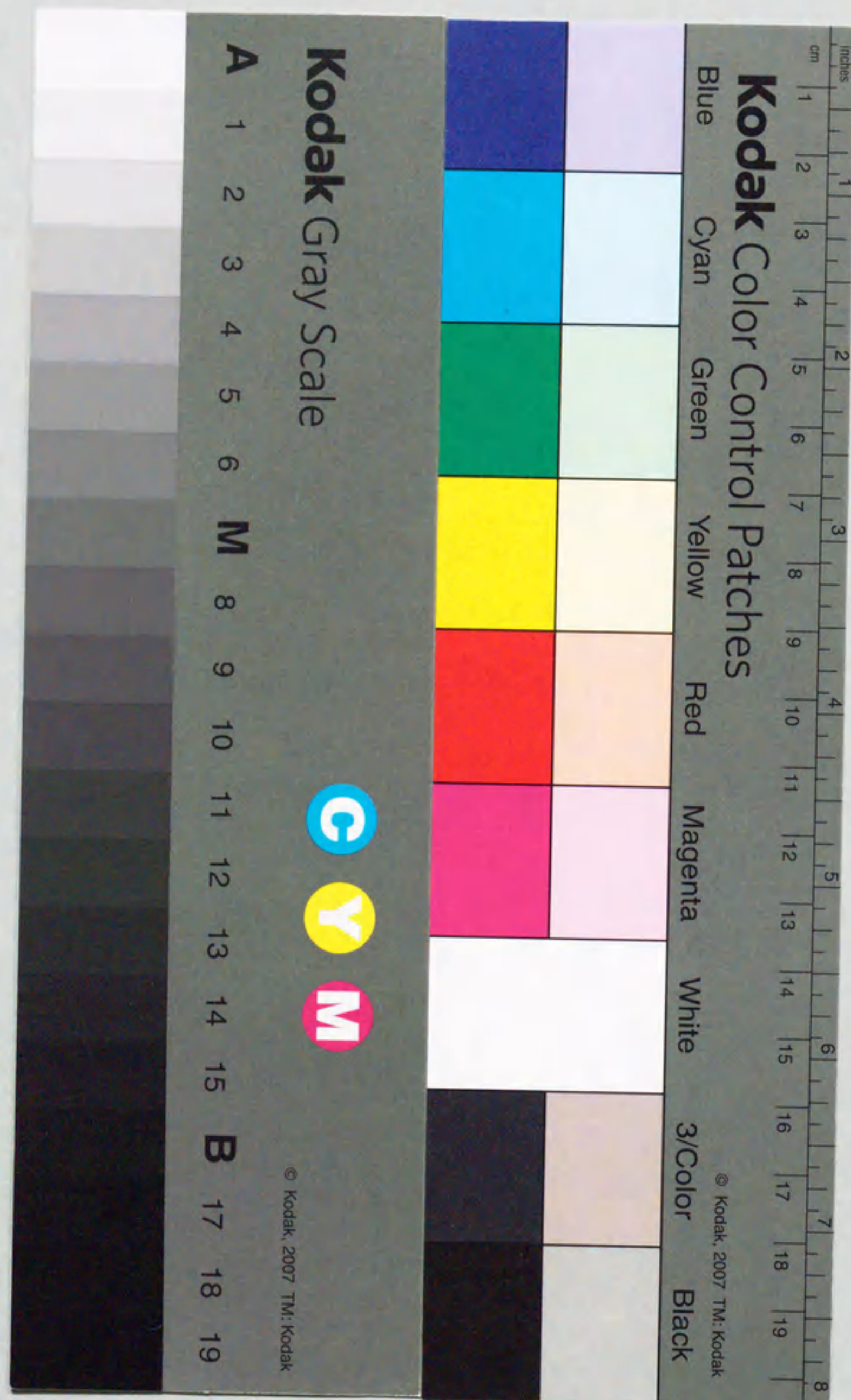


報告番号 乙第 5251 号

STUDIES ON NEIGHBORING GROUP PARTICIPATION AND STERIC PROTECTION IN CARBENE CHEMISTRY

KATSUYUKI HIRAI



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AND STERIC PROTECTION IN CARBENE CHEMISTRY

1997

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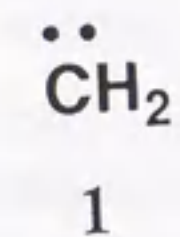
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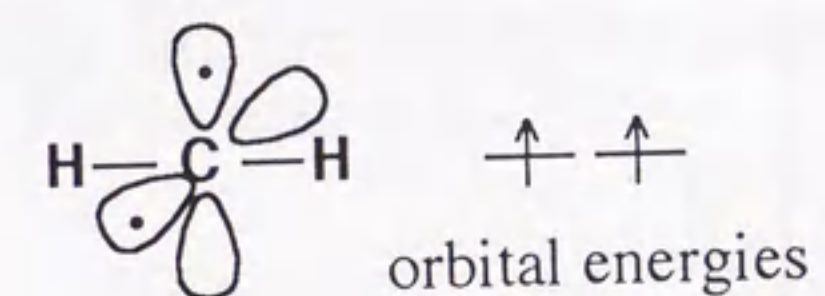
Chapter 1 General Introduction

1-1 Electronic Structure and Energetics of Carbene

Methylene (**1**) is the simplest representative of the family of carbenes. Formally, it results from the removal of two hydrogen atoms from methane. Since the central atom is surrounded by electron sextets, it is said to be electron deficient. Not surprisingly, therefore, it normally reacts as strong electrophiles, but the electrophilicity of carbenes is strongly influenced by substituents.

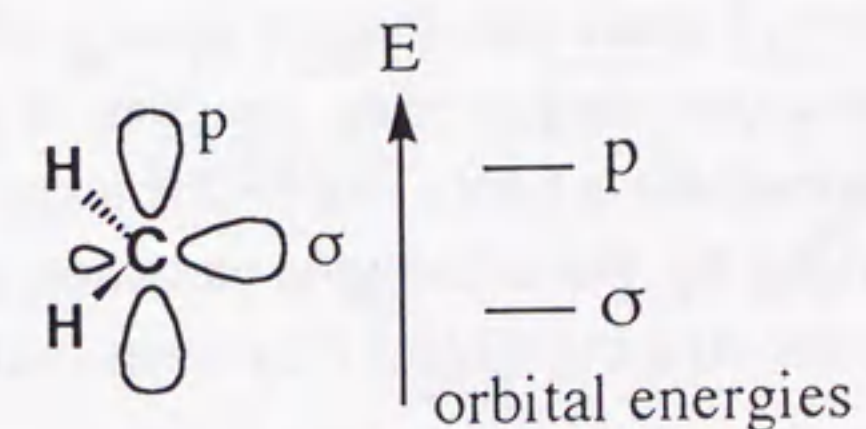


If methylene is linear, it would have two degenerate p orbitals, and Hund's first rule would predict a triplet ground state.



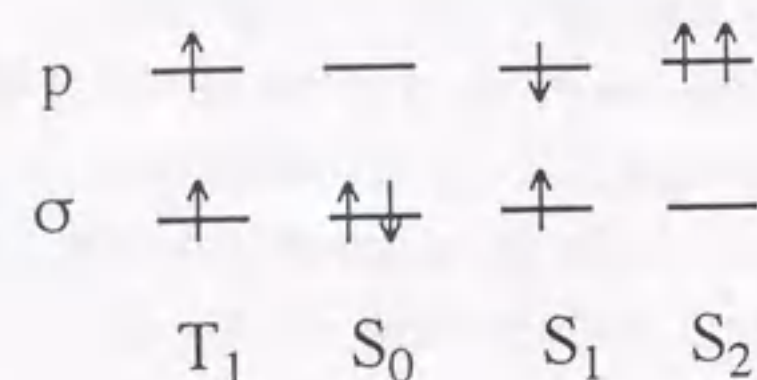
Degenerate orbitals in linear CH₂

If methylene is not linear, the two orbitals will become different: the one in the molecular plane (the σ orbital) will acquire s character and thereby become stabilized. The other orbital (p) remains largely unchanged.



Whether or not the species will now be a singlet depends on the energy separation between the two states. It has to be large enough to overcome the electron correlation energy, that is, the energy required to bring two electrons together in one orbital.

Therefore, if the energy spacing is small, the species will still have a triplet ground state. The following electronic states can exist:



It is now known that T₁ is the ground state. S₀ is an excited singlet state, and S₁ is a doubly excited singlet state. The ordering of the state energies is given in Figure 1. Each species represents a discrete entity.

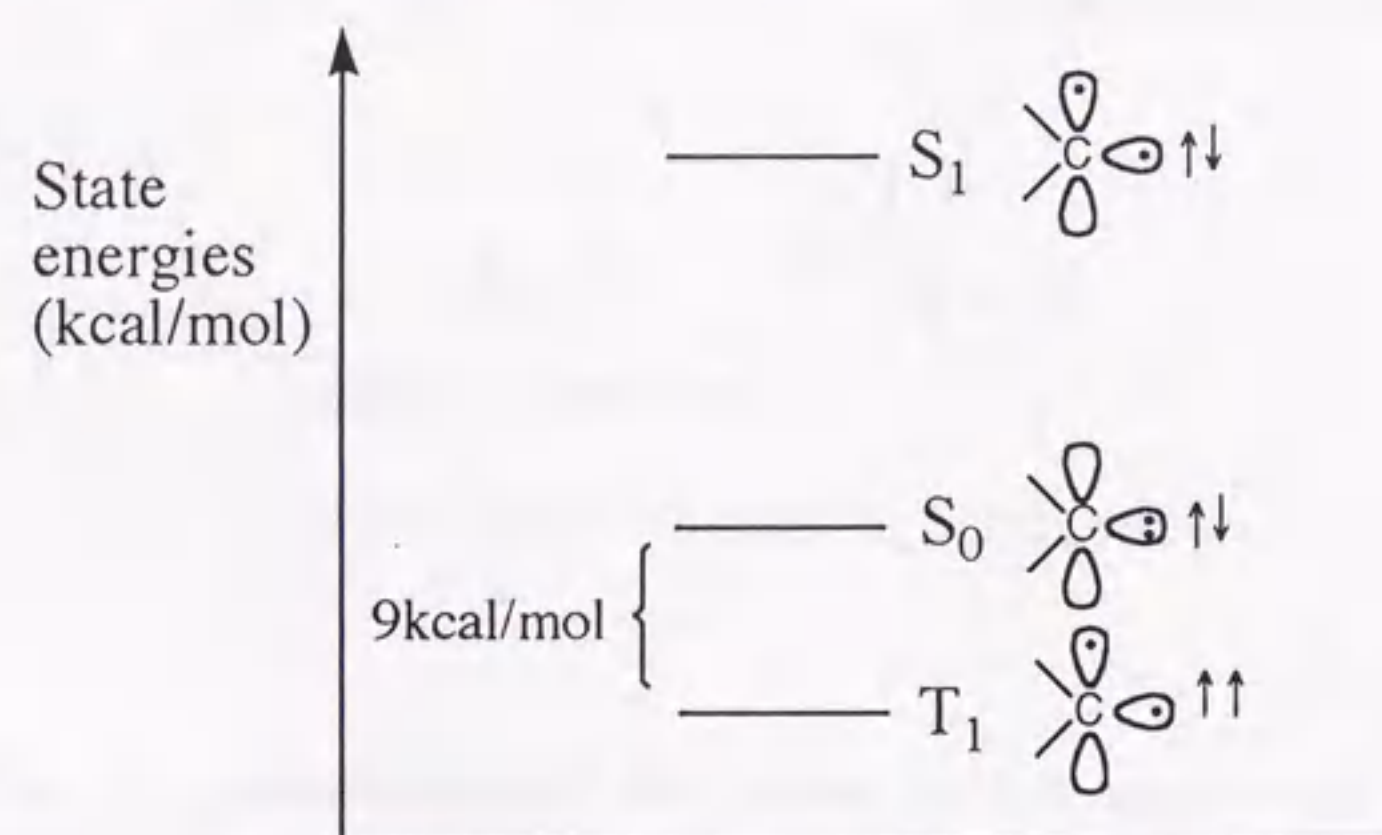


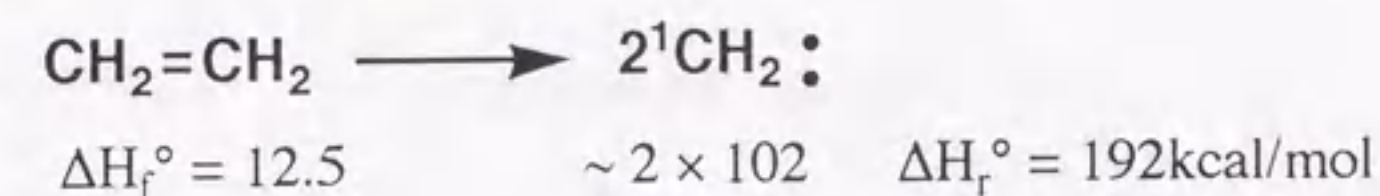
Figure 1. Electronic states of methylene

It has been established¹⁻⁴ 15 years ago that the energy difference between the lowest triplet and singlet states (the singlet-triplet splitting) is quite small, probably around 9 kcal/mol, and that the carbene is bent. The H-C-H angle is approximately 136° in the triplet and 102° in the singlet S₀. For substituted carbenes, singlet-triplet splittings of only a few kcal/mol are known, and the singlet may even become the ground state (e.g., in the halocarbenes).

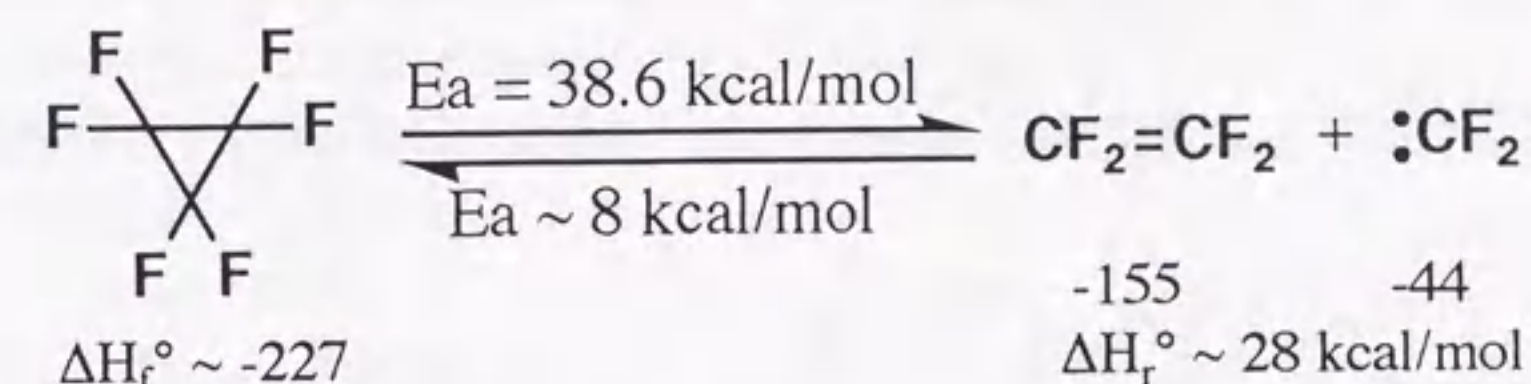
1-2 Generation of Carbene

The general methods, and a few special ones, of preparing carbenes are collected in Scheme 1. The most universal methods are the decomposition of diazo compounds.

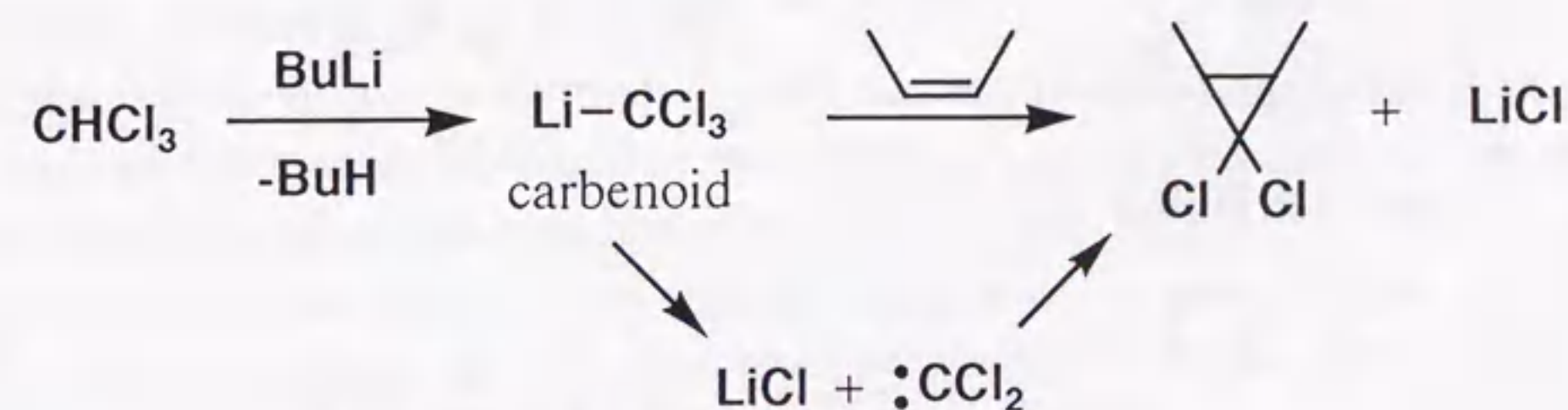
Common for the homolytic methods is the breaking of rather weak bonds with expulsion of stable, neutral fragments like N₂ and CO. The breaking of a C=C bond, in contrast, is a strongly endothermic process,



which can be achieved only in very special cases where the π bond is twisted due to steric repulsion between substituents [e.g., tetra(1-naphthyl)ethylene].⁵ The expulsion of a carbene from a three-membered ring is much less endothermic, and the relatively stable difluorocarbene can be generated in this way.⁶



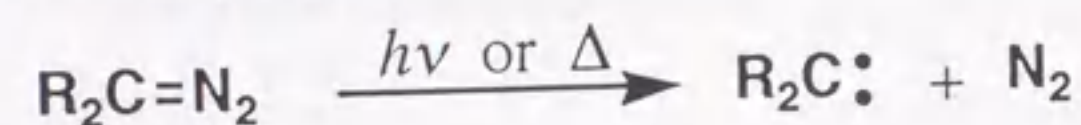
Special attention should be drawn to the so-called carbenoids, that is, compounds that behave like carbenes, although often they are complexed rather than free. For example,



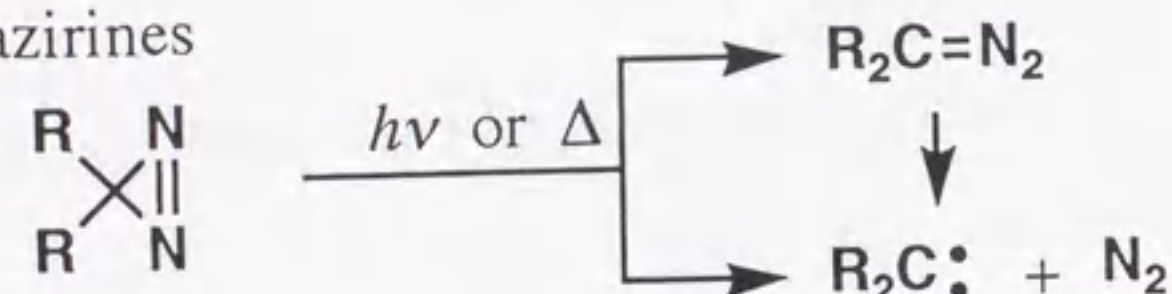
This carbenoid can be considered a complex between :CCl₂ and LiCl. On heating, it dissociates into the carbene and lithium chloride.⁷

Scheme 1

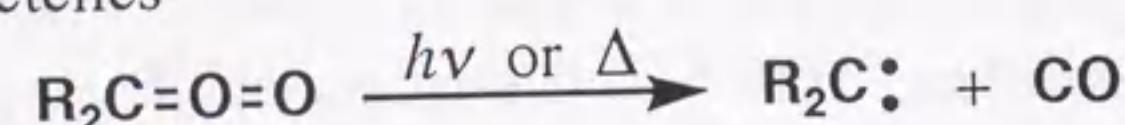
Diazo compounds



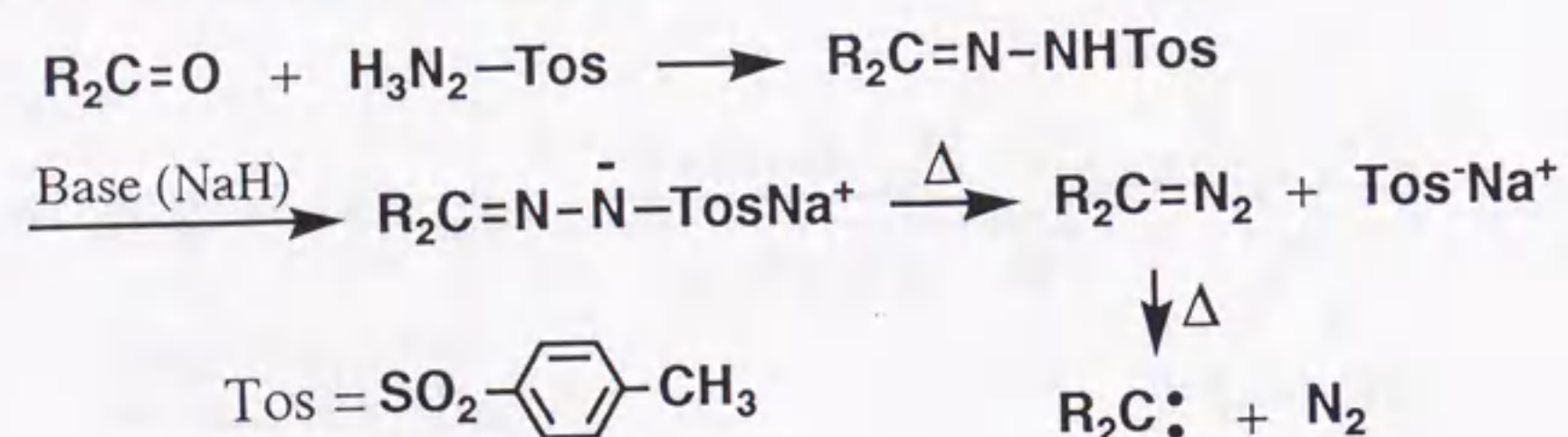
Diazirines



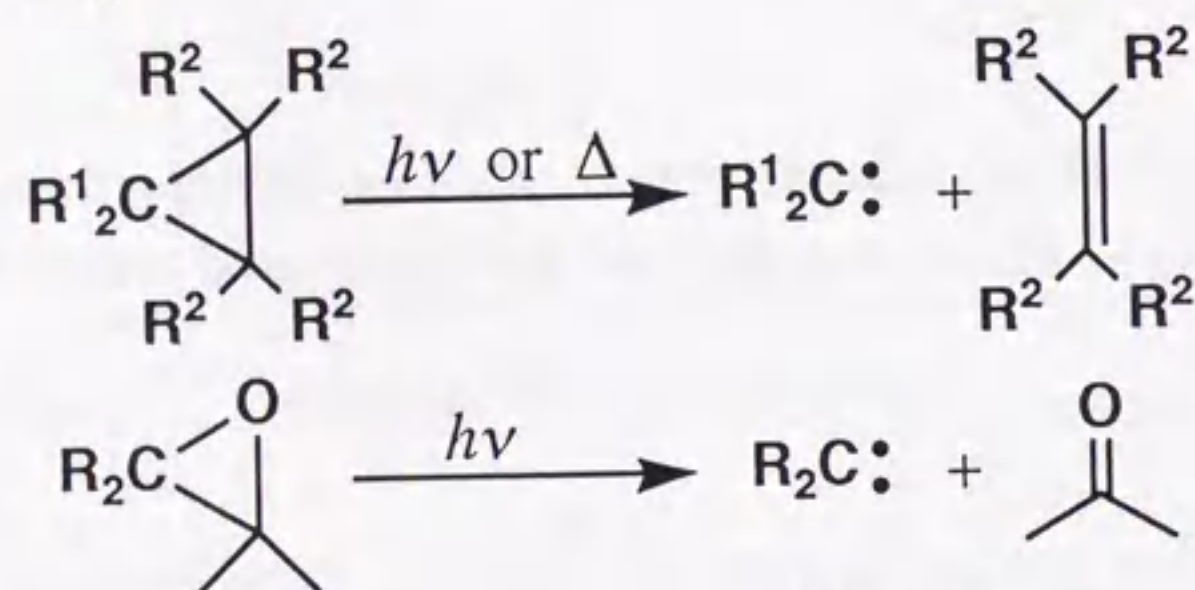
Ketenes



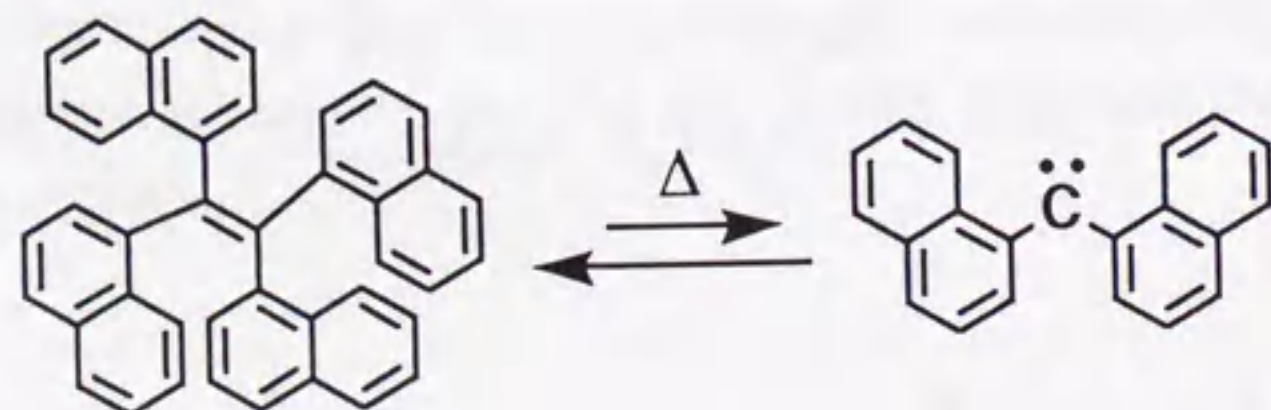
Bamford-Stevens Reaction



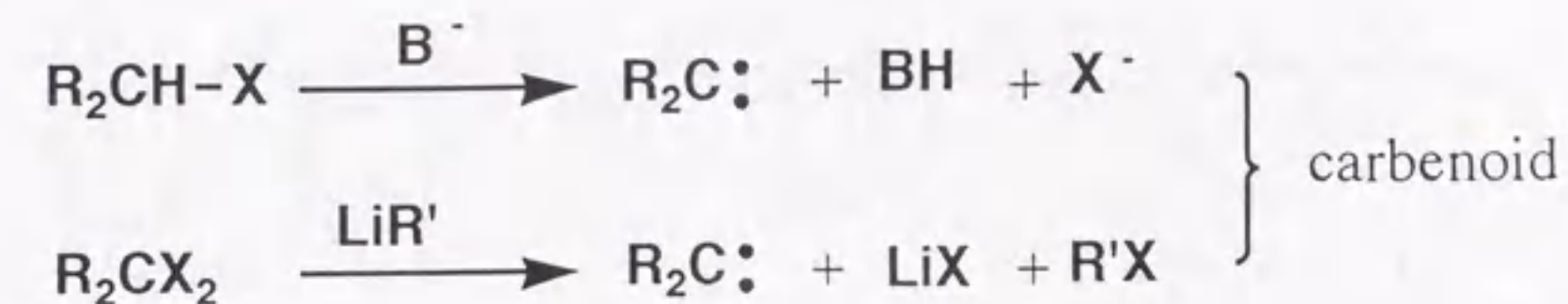
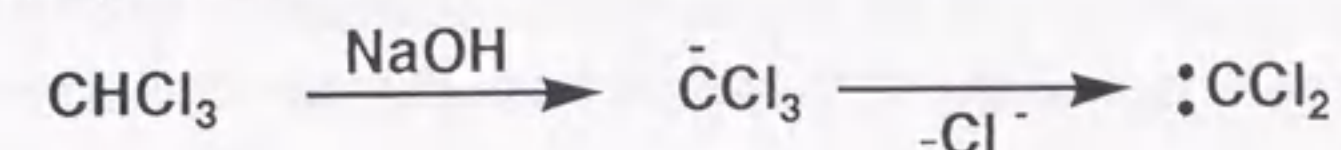
Small Rings



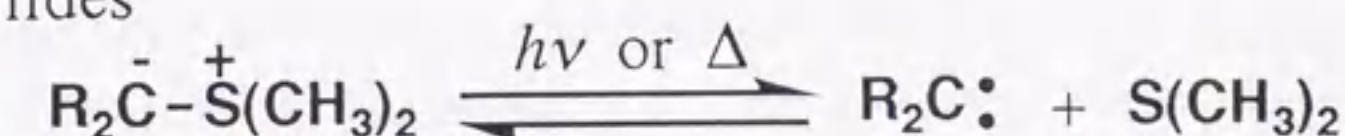
Strained π -Bonds



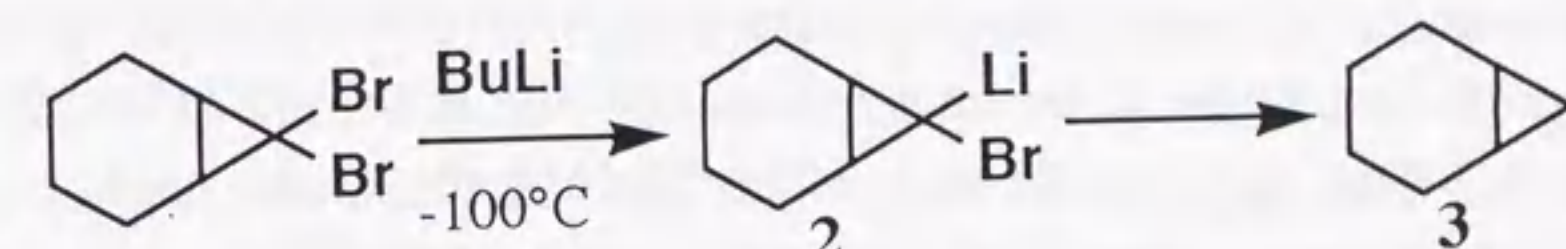
Alkyl Halides



Ylides



Compounds such as **2** are obtained in metal-halogen exchange reactions and can be directly observed by low-temperature ^{13}C NMR spectroscopy.⁸ Compound **2** may be regarded as the carbenoid derived from the corresponding cyclopropylidene **3** and lithium bromide.

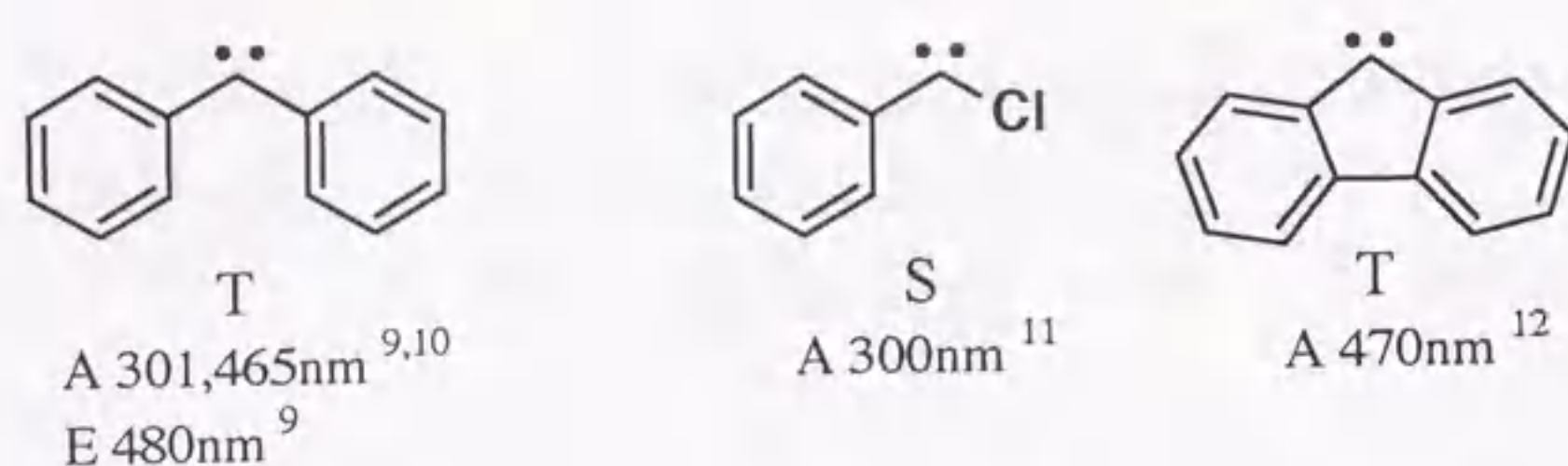


1-3 Direct Observation of Carbene

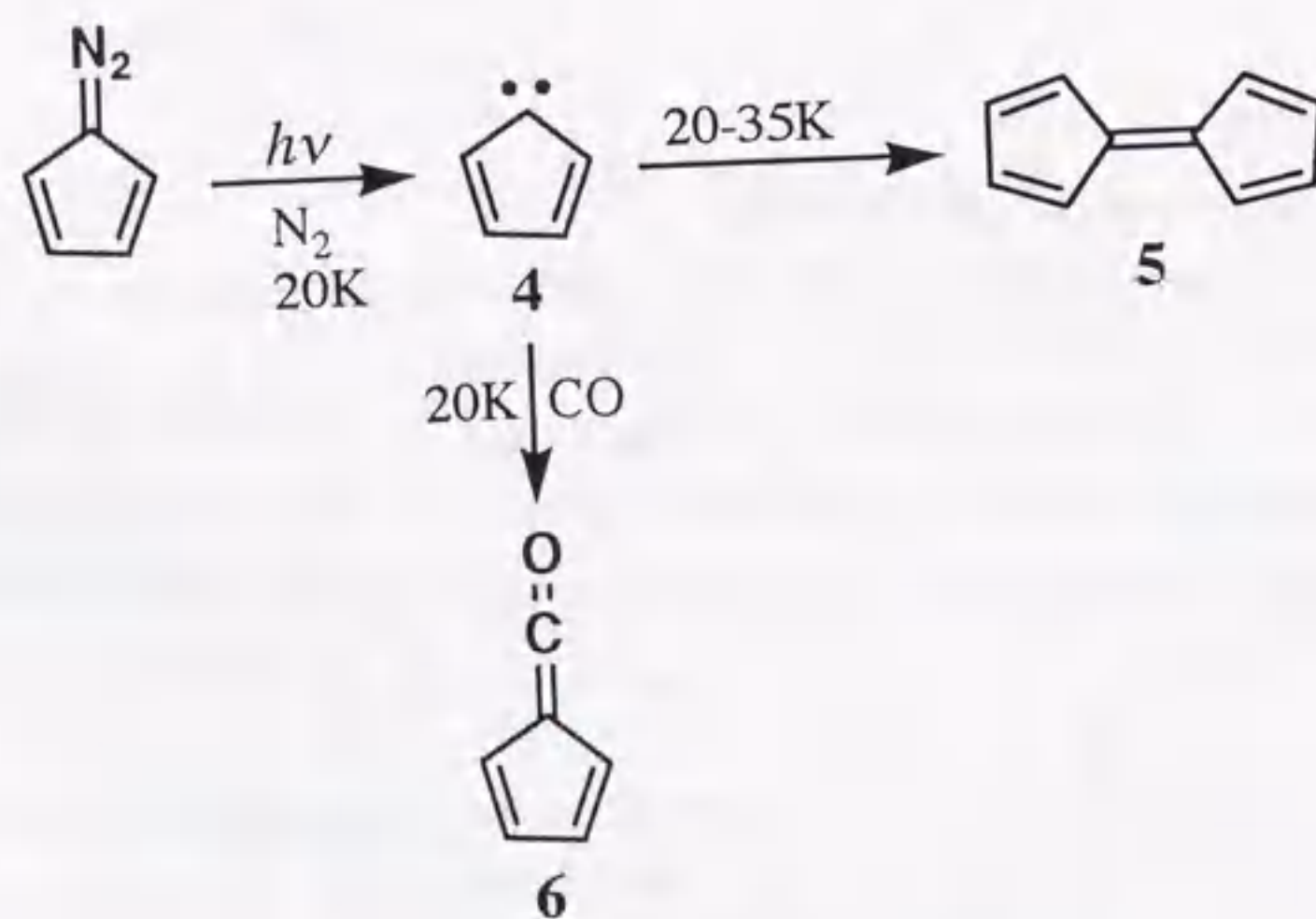
Since carbenes are short-lived and highly reactive species, a direct physical detection requires special techniques. The lifetimes can be prolonged by removal of reaction partners. Spectroscopic observations are therefore made in the gas-phase either at low pressure or with an inert gas as diluent, or at low temperatures, typically 4-77K, in a matrix or glassy solution. The reactive species are often generated by flash photolysis.

(1) *Optical Spectroscopy* In order to observe carbenes in reacting systems in solution, a much more stringent time resolution is required. Using laser flash photolysis with a time resolution in the nanosecond or picosecond range, a number of arylcarbenes have been directly observed by UV spectroscopy. Such studies are of the utmost

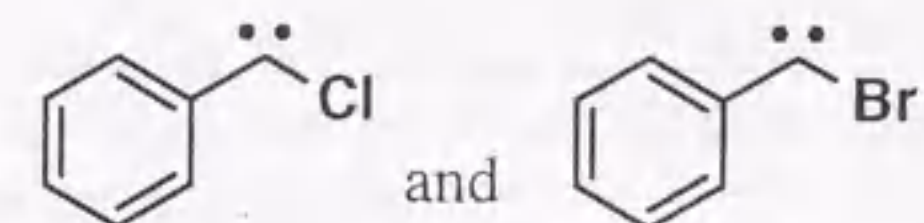
importance since they allow a direct determination of the rate constants for carbene reactions. Some triplet (T) and singlet (S) arylcarbenes detected in this manner are given below together with some absorption (A) and emission (E) maxima.



Of course, the mere observation of an absorption (or emission) line does not prove that a carbene has been detected. Elaborate studies were necessary before the absorption maximum of triplet fluorenylidene could be unambiguously assigned.¹²⁻¹⁴ In order to obtain infrared spectra of carbenes it is necessary both to have a higher concentration of the species and to preserve it for a longer time. Therefore, low-temperature matrix isolation is used. The most convenient means of producing carbenes is again photolysis of a diazo compound, but thermal reactions may also be employed. For example, cyclopentadienylidene (4) has been obtained by matrix photolysis at 12-20K and identified by its UV (λ_{max} 296nm) and IR spectra (strongest band at 703cm⁻¹). The carbene dimerized to fulvalene (5) above 20K, or, when generated in a CO matrix, reacted with the host to give the ketene 6.¹⁵



(2) *ESR Spectroscopy* In order for a carbene to be observable by ESR, it must be in the triplet state. As mentioned earlier, the halocarbenes have singlet ground states. The same appears to be true for phenylhalocarbenes,



which cannot be observed by ESR spectroscopy.

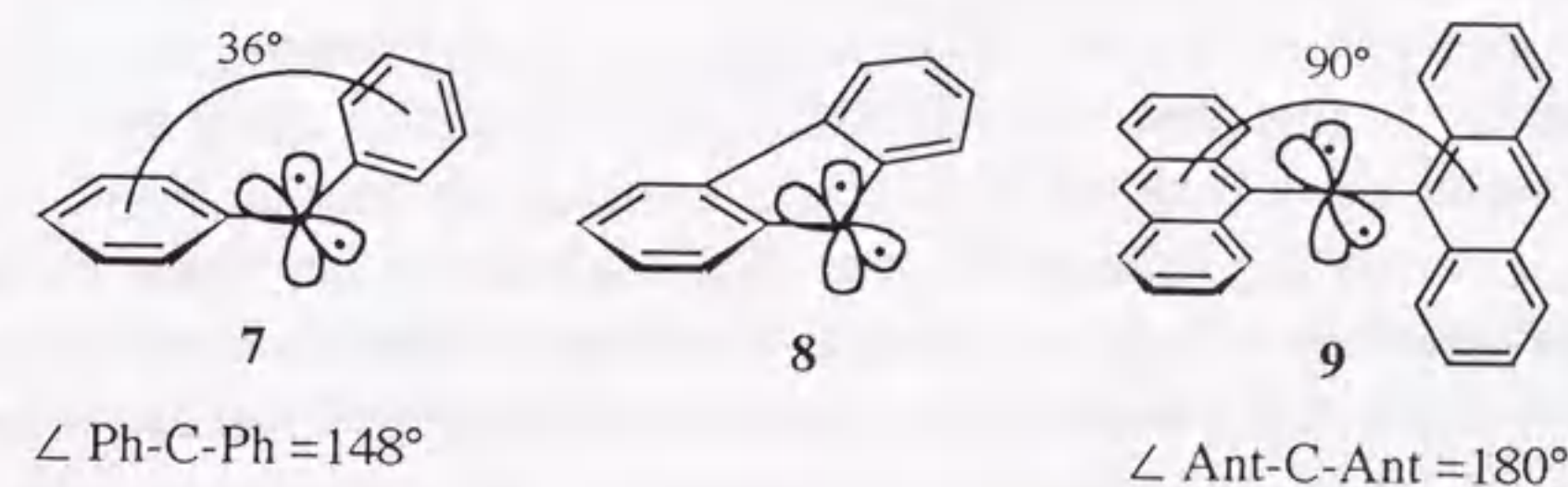
The principal information extracted from ESR spectra of triplet carbenes are the zero-field splitting (zfs) parameters D and E , which measure the magnetic dipole interaction of the unpaired electrons in the absence of an external field.^{16,17}

$$D = [(r^2 - 3z^2) / r^5] \approx (1 / r^3)$$

$$E = [(y^2 - x^2) / r^5]$$

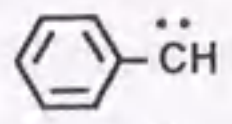
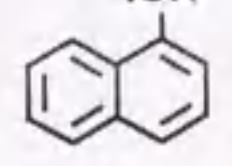
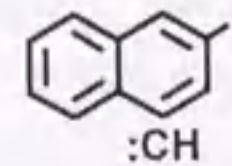
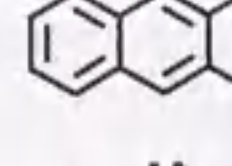
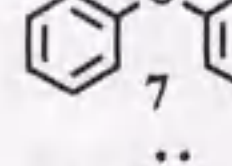
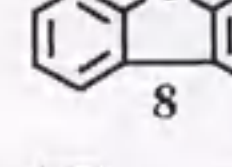
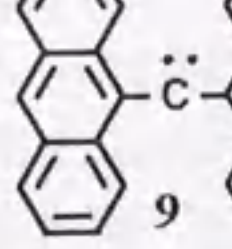
D is a measure of the average distance r of the unpaired electrons and thus allows the determination of the amount of delocalization in carbenes with conjugated π -systems. E measures the difference of the magnetic dipole interaction along the x and y axes and allows one to estimate the bond angle at the carbene center. Especially the E/D ratio is frequently used to estimate the bond angle.¹⁸ E is related to the s character of the in-plane singly occupied orbital. For a linear carbene $E=0$ is expected, while decreasing the bond angle leads to a large value for E .

The ESR spectroscopic data for several carbenes are shown in Table 1. In diphenylcarbene (7), one could expect a low D value due to conjugation of one p electron with each benzene ring. However, comparison with fluorenylidene (8), which certainly is bent and in which one electron is forced to occupy the in-plane σ orbital, indicates almost the same degree of delocalization in the two carbenes. ESR measurements on diphenylcarbene in a host matrix of 1,1-diphenylethylene have shown that the carbene is not only bent, but the phenyl groups are twisted at a dihedral angle of 36°.²²



A linear carbene is obtained in the 9,9-di(anthryl)carbene²¹ (**9**): $E=0.0$. In this case, a bent structure would induce severe sterical hindrance between the two large substituents.

Table 1. ESR Parameters for Triplet Carbenes

carbenes	$D / hc \text{ (cm}^{-1}\text{)}$	$E / hc \text{ (cm}^{-1}\text{)}$	Ref
:CH_2	~ 0.6881	~ 0.00346	19
$(^t\text{C}_4\text{H}_9)_2\text{C:}$	0.689	0.0039	20
	0.5098	0.0249	21
	anti: 0.4555 syn: 0.4347	0.0202 0.0208	21
	anti: 0.4711 syn: 0.4926	0.0243 0.0209	21
	0.3008	0.0132	21
	0.4050	0.0194	21
	0.4078	0.0283	21
	0.3008	0.0	21

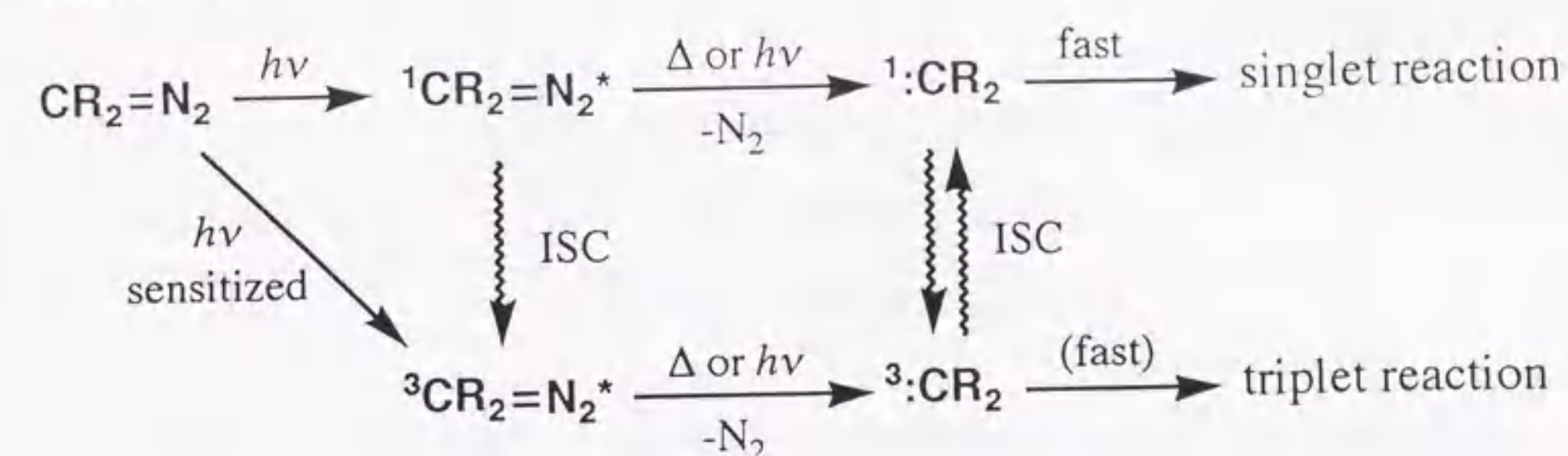
1-4 Reaction Types of Carbene

The only rigorous way to ascertain that a particular reactive intermediate is involved in a given reaction is to observe it directly and monitor its reaction with a spectroscopic method. Kinetics alone may, of course, give evidence for the involvement of an intermediate, but only the combination with chemical intuition will define its nature. Since the rate constants for carbene reactions in solution typically fall in the range 10^6 – $10^9 \text{ M}^{-1}\text{s}^{-1}$, the upper limit being the diffusion-controlled rate, very fast spectroscopic methods are required. Nanosecond and picosecond flash photolysis have been

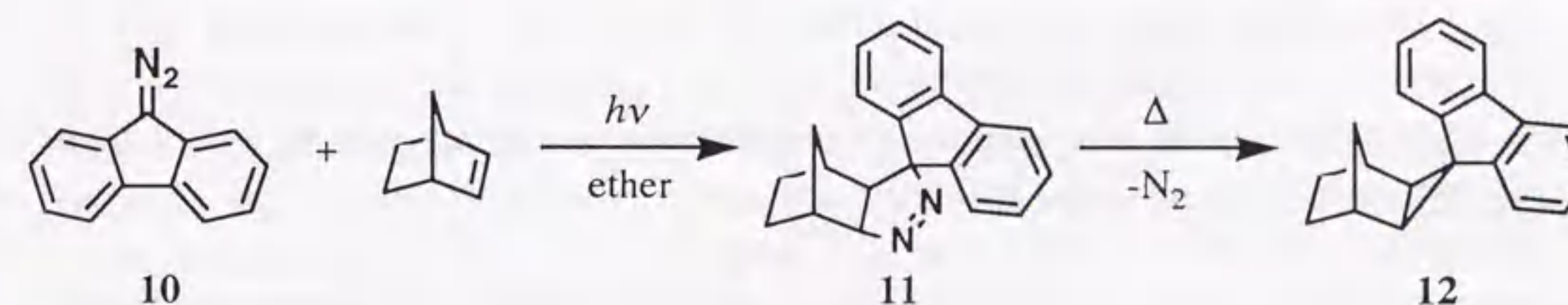
mentioned. The decay of an intermediate may be followed by absorption¹⁰⁻¹³ or emission²³ UV or by ESR spectroscopy.²⁴ An intermediate may be identified by static spectroscopy of low-temperature matrices or glassy solutions, but this does not necessarily prove that the same intermediate is involved in a chemical reaction at, say, room temperature. A carbene observed by ESR at low temperature will be the (ground state) triplet, but the corresponding singlet and other intermediates possibly involved in a solution reaction will escape detection.

A general reaction scheme, exemplified for the decomposition of a diazo compound, can be formulated as follows:

Scheme 2



The rate determining step is the formation of carbene. It may reasonably be expected, therefore, that the rate of decomposition of the diazo compound is essentially independent of solvent and additives. In many instances, the diazo compound can react directly with the substrate, leading to the same product as that expected from a carbene reaction.²⁵ This may be detected kinetically, or, in favorable case, by isolation of the primary reaction product. As an example, the photolysis of diazofluorene (**10**) in

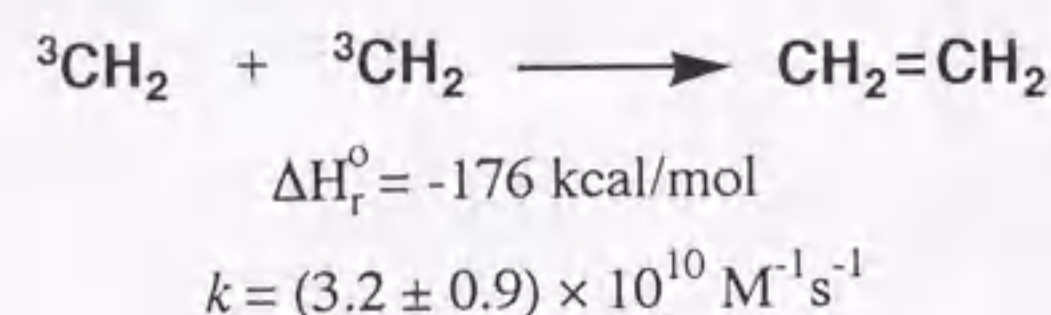


norbornene results in the precipitation of the pyrazoline **11** which is thermally converted to the cyclopropane **12**, the expected product of carbene addition to a double bond.^{25a}

The N_2 expulsion from pyrazolines like **11** proceeds with activation energies between 30 and 40 kcal/mol, that is, about the same as required to decompose diazo compounds. Singlet excited diazo compounds may undergo intersystem crossing to the triplet excited states before decomposition to carbenes. Furthermore, the singlet and triplet carbenes can, themselves, interconvert. If the singlet-triplet splitting is small, this interconversion will be fast.

If the singlet is the ground state (e.g., in the halocarbenes), there is less complication: only singlet reaction is expected.²⁶ If the triplet is ground state, an initially formed singlet carbene will in time convert to the triplet.

(1) *Dimerization* Triplet carbenes, like radicals, dimerize in a very fast and exothermic reaction:²⁷



The recombination of two triplets to give a singlet product is spin-allowed.

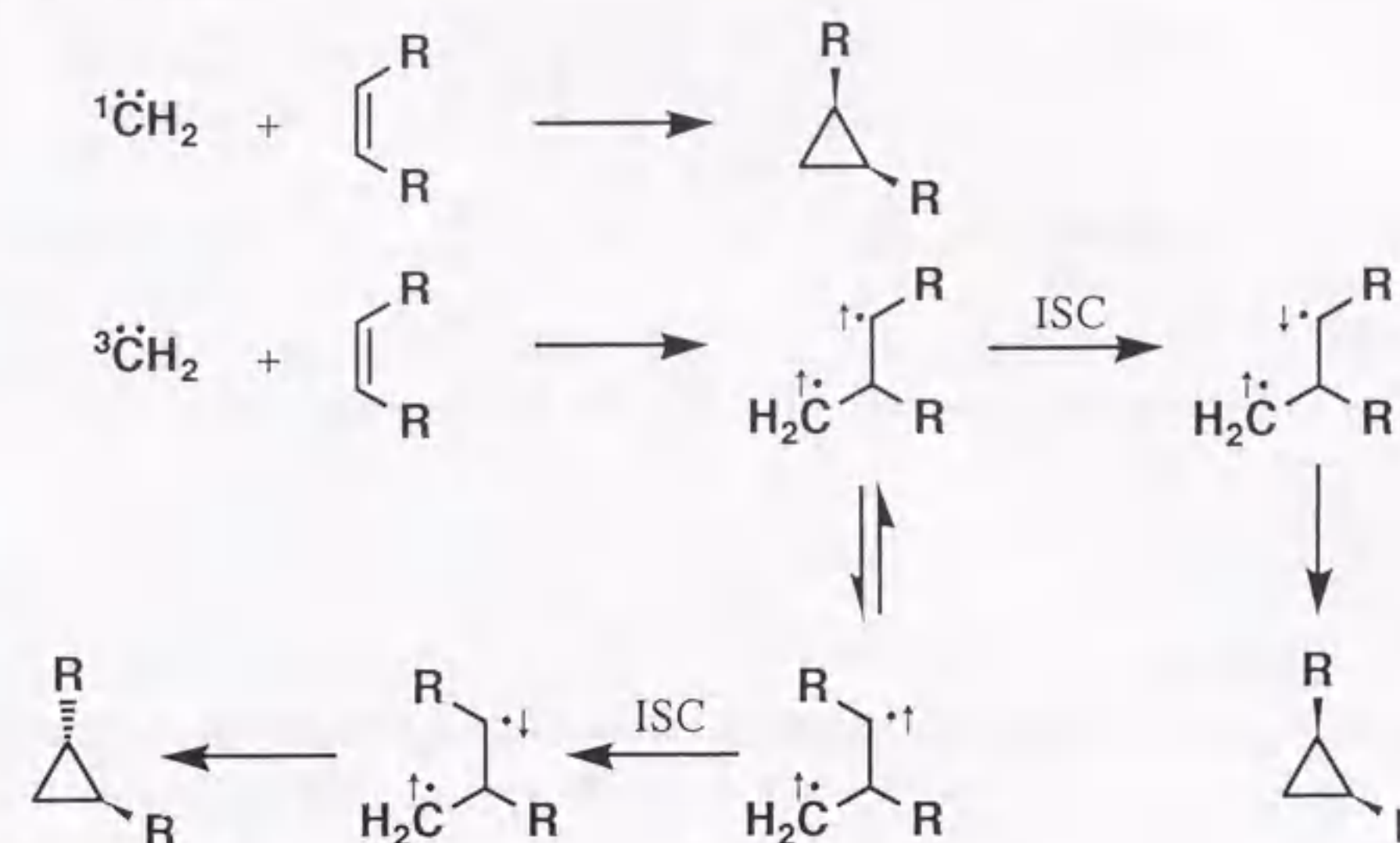
The efficiency of this process obviously depends on the concentration of the carbene. In solution, "dimers" are often formed by attack of the carbene on the carbene precursor, whose concentration is much higher:



This reaction also leads to azines. The azines themselves decompose at much higher temperatures with predominant N-N bond cleavage.

(2) *Addition to Double Bonds* Skell and Woodward²⁸ argued that the addition of a singlet carbene to an olefin could be a one-step reaction, two new bonds being formed simultaneously. A triplet, in contrast, cannot give a cyclopropane in a one-step reaction, since this process is spin-forbidden. Therefore, it was postulated that the triplet would add in two steps, leading first to a triplet diradical intermediate (Scheme 3).

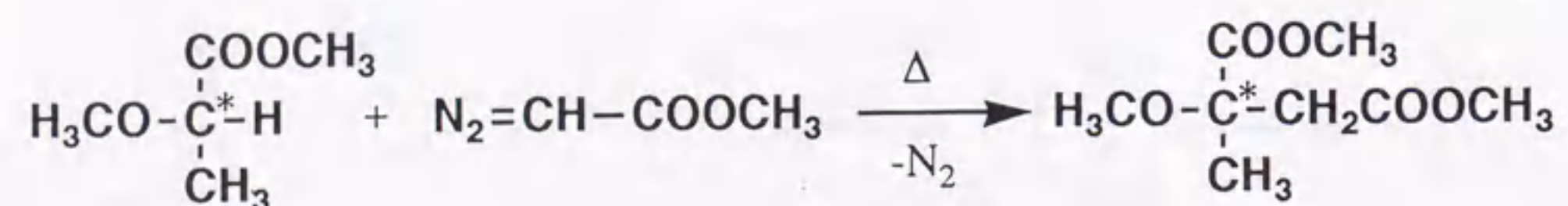
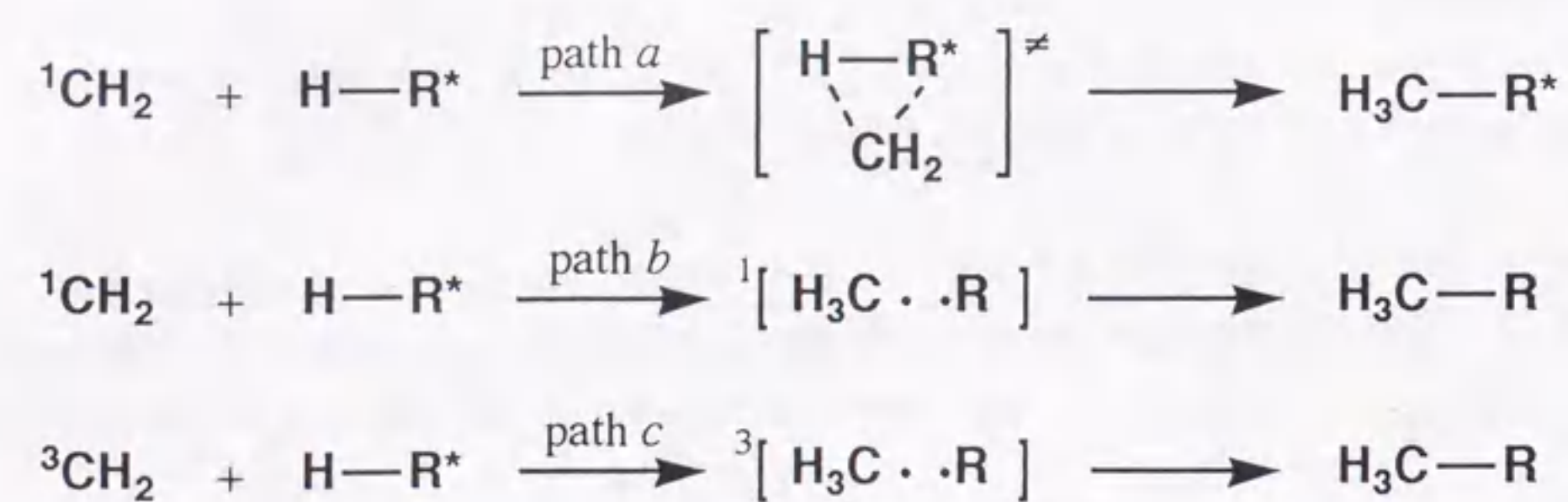
Scheme 3



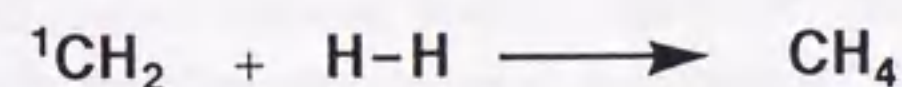
Since rotations can take place in this intermediate prior to intersystem crossing, loss of stereochemistry would result. Thus the Skell rule can be formulated: Singlet carbenes add to olefins stereospecifically; triplet carbenes, nonstereospecifically. If, however, the rate of spin inversion in the 1,3-diradical is much higher than the rate of rotation, the triplet may still add stereospecifically. Likewise, there is no rule that forbids the singlet carbene to add in a two-step manner. We have seen, however, that the singlet 1,3-diradical is not a stable intermediate, but rather a transition state. Therefore, the addition of singlet carbenes to double bonds should indeed be energetically concerted one-step reactions.

(3) *Insertion into C-X bonds* Carbenes insert into single bonds, the most important being the C-H insertion. As with the addition to double bonds, one can imagine a direct insertion of a singlet carbene (Scheme 4, path a); this has come to be known as the Doering-Prinzbach mechanism. It has also been suggested that the singlet carbene abstracts a hydrogen atom to give a singlet radical pair, which then recombines (Benson-DeMore mechanism, path b).²⁹ For triplet reactions, there is general agreement that an abstraction-recombination path (path c) is followed: Many attempts to distinguish path a and b for the singlet reaction have been reported, and it now seems clear that path a is the normal course. If path a is followed, the reaction should proceed with retention of configuration; that is, if RH is optically active, the product should maintain the activity. Indeed, this is usually the case.³⁰

Scheme 4

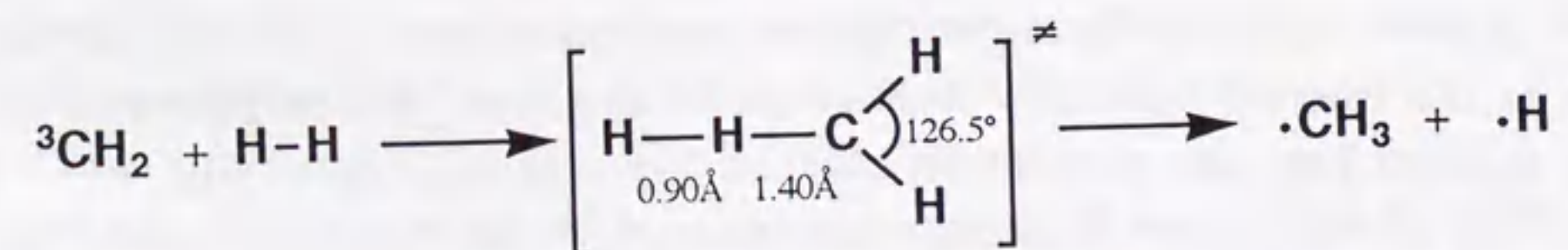


Ab initio quantum-chemical calculations³¹ on the simplest singlet carbene reaction



fully support the mechanism given in path a, that is, three-center (but unsymmetrical) reaction which proceeds without activation energy.

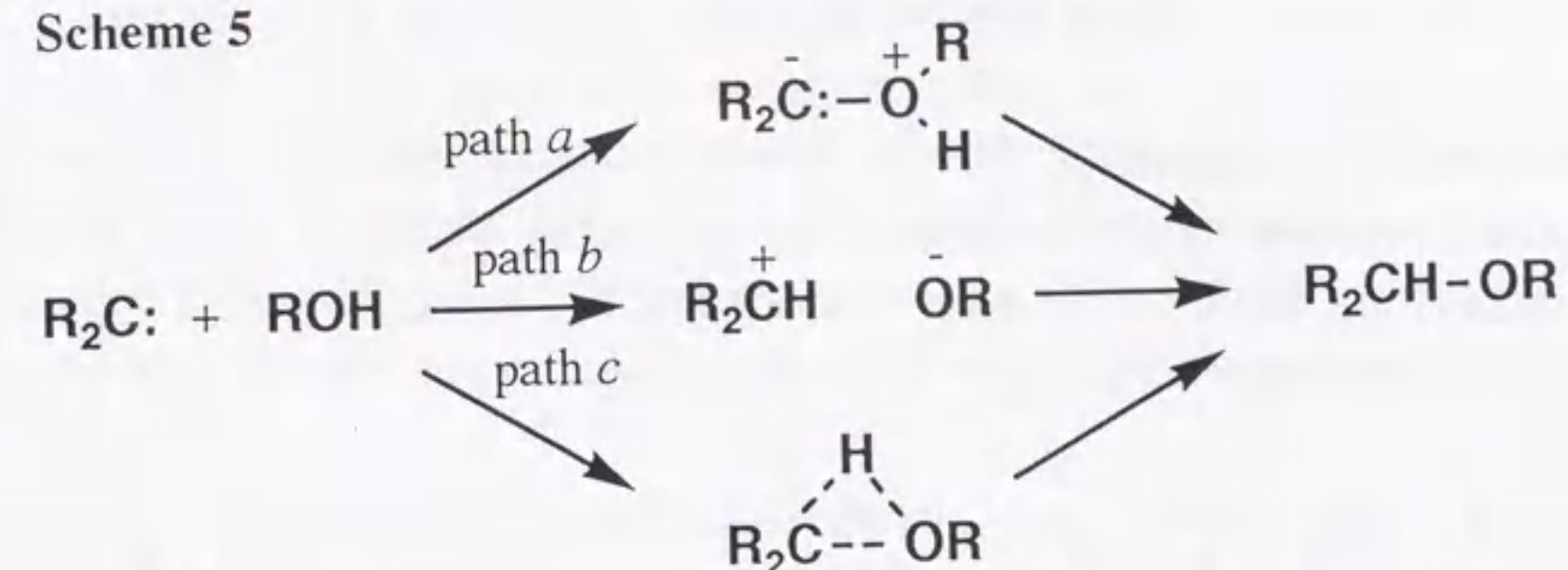
Analogous calculations³¹ for the triplet insertion favored the linear transition state shown. This will lead to abstraction-recombination in accord with path c above. The calculated activation energy was 15 kcal/mol.



In contrast, the insertion of singlet carbenes into O-H bond has been discussed primarily in terms of stepwise mechanisms: (path a) electrophilic attack of the carbene on the oxygen atom, followed by proton transfer (ylide mechanism), and (path b) protonation

of the carbene to give a carbocation (ion pair), followed by nucleophilic substitution (carbocation mechanism) (Scheme 5).^{32,33} A concerted process (path c) cannot be excluded a priori but has not received definitive experimental support. The application of

Scheme 5

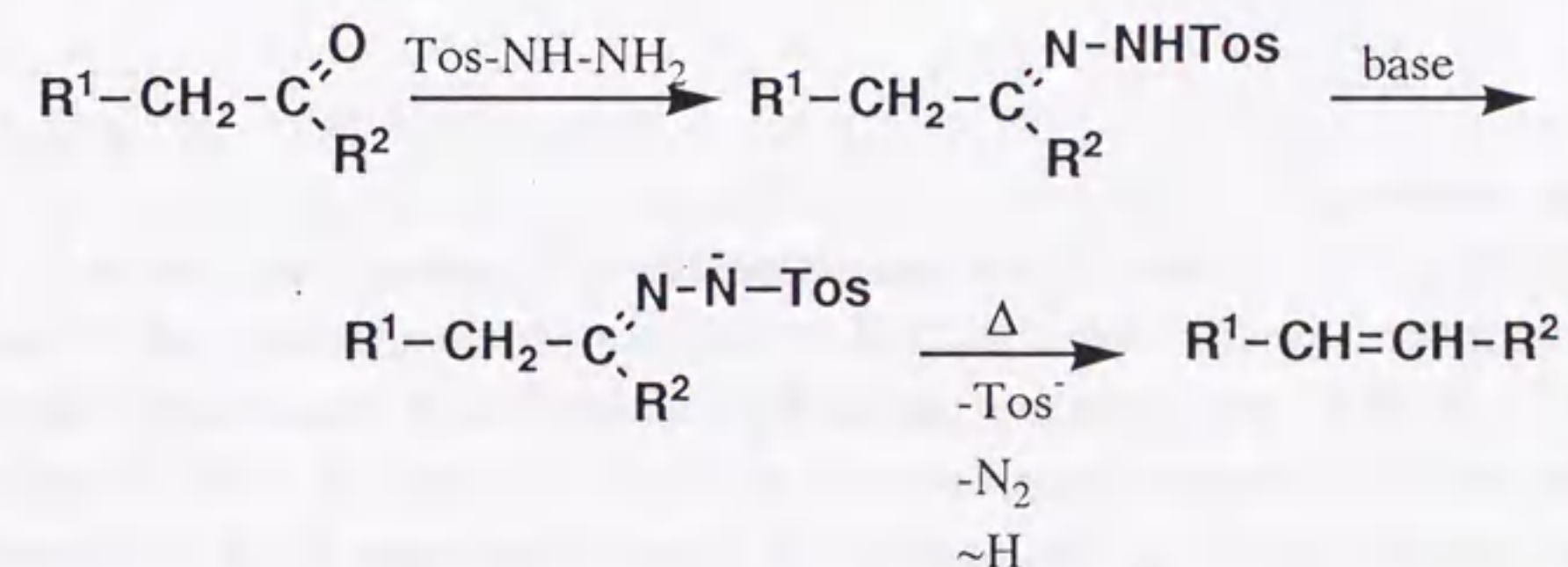


laser flash photolysis(LFP) to O-H insertion reactions recently has provided a rich harvest, including the detection of carbocations as transient intermediates.³⁴⁻³⁸

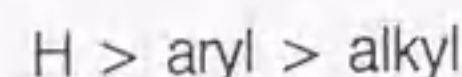
(4) *Rearrangements Hydrogen Shifts.* The 1,2-hydrogen shift in a singlet carbene is one of the most general and versatile carbene reactions:



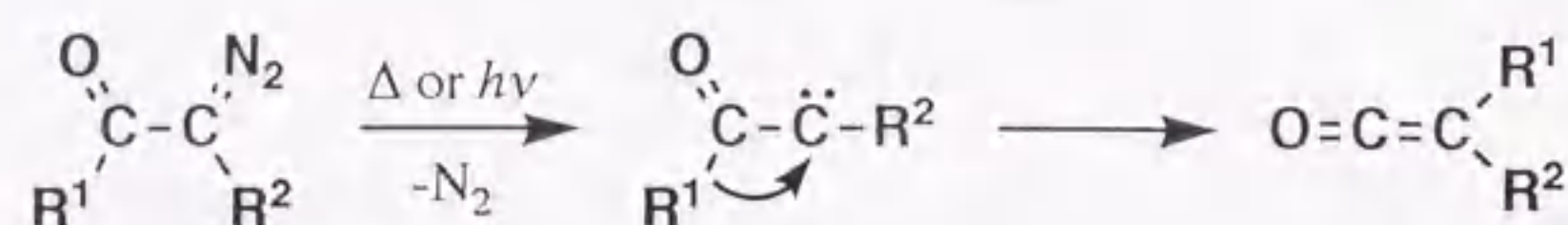
It constitutes the crucial step in the Bamford-Stevens reaction, whereby a ketone (or aldehyde) possessing at least one α -hydrogen atom is converted to an alkene:



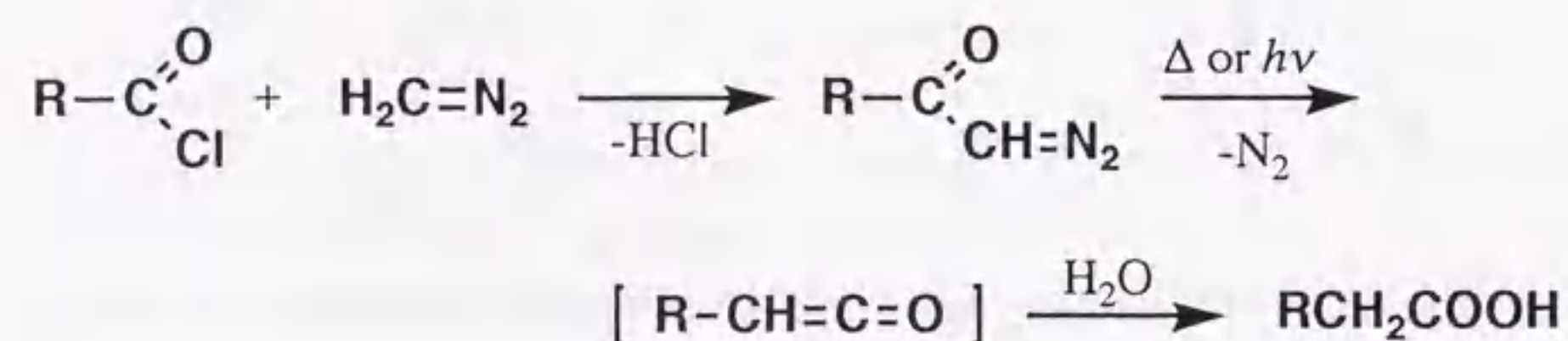
The hydrogen shift can be regarded as an insertion into an α -C-H bond and is analogous to the Wagner-Meerwein rearrangement in carbocations. Alkyl and aryl groups migrate too. The migratory aptitude increases in the series



Wolff-Type Rearrangements. The thermal or photochemical reorganization of an α -diazocarbonyl compound to give a ketene is known as the Wolff rearrangement. For the sake of convenience, we include under this heading the analogous rearrangements of thio-, imido-, and vinyl-carbenes.



The decomposition of diazoketones is usually formulated as a carbene reaction, but, as shown further on, this may not always be correct. The ketene formed as a product is rarely isolated as such. Rather, it is converted to a carboxylic acid or an ester by performing the reaction in aqueous or alcoholic solution, as in the well-known Arndt-Eistert homologization:³⁹



1-5 Carbene Philicity

Singlet carbenes have been experimentally classified as electrophiles, nucleophiles, or ambiphiles depending on their selectivity toward alkenes.⁴⁰ Electrophilic carbenes are described as being more reactive toward electron-rich alkenes such as tetramethylethylene, whereas nucleophilic carbenes react faster with electron poor alkenes such as ethyl acrylate. Ambiphilic carbenes react more rapidly with olefins substituted with either electron-donating or electron-withdrawing groups than with 1-pentene or 1-hexene. Moss has developed a method of quantifying the olefinic

selectivity of carbenes with a free energy relationship that yields a selectivity index m_{CXY} . The relative rates of addition of the carbene under investigation (CXY) with a standard set of alkenes are plotted against the same measurements for CCl_2 ($m_{\text{CCl}_2} = 1.00$) to obtain m_{CXY} as the slope of a log-log correlation.

An electrophilic carbene has a relatively low-lying lowest unoccupied molecular orbital (LUMO or p) and the dominant interaction is carbene LUMO (p) with an alkene highest occupied molecular orbital (HOMO or π). If electron donation from the substituents X and Y is strong enough, the dominant interaction will become carbene HOMO (σ) with alkene LUMO (π^*); the carbene is now nucleophilic. The "border" of electrophilicity and ambiphilicity appears to be experimentally located at $m_{\text{CXY}} \approx 1.5$.

Table 2. Selectivity Indices and Differential Orbital Energies for Carbene-Alkene Additions

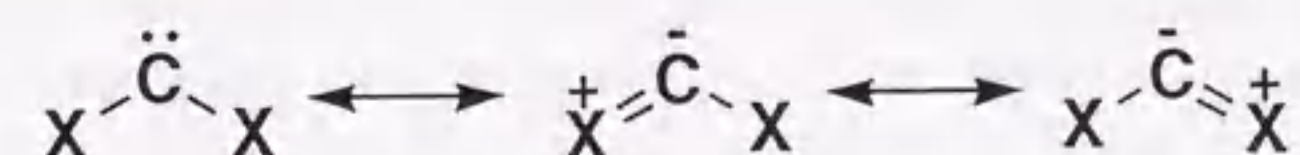
carbenes	m_{CXY} (obsd)	m_{CXY}^a (calcd)	$p-\pi^b$ (eV)	$\pi^*-\sigma^b$ (eV)	
CH_3CCl	0.50	0.58			} electrophilic
PhCCl	0.83	0.71			
CCl_2	1.00	0.97	10.82	13.22	
CF_2	1.48	1.47	12.40	15.16	} ambiphilic
CH_3OCCl		1.59	12.97	12.60	
CH_3OCF		1.85			} nucleophilic
$\text{C}(\text{OCH}_3)$		2.22	14.60	12.59	

^a $m_{\text{CXY}} = -1.10\sum_{\text{X,Y}}\sigma_{\text{R}}^+ + 0.53\sum_{\text{X,Y}}\sigma_{\text{I}} - 0.31$. ^b Calculated for ethylene.

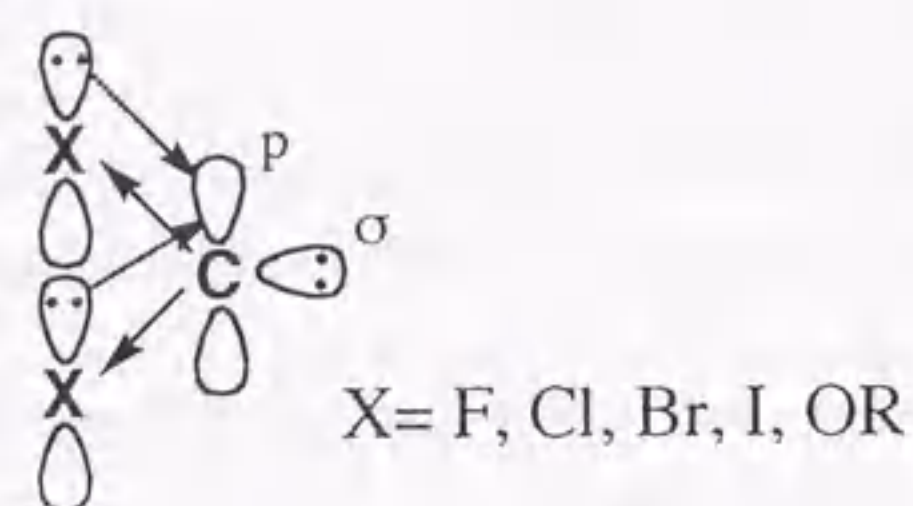
Recently, LFP studies⁴¹ revealed "latent ambiphilicity" of PhCX ; that is, the electron-withdrawing cyano or methoxycarbonyl substituents make $\text{CH}_2=\text{CHR}$ more reactive toward PhCF or PhCCl than does the butyl substituent of 1-hexene. These data caution against the previous characterization of arylhalocarbenes as electrophilic.

1-6 Lone-Pair Stabilization and π Conjugation

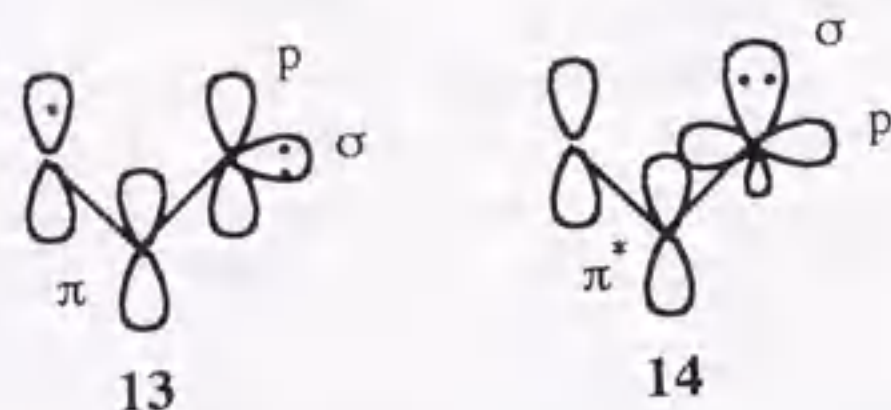
It was mentioned earlier that the halocarbenes and phenylhalocarbenes appear to have singlet ground states. This contention derives from the fact that ESR spectra cannot be obtained nor can the carbenes be "deactivated" to triplets by dilution. Quantum chemical calculations also indicate singlet ground states.^{26,42,43}



This can be accounted for in terms of the resonance structures in which the halogen atoms donate electrons into the empty carbene p orbital. Because the halogens are more electronegative than carbon, there will be a strong concomitant σ polarization in the opposite direction. Thus, the σ core of the carbene carbon becomes more positive, but back-donation from the halogen lone pairs increases the p- π electron density on carbon.

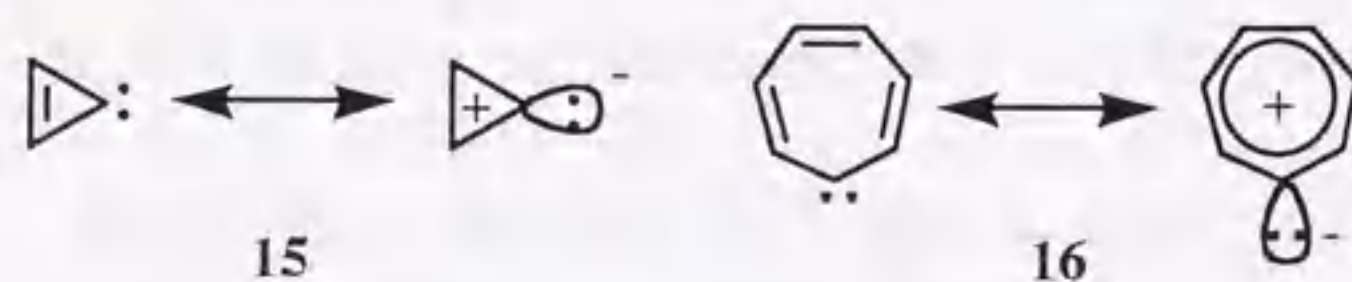


The conjugation of a singlet carbene with a flanking π system will create a delocalized system (**13**) isoelectronic with the allyl cation. The carbene LUMO is raised in energy, and the carbene becomes less electrophilic. If, however, the flanking

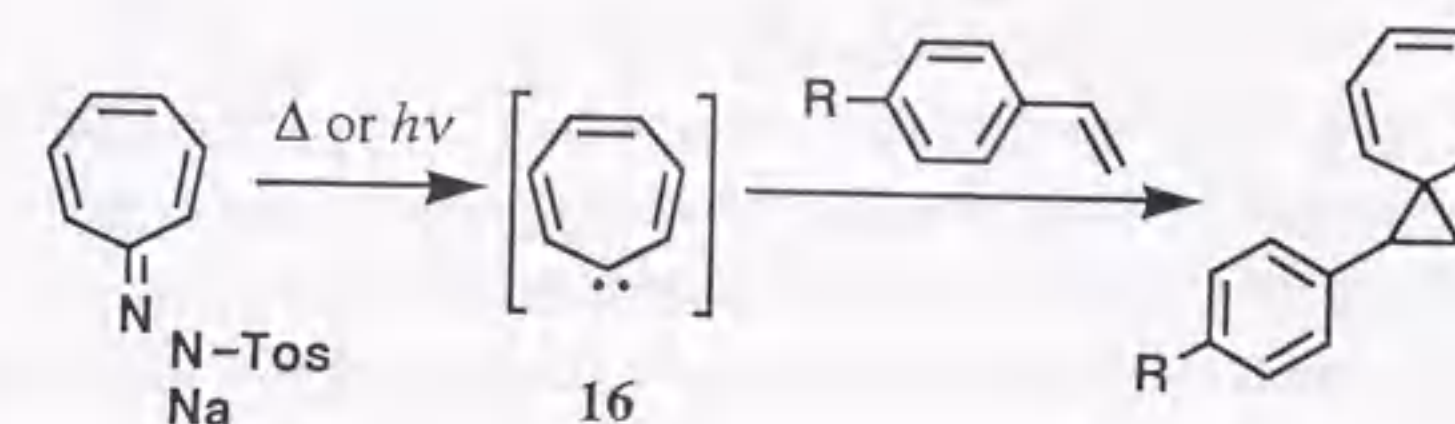


π system is itself electrophilic, that is, it has a low-lying LUMO, a system isoelectronic with the allyl anion may obtain (**14**). Here, the carbene HOMO is stabilized, whereas the vacant p orbital (the carbene LUMO) remains unaffected. It was already mentioned that arylcarbenes can behave as either nucleophiles or electrophiles, depending on the nature of the π system.

The electrophilicity of a carbene can be reduced by incorporation of the vacant p orbital into an aromatic system. Thus, cyclopropenylidene (**15**) and cycloheptatrienylidene (**16**) are Hückel aromatics in the σ^2 configuration, obeying the $4n + 2$ rule:



This leads to a stabilization of the singlet states and a destabilization of the triplet states. The latter would be $4n + 3$ electron systems having one electron in an antibonding orbital. The observed chemistry^{44,45} supports the conclusion that these carbenes are nucleophilic singlets. **16** gives a positive ρ values (+1.05) for the addition to styrenes.⁴⁵



1-7 Summary

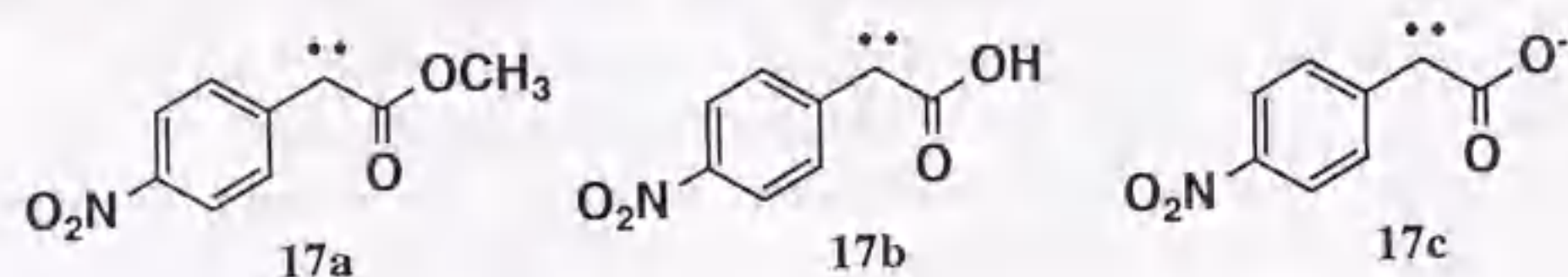
Two electronic states of carbenes, singlet and triplet, can each be detected spectroscopically, and their chemistry is distinct. The effect of substituents on the magnitude of the singlet-triplet energy gap may be dissected into steric, primarily bond angle and electronic components. Both contraction of the carbene-carbon bond angle and electron donation into the vacant p orbital favor the singlet state. For example, many carbenes with heteroatoms attached directly to the central carbon have singlet ground states, the excited states being experimentally inaccessible. On the contrary, expansion of the carbene-carbon bond angle favors the triplet state.

One of the most dramatic effects of substituents in organic reactions is neighboring group participation where the intramolecular association of one group in a molecule exerts a significant effect on the reactivity of another. If a strong electron donor as a participant is introduced in a carbene molecule, the effect of the neighboring group may stabilize the singlet state of the carbene such as electron donation of halogen atoms bonded directly to the carbenic carbon or direct π conjugation with the carbenic carbon.

In the nucleophilic displacement reaction, it is well-known that neighboring anionic groups such as carboxylate or phosphonate groups act as one of the most effective participants. On the basis of this idea, in order to stabilize the singlet state of carbene, the acid anion groups were introduced under a carbene molecule and the reactivities of the carbene were investigated.

Thus, in part 1, effects of carboxylate and phosphonate groups on carbene reactivities are discussed. Chapter 2 describes the effect of neighboring carboxylate group, which has been known to act as the most effective participants in the nucleophilic displacement reaction, on carbene reactivities. Reactivities of (alkoxycarbonyl)carbenes are shown to be dramatically changed as one substitutes the ester group with carboxylate group. Thus, (methoxycarbonyl)- or carboxyl(4-nitrophenyl)carbene (**17a**)

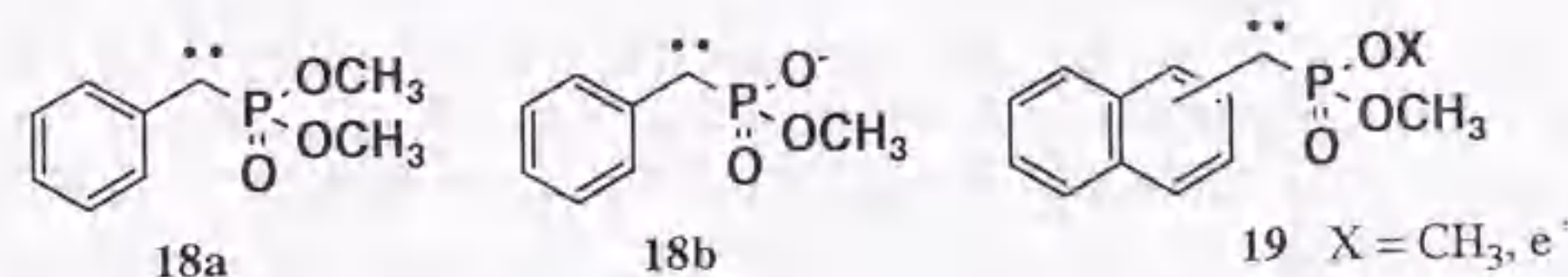
and **17b**, respectively), generated by photolysis of the corresponding diazo compounds in a binary mixture of 2-methyl-2-butene and methanol, gives both cycloaddition products to the butene and OH insertion products into methanol, the relative reactivities (k_{OH}/k_{add}) being 0.3-0.5. In marked contrast, the "carboxylate" carbene (**17c**) generated from the sodium salt of the diazoacetate under the same conditions produces mostly the OH insertion product at the expense of the cyclopropanes, k_{OH}/k_{add} being > 100 . The marked effect of the carboxylate group is nicely explained in terms of the participation by the neighboring carboxylate group, which interacts strongly with the vacant p orbital of the singlet carbene, resulting in the reduction of the electrophilicity. The competition experiments using two sets of alkenes with different electron density also support the above idea. Thus, **17c** is > 2000 times more reactive to α -chloroacrylonitrile relative to 1-hexene while **17a** is only 3-4 times more reactive. More intriguingly, a Hammett treatment of the addition of **17** to a series of substituted styrenes demonstrates that philicity of the carbene is converted from electrophilic to nucleophilic in going from **17a** to **17c**. The geometries of the singlet state of the parent carboxylate carbene optimized by the ab initio molecular orbital using the STO-3G basis set is very much like that of α -lactone anion, where strong interaction between carboxylate oxygen anion and the vacant p orbital is possible. ESR studies show, however, that both **17a** and **17c** have a triplet ground state with comparable thermal stability and that geometry of the triplet state is not affected by the neighboring carboxylate group.



Chapter 3 describes the effect of neighboring phosphonate group on carbene reactivities. Reactivities of (dimethylphosphonyl)carbenes are shown to be dramatically changed as one substitutes the diester group with the mono anion group. Thus, phosphonate ester carbenes (**18**), generated by photolysis of the corresponding diazo compounds in a binary mixture of 2-methyl-2-butene (or 1-hexene) and methanol, gives cycloaddition products to the alkene and OH insertion products into methanol, the relative reactivities (k_{OH}/k_{add}) being 0.84-3.96. In marked contrast, the "phosphonate anion" carbenes generated from the corresponding sodium salts under the same conditions produces mostly the OH insertion products at the expense of the cyclopropanes, k_{OH}/k_{add} being 16.1-163. The marked effect of the phosphonate group is nicely explained in terms of the participation by the neighboring phosphonate group, which interacts strongly with the vacant p orbital of the singlet carbene, resulting in the reduction of the electrophilicity. The competition experiments using two sets of alkenes

with different electron density also support the above idea. Thus, **18b** is > 340 times more reactive to acrylonitrile relative to 1-hexene while **18a** is only 3.34 times more reactive.

More intriguingly, photolysis of dimethyl α -ketodiazophosphonate in methanol afforded the Wolff rearrangement product and the two hydrogen abstraction product. Photolysis of the corresponding sodium salt gave, however, only the Wolff rearrangement product. The geometries of the singlet state of the parent phosphonate carbene optimized by PM3-UHF(P) method is very much like that of oxaphosphirane anion, where strong interaction between phosphonate oxygen anion and the vacant p orbital is possible. ESR studies show, however, that both **18a** and **18b** have a triplet ground state with comparable thermal stability and that geometry of the triplet state is not affected by the neighboring phosphonate group. LFP studies show that naphthyl(phosphonyl)carbenes (**19**) have a triplet state and that lifetimes of the triplet state in a degassed benzene are 20-37 μ s regardless of the substituents.

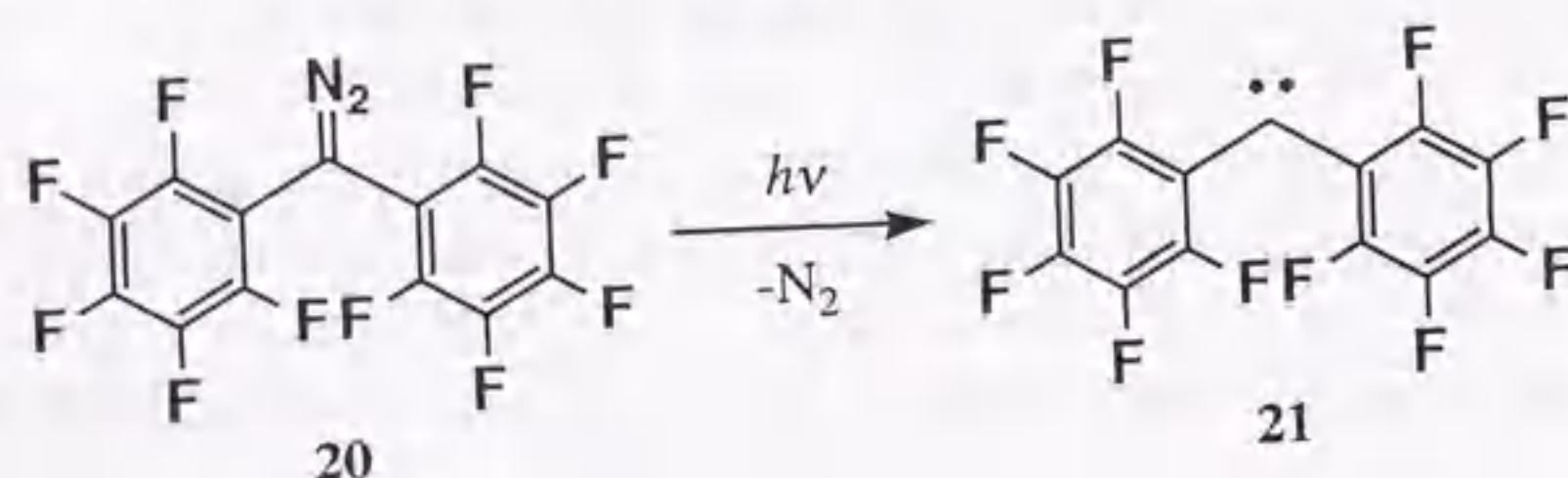


Triplet carbenes are recently attracted as an unit of organic molecules with very high-spin ground states. However, the polycarbenes,⁴⁶⁻⁴⁸ which involve several triplet diphenylcarbene units, are usually highly unstable but can be kept only at cryogenic temperature. Therefore, design of stable triplet diphenylcarbenes is desired.

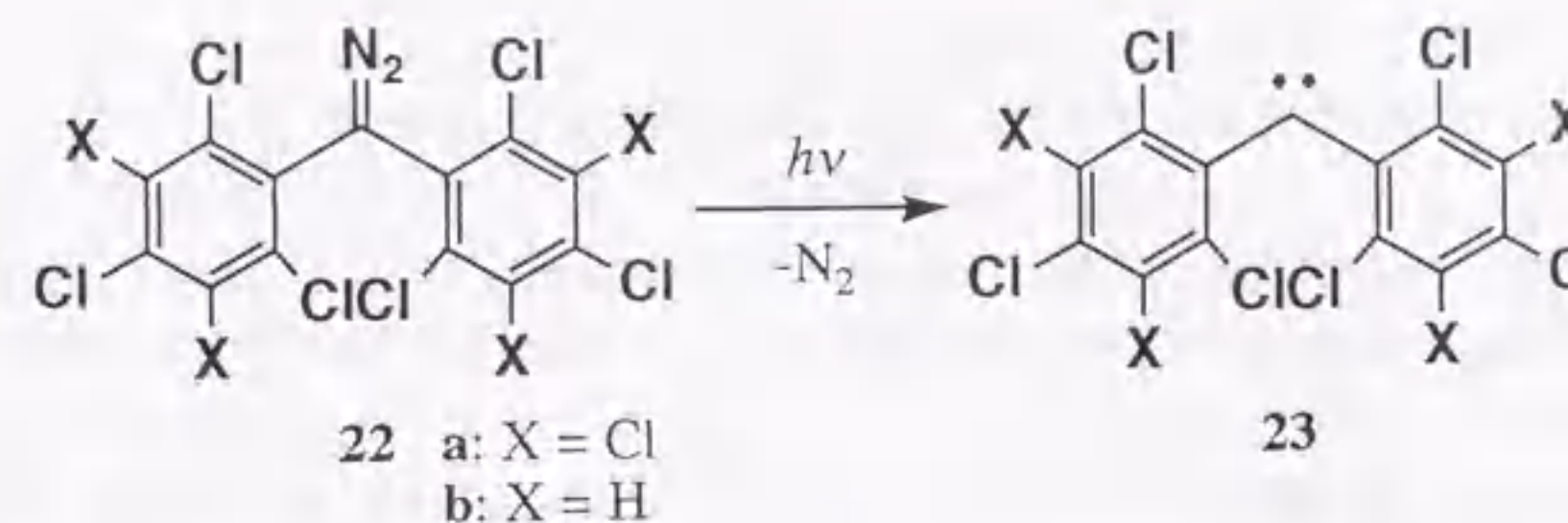
Introduction of some substituents at four ortho positions of diphenylcarbene not only protects the carbene center from some external reagents to make the carbene to be kinetically stable, but also must stabilize the triplet state of the carbene relative to the singlet because of expansion of carbene-carbon bond angle by steric repulsion of the ortho-substituents on a phenyl ring with that on another phenyl ring. In order to isolate a triplet carbene at room temperature, the reactivity of triplet diphenylcarbenes with sterically bulky protection groups was investigated. Thus, in part 2 the steric protection in diphenylcarbene chemistry is discussed.

Chapter 4 describes the chemistry, kinetics, and spectroscopy of decafluoro-diphenylcarbene(**21**). Thus, bis(pentafluorophenyl)diazomethane (**20**) was prepared, and reactivities of **21** generated by photolysis of **20** were investigated not only in terms of product analysis but also by using matrix isolation spectroscopy as well as laser flash photolysis techniques. Product distributions observed in the reactions of **21** in benzene, cyclohexane, and trans-1,2-dichloroethylene suggested that **21** reacted with those substrates with moderate reactivities toward carbene mostly in its singlet state

presumably owing to the increased electrophilicity induced by fluorine substituents while the reaction with the alkane C-H bonds in concerted fashion was retarded partly due to steric effect in the singlet state which thus decayed to the triplet states that underwent predominantly H atom abstraction forming tetraarylethane. Photolysis of **20** in Ar matrix at 10K produced **21** which was observed by IR and UV and shown to react with doped O₂ to produce ultimately perfluorobenzoate by way of the carbonyl oxide and dioxirane, both intermediates being characterized by IR and UV/vis spectroscopy. Laser flash photolysis of **20** in acetonitrile solution produced a transient absorption ($\lambda_{\text{max}} = 320\text{nm}$) due to bis(pentafluorophenyl)methyl radical obviously produced by H atom abstraction of the triplet **21**, which was trapped by oxygen to generate the perfluorobenzophenone oxide showing its absorption maximum at 400nm ($\tau = 5\text{ms}$) and also by 1,4-cyclohexadiene to form the methyl radical with the rate constant of $1.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. The lifetime of the triplet **21** was estimated to be $\sim 1\mu\text{s}$.

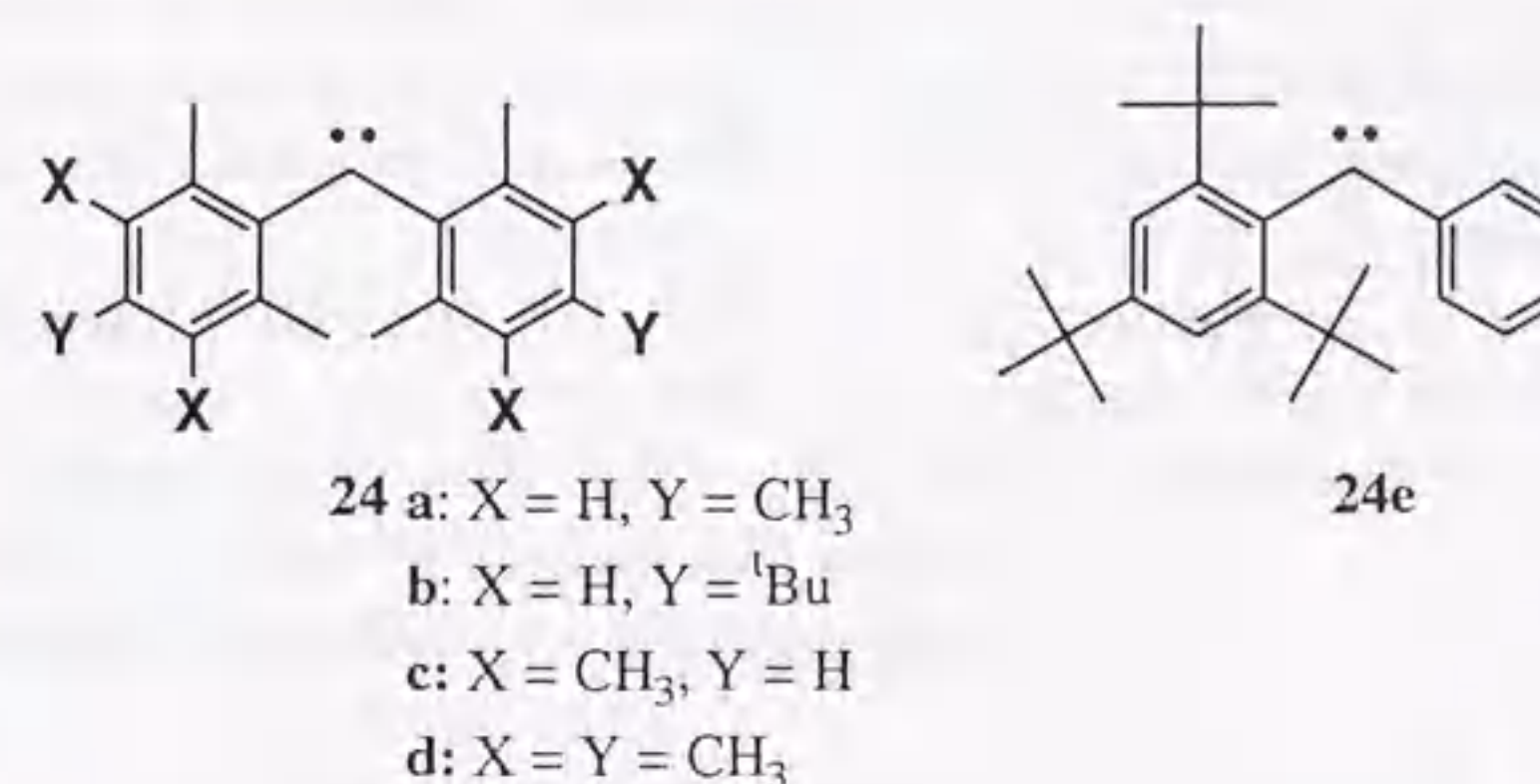


Chapter 5 describes the chemistry, kinetics, and spectroscopy of decachlorodiphenylcarbene (**23a**). Thus, bis(pentachlorophenyl)diazomethane (**22a**) was prepared, and reactivities of **23a** generated by photolysis of **22a** were investigated not only in terms of product analysis but also by using flash photolysis techniques. Although the major reaction found for **23** was dimerization forming perchlorotetraphenylethylene and was essentially similar to that observed for 2,2',4,4',6,6'-hexachlorodiphenylcarbene (**23b**), product distribution clearly indicated that the carbenic center in **23a** is more rigidly protected than that in **23b** by the four ortho chloro substituents which are buttressed by the four meta chloro groups. Irradiation of **22a** in a 2-methyl-tetrahydrofuran glass at 77K resulted in the appearance of the absorption due to triplet **23a** at 356, 493, and 525nm. Flash photolysis of **22a** in benzene solution produced a transient absorption due to **23a** at 357nm, which decayed in second order in accordance with the product analysis data. The rate constant for dimerization of **23a** was determined to be $(2.5 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, 3 orders of magnitude smaller than that of unsubstituted diphenylcarbene. The triplet carbene (**23a**) was trapped by oxygen to generate the perchlorobenzophenone oxide showing its maximum at 390nm ($t_{1/2} = 510 \pm 9\text{ms}$) and also by 1,4-cyclohexadiene to produce bis(perchlorophenyl)methyl radical ($\lambda_{\text{max}} = 376\text{nm}$) with the rate constant of $6.2 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$.



Chapter 6 describes the chemistry, kinetics, and spectroscopy of polyalkyldiphenylcarbenes (**24**) i.e., dimesityl-, bis(4-*tert*-butyl-2,6-dimethylphenyl)-, diduryl-, bis(pentamethylphenyl)-, and (2,4,6-tri-*tert*-butylphenyl)phenyl-carbene. The major reaction found for dimesitylcarbene (**24a**) in degassed benzene was dimerization forming tetramesitylethylene, while bis(pentamethylphenyl)carbene (**24d**) gave insertion into the C-H bond of the *o*-methyl group under the same conditions. Product distribution indicates that the carbenic center in **24d** is more rigidly protected by the four methyl groups at the ortho positions than that in the other methylated carbenes. The reaction observed for (2,4,6-tri-*tert*-butylphenyl)phenylcarbene (**24e**) in benzene, cyclohexane, or even methanol was only insertion into the C-H bond of the *o*-*tert*-butyl group.

The single-crystal ESR studies show that didurylcarbene (**24c**) have a triplet ground state with high thermal stability and that the phenyl rings of the triplet state is perpendicular to each other. The geometries of **24c** optimized by AM1 UHF MO methods also indicate the perpendicular structure. LFP studies show that lifetimes of the triplet state of **24a**, **b**, **c**, **d**, and **e** in a degassed benzene are 667, 1610, 555, 263, and 0.12ms, respectively.



References and Notes

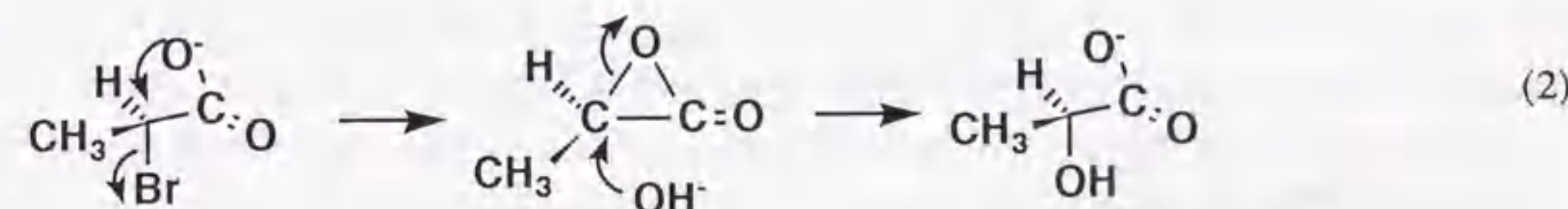
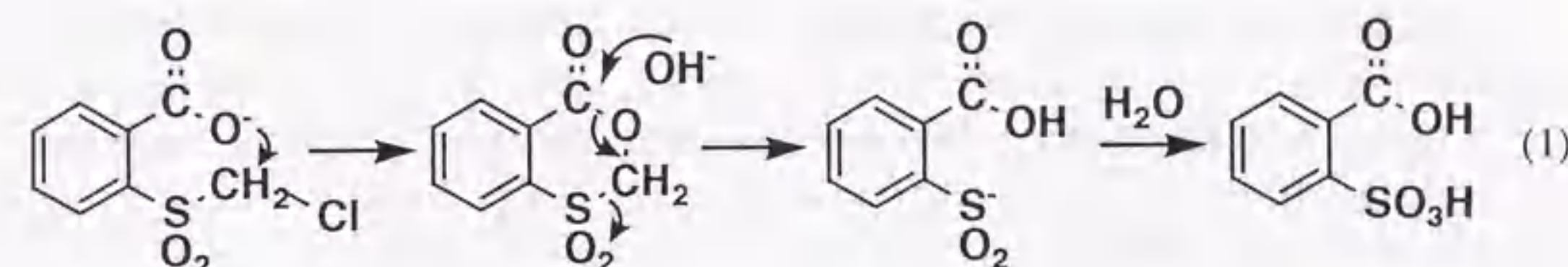
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Part 1

Neighboring Group Participation in Carbene Chemistry

What is the most dramatic and therefore impressive effect of substituents in organic reactions is neighboring group participation¹⁻³ where the intramolecular association of one group in a molecule exerts a dramatic effect on the reaction course of the other. Thus, in the nucleophilic displacement (S_N) reaction, the reactions proceed particularly rapidly and/or with retained stereochemistry when the nucleophile and the leaving group are in the same molecule. In these molecules, internal nucleophiles become bonded (fully or partially) to the electron-deficient center for an interval of time during the reaction's progress. For example, *o*-(chloromethylsulfonyl)benzoate undergoes hydrolysis quite easily under the conditions where its para isomer is completely inert (eq 1),⁴ and the hydrolysis of α -bromopropionate proceeds with retention of configuration of the α -carbon (eq 2).⁵ These results are nicely explained in terms of intramolecular



displacement leading to lactones which subsequently undergo attack by the solvent nucleophiles. Such intramolecular displacement, which has been termed anchimeric assistance or neighboring group participation, occurs not only in appropriate organic systems but also in many biological processes.

In carbene chemistry,^{6,7} although substituent effects have sustained a high level of attention over the past 20 years, the effect of substituents which are directly bound to, or conjugated with the carbene center has been of primary interest, and no study of such magnitude has been made for the effect of substituents which are insulated from direct conjugation with the carbenic atom.

Moreover, the effect of neighboring groups on the reactivity of carbene⁹ has been much less dramatic than that in carbenium ion chemistry. This is apparently because carbenes are usually much less electrophilic than carbenium ions. Another reason which should be pointed out here may be that the internal nucleophiles which have been used in carbene reactions are heavily weighted with neutral heteroatom substituents, e.g., ether, carbonyl and halogens.⁸

It is rather surprising to note here that little is known about the effect of neighboring anionic groups such as carboxylate, phosphonate, or sulfonate anions, all of which have been known to act as the most effective participants in the nucleophilic displacement reaction.² One would easily expect that such anionic groups should exert a much more dramatic effect even upon the reactivities of the electrically neutral six electron companion, carbene.

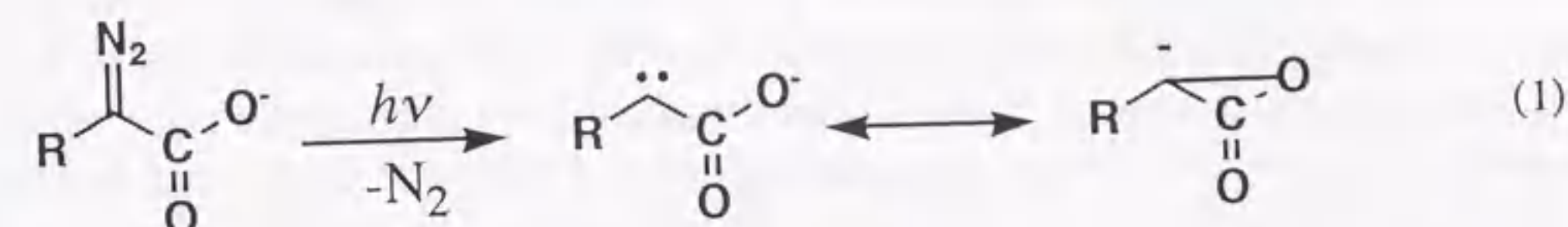
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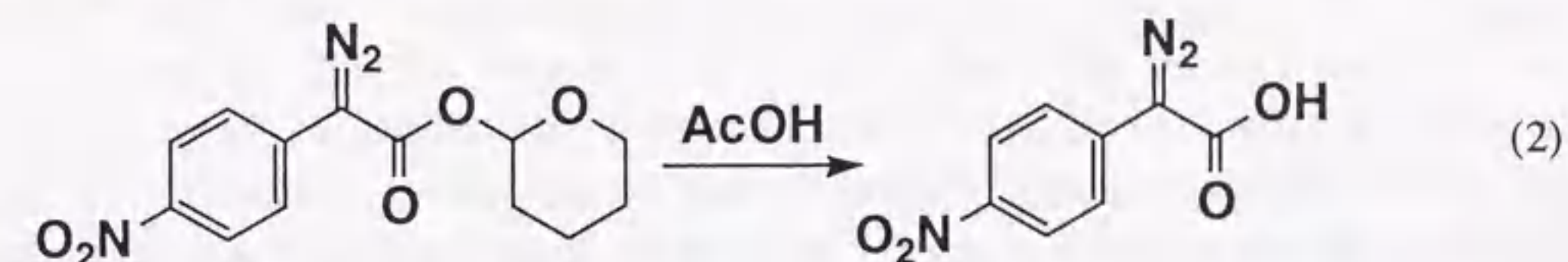
Chapter 2 Effect of Neighboring Carboxylate Group on Carbene Reactivities¹

2-1 Introduction

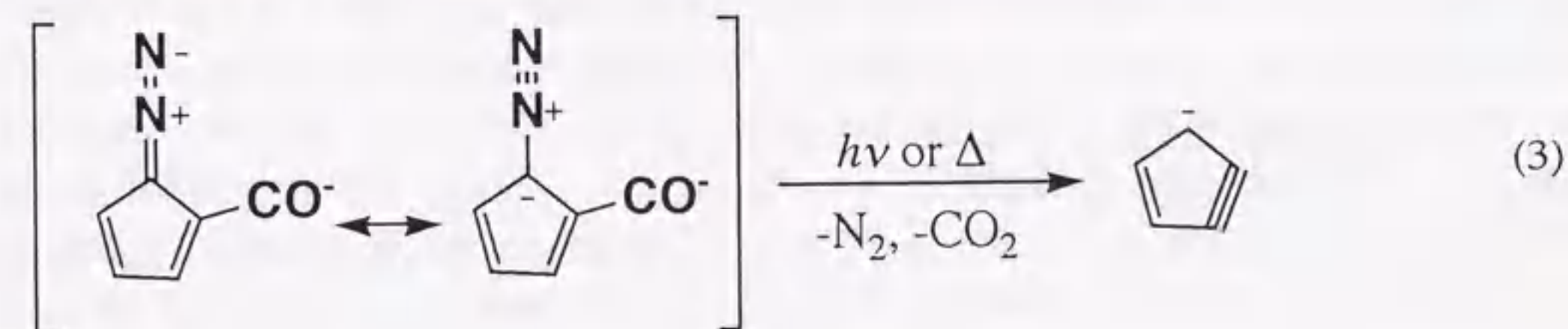
In this chapter, effects of neighboring carboxylate group on carbene reactivities are discussed. Thus, we have examined the chemistry of carboxylate carbenes generated photochemically from diazo carboxylic acid derivatives (eq 1).



Although it is expected that a carboxylate anion group is one of most effective participants on carbene reaction, the generations of carbenes with carboxylate groups, so far, were scarcely reported. Thus, in 1969, Schank have reported the successful preparation of α -diazocarboxylic acid from the corresponding tetrahydropyranyl ester (eq 2).² Treatment of the ester with acetic acid gave α -diazo-4-nitrophenylacetic acid as a yellow solid. However, no attempts to generate carbenes by photolysis or thermolysis of this diazo carboxylic acid and the anion derivatives have been made.

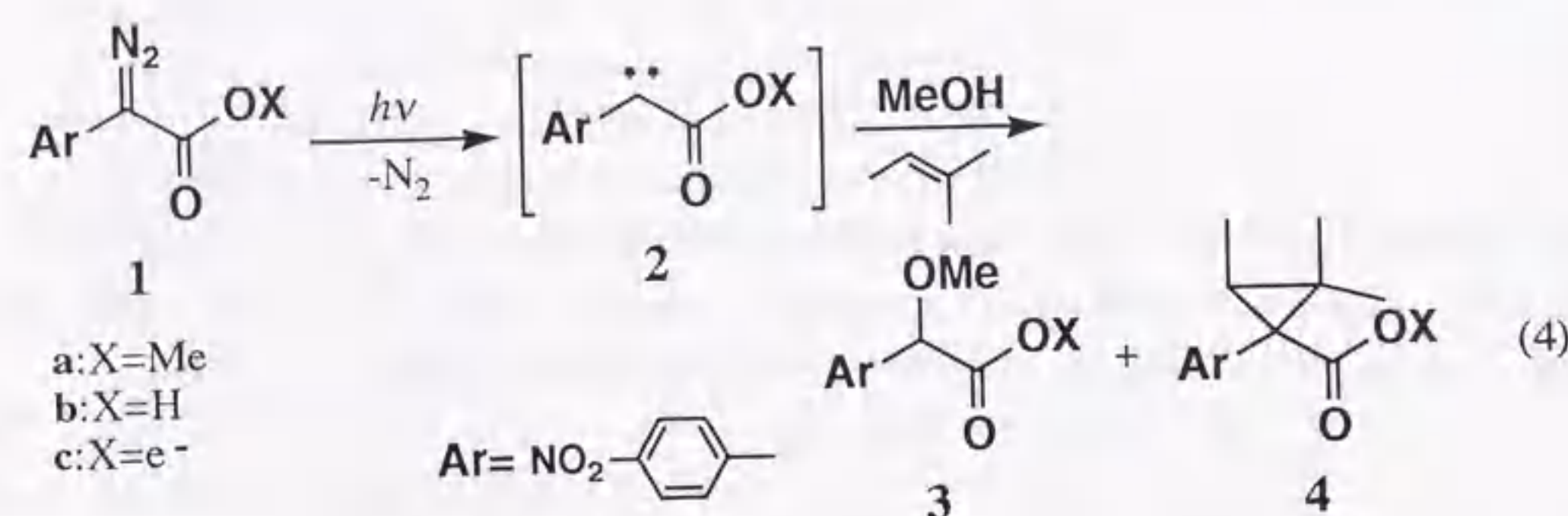


Only one example of decomposition of a diazo carboxylate was reported in 1971. Thus, Martin et al. have described the preparation and the reaction of the diazocyclopentadiene carboxylic acid and the corresponding salt.³ The thermal or photolytic decompositions of the diazocarboxylate released a nitrogen and a carbon dioxide to give dehydrocyclopentadienyl anion (eq 3). In this case, however, it seems that the carboxylate carbene was not generated since elimination of a nitrogen and a carbon dioxide would take place in this compound at the same time.



2-2 Product Analysis

(1) *Insertion-Addition Selectivity* Irradiation of methyl (*p*-nitrophenyl)diazoacetate (**1a**) in a 1:3.5 binary mixture of methanol and 2-methyl-2-butene afforded α -methoxyacetate **3a** and cyclopropanes **4a** (as a mixture of syn and anti isomers) in 7% and 71% yields, respectively. These products are apparently derived from photolytically generated carbene **2a**, which either underwent insertion into the OH bond of methanol or added to the double bond of the alkene. Similar irradiation of the corresponding free diazo acid **1b**, followed by CH_2N_2 treatment gave essentially the same product mixtures. When the sodium salt of **1b** was irradiated under the same conditions, followed by neutralization and esterification, however, the formation of the cyclopropane was almost completely eliminated and α -methoxyacetate **3a** became the major product isolated (eq 4). Similar irradiation of **1b** in the presence of 2 mol excess of triethylamine also



resulted in the almost exclusive formation of the OH insertion product (Table 1). It is quite probable that the "carboxylate" carbene **2c** must be generated under these conditions since either the sodium diazoacetate or the amine salt of diazoacetic acid was quantitatively recovered unchanged in the dark under the otherwise same conditions.

OH insertion-addition selectivities ($k_{\text{ins}}/k_{\text{add}}$) were calculated by means of the well-established equation of Doering and Henderson⁴ (eq 5) where P_i and P_a are the moles of the OH insertion product and the cyclopropanes and I_i and I_a are the initial moles of methanol and the butene, respectively. The data are listed in Table 2. Included in the table for comparison are insertion-addition selectivities of the carbenes having various

$$k_{\text{rel}} = \frac{k_{\text{ins}}}{k_{\text{add}}} = \frac{P_i}{P_a} \frac{I_a}{I_i} \quad (5)$$

Table 1. Photolysis^a of (4-Nitrophenyl)diazoacetate (**1**) in a Binary Mixture (1:3.5) of Methanol-2-Methyl-2-butene

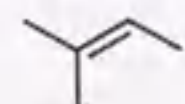
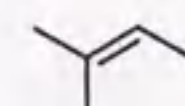
diazo ester (X)	yield, ^b %	
	3	4 (syn:anti) ^c
1a (Me)	9.2	90.8 (1:0.89)
1b (H)	12.3	87.7 (1:1.2)
1c (e ⁻) ^d	96.4	3.6 (1:0.50)
1c (e ⁻) ^e	>99.9	<0.1 (-)

^aIrradiations were carried out on 5 mL of degassed solutions with 300W high-pressure mercury arc equipped with a Corning CS-052 filter. ^bDetermined by GC on the basis of **1** used. ^cStereoselectivity of cyclopropanation, syn-aryl/dimethyl. ^dDiazo acid(**1b**) was irradiated in the presence of 5 mol excess of triethylamine. ^eSodium diazoacetate (**1c**) was used.

neutral ester residues X (**2d-h**). It is evident from the data in the table that the neighboring carboxylate group exerts a tremendous effect on the relative reactivities of carbene **2**. Thus, the carbene derived from **1c** is shown to be some 300 times more reactive toward methanol, relative to alkene, than those derived from the diazo ester (**1a,d-h**) and the diazo acid (**1b**). A similar dramatic effect of the carboxylate group was observed in the competition reaction using benzene instead of the butene and ethyl mercaptan instead of methanol (Table 2).

The difference in the reactivity caused by the carboxylate group is obviously too great to be attributable to a difference in inductive, conjugative, or steric effects, but can be better explained in terms of the neighboring group participation. It is well documented in S_{N} reactions that the carboxylate group functions as a neighboring group participating in the reaction while the carboxy and ester groups lose a great deal of their effectiveness as a participants.⁵ It is quite reasonable, then, to assume that the neighboring carboxylate group can also interact with the vacant p orbital of a singlet carbene. Such interaction should greatly reduce the electrophilicity of the carbene toward external reagents by filling its vacant p orbital. (Methoxycarbonyl)arylcarbenes (**2a**) which we used in this study should be classified as typically electrophilic carbenes and therefore react by accepting electrons from the external substrates, e.g., methanol and butenes, into the empty p orbital. Once a carboxylate group is introduced, the vacant p orbital interacts effectively with the internal carboxylate oxygen anion as depicted by **2c** in Scheme 1 and therefore is no longer available to the external

Table 2. Effects of Carboxylate Groups on the Insertion-Addition Selectivities of Carbenes (**2**)^a

diazo ester (X)	substrates		relative reactivity: k_A/k_B^b
	A	B	
1a (Me)	MeOH		0.34
1b (H)			0.48
1c (e ⁻) ^c			>100
1d (ⁿ C ₆ H ₁₃)			0.37
1e (^t Bu)			0.35
1f (CH ₂ CF ₃)			0.21
1g (CH ₂ CN)			0.30
1h (CH ₂ CH ₂ CN)			0.20
1a (Me)	MeOH	PhH ^d	13
1c (e ⁻) ^c			>1000
1a (Me)	EtSH ^e		5.1
1c (e ⁻) ^c			>100

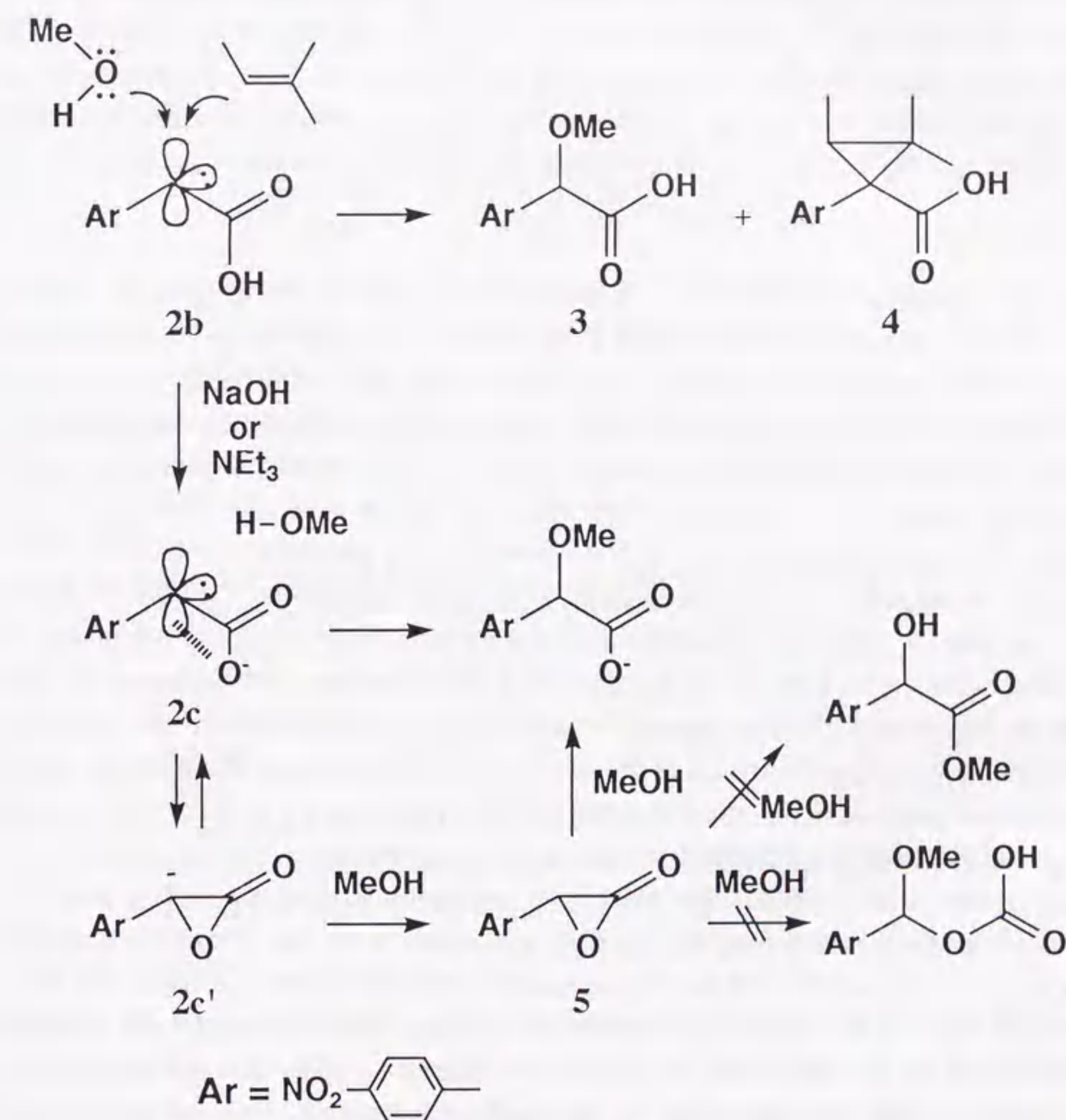
^aCarbenes were generated in a binary mixture of two substrates A and B. ^bCalculated from the mole fraction of products and substrates. ^cDiazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine. ^dNorcaradienes were formed. ^eSH insertion product was formed.

reagents. In other words, the carbenes tend to behave as nucleophiles via the carbenic lone pair rather than as electrophiles. Simple alkenes such as 2-butene are efficient trapping agents for many electrophilic carbenes, but not always reactive toward nucleophilic carbenes.⁶ On the other hand, methanol is known to be very reactive to both electrophilic and nucleophilic carbenes, since the former carbene can attack the lone pair electron of oxygen while the latter undergoes protonation.⁷ Thus, the carboxylate carbene (e.g., **2c**) showed enhanced reactivity toward alcohol relative to the alkenes (Scheme 1).

It may be possible that carbene **2c** can be covalently bonded to the internal carboxylate group leading to the formation of an α -lactone anion **2c'** which then undergoes protonation to give α -lactone **5**.⁷ Subsequent nucleophilic cleavage of **5** by a nucleophile, e.g., methanol, affords the formal OH insertion product. Neither α -

hydroxyacetate nor carbonate, both of which were expected to be formed according to the above mechanism, were detected in the present reaction mixture, however. This is not surprising since α -lactones generally undergo⁸ nucleophilic attack on the carbon adjacent to the C=O group to give an α -substituted acetate, e.g., **3**. For instance, treatment of α -(bromophenyl)acetic acid in methanol with triethylamine produced α -(methoxyphenyl)acetic acid, which could be formed from α -lactone intermediate.⁸

Scheme 1

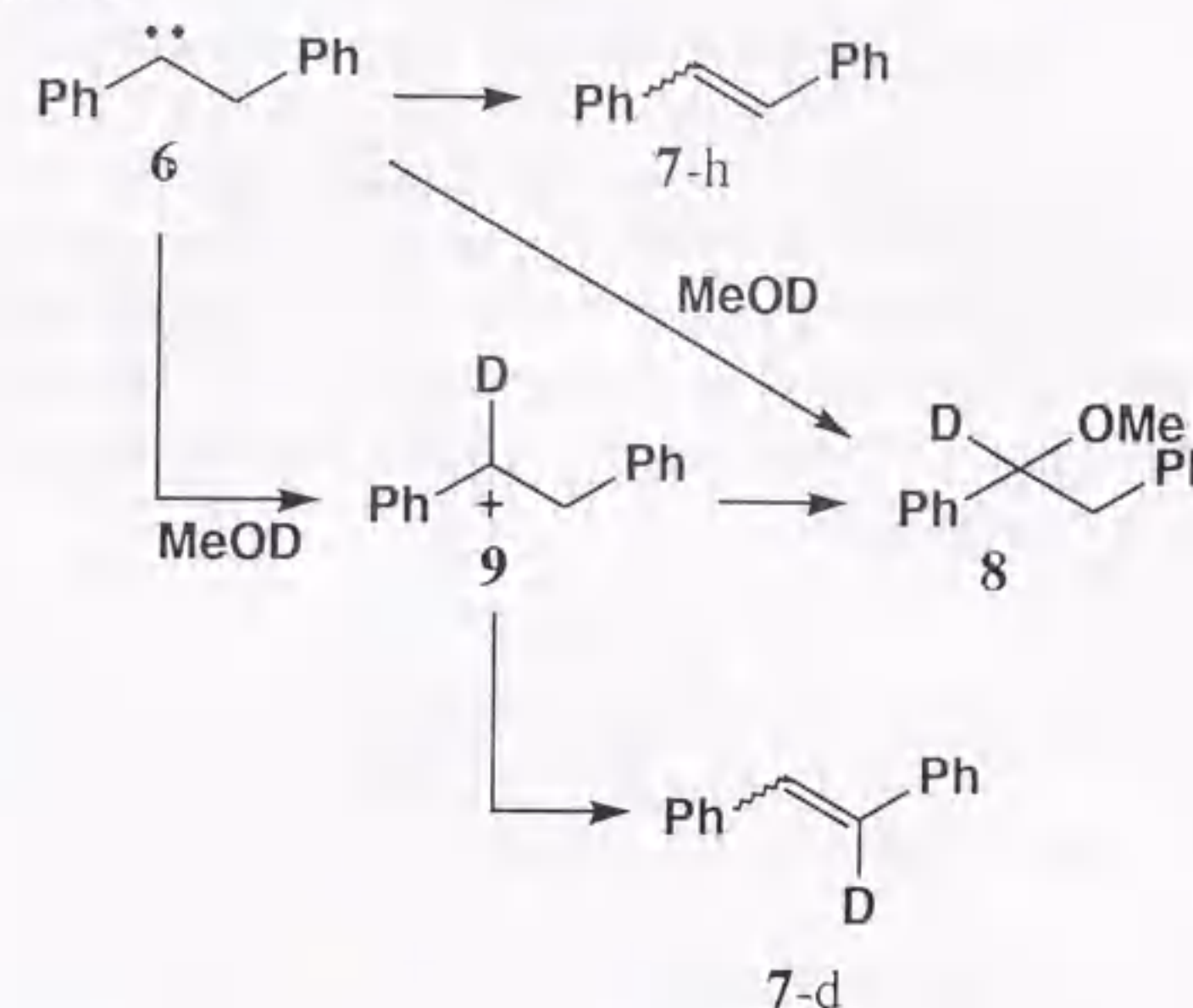


It has been reported⁹ that α -lactones tend to polymerize in the absence of efficient trapping agents to afford polyesters, which undergo alcoholysis upon heating in alcohol to give α -alkoxy acid. So we irradiated the amine salt of diazo acid (**1b**) in anhydrous

benzene which does not react either with carboxylate carbene **2c** nor with α -lactone **5**. No trace of α -methoxy acid **3c** was formed, however, when the photolysis mixtures were refluxed with methanol. The only volatile products detected were *p*-nitrobenzoic acid (5.9%) and *p*-nitrobenzaldehyde (4.2%), both of which were presumably derived by oxidative cleavage of the carboxylate-participating carbene. Since the intermediates generated by irradiation of the neutral diazo compound (**1a** and **b**) were much less susceptible to the oxidation under similar conditions, the formation of these oxidative products can be interpreted as indicating the anionic nature of the intermediate involved in the photolysis of **1c**. Although the results can not afford clear evidence for the presence of α -lactone, its intervention cannot be rigorously excluded. However, the results cannot tell us whether the carboxylate-participating carbene contains a full or partial bond between the divalent carbon and carboxylate oxygen. In order to obtain more insight into the nature of the intermediate, the following labeling experiments were done.

(2) *Mechanism of OH Insertion* It has been shown⁹ that the philicity of carbene toward alcohols can be roughly judged from deuterium incorporation in the alkene. Carbenes with readily accessible 1,2-hydrogen migration channels incorporated deuterium into the alkene in the presence of MeOD. Thus, 1,2-diphenyl-ethylidene (**6**) generated in MeOD afforded *E*- and *Z*-stilbenes (**7**) in which deuterium was incorporated, along with 1-deuterio-1,2-diphenylethyl methyl ether (**8**). The results can be interpreted as indicating that the phenylcarbenes(**6**) generated in alcohol either undergo 1,2-H migration to yield the stilbenes (**7-h**) or are protonated¹⁰ by the alcohol to give carbocation **9**, which subsequently eliminates a proton and produces the alkene or undergoes nucleophilic trapping by the alcohol to produce the ether (Scheme 2). The findings do not indicate that all the ethers are formed via protonation of the carbene. More probably it implies that some of the carbenes should undergo electrophilic attack on the oxygen lone pair of the electron since the phenylcarbenes, e.g., **6**, are recognized to be typical electrophiles. However, it should be noted that the extent of incorporation into the alkene should reflect the philicity of carbenes toward alcohol. Thus, we examined the effect of the neighboring carboxylic groups on the extent of deuterium incorporation in alkene formed from 1-carboxyl-2-phenylethylidene (**11b**) in MeOD in order to get more evidence for the proposed change in the mechanism for OH insertion as it goes from **2a, b** to **2c**. The results are summarized in Table 3 which includes the corresponding ester carbene **11a** for comparison purposes. Intriguing effects of carboxylate anions were observed not only in the percentage of deuterium incorporation but also in product distributions. Thus, the ester carbene **11a** derived from **10a** afforded the alkenes (**12**) almost exclusively as a result of 1,2-H migration (eq 6). This is in accord with the general observation¹¹ that the singlet carbenes with readily accessible

Scheme 2



intramolecular reaction channels are not efficiently trapped by external reagents. Once the carboxylate group is introduced, however, the carbene **11b** becomes relatively

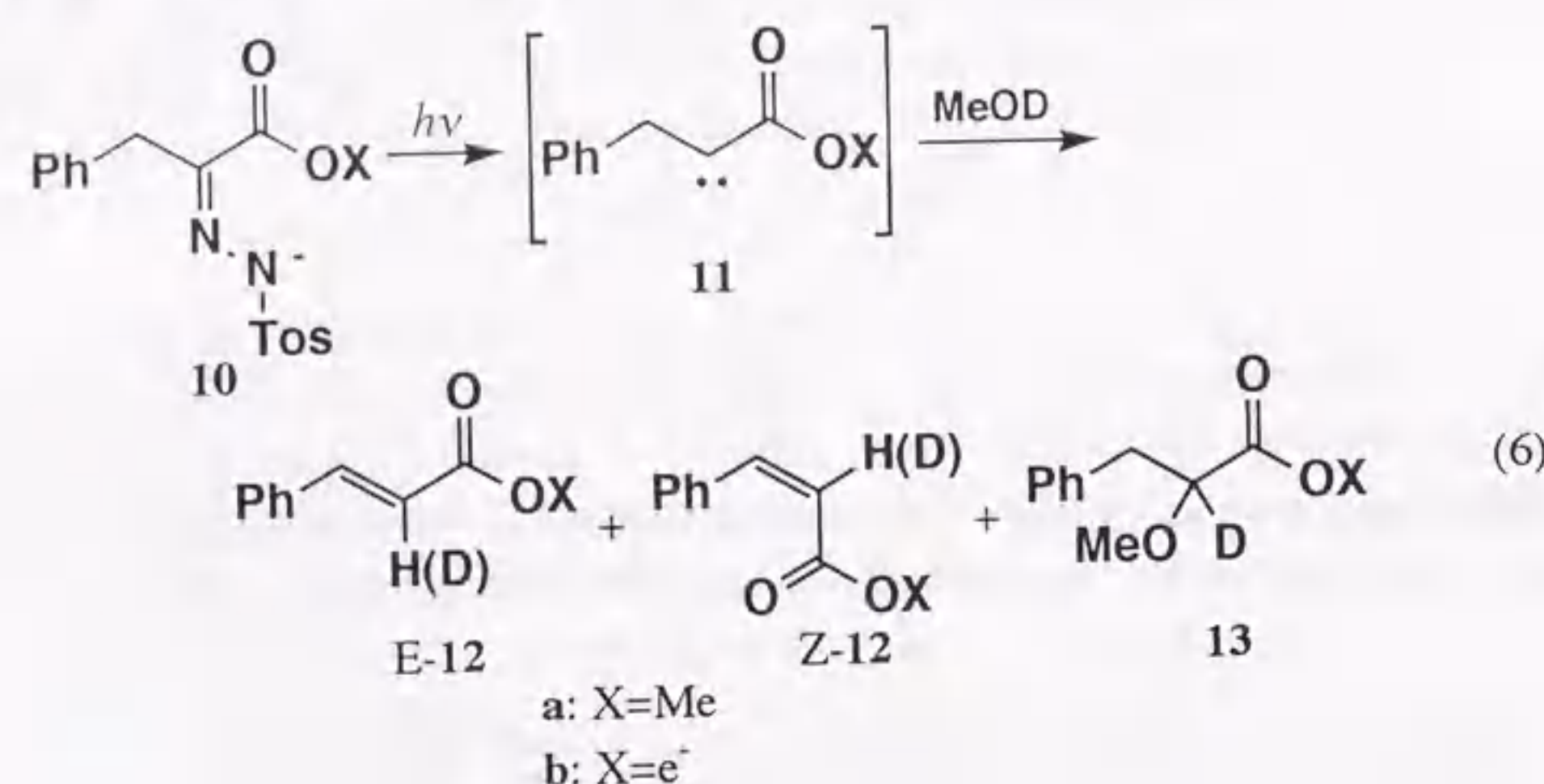
Table 3. Photolysis^a of Sodium 2-Tosylhydrazonate **10** in MeOD

10 (X)	yield, ^b % (D _{incorp} , ^c %)		
	<i>E</i> -12	<i>Z</i> -12	13
a (Me)	48.1 (<0.1)	42.5 (<0.1)	1.4 (~100)
b (e ⁻)	6.6 (28.9)	7.4(1)	27.9 (~100)

^aSee footnote a to Table 1. ^bDetermined by GC on the basis of **10** used. ^cDetermined by GC-MS.

efficiently trapped by methanol, giving α -methoxybenzylacetate (**13**) at the expense of the alkenes (**12**). This is again explained in terms of the neighboring carboxylate group participation by which the electrophilicity of the carbene is greatly reduced. The mechanism¹² of the 1,2-H shift involves an electrophilic pull of hydride through the vacant p orbital of the singlet carbene. Thus, the decrease in the 1,2-H shift again reflects the reduction of electrophilicity, most probably as a result of the neighboring carboxylate group participation. The extent of deuterium incorporation into **12** is

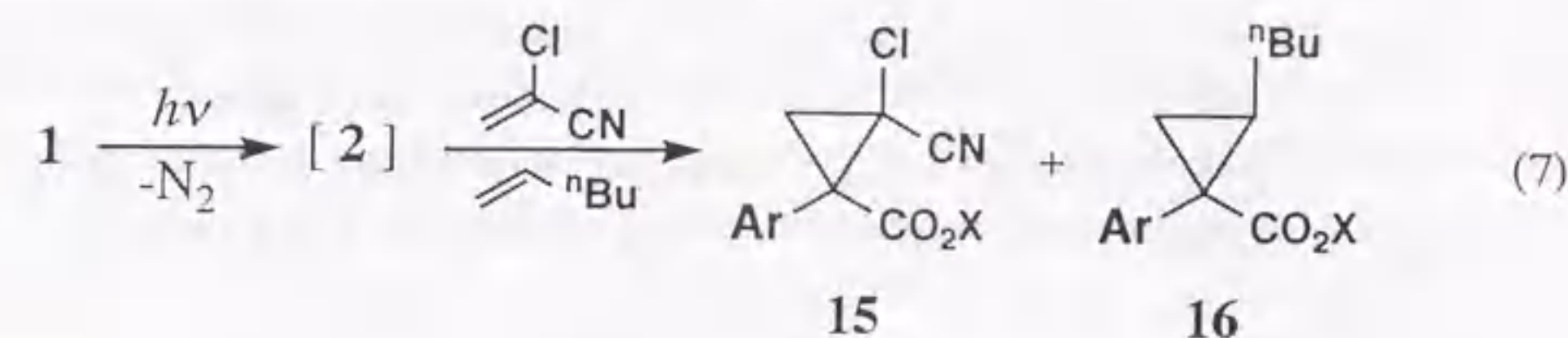
markedly increased as one changes the neighboring group from ester to carboxylate anion, as was to be expected. The deuterated alkenes apparently arise from a carbocation ($\text{PhCH}_2\text{C}^+\text{HCO}_2^-$, **14**) which should be formed by protonation of carbene **11b** or α -lactone anion derived from **11b**, or both. Thus, the above results provide evidence to support the idea that the carboxylate-participating carbenes should undergo protonation by methanol at least more extensively than the ester carbene. The dominant formation of the unlabeled alkenes (**12**) in the MeOD run indicates that not all the carboxylate carbenes (**11b**) react in the participated forms at least in this carbene system. In other words, some of them undergo 1,2-H migration before they are affected by the neighboring carboxylate group.



(3) *Selectivity in Cyclopropanation* The electrophilic and nucleophilic character of carbenes are not absolute. Any carbene can show both electrophilic and nucleophilic characteristics depending on the nature of reagents with which the carbene reacts. Carbenic philicity¹³ has been relatively well characterized on the basis of reactivities toward electron-rich and electron-poor alkenes. Thus, it is of immediate importance to know how the philicity is affected by the neighboring carboxylate participation as based on cyclopropanation selectivity.

Since the carboxylate-participating carbene showed little tendency to react with simple alkenes such as 2-methyl-2-butene, we examined its reactivity toward an electron-deficient alkene, e.g., acrylonitrile. Although conceptually simple, such studies using diazo compounds as precursors for carbene are complicated by the thermal 1,3-dipolar cycloaddition of the diazomethane, especially to electron-poor alkenes, which give pyrazoline that spontaneously decomposes into cyclopropane.¹⁴ Fortunately, however, the diazo ester as well as the acid salt **1** were found to be relatively unreactive

toward these alkenes. For example, when the diazo compound and chloroacrylonitrile were allowed to stand for 2 h at 50°C, only a small amount (<5%) of the expected cyclopropanes (**15**) were formed (eq 7). Irradiation of the diazo compounds in a binary



mixture of 1-hexene and the acrylonitrile were thus carried out at -10°C for 0.5 h, where the thermal route to cyclopropanes was negligible. The selectivities determined from the product and substrate ratio by using eq 5 for the carbenes of carboxylic acid derivatives are listed in Table 4, which clearly indicates that the philicity was dramatically changed as the ester group was converted to a carboxylate anion group. Thus, the carbene derived from **1c** is shown to be some 600 times more reactive toward chloroacrylonitrile, relative to 1-hexene, than those derived from **1a** and **1b**. The carboxylate-participating carbene is shown to be essentially unreactive toward simple alkenes such as hexene, as has been observed for other typical nucleophilic carbenes, e.g., dimethoxycarbene¹⁵ and (dimethylamino)methoxycarbene.¹⁶

Table 4. Effects of Carboxylate Groups on the Selectivity in Cyclopropanation^a

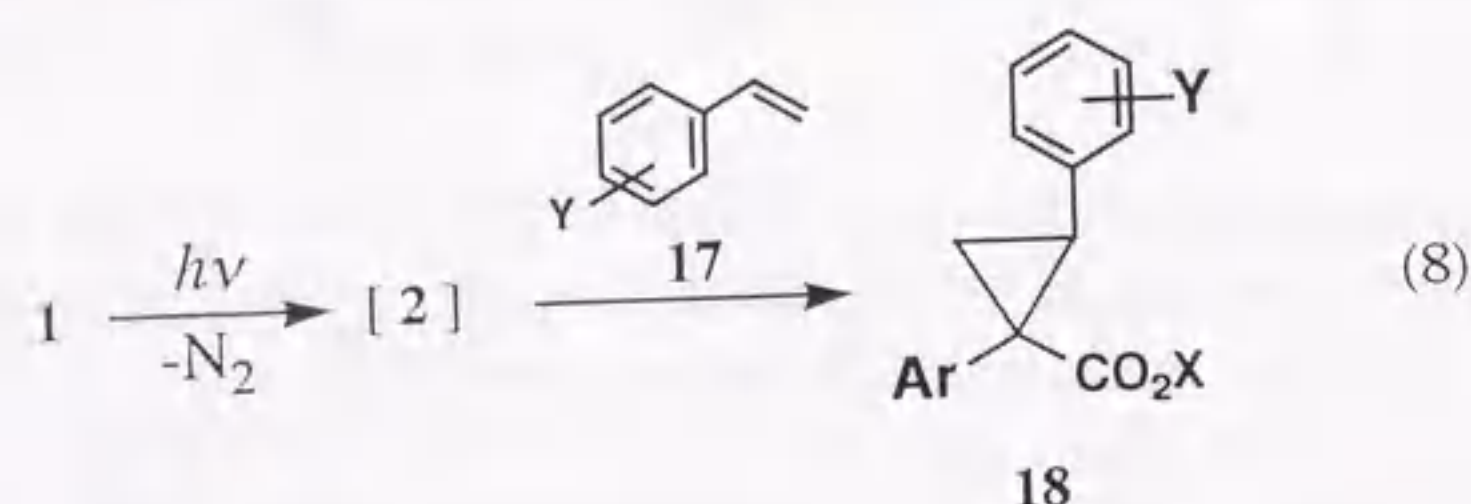
diazo ester (X)	yield, ^b %		k_a/k_b^c
	15	16	
1a (Me)	54.9	43.2	3.51
1b (H)	42.9	48.3	2.48
1c (e ⁻) ^d	78.9	<0.1	>2000

^aSee footnote a to Table 1. ^bDetermined by GC. ^c $k_{\text{chloroacrylonitrile}}/k_{\text{1-hexene}}$ calculated from the mole fraction of products and substrates.

^dDiazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine.

(4) *Hammett Studies* The philicity of carbenes has been examined more quantitatively and generally by a Hammett treatment of the addition of carbene to a

series of substituted styrenes. Thus, to date, a variety of carbenes¹⁷ has been classified according to the Hammett ρ values estimated from the addition of carbenes to styrenes and therefore a philicity spectrum among some typical carbenes can be easily obtained. It is desirable then, to know more quantitatively the extent of nucleophilicity caused by the neighboring carboxylate group. More importantly, a Hammett treatment would be expected to provide evidence that philicity of the carbene can be converted from electrophilic to nucleophilic by changing the carbenic substituent from an ester group to an acid anion. Fortunately, the carboxylate-participating carbene adds to a series of



substituted styrenes (**17**) to give cyclopropanes (**18**) and hence the Hammett study was possible (eq 8). The relative reactivities were determined by a competition method in which two styrenes were allowed to compete for a limited amount of the carbene. In a typical run, the precursor diazo compounds were irradiated with a high-pressure mercury lamp through a Corning CS-052 filter (>350 nm) at -10°C for 0.5 h. In this run, the ratio of styrene mixed with benzene to the diazo compound was more than 20 to 1. Control experiments again showed that the 1,3 dipolar addition of the diazo compounds was negligibly small ($<5\%$) under these conditions.^{15a} The relative reactivities of the styrenes were then calculated by the conventional equation⁴ (eq 5). The reactions were carried out in duplicate and the results are presented in Table 5, along with the data for the ester carbene **2a**.

Inspection of the results in Table 5 indicates immediately that the ester carbene **2a** undergoes electrophilic cycloaddition while attacking **17** at the C=C bond, whereas the participating carbene undergoes nucleophilic cycloaddition at that bond. The relative rate constants were then correlated with σ parameters according to Hammett. The ρ values of these Hammett plots (Figure 1) were calculated by a least-squares analysis to be $\rho = -0.75$ ($r = 0.954$) for the ester carbene and $\rho = +0.35$ ($r = 0.834$) for the participating carbene. Thus, the present results clearly indicate that the electrophilic ester carbene is converted to nucleophilic by simply substituting ester residue with hydroxide.

To date, some carbenes have been classified as nucleophiles^{17g-i} by the Hammett criterion, although pyrazoline intermediacy is not always rigorously excluded. In this

Table 5. Relative Rate Constants for the Addition of the Carbenes (**2a** and **2c**) to Substituted Styrenes (**17**)

Y in YC ₆ H ₄ CH=CH ₂ (17)	k_Y/k_H^a	
	2a (X=Me)	2c (X=e ⁻) ^b
4-CH ₃	1.46	0.98
H	1.00	1.00
4-Cl	0.61	1.11
4-Br	0.61	1.07
<i>m</i> -Cl	0.62	1.13
<i>p</i> -CN	0.25	2.27

^aAverage of two GC Determinations. ^bDiazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine.

sense, the present positive ρ value of +0.35 for **2c** provides a clear quantitative demonstration of the nucleophilicity of carbene affected by the neighboring carboxylate group. On the other hand, it is not clear whether only the singlet state of the carbene is responsible for the observed positive ρ value since styrenes are known^{18,19} to be

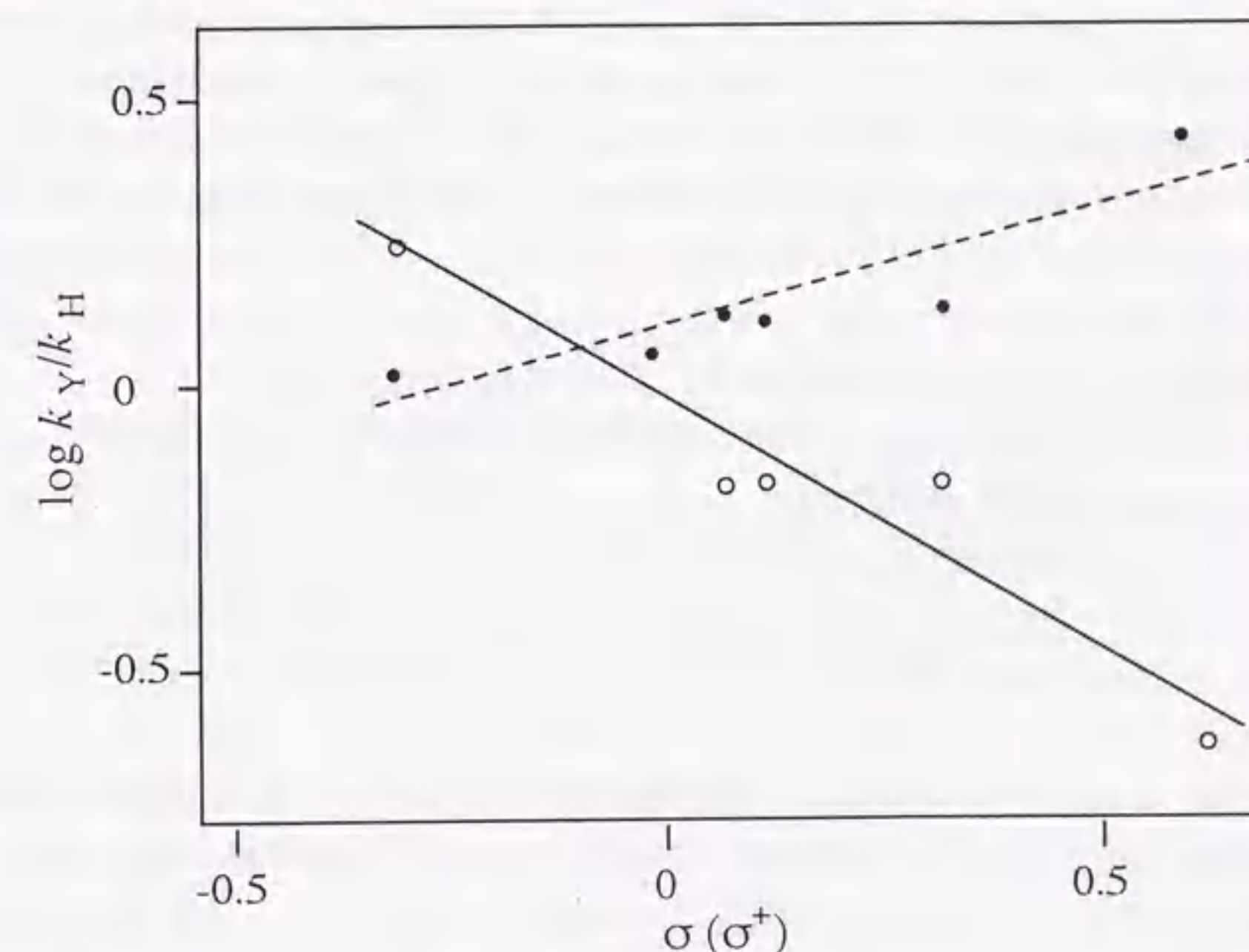


Figure 1. Plot of $\log k_{rel}$ vs σ values for the reactions of carbenes **2a** (—) and **2c** (--) with substituted styrenes.

efficient scavengers for triplet species. However, Hammett studies of addition of triplet carbenes, i.e., 9-xanthylidene^{17j} and diphenylcarbene,^{17k} to styrenes have revealed that triplet arylcarbenes add to styrenes as ambiphiles. The ambiphilicity can be reasonably attributed to electron-donating or electron-withdrawing substituent stabilization of the benzylic radical center in the triplet 1,3-diradical, which is an obligatory intermediate in the triplet carbene addition.^{17k} This rationalization is in accord with indications that benzylic radicals²⁰ and benzylic 1,3-diradicals²¹ can be stabilized by either electron-donating or electron-withdrawing substituents. The linear Hammett relationship even with electron-donating groups observed in the present study suggests that the triplet state would not be involved as a major intermediate and that the singlet state which is able to be affected effectively by the participating carboxylate group (vide infra) is responsible for the observed positive ρ value.

It is quite interesting to compare the ρ value of carbene **2c** with those of carbenes which have been classified^{17g-i} as nucleophiles by Hammett studies. Cycloheptatrienyliene^{17g} showed the largest positive ρ value of +1.05 among the carbenes studied and therefore is now known as the most nucleophilic carbene in the spectrum of Hammett ρ values. Obviously, the nucleophilicity of cycloheptatrienyliene is believed to be caused by incorporation of the vacant p orbital into an aromatic system. The comparison of these ρ values suggests that the nucleophilicity of **2c** is considerably less than that of cycloheptatrienyliene. This means that the overlap between the vacant p orbital and the neighboring carboxylate group in **2c** is less efficient than that of the incorporation of the vacant p orbital into the aromatic system in cycloheptatrienyliene. Apparently, the participation in **2c** would require the formation of a strained, three-membered ring, reducing the effectiveness of the neighboring group participation.

2-3 Detection of Triplet Carbenes by ESR Spectroscopy

Almost all arylcarbenes are known to be triplets in their ground states.²² However, if the perturbation of the electronic structures of the carbene by the neighboring carboxylate group is large enough, it will be possible for the ground state of the carbene **2c** to be a singlet. Thus, in order to assign the ground state for the carbenes and investigate the structures of their triplet states, we tried to measure the ESR spectrum of the carbenes **2**.

Irradiation of methyl (*p*-nitrophenyl)diazoacetate (**1a**) in a rigid glass of ethanol at 15 K in an ESR cavity with Pyrex-filtered UV light produced signals in the range from 140 mT to 820 mT in the X-band ESR spectrum (microwave frequency = 9.296 GHz). The intense signal at 332.7 mT is assigned to doublet radicals presumably formed from chemical reactions of the carbene with matrices. The signals at 147.3, 441.7, 594.7 and 815.2 mT are assigned to Hz, Hx, Hy, and Hz transitions of a triplet, respectively. The

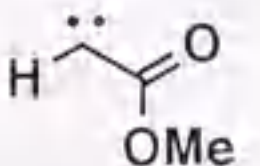
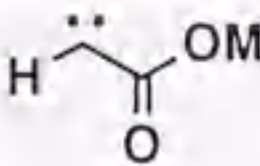
weak but significant signals detected at 465.2 and 576.0 mT show the presence of a minute quantity of another triplet species. Two Hz transitions of the minor triplet species are thought to overlap with those of the major species. The zero-field splitting (zfs) parameters are calculated to be $D = 0.4530 \text{ cm}^{-1}$ and $E = 0.0377 \text{ cm}^{-1}$ for the major species, and $D = 0.4521 \text{ cm}^{-1}$ and $E = 0.0274 \text{ cm}^{-1}$ for the minor species, respectively. It is quite reasonable that these triplet species are regarded as triplet carbenes in their triplet states, because their zfs parameters are in the range of the values reported on various arylcarbenes.²² Thus it is concluded that the irradiation of **1a** in a rigid glass produces two isomeric triplet carbenes which are distinguished by their E values.

In contrast, the spectra recorded after the irradiation of sodium (*p*-nitrophenyl) diazoacetate (**1c**) contained a series of signals due to a single triplet carbene together with an intense doublet signal. It is noted that the resonance positions of the carbene differ from those of the major species generated by the irradiation of the ester **1a** and they are rather close to those of the minor one. The zfs parameters of the carbene in the triplet state are calculated to be $D = 0.4572 \text{ cm}^{-1}$ and $E = 0.0271 \text{ cm}^{-1}$.

Comparing the D values observed for the carbene **2a** with that reported for (*p*-nitrophenyl)carbene ($D = 0.4859 \text{ cm}^{-1}$),²⁷ it is indicated that the distance between the two unpaired electrons is longer in **2a** than in (*p*-nitrophenyl)carbene. The decrease of the D value in the carbene **2a** is reasonably explained by the delocalization of the π spin onto the carbonyl oxygen.

Hutton and Roth reported that the ESR spectra of carbomethoxycarbene (**19**) showed two sets of triplet signals with slightly different zfs parameters.²³ They assigned the major isomer with the lower D value to the carbene with trans conformation and the minor isomer with the higher D value to the cis isomer, by taking into account the contribution of the spin density on the carbonyl oxygen to the zfs parameters. Their assignment is summarized in Table 6. It is not surprising that the geometric isomerism is

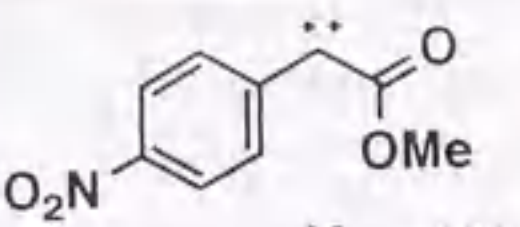
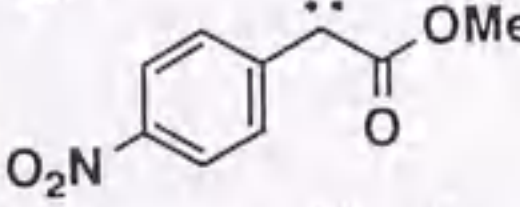
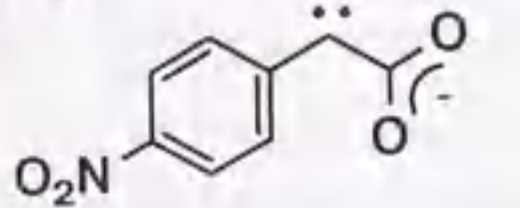
Table 6. Assignment of the Zero-Field Splitting Parameters to the Geometric Isomers of **19**^a

carbenes (19)	$D, \text{ cm}^{-1}$	$E, \text{ cm}^{-1}$	E/D
 (trans) ^b	0.617	0.053	0.086
 (cis)	0.663	0.030	0.045

^aRef 23. ^bThe major isomer.

also observed for the carbene **2a**, since the π spin in **2a** is expected to be delocalized largely on the carbonyl oxygen as mentioned above. Moreover a large decrease of the E/D value is observed in going from the major to the minor isomer of **2a**. This tendency is in harmony with that reported in the geometric isomers of **19** shown in Table 6. Thus the two isomeric carbenes observed by the irradiation of **1a** are reasonably identified as the geometric isomers of carbene **2a**; the major isomer is assigned to the trans **2a-t**, and the minor is assigned to the cis isomer **2a-c**. The zfs parameters and their assignments are summarized in Table 7.

Table 7. The Zero-Field Splitting Parameters for Carbenes **2a** and **2c**

carbenes		D, cm^{-1}	E, cm^{-1}	E/D
	(2a-t)	0.4530	0.0377	0.0832
	(2a-c)	0.4521	0.0274	0.0606
	(2c)	0.4572	0.0271	0.0593

It should be emphasized again that the zfs parameters of the carboxylate carbene **2c** are different from those of the major isomer **2a-t** and almost identical with those of the minor isomer **2a-c**. There are several possible explanations for this result. First, the conformation of the carboxylate carbene **2c** could be identical with that of the minor isomer of the ester. This possibility seems unlikely, because it is reasonable to think that the two oxygen atoms of the carboxylate anion become equivalent in polar solvents such as ethanol, so that the phenomenon of geometric isomerism is impossible in **2c**. The second possibility is that the angle of the divalent carbon of the carbene **2c** would be quite different from that of **2a-t**. This explanation would be possible if the intramolecular interaction of the carboxylate anion with the carbenic center resulted in structural changes of the triplet carbene in a rigid glass. The E/D value is known to reflect the angle of the divalent carbon; the increase of the angle results in the decrease of the E/D values.²⁴ However, in the case of the carbenes with unsymmetrical π spin distribution such as carboalkoxycarbenes, the spin distribution plays an important role in the determination of the zfs parameters. Therefore, the smaller E/D value of the carboxylate carbene **2c** does not necessarily indicate the larger angle of the divalent carbon of **2c**.

The significant differences between the zfs parameters in the isomeric carbomethoxycarbenes (**19**) have been attributed not to the different spin densities and angles of the divalent carbons, but to the different spin distributions, that is, the different contributions of the π spin density on the carbonyl oxygen to the parameters.²³

The most probable explanation for the drastic changes of zfs parameters in the carboxylate carbene **2c** is that the contribution of the carbonyl oxygen to the zfs parameters is eliminated in **2c** because of the disappearance of the carbonyl functional group. The zfs parameters of the major isomer of **2a**, which is assigned to the trans isomer **2a-t**, is thought to be predominantly governed by the large spin density on the carbonyl oxygen, as discussed by Hutton and Roth.²³ Since in the cis isomer of **2a** the contribution of the carbonyl oxygen to the zfs parameters is small, the parameters are thought to reflect the spin density and the angle of the divalent carbon atom. The agreement of the zfs parameters of the cis isomer **2a-c** with those of the carboxylate carbene **2c** seems to imply that the contribution of the carboxylate anion to the π spin density at the divalent carbon and to the structure of the carbene is negligible in the triplet state.

The spin multiplicities of the ground state of the carbenes, **2a** and **2c**, were determined from the temperature dependence of the intensities of their ESR signals.

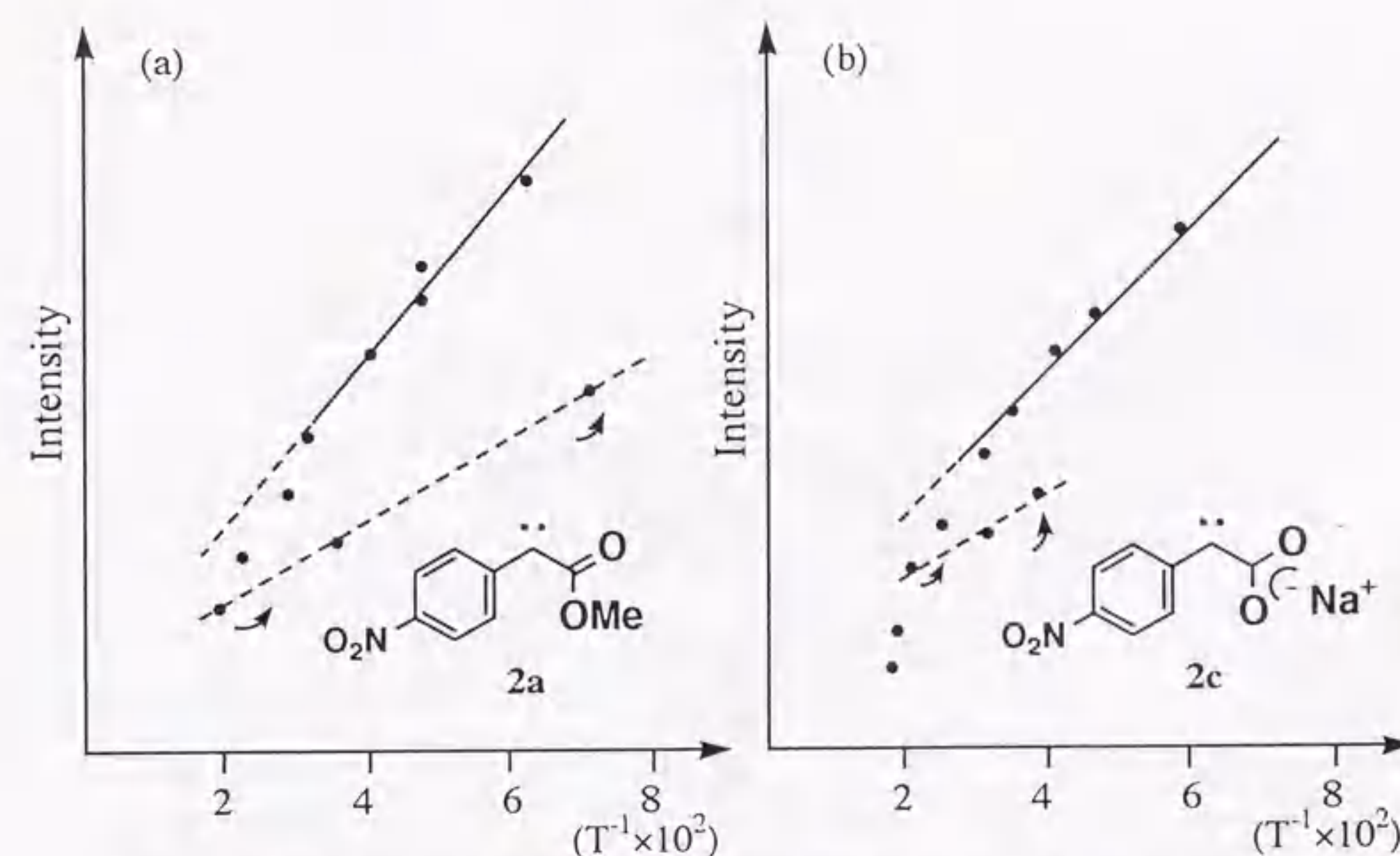


Figure 2. Curie plots of triplet signals after the photolysis of **1a** (a) and **1c** (b). Arrow and dotted lines indicate reproduction of the intensity of triplet signals upon lowering the temperature after warming up to ca. 50K.

The intensities of both carbenes, **2a** and **2c**, decreased linearly with the reciprocal of the temperature in the range of 10-30 K, as shown in Figure 2. The linear relations indicate that both carbenes are likely to have a triplet ground state, though the possibility can not be excluded that the triplet lies ca. 10 cal/mol above the singlet ground state. The plots deviated irreversibly from the line at above 30 K, but linear relations were obtained again by lowering the temperature as indicated by the arrows and the dotted line in the figure. These results are explained by a partial loss of carbenes at the higher temperature, owing to the chemical reactions of the triplet with a matrix or of a more reactive singlet state populated thermally. Thus the thermal stability of the triplet carbene **2c** in a rigid matrix is found to be comparable to that of **2a**.

The ESR studies revealed that the carboxylate carbene **2c** had a triplet ground state. Moreover we have obtained no evidence for the interaction of the carboxylate anion with the carbenic center in the triplet state of **2c**. Thus the results obtained for the triplet state by the ESR spectroscopy present a striking contrast to the reactivities of the

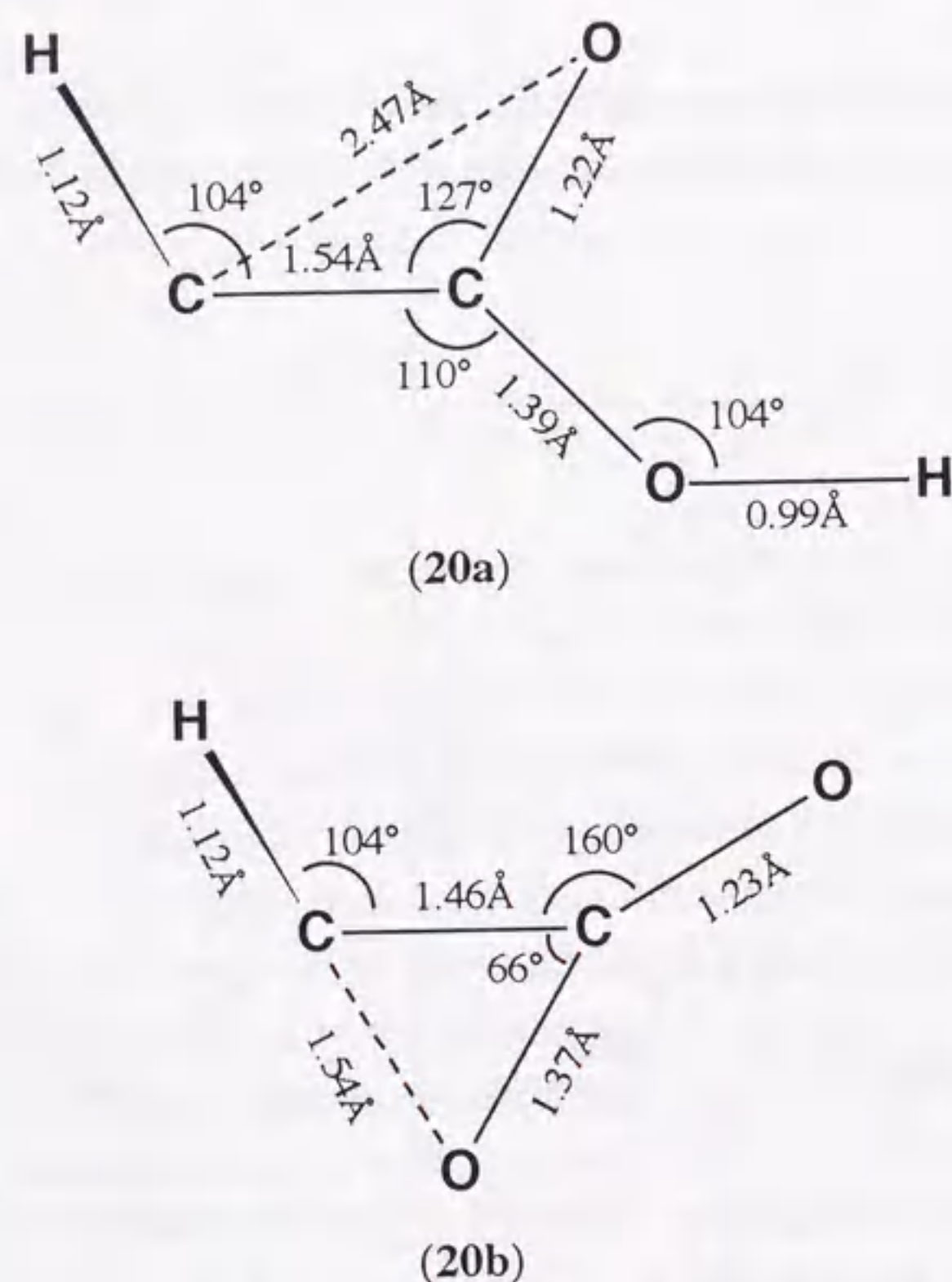


Figure 3. Optimized geometries for the singlet acid carbene HCCO_2H (**20a**) and the singlet carboxylate carbene HCCO_2^- (**20b**). Bond lengths are in angstroms and angles are in degrees.

singlet state in fluid solutions. This seems to be because the interaction of the vacant p orbital of the carbene in the singlet state with the carboxylate anion moiety is more effective than that of the half-occupied p orbital in the triplet state.

2-4 Theoretical Calculations

Ab initio MO calculations offer further corroborating evidence for the neighboring participation of the carboxylate group on carbene chemistry. The geometries of the singlet state of the parent carboxylic acid (**20a**) and the carboxylate carbene (**20b**) optimized by ab initio molecular orbital using the STO-3G basis set are shown in Figure 3. Inspection of the optimized geometries immediately reveals that the geometry changes dramatically in going from acid carbene to anion carbene. Thus, in the carboxylate carbene, the $\text{C}_1\text{-C}_2\text{-O}_2$ bond angle is expanded up to 160° whereas the $\text{C}_1\text{-C}_2\text{-O}_1$ bond angle is contracted to 66.0° and consequently the distance between

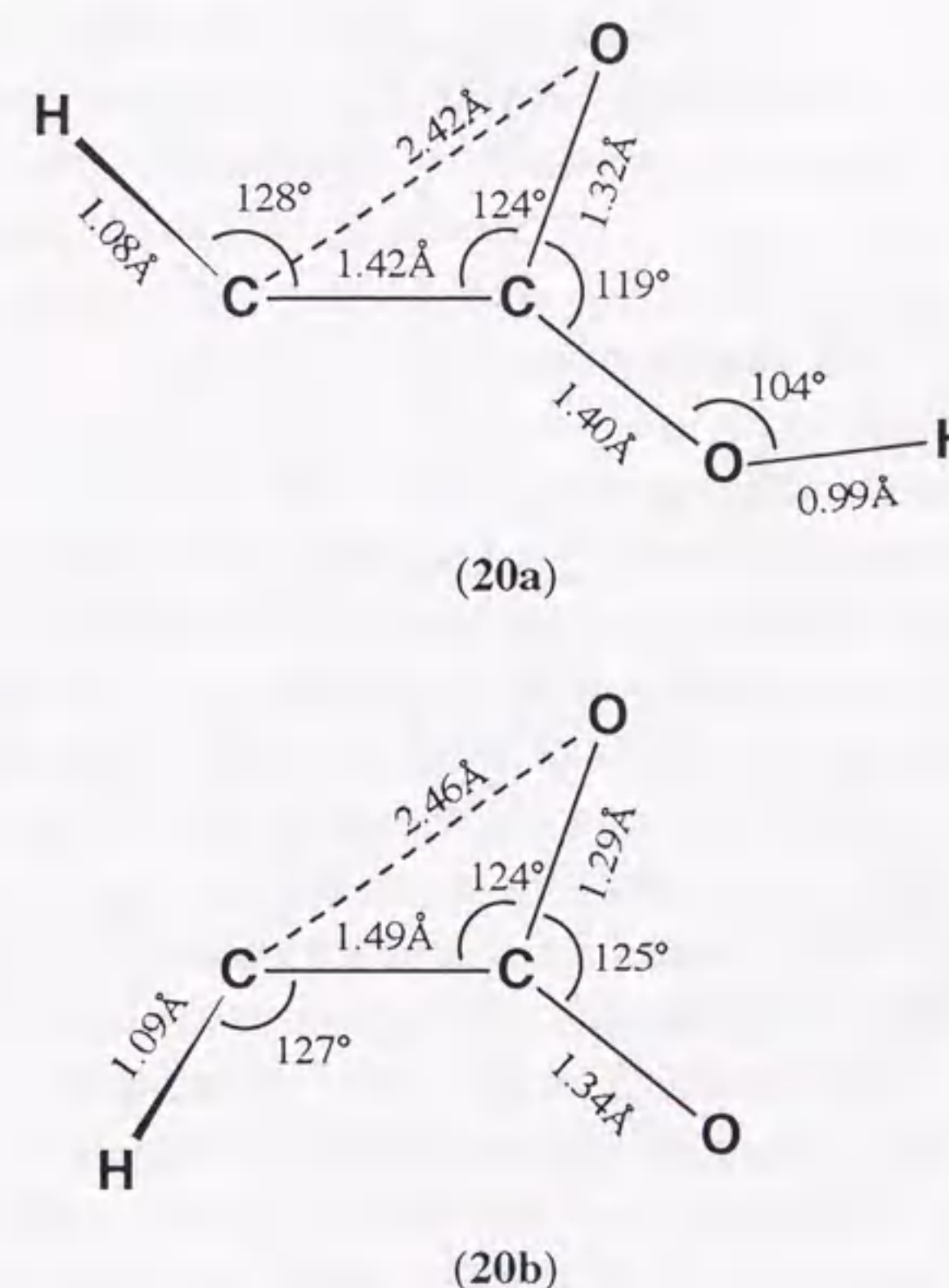


Figure 4. Optimized geometries for the triplet acid carbene HCCO_2H (**20a**) and the triplet carboxylate carbene HCCO_2^- (**20b**). Bond lengths are in angstroms and angles are in degrees.

carbenic carbons and oxygen anions is calculated to be 1.54 Å, which is as short as that of a carbon-carbon single bond. The whole geometry of **20b** is then very much like that of an α -lactone anion, suggesting that there should be strong interaction between a carbenic carbon and an oxygen anion, as has been proposed from the product analysis studies. Obviously, no such interaction is expected from the inspection of the geometry of acid carbenes (**20a**).

Optimized geometries of the corresponding triplet carbene were also calculated by using the same basis set and are shown in Figure 4 for comparison purposes. It is immediately clear that no significant change in geometries is seen in going from acid to anion carbenes in the case of the triplet. This is again in accord with the spectroscopic observation that the geometries of the triplet carbene are not significantly affected by the neighboring groups.

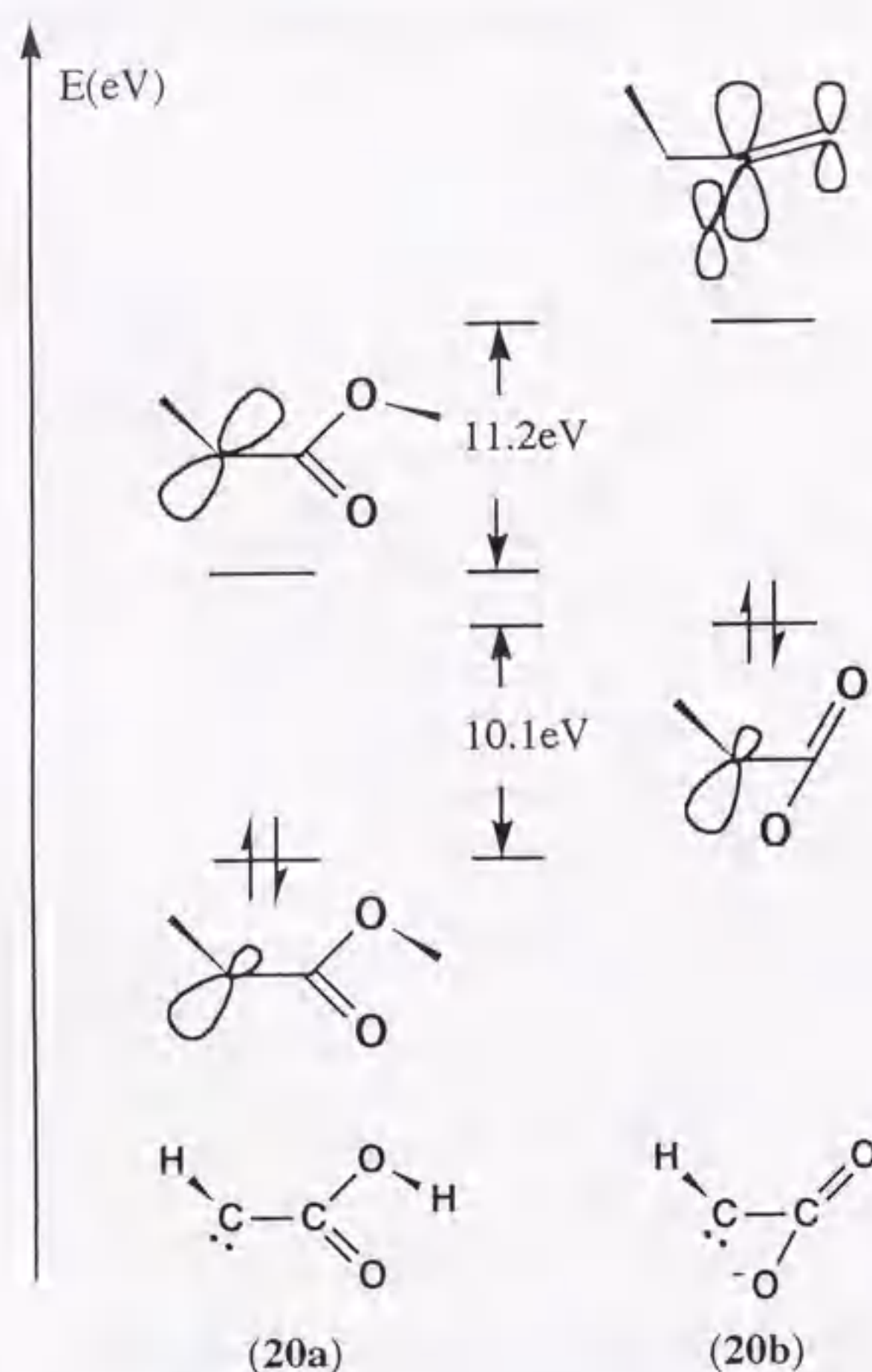


Figure 5. Energies and shapes of the frontier orbitals of singlet **20a** and **20b**.

Energies of frontier MO also support the idea that the carboxylate carbene is more nucleophilic than acid carbenes (Figure 5). Thus, the energies of HOMO as well as LUMO are greatly raised as the neighboring group is changed from acid to acid anion. Obviously, such change in the energy predicts that the interaction with the carbene HOMO becomes more favorable than that with the LUMO, as is observed.

2-5 Summarizing Discussion

The present results demonstrate that typical neighboring groups such as carboxylate groups, which have been known to exert a dramatic effect on nucleophilic displacement, show similar dramatic effects on the fate of carbenes. Impressive changes in the reactivity in going from carboxylic acid to the carboxylate anion group, which have been well documented in the solvolysis reaction, are also shown to exist in the carbenic reactions. Such a dramatic effect of substituents have not been preceded in the reaction of carbenes, which are electronically neutral and therefore much less susceptible to the electronic change in substituents.

All of these findings clearly provide concrete evidence that carbenic reactivities are susceptible to a similarly dramatic influence of the participants as that established in electrically positive six electron companions.

Rate enhancement and retained stereochemistry have served as useful tests for the neighboring group participation in the solvolysis reaction. In carbene chemistry, no diagnostic tests for neighboring group participation have been established. Obviously, stereochemical tests which have been used in carbenium chemistry can not be applied to carbene chemistry since carbenes have no stereochemical handle. Here we propose that the relative reactivity changes reflecting rate enhancement can be used as a useful and convenient test for neighboring group participation. Thus, electrophilic to nucleophilic inversion caused by typical participants can be most easily judged by simply examining the OH insertion-cyclopropanation selectivities. Cyclopropanation selectivity determination using a proper set of two electronically different alkenes offers corroborating evidence, and philicity determination using the Hammett treatment of the addition to a series of substituted styrenes enables more quantitative evaluation of the degree of the participation. Those tests can conveniently be used as an equally attractive diagnosis for the neighboring group participation in carbene chemistry.

In spite of the chemical evidence that the reactivities of carbenes are dramatically changed as a result of the strong perturbation by the neighboring carboxylate group, ESR studies provided unequivocal evidence that the ground-state multiplicities are not affected by the neighboring group. It is very important to note here in this connection that the geometrical changes of the molecules are usually very difficult in rigid organic matrices at this low temperature. For example, it has been reported²⁵ that when a

carbene is generated in microscopically rigid glass, it has the best geometry and the conformation dictated by the precursor and undergoes irreversible structural change to the thermodynamically most stable geometry as the media become soft at high temperature. Thus, it is probable that the present carbenes have, from their birth from the diazo precursor at low temperature in rigid glass, the geometry which should reflect the geometry and the conformation of the precursor. Efficient interaction of the carbenic p orbital with the neighboring anion group is not attained in the nascent geometry of the carboxylate carbene and a structural movement against steric demand imposed by the highly rigid environments will be required in order to maximize the overlap between the orbitals. Temperature studies of ESR signals showed that the structural change was not attained at least in the triplet manifold. This is presumably due to the ineffective interaction of the half-occupied p orbital with the anion moiety. Although the ESR studies give us no information on the geometrical change in the singlet state of carbenes, it is now well documented²⁶ that the reactions of carbene within rigid organic matrices are strongly affected by that rigidity. Moreover, the ionic nature of the participating carbene (e.g., **2c** or **2c'**) must be strongly favored by the solvation, which is apparently not attained in rigid matrices.

Finally, it is important to consider whether the interaction between the carbene center and a neighboring anion group is partial or full. The theoretical calculation on model carbene (**20b**) suggests that the bond length between carbenic carbons and oxygen anions is indistinguishably close from that known for cyclopropane itself, suggesting full bonding that forms an α -lactone anion or an oxaphosphirane anion is possible. It is probable that α -lactone or oxaphosphirane formed by protonation of its anion may intervene in the reaction in protic substrates, e.g., methanol. The intermediates undergoing cyclopropanation to the alkenes, on the other hand, seem to have a carbenic character unlike α -lactone, oxaphosphirane or its anion. Unfortunately, we have no experimental means to make a clear distinction between the carboxylate carbene and α -lactone anion or between the phosphonate carbene and oxaphosphirane anion at present. It is very tempting then to assume the carboxylate carbene (**2c**) and the α -lactone anion (**2c'**) are in equilibrium. Apparently, further experimental, as well as theoretical, studies are needed to clarify these points.

Experimental

General Methods. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrophotometer, and ¹H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in CDCl₃ with Me₄Si as an internal reference. The mass spectra

were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column A was prepared from 10% SE-30 on Diasolid L (5.0 mm \times 2.0 m); column B consisted of 5% PEG-20M on Diasolid L (5.0 mm \times 1.0 m). Thin-layer chromatography was done on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was carried out on silica gel (ICN for dry column chromatography).

ESR Measurements. The diazo compounds were dissolved in ethanol (ca. 5×10^{-3} M) and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The sample was cooled in an optical transmission ESR cavity at 15 K with an Air Products LTD-3-100 liquid helium transfer system, and irradiated with an Ushio USH-500D 500-W high-pressure mercury lamp and a Pyrex filter. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100kHz field modulation). The signal positions were read by the use of a Varian E-500 NMR gaussmeter.

Irradiations for Product Identification. In a typical run, a solution of the diazo compounds (ca. 100 mg) in substrate (5 mL) was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The resulting solution with the diazoacetic acid **1b** and acetate **1c** was neutralized and treated with diazomethane shortly after the irradiation. The irradiation mixtures were then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS. These fully characterized products were then used as "authentic" compounds for product identification by coinjection in GC-MS.

Irradiations for Analytical Purposes. All irradiations outlined in Tables 1-5 and 8-12 were carried out in a Pyrex tube of 5.0-mL capacity at below 10 °C. In order to avoid ambiguity of the relative yields due to the oxidation, the solution was degassed by subjecting the samples to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} mmHg before irradiation. Irradiation was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC as well as GC-MS comparisons with authentic samples and product distributions were conveniently determined by standard GC techniques.

General Comments concerning the Competition Experiments. These were carried out on binary mixtures of two substrates under the carefully controlled conditions. Thus, the precursory diazo compounds (0.1 mmol) were dissolved in the solvents (5 mL) consisted from large excess of the two substrates. Generally no solvents

were used to avoid possible effect of solvent on the reactivities of carbenes. The reaction mixtures were degassed and irradiated as described above and product ratios were determined on a Yanagimoto gas chromatograph equipped with a calibrated flame ionization detector, coupled to a Shimadzu C-R1B digital electronic integrator. The reaction mixtures with the diazoacetic acid (**1b**) and acetate (**1c**) were treated with diazomethane before the GC analysis. Control experiments exclude the possible photoconversion of the products during the irradiation period and also demonstrate that no reaction occurs in the absence of light. Experiments were duplicated, and average deviations from the mean values were all <3%.

The runs using alkenes with electron-deficient double bond were carried out at a lower temperature in order to avoid the thermal pyrazoline pathway. Thus, the precursory diazo compounds were added to the substrate mixture precooled to -20 °C and the mixtures were carefully degassed and irradiated at -10 °C. Control experiments exclude the formation of cyclopropanes in the absence of light under these conditions.

Preparation of (4-Nitrophenyl)diazoacetic Acid Derivatives 1a-c. (4-Nitrophenyl)diazoacetic acid (**1b**) was prepared according to the procedure of Schank² by diazo group transfer of tetrahydropyranyl (4-nitrophenyl)diazoacetate with tosyl azide followed by the acid-catalyzed hydrolysis of the resulting diazo ester. The sodium salt of the diazoacetic acid was obtained by the treatment of **1b** with NaOMe in absolute ether followed by the filtration and washing with the ether. Both **1b** and **1c** were considerably stable in the dark at 0 °C. All other (4-nitrophenyl)diazoacetates (**1d-h**) were prepared by the diazo group transfer of the corresponding phenylacetate with tosyl azide according to the slightly modified method of Regitz.²⁷ Typically, to a solution of the ester (10 mmol) and triethylenediamine (20 mmol) in anhydrous acetonitrile (20 mL) was added an acetonitrile solution of tosyl azide (10 mmol) at 0-5 °C under vigorous stirring in the dark. The progress of the reaction was carefully monitored by TLC and after almost all of the starting materials were consumed, the reaction mixture was poured into water (150 mL) to give orange to yellow crystalline of **1**, which was filtered and washed with water and a small amount of cold methanol. The crystalline product dried under reduced pressure (10⁻¹ Torr) at room temperature was found to be pure spectroscopically. Spectral data are given in Table 8.

Preparation and Decomposition of Sodium Salt of 1-Phenyl-2-ketopropionic Acid Tosylhydrazonate (15) in MeOD. 1-Phenyl-2-ketopropionic acid²⁸ (0.67 g, 4.1 mmol) was dissolved in methanol (20 mL). To this was added an equivalent amount (0.76 g, 4.1 mmol) of (*p*-tolylsulfonyl)hydrazine. The mixture was stirred until the tosylhydrazine dissolved to give a pale yellow solution. After standing for 3 days at room temperature, the precipitate was filtered, washed with cold methanol, and

dried under vacuum (1.20 g, 3.6 mmol), yield, 88.1%, mp 170-175 °C; ¹H NMR (CDCl₃) δ 7.75 (2 H, d, *J* = 8.0 Hz), 7.60-7.05 (7 H, m), 3.76 (2 H, s), 2.43 (3 H, s).

The acid tosylhydrazone (0.10 g, 0.3 mmol) thus obtained was dissolved in absolute ether (10 mL) and treated with excess of CH₂N₂. Evaporation of the solvent afforded the corresponding methyl ester as a yellow oil in quantitative yield; ¹H NMR (CDCl₃) δ 7.77 (2 H, d, *J* = 8.0 Hz), 7.34 (2H, d, *J* = 8.0 Hz), 7.25 (5 H, bs), 4.25 (2 H, s), 3.74 (3 H, s) 2.43 (3 H, s).

To a suspension of sodium hydride (50 mg of NaH in oil (50%)) was washed with dry ether, 0.6 mmol) in dry THF (5 mL) was added tosylhydrazone (0.30 mmol for the acid, 0.6 mmol for the ester). The mixture was stirred for 1 h under argon and the precipitate was filtered, washed with cold dry THF under argon atmosphere and dried in vacuum to afford the sodium salt, which was immediately used for the photolysis experiments.

The sodium salt (3 mg) was dissolved in MeOD (Merck, 99.9%, 0.5 mL) in a Pyrex tube. After careful degassing, the mixture was irradiated as described above. A faint pink color and copious gas evolution was observed during the irradiation, indicating the formation and decomposition of the corresponding diazo compounds. The mixture was irradiated until the color disappeared. The photomixture from **15b** was treated with CH₂N₂. The contents of deuterium in the products (**17** and **18**) were conveniently determined by using standard GCMS technique. In order to avoid the possible error due to partial separation of isotopic mixtures by GC, the mass fragmentography technique was employed. Thus, total ion of each mass (*m/e*) were integrated in each GC peaks and used as numerical value in calculation²⁹ of analysis.

The OH Insertion Product (3) of 2 to Methanol. A solution of the diazo compounds (**1**, ca. 50 mg) in dry methanol (5 mL) in a Pyrex tube was irradiated by using a Corning CS-052 filter (>350 nm) at 10°C. After evaporation of the solvent under reduced pressure, the reaction mixture was subjected to silica gel chromatography to afford pure α-methoxy-α-arylacetate (**3**) in about 85-90% yields. NMR and MS data are summarized in Table 9. Anal. (**3e**) Calcd for C₁₃H₁₇NO₅: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.87; H, 6.35; N, 5.07.

The Cycloadducts (4) of 2 to 2-Methyl-2-butene. A solution of the diazo compounds (**1**, ca. 50 mg) in the butene (3 mL) in a Pyrex tube was irradiated under the similar condition employed for the photoreaction in methanol. The reaction mixture was separated by preparative TLC (CHCl₃-*n*-hexane = 1:1) to give isomerically pure 1,1,2-trimethyl-3-(methoxycarbonyl)-3-(4-nitrophenyl)cyclopropanes. NMR and MS data are given in Table 10.

Photolysis of 1a in Benzene. A solution of **1a** (50 mg) in benzene (5.0 mL) was irradiated and the irradiated mixture was separated by preparative TLC (CHCl_3 -*n*-hexane = 3:1) to give 1-(methoxycarbonyl)-1-(4-nitrophenyl)norcaradiene (45 mg) in 74.0% yield: ^1H NMR (CCl_4) δ 8.00-7.15 (4 H, m), 6.31-5.80 (4 H, m), 4.12-4.08 (2 H, m), 3.60 (3 H, s); MS *m/e* (relative intensity) 271 (M^+ , 16), 239 (45), 212 (100), 166 (18). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 65.65; H, 4.71; N, 4.98.

The SH Insertion Product of 2 in Thioethanol. A solution of **1a** (50 mg) in thioethanol (50 mL) was irradiated and the photomixture was chromatographed to afford α -thioethoxy- α -(4-nitrophenyl)acetate (53 mg) in 91.9% yield: ^1H NMR (CDCl_3) δ 8.08 (2 H, d, J = 8.5 Hz), 7.55 (2 H, d, J = 8.5 Hz), 3.50 (1 H, s), 3.70 (3 H, s), 2.52 (1 H, q, J = 7.0 Hz), 2.48 (1 H, q, J = 7.0 Hz), 1.22 (3 H, t, J = 7.0 Hz); MS *m/e* (relative intensity) 255 (M^+ , 3), 196 (100), 195 (71).

The Cyclopropane (20) from 2a and α -Chloroacrylonitrile. A solution of the diazo ester (**1a**, 50 mg) in the acrylonitrile (5 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 -*n*-hexane = 1:1). Removal of the mobile phase under reduced pressure afforded 1-chloro-1-cyano-2-(methoxycarbonyl)-2-(4-nitrophenyl)cyclopropanes (**20**). The major isomer (43 mg, 67.0%) eluted first, followed by the minor isomer (16 mg, 25.0%). The major isomer: ^1H NMR (CDCl_3) δ 8.25 (2 H, d, J = 8.0 Hz), 7.68 (2 H, d, J = 8.0 Hz), 3.79 (3 H, s), 2.68 (1 H, d, J = 7.5 Hz), 2.35 (1 H, d, J = 7.5 Hz); MS *m/e* (relative intensity) 280 (M^+ , 34), 140 (64), 59 (100). The minor isomer: ^1H NMR (CDCl_3) δ 8.25 (2 H, d, J = 8.0 Hz), 7.55 (2 H, d, J = 8.0 Hz), 3.80 (3 H, s), 2.92 (1 H, d, J = 7.5 Hz), 2.13 (1 H, d, J = 7.5 Hz); MS *m/e* (relative intensity) 280 (M^+ , 34), 140 (64), 59 (100). Anal. Calcd for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{Cl}$: C, 51.35; H, 3.23; N, 9.98. Found: C, 51.72; H, 3.16; N, 9.90.

The Cyclopropanes (21) from 2a and 1-Hexene. A solution of the diazo ester (**1a**, 50 mg) in 1-hexene (3 mL) in a Pyrex tube was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 -*n*-hexane = 1:4) to give 1-(methoxycarbonyl)-1-(4-nitrophenyl)-2-butylcyclopropanes (**21**). (Syn- CO_2Me)-**21**: 20 mg (31.8%); ^1H NMR (CDCl_3) δ 8.10 (2 H, d, J = 8.0 Hz), 7.45 (2 H, d, J = 8.0 Hz), 3.62 (3 H, s), 1.63-0.92 (12 H, m); MS *m/e* (relative intensity) 277 (M^+ , 37), 208 (100), 176 (62), 148 (89). (Anti- CO_2Me)-**21**: 12 mg (18.8%); ^1H NMR (CDCl_3) δ 8.15 (2 H, d, J = 8.0 Hz), 7.40 (2 H, d, J = 8.0 Hz), 3.60 (3 H, s), 1.82-0.80 (12 H, m); MS *m/e* (relative intensity) 277 (M^+ , 37), 208 (100), 176 (62), 148 (89).

The Cyclopropanes (23) from 2 and Substituted Styrenes (22). A solution of **1a** and **1c** (50 mg) in substituted styrenes (**22**, 200 mg) and benzene (0.2 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 -*n*-hexane = 2:3) to give isomeric pure 1,2-diaryl-1-(methoxycarbonyl)cyclopropanes (**23**). The isomer ratio was roughly 1:1 and overall yields were about 80-90% in each runs. The NMR and mass spectra of each isomer are given in Table 11 together with the melting points.

Anal. **23** (Y = 4-Me) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.67; H, 5.47; N, 4.41.

Anal. **23** (Y = H) Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.88; H, 5.06; N, 4.53.

Anal. **23** (Y = 4-Cl) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4\text{Cl}$: C, 61.55; H, 4.25; N, 4.22. Found: C, 61.04; H, 4.12; N, 4.04.

Anal. **23** (Y = 4-Br) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4\text{Br}$: C, 54.28; H, 3.75; N, 3.72. Found: C, 54.95; H, 3.53; N, 3.53.

Anal. **23** (Y = 4-CN) Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.05; H, 4.29; N, 8.65.

Anal. **23** (Y = 4- NO_2) Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.90; H, 4.10; N, 8.11.

Table 8. Physical Data of (4-Nitrophenyl)diazoacetates 1a-h

I	X in 1	mp, °C	IR, cm ⁻¹	NMR, δ
a	Me	147.0-149.0	2090, 1708, 1590	8.16(2H, d, J=8.0Hz), 7.60(2H, d, J=8.0Hz), 3.88(3H, s)
b	H	124.3-125.2	2095, 1645	
c	Na	>300	2095, 1612, 1591	
d	ⁿ C ₆ H ₁₃	53.0-55.8	2105, 1705, 1590	8.15(2H, d, J=8.5Hz), 7.58(2H, d, J=8.5Hz), 4.28(2H, t, J=6.0Hz), 1.80-1.30(8H, m), 0.90(3H, t, J=6.0Hz)
e	^t Bu	117.0-118.5	2085, 1685, 1590	8.53(2H, d, J=8.5Hz), 7.55(2H, d, J=8.5Hz), 1.56(9H, s)
f	CH ₂ CF ₃	76.0-83.0	2120, 1720, 1595	8.17(2H, d, J=8.5Hz), 7.70(2H, d, J=8.5Hz), 4.75(2H, q, J=8.0Hz)
g	CH ₂ CN	129.3-132.7	2100, 1720, 1590	8.17(2H, d, J=8.0Hz), 7.57(2H, d, J=8.0Hz), 4.89(2H, s)
h	CH ₂ CH ₂ CN	107.6-110.9	2100, 1705, 1595	8.13(2H, d, J=8.5Hz), 7.55(2H, d, J=8.5Hz), 4.52(2H, t, J=6.0Hz), 2.80(2H, t, J=6.0Hz)

Table 9. NMR and MS Data of α-Methoxy-α-(4-nitrophenyl)acetates 3a,d-h

3	NMR, δ				MS: m/e (rel. intensity)
	Ar	ArCH	MeO	other	
a	8.05(2H, d, J=8.0Hz), 7.52(2H, d, J=8.0Hz)	4.78(1H, s)	3.45(3H, s)	3.70(3H, s)	166(100) 120(30)
d	8.14(2H, d, J=8.0Hz), 7.55(2H, d, J=8.0Hz)	4.75(1H, s)	3.44(3H, s)	4.06(2H, t, J=6.0Hz), 1.65-1.18(8H, m), 0.94-0.80(3H, m)	166(100) 120(22)
e	8.14(2H, d, J=8.0Hz), 7.55(2H, d, J=8.0Hz)	4.62(1H, s)	3.44(3H, s)	1.39(9H, s)	166(100) 120(32)
f	8.20(2H, d, J=8.0Hz), 7.62(2H, d, J=8.0Hz)	4.98(1H, s)	3.49(3H, s)	4.50(2H, q, J=8.0Hz)	166(100) 120(8)
g	8.20(2H, d, J=8.0Hz), 7.62(2H, d, J=8.0Hz)	4.97(1H, s)	3.49(3H, s)	4.77(2H, s)	166(100) 120(29)
h	8.19(2H, d, J=8.0Hz), 7.62(2H, d, J=8.0Hz)	4.92(1H, s)	3.47(3H, s)	4.32(2H, t, J=6.0Hz), 2.70(1H, t, J=6.0Hz), 2.67(1H, t, J=6.0Hz)	166(100) 120(25)

Table 10. NMR and MS Data of 1,1,2-Trimethyl-3-(methoxycarbonyl)-3-arylcyclopropanes 4a,d-h

4 (syn/anti) ^a	NMR, δ		MS: m/e (rel. intensity)
	Ar	other	
a (syn)	8.12(2H, d, J=8.0Hz), 7.32(2H, d, J=8.0Hz)	3.55(3H, s), 1.40-0.80(10H, m)	263(M ⁺ , 20), 248(35), 231(40),
(anti)	8.09(2H, d, J=8.0Hz), 7.42(2H, d, J=8.0Hz)	3.54(3H, s), 1.38-0.80(10H, m)	216(25), 115(38), 73(100)
d (syn)	8.14(2H, d, J=8.0Hz), 7.34(2H, d, J=8.0Hz)	3.97(2H, t, J=6.0Hz), 1.99(1H, q, J=7.0Hz), 1.63-0.82(20H, m)	333(M ⁺ , 7), 249(100), 234(41),
(anti)	8.09(2H, d, J=8.0Hz), 7.42(2H, d, J=8.0Hz)	3.96(2H, t, J=6.0Hz), 1.63-0.80(21H, m)	163(55), 59(47)
e (syn)	8.11(2H, d, J=8.0Hz), 7.32(2H, d, J=8.0Hz)	1.88(1H, q, J=7.0Hz), 1.30(3H, s), 1.28(9H, s), 0.96(3H, d, J=7.0Hz), 0.92(3H, s)	249(50), 163(29), 57(100)
(anti)	8.09(2H, d, J=8.0Hz), 7.43(2H, d, J=8.0Hz)	1.58(1H, q, J=7.0Hz), 1.32(9H, s), 0.80(3H, s)	
f (syn)	8.12(2H, d, J=8.0Hz), 7.33(2H, d, J=8.0Hz)	4.57-4.14(2H, m), 2.03(1H, q, J=7.0Hz), 1.32(3H, s), 1.02(3H, d, J=7.0Hz), 0.98(3H, s)	331(M ⁺ , 41), 231(59), 216(36), 141(100), 115(41)
(anti)	8.08(2H, d, J=8.0Hz), 7.42(2H, d, J=8.0Hz)	4.33(2H, q, J=8.0Hz), 1.57(1H, q, J=7.0Hz), 1.37(3H, d, J=7.0Hz), 1.32(3H, s), 0.84(3H, s)	
g (syn)	8.16(2H, d, J=8.0Hz), 7.33(2H, d, J=8.0Hz)	4.76-4.40(2H, m), 2.08(1H, q, J=7.0Hz), 1.36(3H, s), 1.02(3H, d, J=7.0Hz), 0.97(3H, s)	288(M ⁺ , 55), 231(84), 157(75), 123(90), 115(85),
(anti)	8.11(2H, d, J=8.0Hz), 7.42(2H, d, J=8.0Hz)	4.58(2H, s), 1.57(1H, q, J=7.0Hz), 1.37(3H, d, J=7.0Hz), 1.33(3H, s), 0.84(3H, s)	98(100), 69(74)
h (syn)	8.15(2H, d, J=8.0Hz), 7.36(2H, d, J=8.0Hz)	4.37-4.02(2H, m), 2.55(2H, t, J=6.0Hz), 2.04(1H, q, J=7.0Hz), 1.34(3H, s), 1.01(3H, d, J=7.0Hz), 0.95(3H, s)	302(M ⁺ , 29), 285(100), 231(70), 157(80), 115(67),
(anti)	8.11(2H, d, J=8.0Hz), 7.45(2H, d, J=8.0Hz)	4.18(2H, t, J=6.0Hz), 2.56(2H, t, J=6.0Hz), 1.64-1.40(1H, m), 1.37(3H, d, J=7.0Hz), 1.33(3H, s), 0.83(3H, s)	59(85)

^aAr is syn or anti with respect to dimethyl groups.

Table 11. Continued

Y in 18 (syn/anti) ^a	mp	NMR, δ			MS: <i>m/e</i> (rel. intensity)
		Ar	OMe	other	
4-Br (syn)	187.0-188.5°	7.96(2H,d, <i>J</i> =8.0Hz), 7.16(2H,d, <i>J</i> =8.0Hz), 7.14(2H,d, <i>J</i> =8.0Hz), 6.63(2H,d, <i>J</i> =8.0Hz)	3.65(3H,s)	3.13(1H,dd, <i>J</i> =7.0,9.0Hz), 2.12(1H,dd, <i>J</i> =6.0,9.0Hz), 1.89(1H,dd, <i>J</i> =6.0,7.0Hz)	377(M+2,73), 375(M ⁺ ,73),237(76), 218(77),201(83), 199(85),89(100)
		(anti) 102.0-106.0°	8.18(2H,d, <i>J</i> =8.0Hz), 7.60(2H,d, <i>J</i> =8.0Hz), 7.43(2H,d, <i>J</i> =8.0Hz), 7.18(2H,d, <i>J</i> =8.0Hz)	3.35(3H,s) 2.82(1H,dd, <i>J</i> =7.0,9.0Hz), 2.39(1H,dd, <i>J</i> =6.0,7.0Hz), 1.69(1H,dd, <i>J</i> =6.0,9.0Hz)	
4-CN (syn)	b	7.95(2H,d, <i>J</i> =8.0Hz), 7.33(2H,d, <i>J</i> =8.0Hz), 7.15(2H,d, <i>J</i> =8.0Hz), 6.84(2H,d, <i>J</i> =8.0Hz)	3.69(3H,s)	3.22(1H,dd, <i>J</i> =4.0,4.0Hz), 2.33-2.19(1H,m), 2.10-1.95(1H,m)	322(M ⁺ ,100),290(45), 263(20),217(44), 146(62)
		(anti) b	8.16(2H,d, <i>J</i> =8.0Hz), 7.62-7.45(6H,m)	3.33(3H,s) 2.84(1H,dd, <i>J</i> =4.0,4.0Hz), 2.55-2.40(1H,m), 1.67(1H,dd, <i>J</i> =3.0,4.0Hz)	

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^aAr is syn or anti with respect to Ar'. ^bLiquid.

Table 11. NMR and MS Data of 1,2-Diaryl-1-(methoxycarbonyl)cyclopropanes (18)

Y in 18 (syn/anti) ^a	mp	NMR, δ			MS: <i>m/e</i> (rel. intensity)
		Ar	OMe	other	
4-Me (syn)	b	7.94(2H,d, <i>J</i> =8.0Hz), 7.15(2H,d, <i>J</i> =8.0Hz), 6.87(2H,d, <i>J</i> =8.0Hz), 6.65(2H,d, <i>J</i> =8.0Hz)	3.67(3H,s)	3.17(1H,dd, <i>J</i> =8.0,9.0Hz), 2.25-2.12(1H,m),2.20(3H,s), 1.90(1H,dd, <i>J</i> =6.0,9.0Hz)	311(M ⁺ ,95), 279(100),252(80), 135(92)
		(anti) b	8.18(2H,d, <i>J</i> =8.0Hz), 7.63(2H,d, <i>J</i> =8.0Hz), 7.25-7.07(4H,m)	3.33(3H,s) 2.85(1H,dd, <i>J</i> =8.0,9.0Hz), 2.47-2.30(1H,m),2.33(3H,s), 1.65(1H,dd, <i>J</i> =6.0,9.0Hz)	
H (syn)	b	7.90(2H,d, <i>J</i> =8.0Hz), 7.21-6.96(5H,m), 6.75-6.63(2H,m)	3.61(3H,s)	3.10(1H,dd, <i>J</i> =8.0,8.0Hz), 2.15(1H,dd, <i>J</i> =6.0,8.0Hz), 1.96(1H,dd, <i>J</i> =6.0,8.0Hz)	297(M ⁺ ,72),265(58), 237(40)
		(anti) b	8.10(2H,d, <i>J</i> =8.0Hz), 7.53(2H,d, <i>J</i> =8.0Hz), 7.17(5H,s)	3.20(3H,s) 2.74(1H,dd, <i>J</i> =8.0,8.0Hz), 2.32(1H,dd, <i>J</i> =6.0,8.0Hz), 1.53(1H,dd, <i>J</i> =6.0,8.0Hz)	192(60),191(58), 121(100)
4-Cl (syn)	180.5-184.0°	7.95(2H,d, <i>J</i> =8.0Hz), 7.13(2H,d, <i>J</i> =8.0Hz), 7.00(2H,d, <i>J</i> =8.0Hz), 6.65(2H,d, <i>J</i> =8.0Hz)	3.65(3H,s)	3.14(1H,dd, <i>J</i> =7.0,9.0Hz), 2.20(1H,dd, <i>J</i> =5.0,7.0Hz), 1.88(1H,dd, <i>J</i> =5.0,9.0Hz)	333(M+2,20), 331(M ⁺ ,65),229(46), 272(42)
		(anti) 103.0-104.5°	8.14(2H,d, <i>J</i> =8.0Hz), 7.56(2H,d, <i>J</i> =8.0Hz), 7.20(4H,s)	3.32(3H,s) 2.82(1H,dd, <i>J</i> =7.0,9.0Hz), 2.37(1H,dd, <i>J</i> =5.0,7.0Hz), 1.68(1H,dd, <i>J</i> =5.0,9.0Hz)	189(54),155(100)

^aAr is syn or anti with respect to Ar'. ^bLiquid.

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Table II. Continued

Y in 18 (syn/anti) ^a	mp	NMR, δ			MS:
		Ar	OMe	other	m/e (rel. intensity)
4-NO ₂ (syn)	175.0-178.0°	7.95(2H, d, $J=8.0$ Hz), 7.86(2H, d, $J=8.0$ Hz), 7.15(2H, d, $J=8.0$ Hz), 6.87(2H, d, $J=8.0$ Hz)	3.66(3H, s)	3.28(1H, dd, $J=4.0, 4.0$ Hz), 2.37-1.96(2H, m)	342(M ⁺ , 34), 325(79), 237(44), 189(80), 166(68), 150(100)
(anti) b		8.15(2H, d, $J=8.0$ Hz), 8.12(2H, d, $J=8.0$ Hz), 7.58(2H, d, $J=8.0$ Hz), 7.46(2H, d, $J=8.0$ Hz)	3.34(3H, s)	2.92(1H, dd, $J=4.0, 4.0$ Hz), 2.48(1H, dd, $J=4.0, 6.0$ Hz), 1.80(1H, dd, $J=4.0, 6.0$ Hz)	

^a Ar is syn or anti with respect to Ar¹. Liquid.

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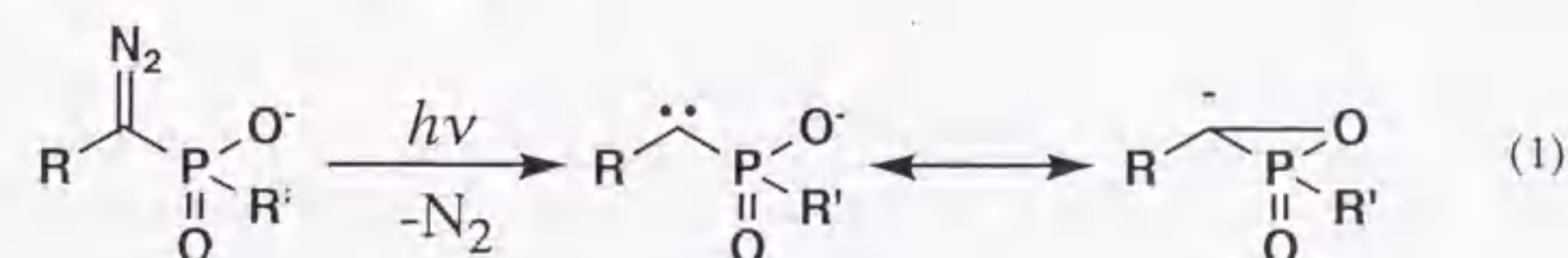
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Chapter 3 Effect of Neighboring Phosphonate Group on Carbene Reactivities

3-1 Introduction

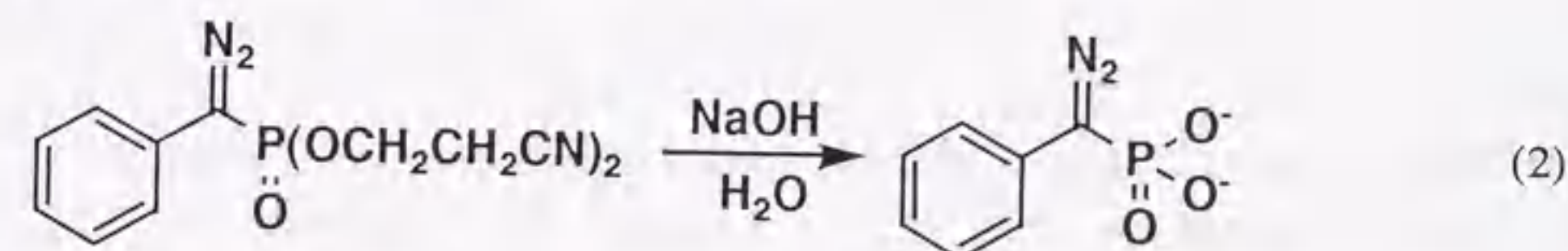
In last chapter, we described that carboxylate anion group acted as an highly effective participant on carbene reactivities. Thus, an interaction of carboxylate anion group with the vacant p orbital of the singlet carbene resulted in the change of carbene reactivities dramatically.

In this chapter, as part of our work on the effect of neighboring anionic groups on the reactivities of carbenes, we have generated carbenes photolytically from the α -diazophosphonate salts and have studied their reactivities both by product analysis and spectroscopic techniques (eq 1).

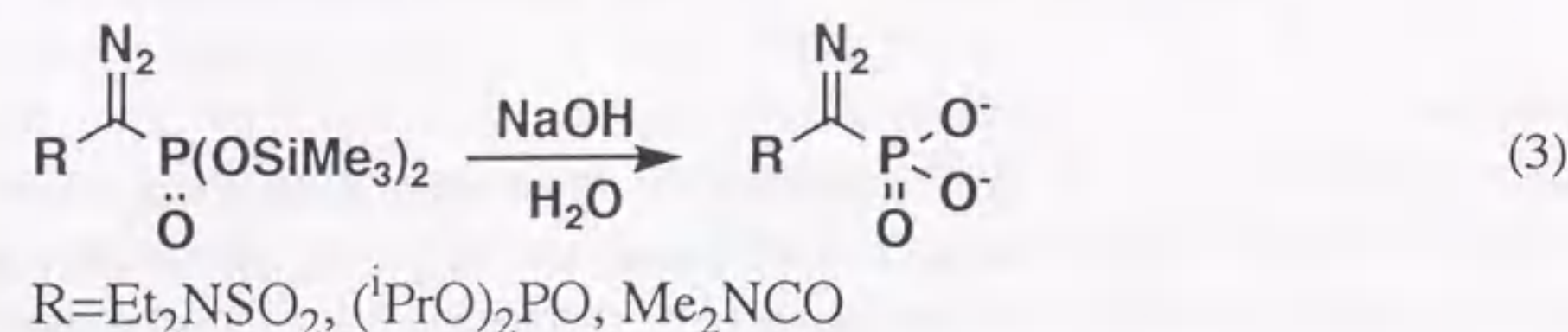


The studies of photolysis process of diazophosphonates and reactivities of the resulting carbenes are also interested from the viewpoint of a photoaffinity labeling probe. That is, since its invention by Westheimer some 30 years ago,¹ the technique of photoaffinity labeling has become an important one for probing macromolecular binding sites and biological targets.² The photolabile moieties employed for this purpose have for the most part been α -diazoo esters or aryl azides. Particular attention has been paid recently to α -diazophosphonic acid salts as potential photolabile mimics of phosphate derivatives, and several α -diazophosphonic acids have been synthesized and characterized.³⁻⁶ However, little is known about the effect of the phosphonate anion on the reactivity of photolytically generated carbenes from the α -diazophosphonate salts.

Same syntheses of α -diazophosphonate salts have been reported. For example, Goldstein et al. have reported the successful preparation of disodium α -diazophosphonate in aqueous solution (eq 2).³ Treatment of dicyanoethyl α -diazobenzylphosphonate with sodium hydroxide gave aqueous solutions of disodium α -diazobenzylphosphonate, although the compound was somewhat unstable even in alkaline solution.



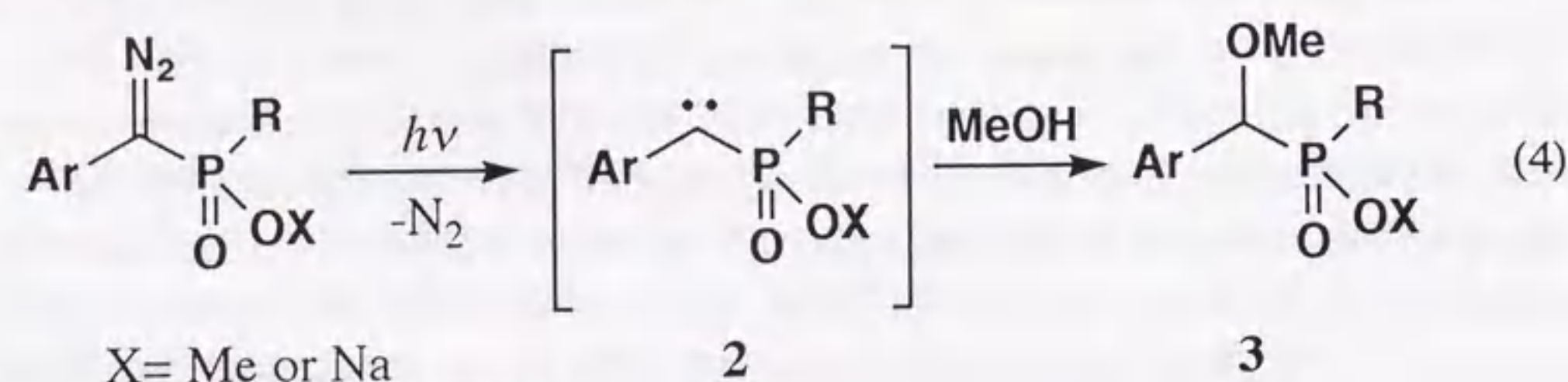
On the other hand, Bartlett et al. have described the preparation of three diazophosphonic acid salts from the bis(trimethylsilyl)esters (eq 3).⁴⁻⁶



If phosphonate carbenes are generated photolytically from these diazophosphonate salts, reactivities of the carbenes must be dramatically different from that of the corresponding ester carbenes.

3-2 Product Analysis

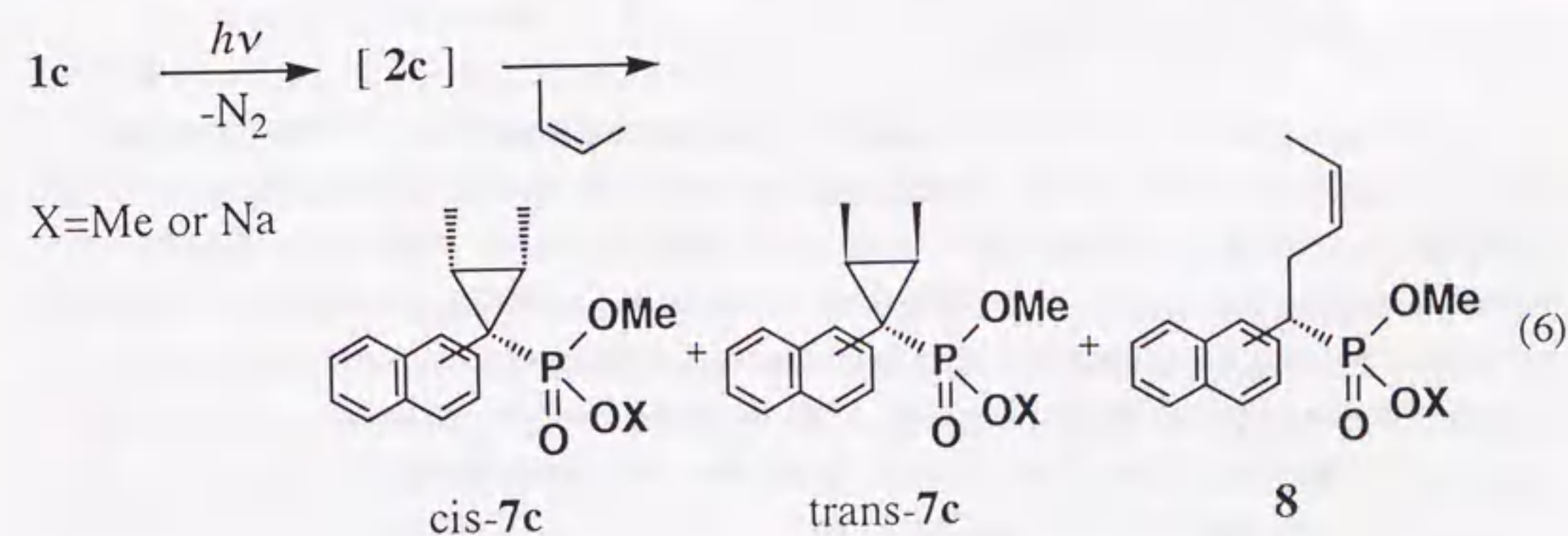
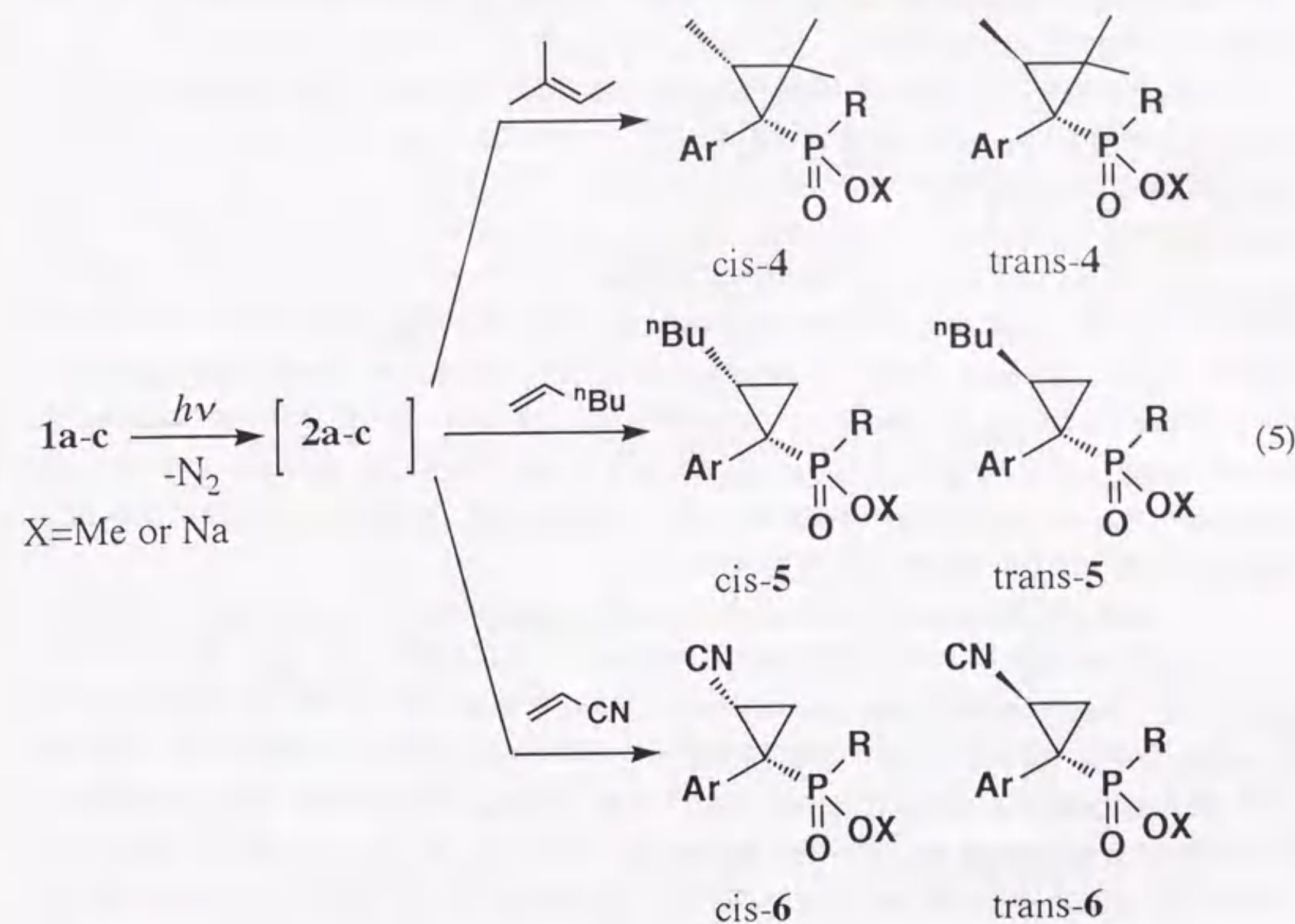
(1) *Photolysis in MeOH* Irradiation (> 300 nm) of a series of diazomethanes bearing phosphoryl groups (**1**) in methanol afforded α -methoxyphosphonate (**3**) as the major products regardless of the substituents (eq 4). These products are apparently derived from photolytically generated carbenes (**2**) which must undergo insertion into the O-H bond of methanol⁷ since the diazo compounds (**1**) were completely recovered unchanged in the dark under otherwise the identical conditions.



(2) *Photolysis in the Presence of Alkenes* Irradiation of **1** in the presence of alkenes resulted in the formation of products, the structures of which were sensitively dependent on the aryl group on carbenic carbon and on the change on the phosphonyl groups.

Thus, photolysis of **1a-c** in alkenes afforded cyclopropanes **4-6** in 83-76 % yield as a mixture of geometrical isomers, which could be separated by gel permeation

chromatography into two fractions, *syn*- and *anti*-isomers (eq 5)⁷. In order to obtain information on the multiplicities of the carbene undergoing cyclopropanation, the carbene was generated in an alkene having a stereochemical handle, i.e., (*Z*)-but-2-ene. Thus, irradiation of α -**1c**(X=Me) in the butene resulted in the formation of cyclopropane α -**7c**(X=Me) again as a mixture of geometrical isomers. ¹H NMR analysis clearly indicated that the cyclopropanes were formed almost exclusively with retention of stereochemistry of the butene, suggesting the participation of the singlet-state carbene.



Essentially similar results were obtained in the photolysis of β -**1c**(X=Me) in the presence of but-2-ene, although an appreciable amount (ca. 10 %) of the product β -**8c**(X=Me) in which the carbene had inserted into the C-H bond of the methyl group was detected in this case (eq 6). This can be explained in terms of the difference in electrophilicity between α - and β -**1c**(X=Me) (vide infra).

In marked contrast, irradiation of the sodium salt of the diazophosphonate, i.e., **1c**(X=Na) in the presence of an alkenes did not result in the formation of the corresponding cyclopropane to an extent which enabled us to examine the stereochemistry of the reaction.

The chemistry of 'parent' naphthylcarbenes (NC) has been examined by product analysis and also by laser flash photolysis.⁸⁻¹⁰ A comparison of the data available on the reactions of α -NC and β -NC with hydrocarbons shows that α -NC exhibits the lower reactivity and the higher singlet character and possesses the smaller singlet-triplet energy gap. Two key molecular structural differences are responsible for the observed difference in the reactivity. First, the α -position of the naphthyl moiety has the largest HOMO orbital coefficient (Hückel 0.425 vs. 0.263). This will lead to greater stabilization of the carbene center by π -p overlap thus making the carbenic center less electrophilic. A second factor which should be taken into account is the interaction between the carbene center and the peri-hydrogen, which as clearly shown from an EPR experiment shows a preference for the syn conformation of α -NC.

The marked difference in the reaction patterns as well as in the reactivities between the α and β -isomers of naphthyl(phosphonyl)carbene **1c**(X=Me) can also be explained in terms of either or both of these two factors. Thus, in the reaction with (Z)-but-2-ene (eq 6), α -**1c**(X=Me) produces only stereospecific cyclopropanation products **7**, while β -**1c**(X=Me) affords the cyclopropanes **7** and C-H insertion products **8**, the formation of which can be explained as indicating either that the β -isomer is more electrophilic and hence can attack even at the C-H bonds of the alkene or that, because of the higher singlet-triplet energy gap, the singlet state of β -isomer decays to the triplet which reacts by abstracting allylic hydrogens from the alkene before it undergoes intersystem crossing to regenerate the singlet.

(3) *Photolysis in Benzene* Irradiation in benzene resulted in the formation of products which were much more dramatically affected by the subtle changes in the carbenic structure. Thus, photolysis of α -**1c**(X=Me) in benzene afforded α -(naphthyl)benzylphosphonate α -**10**(X=Me), formally an insertion product of carbene α -**2c**(X=Me) into the C-H bond of the solvent, as major product along with a trace amount of (naphthyl)methylphosphonate α -**9**(X=Me), whereas similar irradiation of β -**1c**(X=Me) resulted in the formation of a mixture of the norcaradiene β -**11**(X=Me) and cycloheptatriene β -**12**(X=Me), no C-H insertion product, i.e., β -**9**(X=Me) being detected

in this case. Introduction of the phosphonate monoanion group again resulted in a dramatic decrease in the product obtained in the corresponding diester carbene. Thus, irradiation of **1c**(X=Na) in benzene resulted in the formation of **9** at the expense of either α -**10** or β -**11** and β -**12** (eq 7, Table 1).

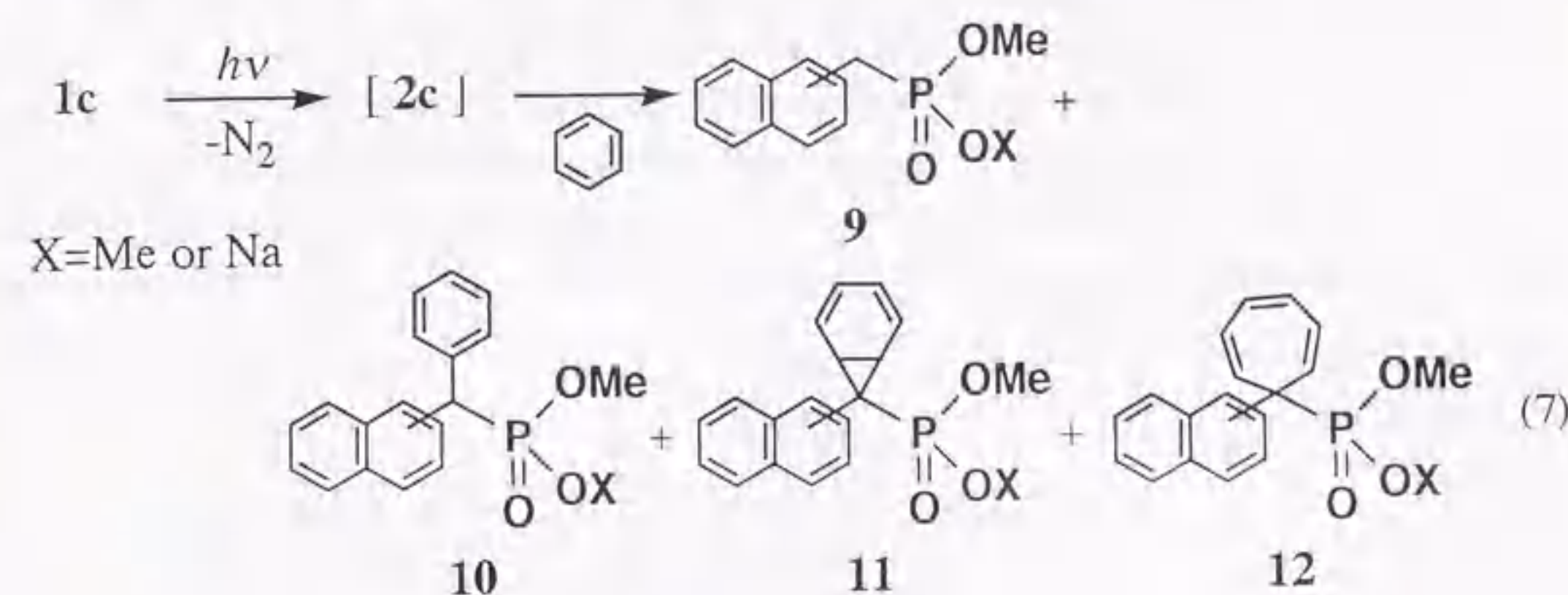


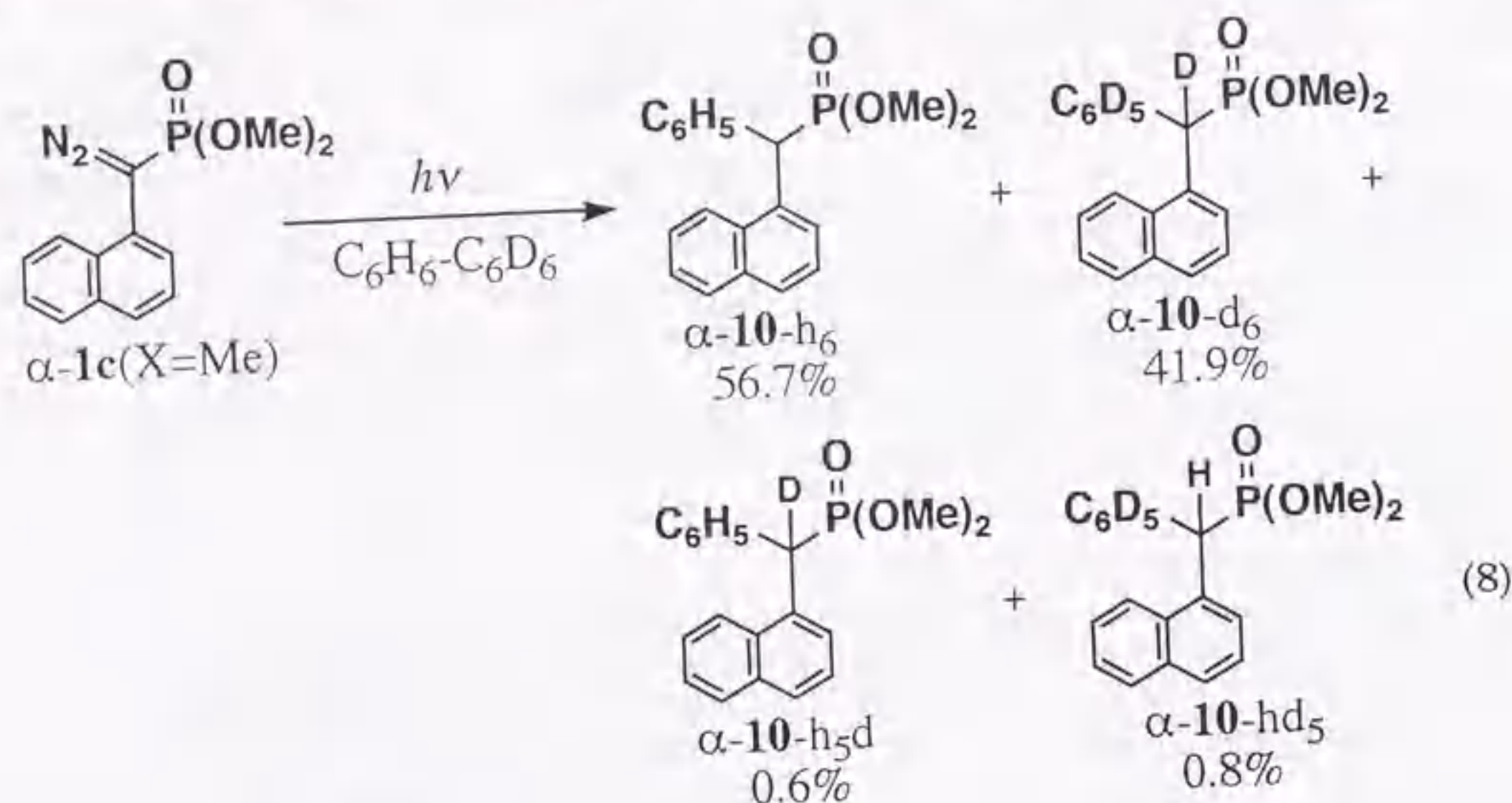
Table 1. Photolysis^a of Diazophosphonate **1c** in Benzene

diazo compd.		yield, ^b %			
	X	9	10	11	12
α - 1c	Me	0.9	96.6	0	0
	Na	43.2	7.7	0	0
β - 1c	Me	2.4	0	52.6	23.5
	Na	44.8	0	3.9	1.8

^aIrradiations were carried out on a 10mM degassed solution of **1c** in benzene at 20°C. ^bDetermined by GC.

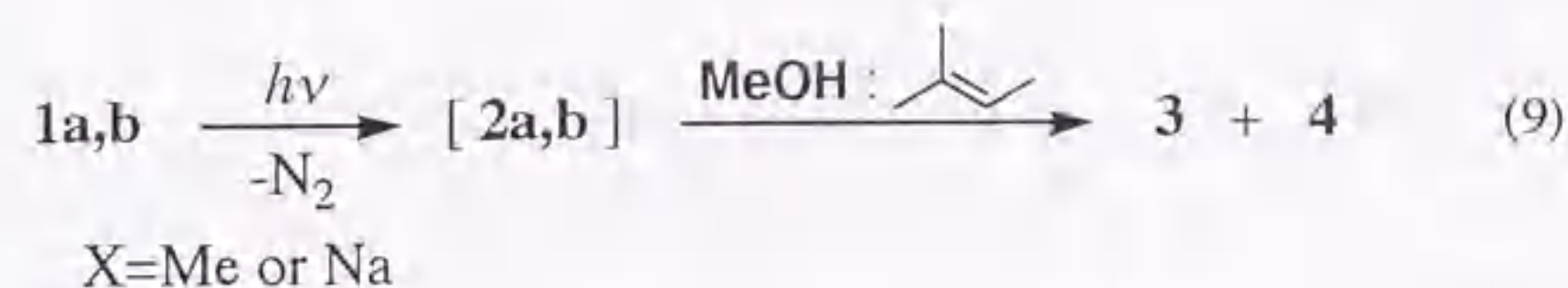
The dramatic difference in the reaction patterns in the reaction of α - and β -**2c**(X=Me) with benzene (eq 7) is rather surprising. The less electrophilic α -**2c**(X=Me) produced **10** which is formally an insertion into the C-H bonds of benzene, while the more electrophilic β -**2c**(X=Me) afforded a mixture of the norcaradiene **11** and cycloheptatriene **12**. Most carbenes react with benzene by initial attack on the π electrons on the aromatic ring to result in the formation of a norcaradiene and/or cycloheptatriene⁷ and the C-H insertion product is observed only in the reaction of highly electrophilic carbene, e.g., (CF₃)₂C:¹¹. It is likely that **10** is produced from the triplet state of α -**2c**(X=Me) by an abstraction-recombination mechanism. In order to check this possibility, the irradiation of α -**1c**(X=Me) was carried out in a 1:1 mixture of C₆H₆ and

C_6D_6 , and the deuterium distributions in the product **10** were determined by the mass spectrometric analysis, which clearly showed that direct insertion products, i.e., α -**10**- h_6 and - d_6 ($X=Me$) were formed almost exclusively (>98%) while the yield of scrambled products detected as only less than 2% (eq 8). The kinetic isotope effect (k_H/k_D) for the formation of **10** was determined to be 1.35 from the product distributions. The results



clearly indicate that the C-H insertion product is formed almost exclusively from the singlet carbene α -**2c** ($X=Me$). Recently Olah and his co-workers have studied the mechanism of the C-H insertion of methylene (CH_2) into benzene using kinetic hydrogen isotope effects as well as theoretical calculations and concluded that, while the insertion of the triplet methylene ($k_H/k_D=12.1\pm1.0$) proceeds through a stepwise mechanism which may involve an intermediate, the mechanism for the singlet methylene ($k_H/k_D=1.34\pm0.04$) seems to follow a concerted pathway although initial formation of π -complexes cannot be excluded.¹² Direct attack of the singlet α -**2c** ($X=Me$) at the C-H bond of benzene is however rather unlikely in the light of the decreased electrophilicity as well as increased steric crowding due to the peri-hydrogen. Presumably it is possible that, as the carbenic center of α -**2c** ($X=Me$) approaches to the π -electrons on the aromatic ring in a manner to form norcaradiene, it will experience severe steric hindrance due to the peri-hydrogen and the phosphonyl group and thus the carbene will be forced to follow the pathway to generate π -complex or a neutral zwitterionic species which will ultimately cascade to **10**. Alternatively, a norcaradiene may be formed which readily undergoes rearrangement to give the insertion product owing to the steric repulsion either as it is formed or during the work-up, although all attempts to detect the norcaradiene (i.e., α -**12** ($X=Me$)) have been unsuccessful to date.

(4) *OH Insertion-Addition Selectivity* Product analysis studies clearly indicate that the reactivities of phosphonyl-carbenes are highly sensitive to the change of the phosphonyl group. In order to obtain more quantitative information, competitive experiments were carried out. Irradiation of dimethyl α -diazobenzylphosphonate **1a** ($X=Me$) in a 1:3.8 binary mixture of methanol and 2-methylbut-2-ene afforded α -methoxyphosphonate (**3**) and cyclopropanes (**4**) (mixture of syn- and anti-isomers) in 17.8 and 81.1% yield, respectively. When the monosodium salt of α -diazobenzylphosphonate **1a** ($X=Na$) was irradiated under the same conditions, followed by neutralization and esterification by CH_2N_2 , however, the formation of the cyclopropanes **4** was greatly reduced and the α -methoxyphosphonate **3** became the major product (eq 9).



O-H insertion-addition selectivities (k_{OH}/k_{add}) were calculated by the equation of Doering and Henderson using the mole fraction of products and substrates and are listed in Table 2. It is evident from the data in Table 2 that the neighboring phosphonate group exerts a dramatic effect on the relative reactivities of the carbene **2**. Thus, the carbene derived from **1a** ($X=Na$) is 20 times more reactive towards methanol relative to the alkene than the carbene derived from **1b** ($X=Me$). A similar dramatic increase in the O-H insertion product in going from the ester to the sodium salt is observed in the photolysis of the diazo derivatives of benzylphosphonate **1b**.

On the other hand, naphthyl(phosphonyl)carbenes **2c** were generated in a binary mixture of methanol and hex-1-ene (1:4.2) and the product yields were determined by GC.

Inspection of the data summarized in Table 2 immediately indicates that the α -diester carbene α -**2c** ($X=Me$) is some three times more reactive towards methanol relative to the hexene than is the corresponding β -isomer β -**2c** ($X=Me$), while the magnitude of the effect of neighboring phosphonate group is much greater in the α -isomer than in the β -isomer as judged from the increase in the relative reactivities by replacing the function with a monoanion.

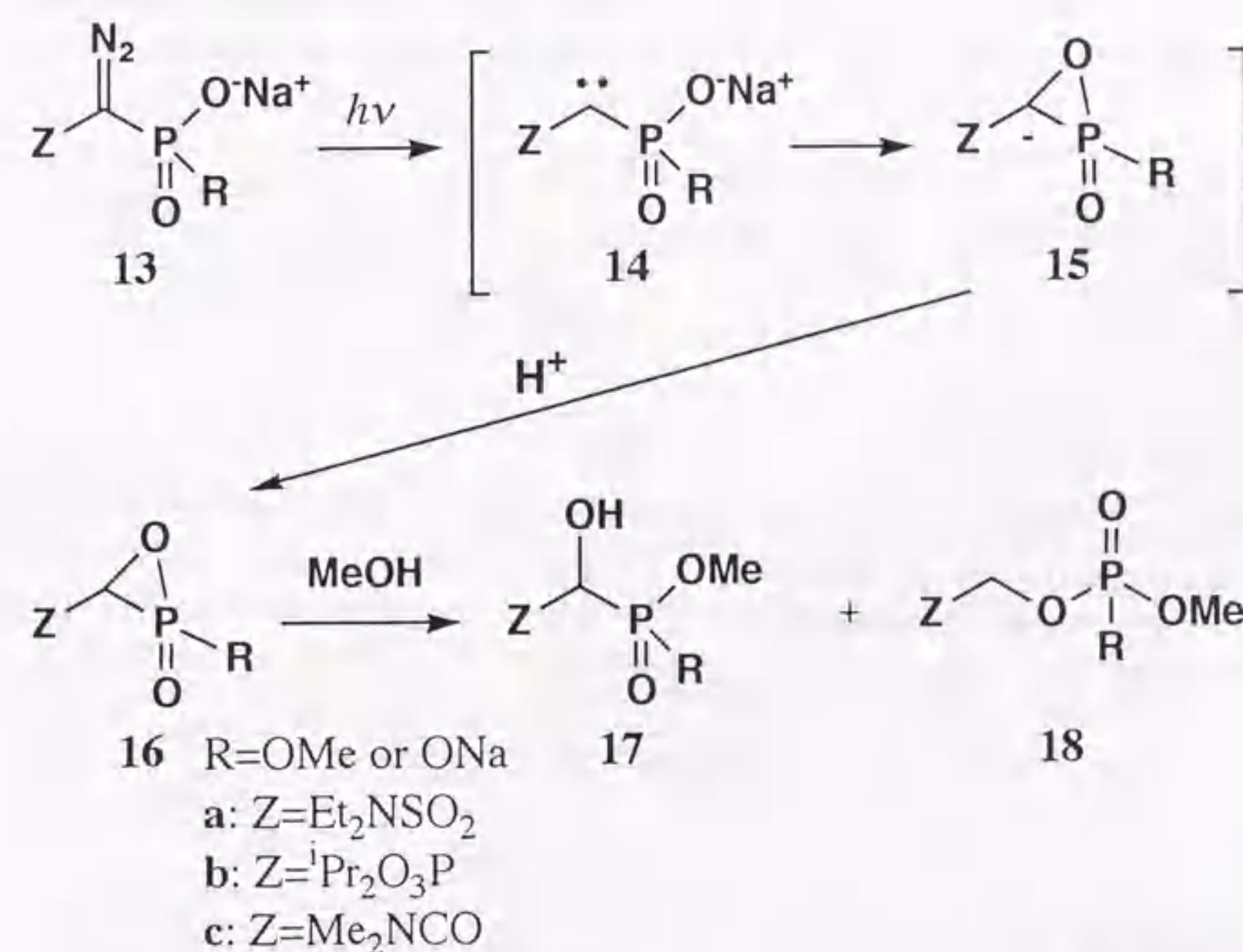
The difference in the reactivity caused by the phosphonate group is obviously too great to be attributable to differences in inductive, conjugative, or steric effects, but can be better explained in terms of neighboring group participation. Thus, it is reasonable to assume that the neighboring phosphonate anion can interact with the vacant p orbital of

diaz. compd.		alkene	yield, ^b %			<i>k</i> _{OH} / <i>k</i> _{add} (<i>k</i> _{rel})
	X		3	4	5	
1a	Me	2-methyl-2-butene	17.8	81.1	-	0.84 (1.00)
	Na		72.5	16.4	-	16.80 (20.0)
1b	Me	hex-1-ene	38.3	57.4	-	2.54 (1.00)
	Na		73.9	13.5	-	20.8 (8.19)
α-1c	Me	hex-1-ene	41.7	-	48.7	3.96 (1.00)
	Na		81.0	-	2.3	163 (41.2)
β-1c	Me	hex-1-ene	19.5	-	72.6	1.24 (1.00)
	Na		69.9	-	20.6	16.1 (13.1)

^bDetermined by GC.

It is important to compare our result with that of Bartlett who reported¹³ that similar phosphonate carbene **14** generated from the mono- or di- sodium salts of the phosphonates **13a**, **13b**, and **13c** in methanol do not undergo O-H insertion into the alcohol but give rise to α -hydroxyphosphonate **17** and/or phosphate **18**; they explained their results in terms of the oxaphosphirane anion **15** intermediate resulting from intramolecular trapping of the carbenes by phosphonate anion and subsequent protonation and reaction with methanol (Scheme 1). The intervention of oxaphosphirane

Scheme 1



66

because of the higher electron density in the α -position of the naphthyl HOMO. Introduction of a phosphonate anion on the α -position will result in further decrease in the electrophilicity of the carbenic center as a result of the intramolecular interaction. Steric factors involved in the reaction should play a more important role. Presumably, approach of the carbenic center to the alkene in a concerted manner must be sterically more hindered than that to an alcohol oxygen in the light of the substituents involved in the reaction center.¹⁴ The difference must be much more dramatic if the protonation mechanism is operative in the reaction with methanol. Such steric problems already present in the reaction of the ester carbene **2c** (X=Me) must become more important in the reaction of the anionic carbene **2c** (X=Na) where reactive intermediate undergoing the reaction is not a free carbene but oxaphosphirane anion type intermediate. Therefore, in the reaction of α -**2c** (X=Na), protonation by methanol is presumably greatly favored over cyclopropanation of the alkene.

(5) *Selectivity in Cyclopropanation* Carbenic philicity has been relatively well characterized¹⁹ on the basis of reactivity towards electron-rich and electron-poor alkenes. Thus, it is of immediate interest to know how the philicity will be affected by the neighboring phosphonate participation on the basis of cyclopropanation. Thus, the

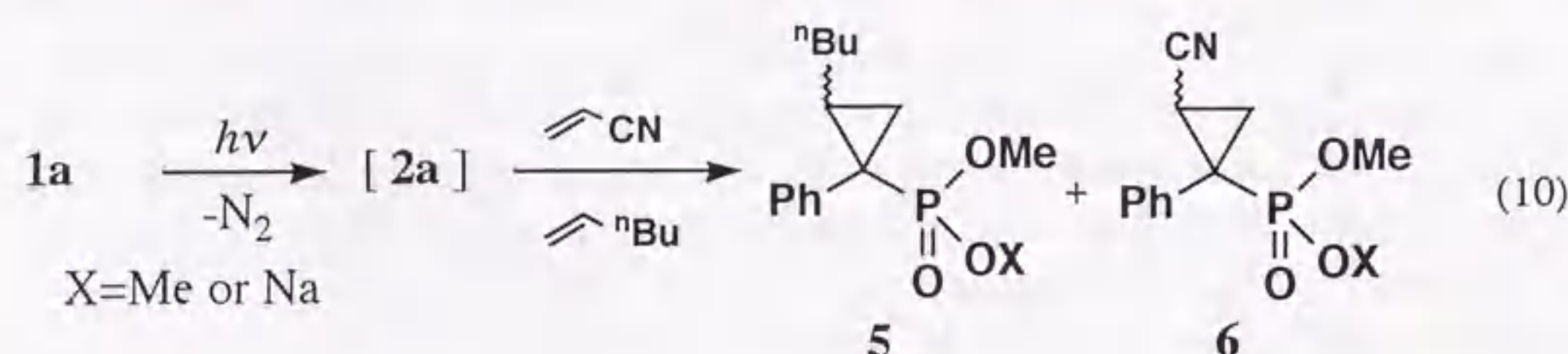


Table 3. Photolysis^a of Diazophosphonate in Alkenes. Effect of Neighboring Phosphonate Groups on Selectivity in Cyclopropanation

diazo compd.	X	yield, ^b %		$k_{ac}/k_{hex.}^c$
		5	6	
1a	Me	60.5	38.1	3.34
	Na	<1	64.2	>340

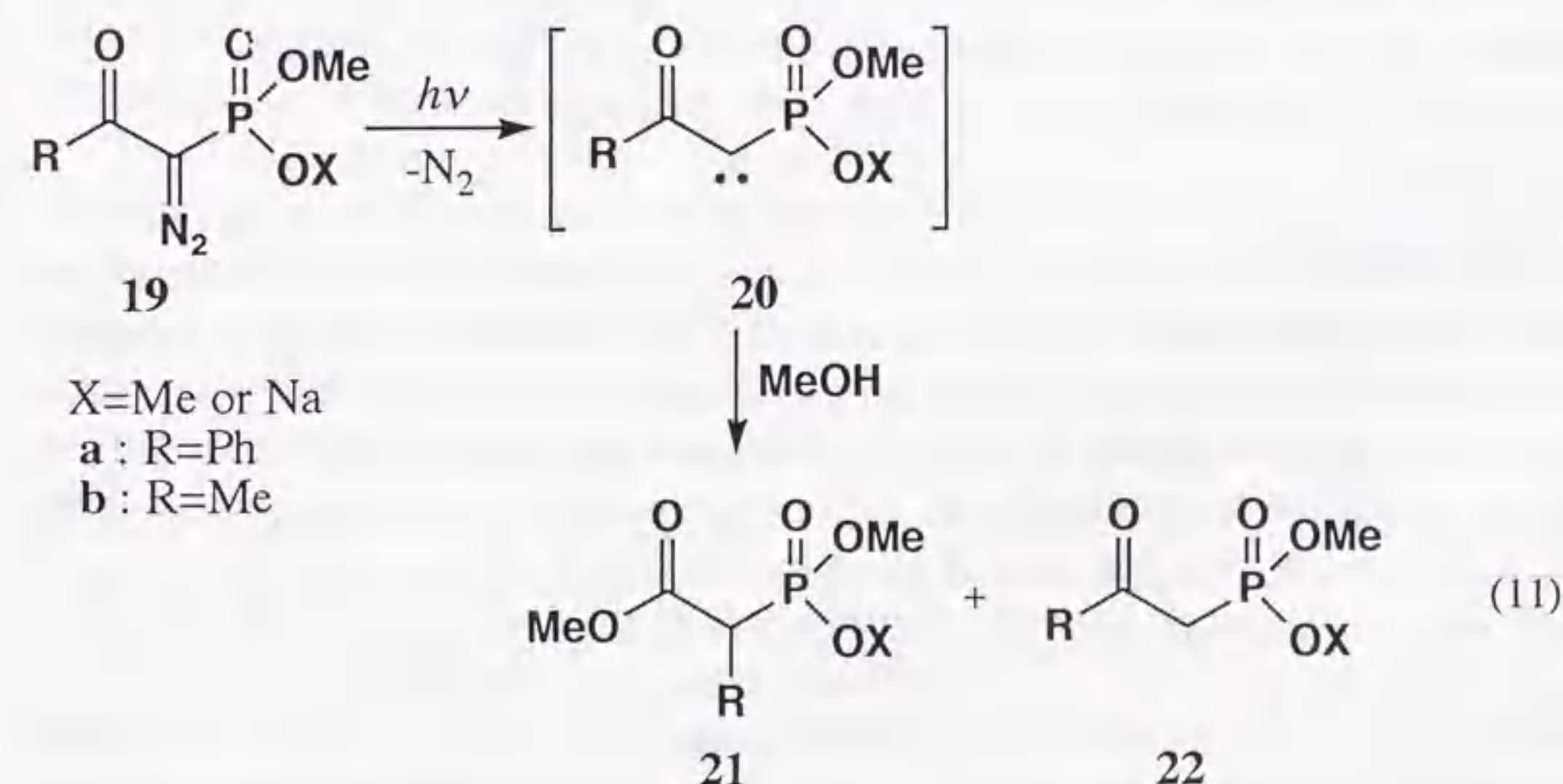
^aIrradiations were carried out on a 10mM degassed solution of **1a** in a 5.3:1 binary mixture of hex-1-ene and acrylonitrile at -10°C. ^bDetermined by GC.

^c $k_{acrylonitrile}/k_{hex-1-ene}$ calculated from the mole fraction of products and substrates.

diazophosphonates **1a** were irradiated in a binary mixture of hex-1-ene and acrylonitrile under conditions in which the thermal 1,3-dipolar cycloaddition of the diazo compound especially to the electron-poor alkene leading to cyclopropane via pyrazoline was negligible,^{22b} and the selectivities were determined from the product and substrate ratio. The results in Table 3 clearly indicate that the philicity was dramatically changed from slightly electrophilic to highly nucleophilic in going from ester carbene to anion carbene. Thus, the phosphonate anion carbene shows little reactivity towards normal simple alkenes, as has been observed for most typical nucleophilic carbenes, e.g., dimethoxycarbene,¹⁵ diamino- and amino(alkylthio)-carbenes.¹⁶

(6) *Selectivity in Intramolecular Reaction* In intramolecular reactions of carbene there are the reaction of the singlet state such as Wolff rearrangement and the reaction of the triplet state such as phenyl migration. If the neighboring phosphonate participation stabilized only the singlet state of the carbene, the decay path of the carbene must be dramatically affected by the participation.

Irradiation of dimethyl α -diazophenacyl-phosphonate **19a** (X=Me) in methanol afforded α -methoxycarbonylbenzylphosphonate **21a** and phenacylphosphonate **22a** in a ratio of ca. 1:1 (eq 11). However, when the monosodium salt of α -diazophenacylphosphonate **19a** (X=Na) was irradiated under the same conditions,



followed by neutralization and esterification by CH_2N_2 the formation of the phenacylphosphonate **22** was almost completely eliminated and the benzylphosphonate **21** became the sole isolable product. A similar but less dramatic

effect of ester residue was also observed in the photolysis of the diazo derivatives of acetonylphosphonate **19b** (eq 11, Table 4).

Table 4. Photolysis^a of α -Ketodiazophosphonate **19** in Methanol

diazo compd.	X	yield, ^b %	
		21	22
19a	Me	41.2	32.6
	Na	46.1	0
19b	Me	87.5	12.3
	Na	79.5	0

^aIrradiations were carried out on a 10mM degassed solution of **19** in methanol at 0°C. ^bDetermined by GC.

It is probable that these products are derived from the photolytically generated carbene **20**, which either undergoes the Wolff rearrangement (WR) leading to **21** or abstracts two hydrogens from the solvent giving rise to **22**. Accepting¹⁷ that the WR takes place in the singlet state of keto carbene while the double hydrogen abstraction is a characteristic reaction of the corresponding triplet, the results suggest that the neighboring phosphonate anion group completely suppresses the reaction from the triplet state of carbene. This can be interpreted as indicating that the singlet state is stabilized by the neighboring phosphonate group as a result of the intramolecular interaction with the vacant p orbital, thus, preventing the intersystem crossing to the triplet state.

Evidence to support the idea that the neighboring phosphonate anion can strongly interact with the carbenic center was obtained when the effect of phosphonate groups on the reaction patterns of the carbene was studied by systematically changing the carbenic substituents. Thus, generation of phenylphosphonylcarbene **2a** by irradiation of the corresponding diazomethane **1a** in methanol afforded O-H insertion product **3a** into the alcohol irrespective of substituents X. Similar generation of ester carbene **2d** (X=Me) also afforded O-H insertion product **3b** along with **25b**, the latter being formed as a result of phenyl migration followed by addition of the solvent.¹⁸ Irradiation of the sodium salt of **1d** (X=Na) gave, however, phosphonate **23b** at the complete expense of **3b** and **25b**. However, generation of methoxycarbonyl carbene **2e** (X=Me) in methanol afforded O-H insertion product **3c** as a major product, while similar generation of the corresponding phosphonate anion carbene **2e** (X=Na) again resulted in the almost complete elimination of **3e** but gave rise to the formation of α -hydroxyphosphonate **24e** in this case (eq 12, Table 5).

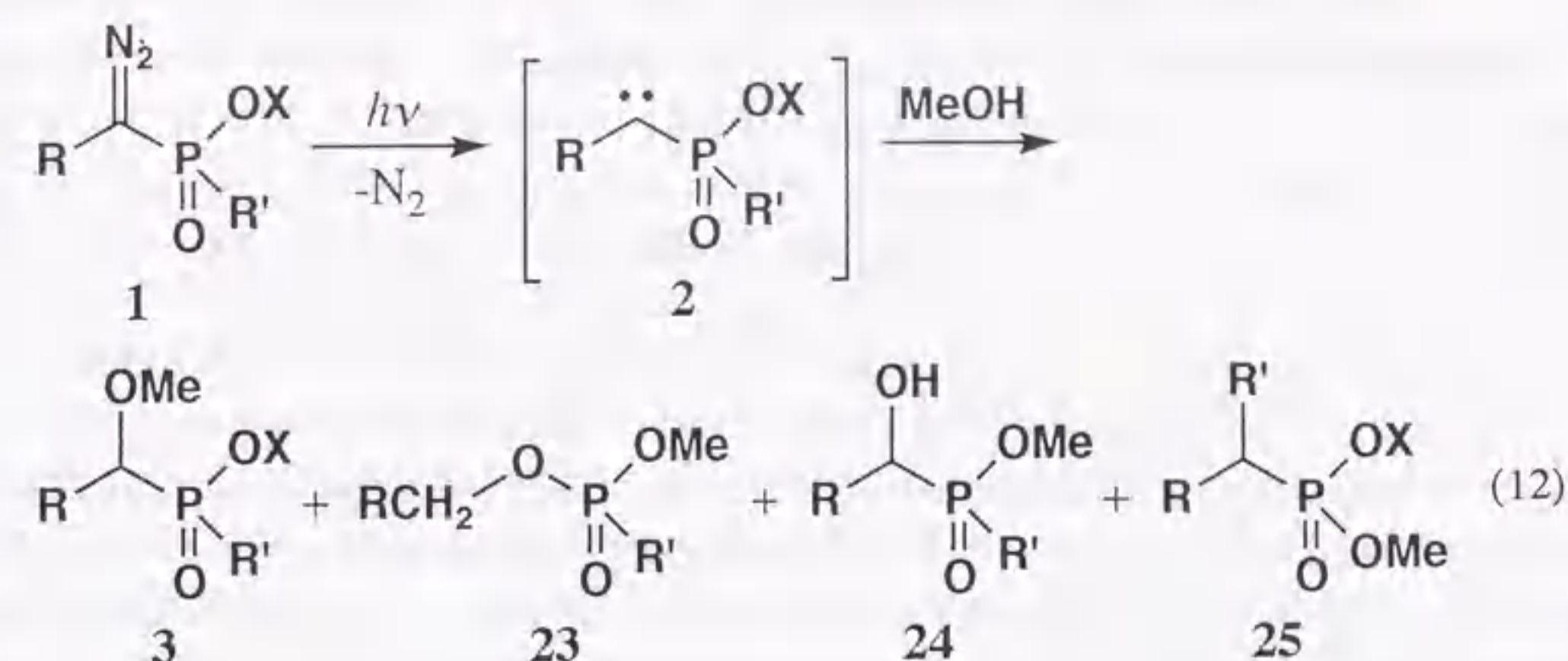


Table 5. Photolysis^a of Diazophosphonate **1** in Methanol

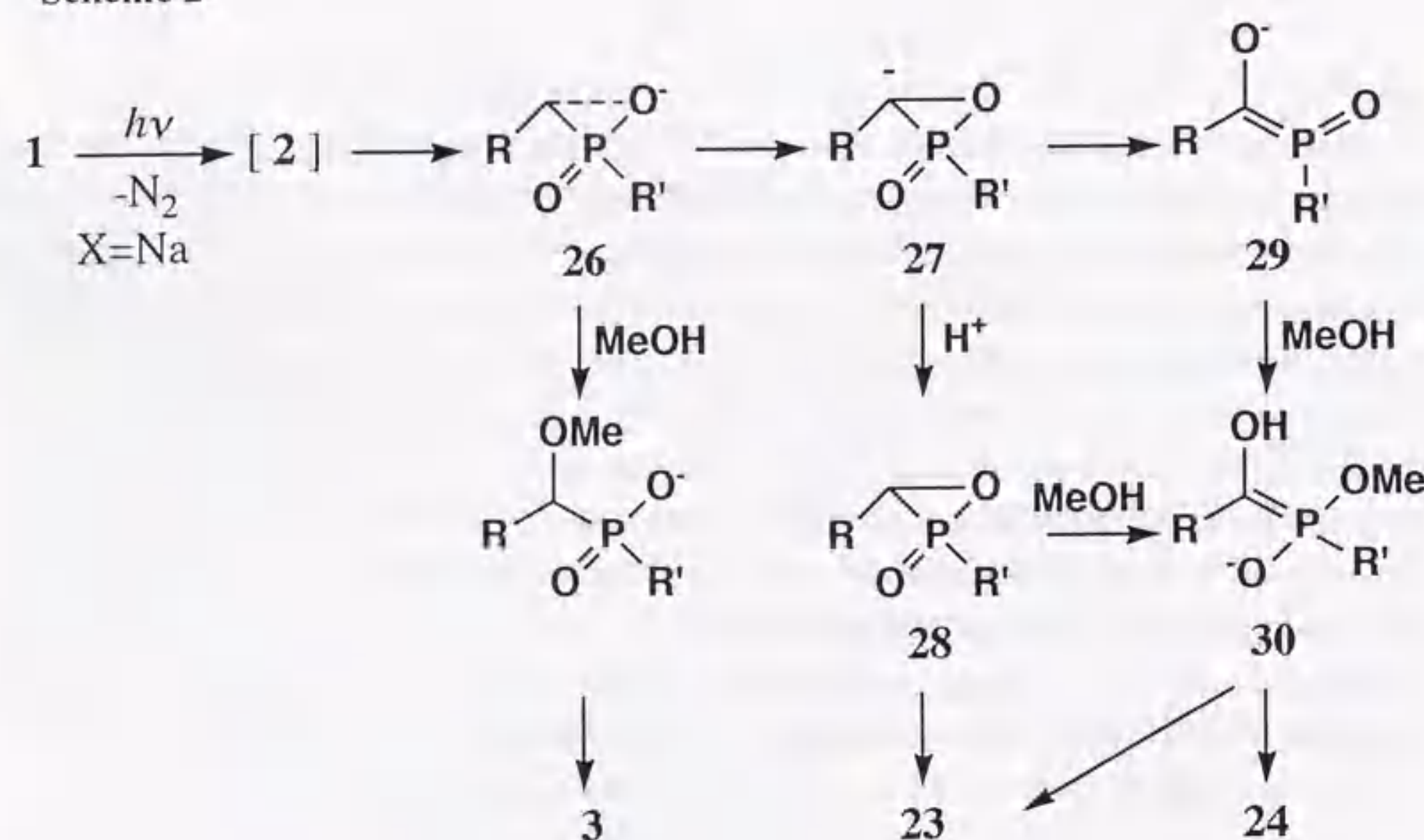
diazo compd.	1	R	R'	X	yield, ^b %			
					3	23	24	25
a		Ph	OMe	Me	>99	0	0	0
				Na	>99	0	0	0
d		H	Ph	Me	48.7	0	0	35.1
				Na	5.4	52.9	0	1.8
e		MeO ₂ C	OMe	Me	>99	0	0	0
				Na	0	0	>99	0

^{a,b}See footnotes in Table 4.

The results clearly showed that the neighboring phosphonate groups exerted enormous effects not only on both the product distribution and the reaction products; the mode of participation seemed to be sensitive to the carbenic substituents. The formation of apparently migrated products, i.e. **23** as well as **24** strongly suggest that the phosphonate anion becomes bonded fully or partially to the carbenic center during the progress of the reaction. These products are similar to the migration products **17** and **18** isolated by Bartlett et al.. Although a similar mechanism can be applied to explain the present results, the sensitivity of bond fission selectivity on carbenic substituents cannot be explained in terms of the common oxaphosphirane intermediate **27**. For example, it has been shown¹⁹ that the opening of the ring in azaphosphirane as a result of nucleophilic attack at phosphorus occurs with P-N bond breaking but P-C bond fission increases as electron withdrawing groups are introduced on the α -carbon. On the contrary, completely reversed trends were observed in the present reactions. Moreover, exclusive formation of the O-H insertion product **3** from carbene **2a** can be interpreted as

indicating that the nucleophilic attack should occur on benzyl carbon of the oxaphosphirane intermediate in this case. The results are then better explained by assuming that the extent of the interaction between the carbenic center and oxygen anion is sensitively changed as carbenic substituents change from Ph(**2a**) to H(**2d**) to MeO₂C(**2e**). Thus, **2a** is stabilized by the interaction of its vacant p orbital with the aromatic π orbital and, therefore, less susceptible to accept a negative charge developing at benzyl carbon atom in the transition state for the formation of oxaphosphirane intermediates. It is reasonable then to regard **2a** as a typical phosphonate participating carbene (e.g. **26**) that can react with methanol via protonation to give **3a**. However, the parent phosphinylcarbene (**2b**) should be strongly electrophilic and will be quenched by the neighboring phosphonate oxygen anion leading to the oxaphosphirane anion **27**, which is then immediately protonated by the solvent to give the oxaphosphirane intermediate **28**. Nucleophilic attack of the solvent on phosphorus followed by P-C bond breaking would give the observed product **23d**. Absence of the P-O bond fission product, i.e. **24d** in the reaction mixture is not clear at present. It is well-known, however, that α -hydroxyphosphonates rearrange to phosphates when treated with a catalytic amount of base. It may be that **24d** is simply unstable under these conditions and undergoes rearrangement to give **23d**. Carbene **2e** is also expected to be highly electrophilic and will be trapped by intramolecular phosphonate oxygen anion leading to oxaphosphirane anion. The anion must be stabilized by the adjacent CO as well as P=O and should undergo Wolff-type rearrangement of the oxygen anion giving

Scheme 2



rise to the Wolff intermediate, i.e. metaphosphinate **28**, which undergoes addition of the alcohol to produce **24e**. It is well documented²⁰ that methyleneoxophosphorane bonds are efficiently trapped by the alcohol (Scheme 2).

2-3 Detection of Triplet Carbenes by ESR Spectroscopy

(1) *Phenylphosphonylcarbenes (2a)* Irradiation of dimethyl α -diazobenzylphosphonate [**1a**(X=Me)] in ethanol at 15 K with Pyrex-filtered UV light produced two sets of signals characteristic of the carbenes in the triplet states, together with the intense signal at 332.2 mT due to radicals formed by reactions of the carbene with matrices. The signals of the major triplet species appeared at 187.4, 489.2, 573.6, and 851.8 mT, which were assigned to Hz, Hx, Hy, and Hz transition, respectively. Though Hz (low field), Hy, and Hz (high field) transitions of the minor triplet were observed at 152.8, 560.6, and 818.3 mT, respectively, no Hx transition of the minor isomer was detected due to overlapping with the intense signal of the major species. The zero-field splitting (zfs) parameters are calculated to be $D = 0.4866 \text{ cm}^{-1}$, $E = 0.0206 \text{ cm}^{-1}$, and $D = 0.4558 \text{ cm}^{-1}$, $E = 0.0176 \text{ cm}^{-1}$ for the major and minor species, respectively (Table 6). The zfs parameters of the parent phenylcarbene are reported to be $D = 0.5098 \text{ cm}^{-1}$ and $E = 0.0249 \text{ cm}^{-1}$.¹⁹ A considerably smaller D values of the phosphonylcarbene [**2a**(X=Me)] than that of the parent carbene show the delocalization of the π spin onto the phosphonate moiety.

Table 6. The Zero-Field Splitting Parameters for Carbenes **2a** and **2b**

carbenes	X	D, cm^{-1}	E, cm^{-1}	E/D
2a	Me	0.4866	0.0206	0.0423
		0.4558	0.0176	0.0386
2b	Na	0.4942	0.0194	0.0393
		0.6681	0.0074	0.0111
	Na	0.6585	0.0078	0.0118

The ESR detection of two triplet carbenes in matrices was already reported for the naphthylmethylenes,²² the vinylmethylenes,²³ and alkoxycarbonylcarbenes.²⁴ The observation of two similar but nonidentical carbenes in matrices was explained in terms of geometric isomerism in the triplet carbenes. In the case of alkoxycarbonylcarbenes, the π spin density on the carbonyl oxygen largely contributes to the zfs parameters of two geometric isomers. Since the π spin in **2a**(X=Me) is expected to be delocalized on the phosphonyl oxygen atom (P=O), it is reasonable to think that the rotational isomers in **2a**(X=Me) based on the restricted rotation about the carbon-phosphorus bond have

different zfs parameters. Thus the two triplet carbenes observed in the irradiation of **1a**(X=Me) would be assigned to the two rotameric isomers in **2a**(X=Me).

In contrast, photolysis of the monosodium salt of α -diazobenzylphosphonate **1a**(X=Na) produced the signals due to a single triplet carbene at 195.3, 494.4, 574.2, and 860.1 mT, together with a signal of doublet radical at 332.8 mT. The zfs parameters of the carbene are calculated to be $D = 0.4942 \text{ cm}^{-1}$ and $E = 0.0194 \text{ cm}^{-1}$. These values are close to those of the major species of the phosphonylcarbene [**2a**(X=Me)]. In the monosodium salts, the two oxygen atoms of the phosphonate anion moiety is thought to be equivalent in ethanol, so that the contribution of the oxygen atom to the zfs parameters is largely eliminated. It seems to be the reason why the geometric isomers were not observed in **2a**(X=Na). A detailed discussion of the contribution of the carbonyl oxygen to the zfs parameters in the carboxylate carbene was described in chapter 2.

In order to determine the spin multiplicity of the ground states of the carbenes **2a**, the temperature dependence of the intensities of their ESR signals was examined. As shown in Figure 1, the signal intensities of both carbenes decreased linearly with the reciprocal of the temperature in the range of 10-50 K. However, the plots deviated irreversibly from the line at above 50 K. These results indicate that these carbenes probably have triplet ground states, and are partially lost at above 50 K presumably due to chemical reactions with the matrices.

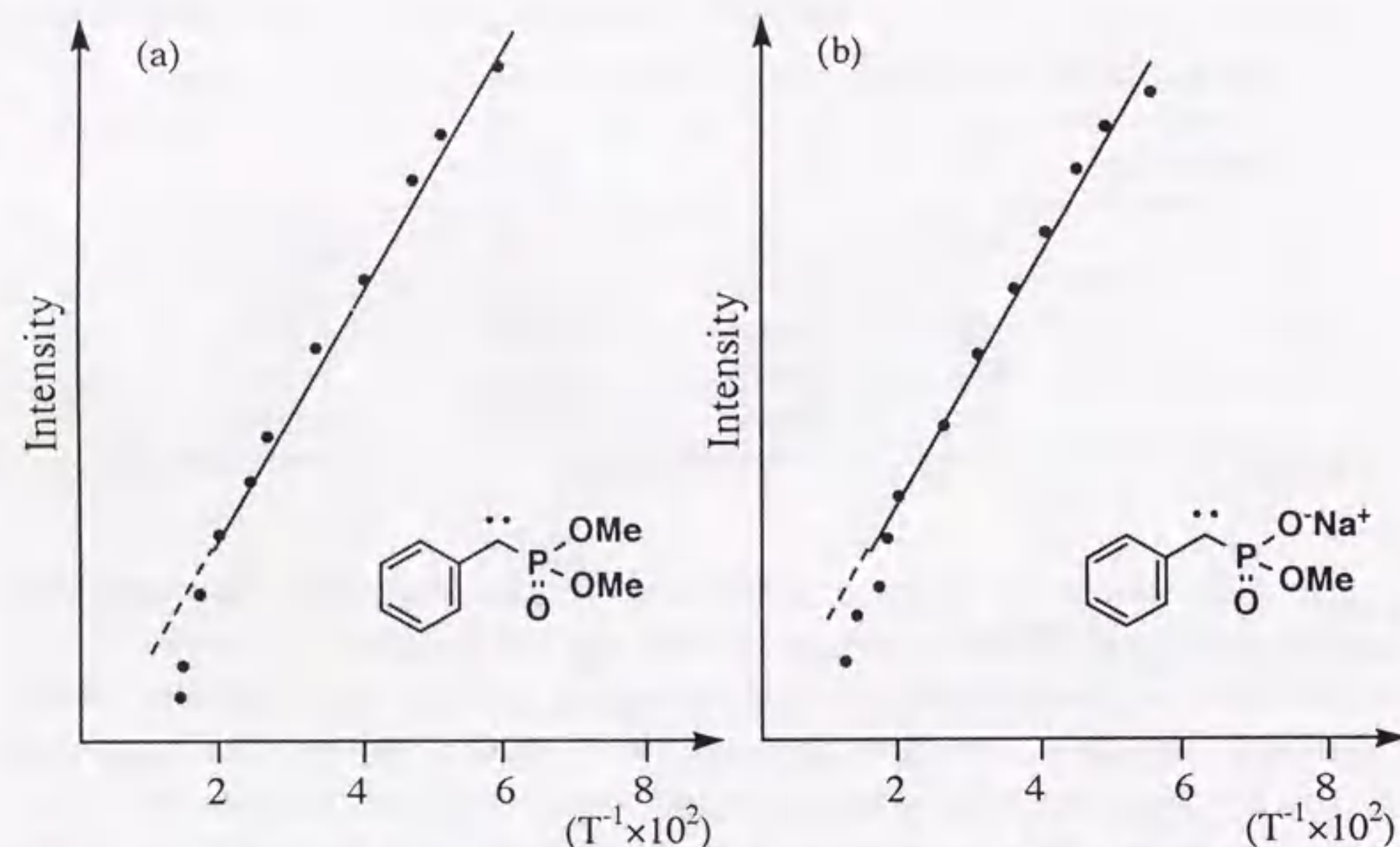


Figure 1. Curie plots of triplet signals after the photolysis of **1a**(X=Me) (a) and **1a**(X=Na) (b).

The ESR studies reveal that the phosphonate carbene **2a**(X=Na) has a triplet ground state, and that the structure and the thermal stability in matrices of the triplet state of **2a**(X=Na) are almost identical with those of the phosphonylcarbene (**2a**(X=Me)).

(2) *Phosphinylcarbene (2d)* Irradiation of methyl diazomethylphenylphosphinate [**1d**(X=Me)] in ethanol at 11 K with Pyrex-filtered light gave an intense signal at around 333 mT and weak signals of a triplet species at 383.0, 570.2, 602.8, and 1047.4 mT. The triplet species are identified as the phosphinate carbene [**2d**(X=Me)], the zfs parameters of which are evaluated to be $D = 0.6681 \text{ cm}^{-1}$ and $E = 0.0074 \text{ cm}^{-1}$. The ESR spectrum obtained by the irradiation of sodium salt of diazomethylphenylphosphinate **1d**(X=Na) under the same conditions resembled the spectrum obtained from **1d**(X=Me). The signals of the triplet carbene **2d**(X=Na) appeared at 372.0, 567.6, 601.9, and 1037.1 mT, from which the zfs parameters were calculated to be $D = 0.6585 \text{ cm}^{-1}$ and $E = 0.0078 \text{ cm}^{-1}$.

The D values of the phosphinate carbenes **2d** are moderately close to those of methoxycarbonylcarbene (**31**), while the E values are considerably smaller than those of **31**.²⁵ No simple explanation can be given for the origin of the small E values of **2d**, since many factors, that is, the spin density and angle at the divalent carbon, and the spin distributions and geometry of the phosphinate moiety, contribute to the zfs parameters.

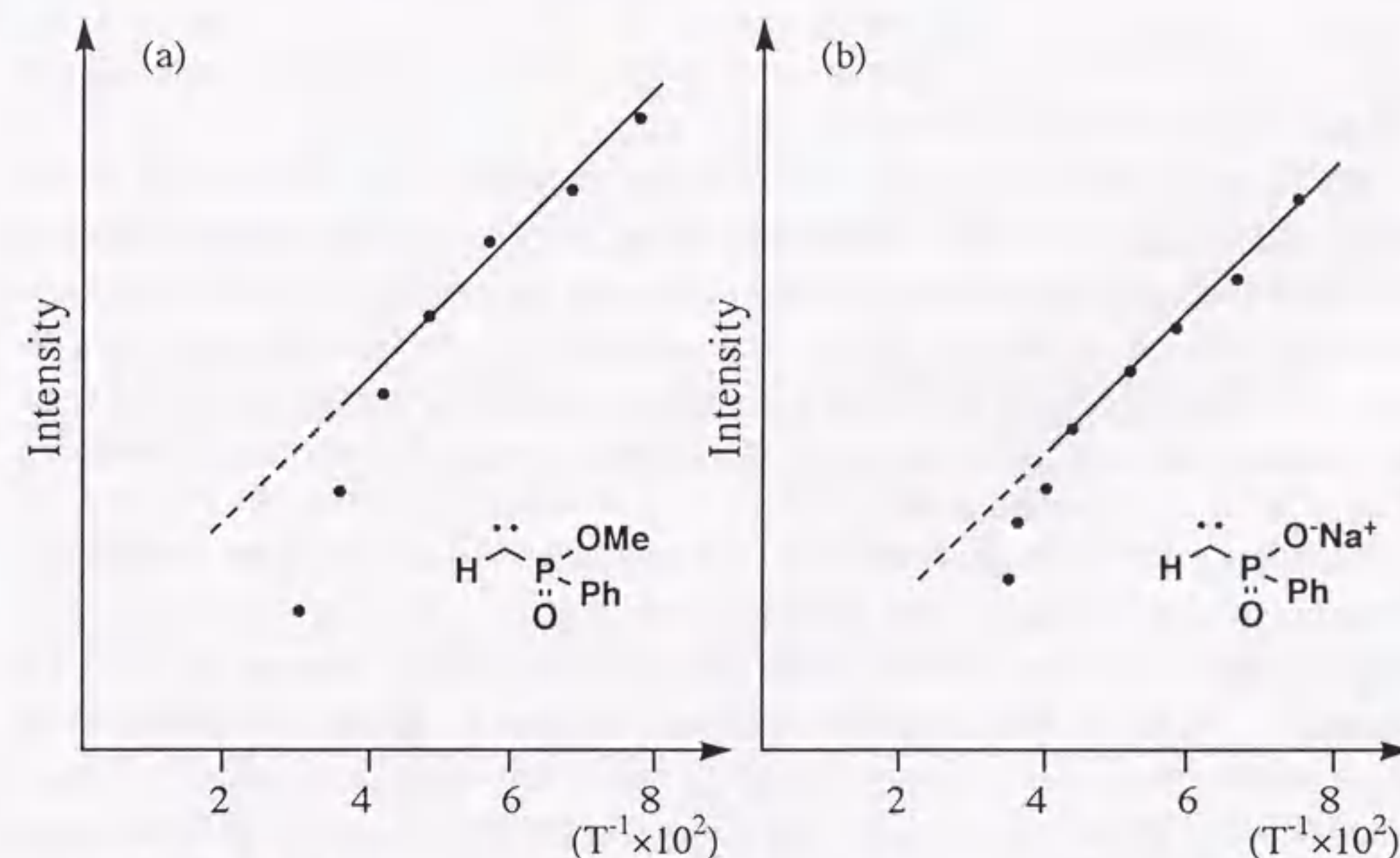


Figure 2. Curie plots of triplet signals after the photolysis of **1d**(X=Me) (a) and **1d**(X=Na) (b).

The temperature dependence of the signal intensities of the phosphinate carbenes **2d**(X=Me) and **2d**(X=Na) are shown in Figure 2. Reproducible linear relationship of the intensities vs. the reciprocal of temperature was obtained only in the temperature range of 11-25 K in both carbenes. These results show that the phosphinate carbenes **2d**(X=Me) and **2d**(X=Na) probably have triplet ground states, and react with the matrices at above 25 K. In analogy with a series of phosphonyl-carbenes **2a**, no effects of the phosphinate anion on the structure and the reactivity in matrices can be detected in the triplet state of the carbenes **2d**.

3-4 Detection of Triplet Carbene by UV/vis Spectroscopy

(1) *Steady-state Irradiation in Frozen Media* Irradiation ($\lambda > 300$ nm) of α -**1c**(X=Me) in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of the new absorption bands as the absorption due to α -**1c** was consumed, as is shown in Figure 3. The new absorption consisted of two identifiable features. There were sharp, intense UV bands centered at 375 nm and the visible portion of the spectrum showed two weak and broad overlapping bands with apparent maxima at 490, 530 and 570 nm. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming to room temperature and refreezing at 77 K led to complete disappearance of the characteristic absorption bands. The optical absorption spectra of several arylcarbenes in frozen media have been assigned and typically they consist of an intense UV band and a weak visible transition.²⁶ These features are present in the spectrum obtained in the photolysis of α -**1c**(X=Me). Thus, the absorption spectrum is attributable to the phosphonylcarbene α -**2c**(X=Me).

Photolysis of the monosodium salt of the diazomethane, i.e., α -**1c**(X=Na) under similar conditions also resulted in essentially similar absorption bands at the expense of the original absorption due to the precursor compound [Figure 3(b)]. Thus, again there were sharp, intense UV band at 365 nm and weak visible bands with apparent maxima at 525 and 568 nm and all the absorption bands completely disappeared when the matrix was thawed to room temperature. Thus, the transient absorption was ascribable to the carbenic phosphonate α -**2c**(X=Na).

Essentially similar absorptions were observed with the β isomer of the carbenes β -**2c** and the absorption maxima are summarized in Table 7. There were no significant changes in the spectrum of the carbene on changing from the diester group to the monoanion. However, the thawing experiment indicated an appreciable difference in thermal stability between the ester carbene **2c**(X=Me) and anion carbene **2c**(X=Na). Thus, gradual thawing of the matrix containing the carbenes **2c** at identical warming rates indicated that the characteristic absorption of the ester carbene disappeared at around 90 K while the absorption bands due to the anionic-carbene **2c**(X=Na) remained even at

110 K. Thus, carbene seems to be thermodynamically stabilized by anionic phosphonate groups.

In spite of those impressively large differences in reactivity on going from the ester to the anionic carbenes, subtle differences in the spectroscopic behavior between the two carbenic systems are rather surprising. However, careful examination of the data provides important information which supports the involvement of neighboring

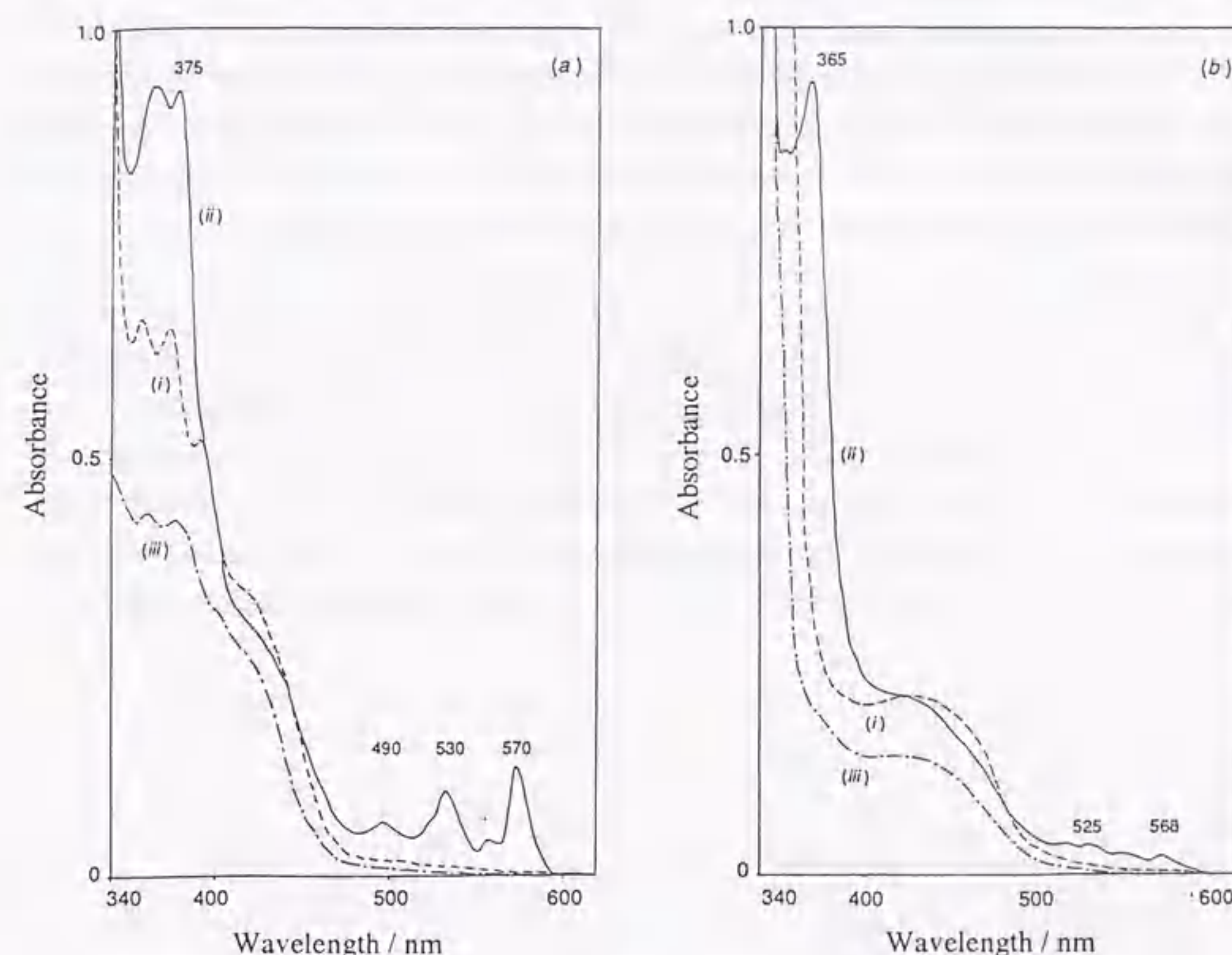


Figure 3. (a) UV/vis spectrum of transient products obtained by photolysis of α -**1c**(X=Me)(a) and α -**1c**(X=Na)(b): (i) UV/vis spectrum of α -**1c** in MTHF at 77K. (ii) Same sample after irradiation ($\lambda > 350$ nm). (iii) Same sample after thawing the matrix.

Table 7. Spectra of Carbenes **2c** in 2-Methyltetrahydrofuran Matrix at 77K

carbenes	X	λ_{max} / nm
α - 2c	Me	375, 490, 530, 570
	Na	365, 525, 568
β - 2c	Me	370, 510, 543, 590
	Na	378, 498, 535, 575

phosphonate participation. First, there is no significant difference in the spectrum of the carbenes in terms of the intensity on changing the the phosphonyl group to the phosphonate anion. Only slight changes in the maximum are observed but no systematic shifts are apparent (Table 7). On the assumption that these transient absorption bands observed in organic matrix at 77 K are due to the triplet carbenes, these results can be interpreted as indicating that the neighboring phosphonate group exerts little effect on the triplet state of the carbene. This is reasonable since in the singlet, phosphonate anion can effectively interact with the vacant p-orbital involving a two-electron stabilization while for the triplet, the interaction is only a one-electron, if any, and should be much less effective. The apparent thermal stability of the triplet phosphonate carbene **2c**(X=Na) may be explicable in terms of the stabilization by the neighboring phosphonate group even by the one-electron net interaction.

(2) *Laser Flash Photolysis in Fluid Solution* Flash photolysis of α -**1c**(X=Me) (3.8×10^{-4} M) in a degassed benzene solution at room temperature with the output of a XeCl excimer laser (308 nm, pulse width 12 ns) gave the transient absorption spectrum shown in Figure 4. The transient spectrum consisted of two identifiable features, a sharp, relatively intense UV absorption with a maximum at 380 nm and a broad, weak absorption extending from 500 to 600 nm, all of which appeared to rise within the pulse width of the laser and disappeared with similar kinetic behavior over a period of ca. 100

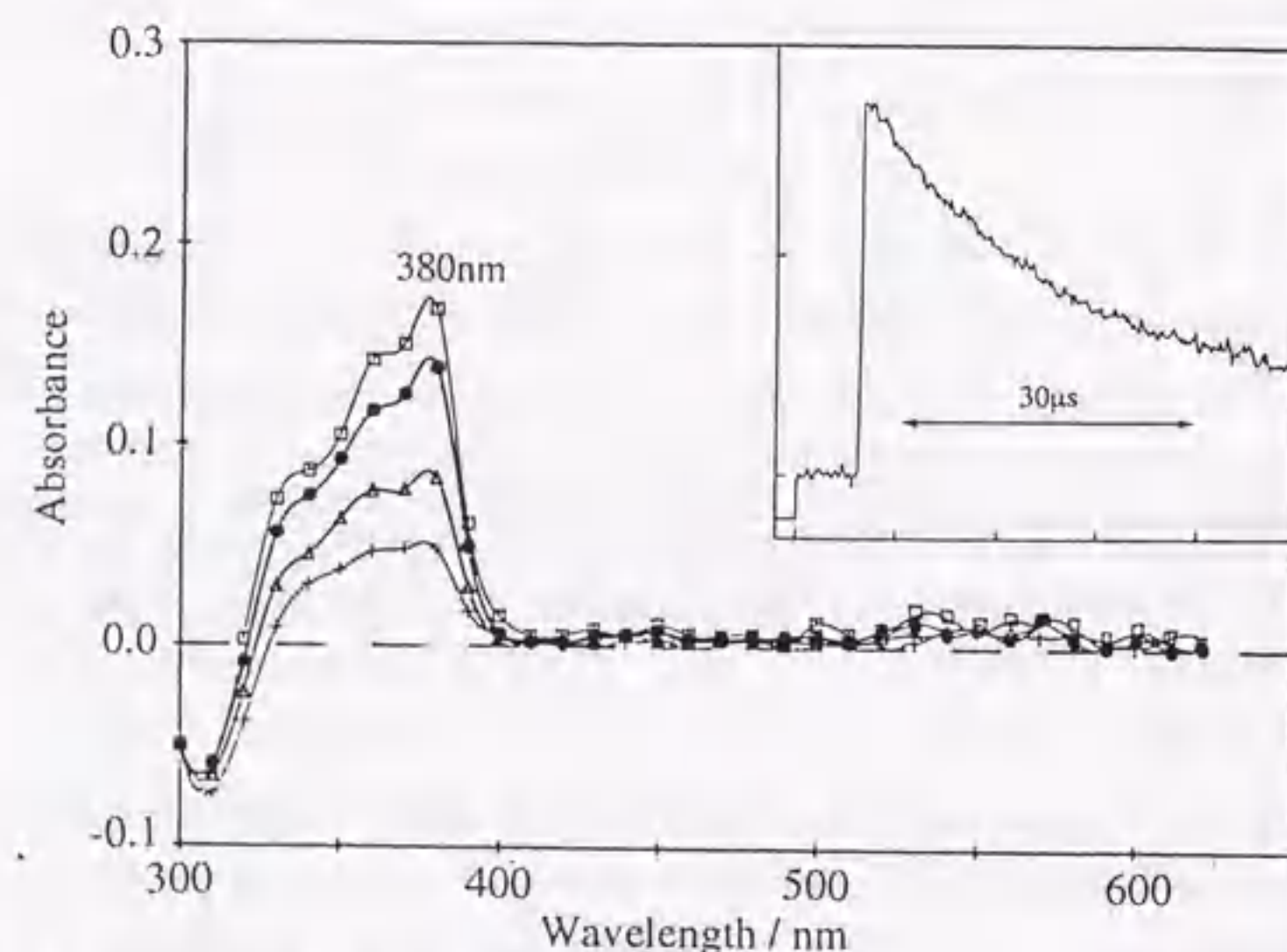
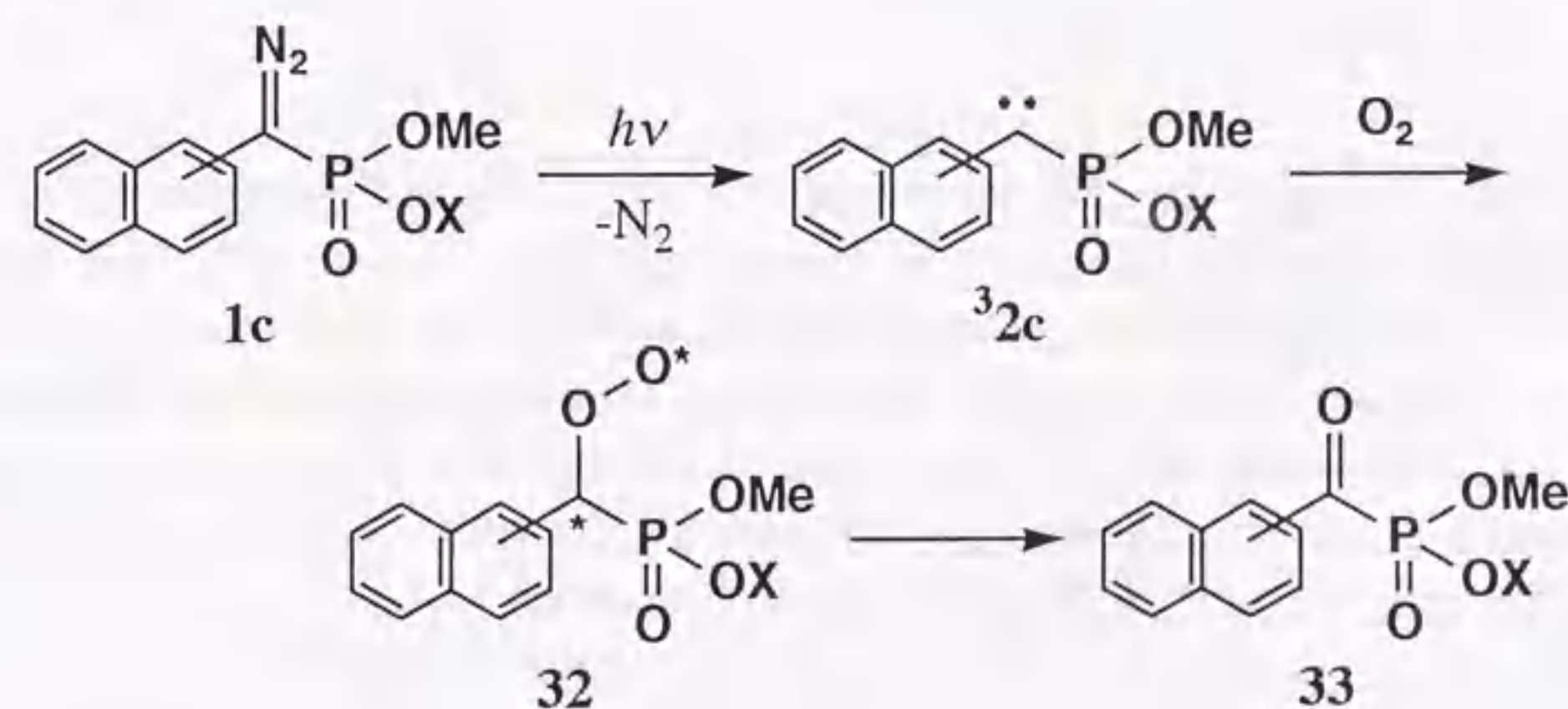


Figure 4. Time-resolved absorption spectra obtained upon 308nm excitation of α -**1c**(X=Me) in degassed benzene at room temperature: \square , 1.2 μ s; \circ , 5.9 μ s; Δ , 20 μ s; +, 41 μ s delay from 308nm laser pulse. Inset shows oscillogram trace monitored at 380nm.

μ s. The spectrum is similar to that measured during the photolysis of α -**1c**(X=Me) in a 2-methyltetrahydrofuran (MTHF) glass at 77 K and was therefore assigned to the carbene α -**2c**(X=Me). The oscillogram trace of the transient absorption due to α -**2c**(X=Me) monitored at 380 nm is shown in the inset of Figure 4. The decay was found to be first order and the lifetime was determined to be 20 μ s.²⁷ This assignment was further supported by a trapping experiment using oxygen. Thus, when flash photolysis of α -**1c** was carried out in aerated benzene solution, the transient absorption bands due to the carbene were observed but decayed very fast and the lifetime was now only 3.0 μ s. A broad absorption band with a maximum at 420 nm appeared (Table 8). The rate of increase in absorbance at 420 nm was practically identical with that of decay of the peak at 380 nm, showing that the carbene **2c**(X=Me), most likely in its triplet ground states, was quenched by O₂ to form a new species. Analysis of the spent solution showed the presence of a large amount of the ketone **33**. It is now well documented²⁸ that arylcarbenes with the triplet ground state are readily trapped by O₂ to give the corresponding aryl carbonyl oxides, which are observed directly either by matrix-isolation techniques or by flash photolysis. These carbonyl oxides usually show rather broad absorption band centered at around 390-450 nm. Thus, the observations can be interpreted as indicating that the triplet carbene **2c**(X=Me) is trapped by O₂ to generate the carbonyl oxide **32**, thus, confirming that the transient absorption at 380 nm quenched by O₂ is due to the triplet **2c**(X=Me).

Scheme 3



Essentially similar observations were obtained with the sodium salt of the diazophosphonate **1c**(X=Na). Thus, laser flash photolysis of **1c**(X=Na) in degassed benzene produced a transient spectrum consisting of sharp UV absorption at 380 nm along with broad visible absorption extending from 500 to 600 nm with lifetime of 26 μ s

ascribable to the carbene **2c**(X=Na). The transient absorption was quenched with O₂ to give a characteristic absorption (λ_{max} at 410 nm) due to the corresponding peroxide **32**. The key difference noted was in the intensities of the transient absorption. Thus, the absorbance of transient absorption due to the carbenic phosphonate **2c**(X=Na) was only a tenth of that of the ester carbene **2c**(X=Me). On the assumption that all the transient absorptions observed in time ranges of the order of microseconds are due to the triplet-state carbene, the marked decrease in the absorbance can be explained, at least in part, as indicating that the reaction of the singlet carbene is much faster than the rate of intersystem crossing in **2c**(X=Na) than in **2c**(X=Me), so that most of the carbene is quenched before it decays to the triplet states.

Table 8. Spectra and Lifetime of Transient Species in Benzene

diazo compd.	X	D/A ^a	carbene 2c		peroxide 32	
			λ_{max} /nm	lifetime/ μ s	λ_{max} /nm	lifetime/ μ s
α - 1c	Me	D	380	20		
		A	380	3.0	420	3.0
	Na	D	380	26		
β - 1c	Me	D	380	4.0	410	4.5
		A	370	2.0	420	2.1
	Na	D	380	27		
		A	380	2.3	420	2.9

^aD, degassed; A, aerated.

There is no significant difference in the lifetime of the triplet carbene between the α - and β -isomers of the ester carbenes **2c**(X=Me) in benzene. This is rather surprising in the light of the significantly different reaction patterns with benzene of α - and β -**2c**(X=Me) (Table 1, eq 7). However, as most of the reactions occur with the singlet-state carbene, direct observation of the singlet state with much faster time-resolution spectroscopy provided data reflecting its chemical reactions. For instance, there are significant differences in the reaction patterns between α - and β -naphthyl nitrenes, obviously because of the similar electronic steric factors as described above and this difference has been nicely explained in terms of the lifetime of the azirine intermediates which are directly observed by laser flash photolysis.²⁹

3-6 Theoretical Calculations

Semiempirical theoretical calculations offer further corroborating evidence for neighboring participation of the phosphonate group on phosphonylcarbene chemistry. The geometries of the singlet state of the parent phosphonic acid **34a** and the phosphonate anion carbene **34b** optimized by PM3-UHF(P) method³⁰ are shown in Figure 5. Inspection of the optimized geometries immediately reveals that the geometry changes dramatically on going from acid-carbene to anion-carbene. Thus, in the phosphonate carbene, the C-P=O bond angle is expanded to 141.4° whereas the C-P-O⁻ bond angle is contracted to 54.2° and consequently the distance between carbenic carbons and oxygen anions is calculated to be 1.50 Å, which is as short as that of a carbon-phosphorus single bond. The whole geometry of **34b** is then very much like that of oxaphosphirane anion, supporting the idea that an oxaphosphirane-anion-type

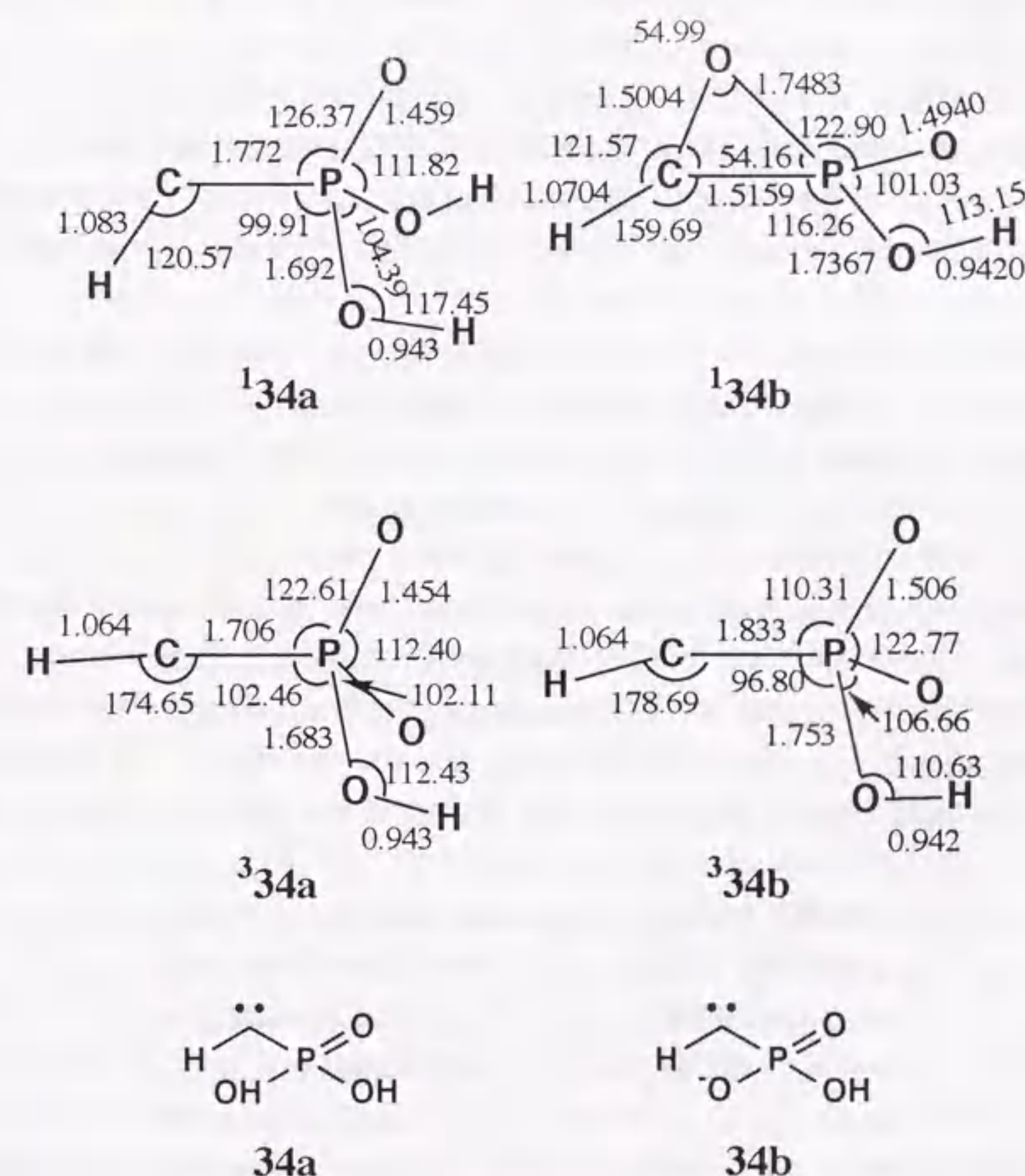


Figure 5. Optimized geometries for the singlet and triplet acid carbenes **34a** and acid anion carbenes **34b** (bond lengths are in Å and angles are in deg).

intermediate is involved in the reaction of phosphonate carbene. No such interaction is expected from the inspection of the geometry of acid carbenes **34a**. Optimized geometries of the corresponding triplet carbene were also calculated and are shown in Figure 5. It is immediately clear that no significant change in geometry is seen on going from acid- to anion-carbene in the case of the triplet. This is again in accord with the spectroscopic observations that the triplet states are little affected by the neighboring phosphonate anion group.

3-7 Summarizing Discussion

The present results demonstrate that the neighboring phosphonate groups also exert prominent effects on the fate of carbenes. The electrophilicity of phosphonylcarbenes is dramatically reduced as one changes the neighboring group from the phosphonate ester to the phosphonate anion group, and phosphonate carbenes are experimentally classified as typical nucleophiles. The migration products in the photolysis of **1d** or **1e** suggest the intermediary formation of oxaphosphirane **28** as a result of the intramolecular trapping of the carbene center by phosphonate anion followed by protonation.

Theoretical calculations offer further corroborating evidence for the formation of oxaphosphirane-anion intermediate **27**, which is protonated to give **28**.

ESR studies provided unequivocal evidence that the ground-state multiplicities are not affected by the neighboring group. Temperature studies of ESR signals showed that the structural change was not attained at least in the triplet manifold. These results are essentially the same as obtained for the carboxylate carbenes and are presumably due to the ineffective interaction of the half-occupied p orbital with the anion moiety.

LFP studies also provided decisive evidence that the ground-triplet state are not affected by the neighboring phosphonate group and the reaction of the singlet state is much faster than intersystem crossing in the phosphonate carbene than in the ester carbene.

It is important to consider the difference in the magnitude of participation caused by the anion group between the phosphonate- and the carboxylate-carbene. The magnitude of the effect caused by the neighboring phosphonate group is considerably smaller than that caused by the neighboring carboxylate group. The reason for this difference in the effectiveness as a participant between carboxylate and phosphonate group must reside partly in the difference in the geometry. Since carboxyl carbon is sp^2 hybridized, carboxylate group must lie in the same plane with the carbenic carbon and therefore the interaction between carbenic p orbital and carboxylate oxygen must be very effective. In the phosphonate carbene, on the other hand, the phosphorus compounds have four substituents arranged tetrahedrally about a phosphorus atom

which is essentially sp^3 hybridized and therefore the overlap between carbenic p-orbital and phosphonate oxygen must be poor.

Experimental

General Methods. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrophotometer, and 1H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). The GC analyses were performed on a Yanagimoto instrument, Model G-80 or Model G-180. The GC column A was prepared from 10% SE-30 on Diasolid L (5.0 mm \times 2.0 m); column B consisted of 5% PEG-20M on Diasolid L (5.0 mm \times 1.0 m). Thin-layer chromatography was done on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was carried out on silica gel (ICN for dry column chromatography or Fuji Davison for column chromatography). Gel permeation Chromatography (GPC) was performed on a JASCO, Model HLC-01 instrument. The GPC column was a Shodex H-2001.

ESR Measurements. The diazo compounds were dissolved in ethanol (ca. 5×10^{-3} M) and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The sample was cooled in an optical transmission ESR cavity at 15 K with an Air Products LTD-3-100 liquid helium transfer system, and irradiated with an Ushio USH-500D 500-W high-pressure mercury lamp and a Pyrex filter. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100kHz field modulation). The signal positions were read by the use of a Varian E-500 NMR gaussmeter.

Low Temperature UV-vis Spectra. Low temperature spectra at (77K) were obtained by using Oxford variable temperature liquid nitrogen cryostat (DN1704) equipped with quartz outer windows and sapphire inner windows. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked quartz cuvette of 1 mm path length and degassed by repeated freeze-degas-thaw cycles at ca. 10^{-5} Torr. The cuvette was placed in the cryostat and cooled to 77 K. After a baseline had been recorded, the sample were irradiated for several minutes in the spectrophotometer with a Halos 300 W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instruments intelligent temperature controller (ITC4).

Laser Flash Photolysis. The sample (10^{-3} - 10^{-4} mol dm $^{-3}$) was dissolved in dry benzene (over benzophenone ketyl), placed in a long-necked 10 × 10 mm (3 - 5 mL) quartz fluorescence cuvette, and degassed by a minimum of four freeze-degas-thaw cycles at pressure near 10^{-5} Torr immediately prior to the flash. Laser flash photolysis was carried out by means of an excimer laser (Lambda Physik EMG-50E, 308 nm) and a xenon arc lamp as excitation and probe light sources, respectively. A transient signal was detected by a combined monochromator, photomultiplier and storage scope (Iwatsu TS-8123) and fed into a microcomputer (Fujitsu FM-11BS) for analysis.

Irradiations for Product Identification. In a typical run, a solution of the diazo compounds (ca. 100 mg) in substrate (5 mL) was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The sodium salts of the diazophosphonate were dissolved in solvents with the minimum amount of 12-crown-4. The resulting solution with the salt of diazophosphonate was neutralized and treated with diazomethane shortly after the irradiation. The irradiation mixtures were then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS. These fully characterized products were then used as "authentic" compounds for product identification by coinjection in GC-MS.

Irradiations for Analytical Purposes. All irradiations outlined in Tables 1-5, 9 and 10 were carried out in a Pyrex tube of 5.0-mL capacity at below 10 °C. In order to avoid ambiguity of the relative yields due to the oxidation, the solution was degassed by subjecting the samples to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} mmHg before irradiation. Irradiation was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC as well as GC-MS comparisons with authentic samples and product distributions were conveniently determined by standard GC techniques.

General Comments concerning the Competition Experiments. These were carried out on binary mixtures of two substrates under the carefully controlled conditions. Thus, the precursory diazo compounds (0.1 mmol) were dissolved in the solvents (5 mL) consisted from large excess of the two substrates. Generally no solvents were used to avoid possible effect of solvent on the reactivities of carbenes. The reaction mixtures were degassed and irradiated as described above and product ratios were determined on a Yanagimoto gas chromatograph equipped with a calibrated flame ionization detector, coupled to a Shimadzu C-R1B digital electronic integrator. The

reaction mixture with the salt of diazophosphonate was treated with diazomethane before the GC analysis. Control experiments exclude the possible photoconversion of the products during the irradiation period and also demonstrate that no reaction occurs in the absence of light. Experiments were duplicated, and average deviations from the mean values were all <3%.

The runs using alkenes with electron-deficient double bond were carried out at a lower temperature in order to avoid the thermal pyrazoline pathway. Thus, the precursory diazo compounds were added to the substrate mixture precooled to -20 °C and the mixtures were carefully degassed and irradiated at -10 °C. Control experiments exclude the formation of cyclopropanes in the absence of light under these conditions.

Preparation of Dimethyl α -Diazobenzylphosphonate 1a(X=Me). Dimethyl benzoylphosphonate toluene-p-sulfonylhydrazone was prepared from dimethyl benzoylphosphonate and toluene-p-sulfonylhydrazide by the procedure of Seyferth,³¹ as a white solid in 84% yield: mp 173-174°C; ^1H NMR (CDCl_3) δ 8.40 (1H, bs), 7.90-7.10 (9H, m), 3.73 (6H, d, $J=11.0$ Hz), 2.44 (3H, s).

A suspension of the tosylhydrazone (10.0 g, 26 mmol) in a solution of sodium carbonate (2.86 g, 27 mmol) in 47 mL of distilled water was stirred at room temperature for 23 hr, during which time the hydrazone slowly dissolved and the solution became orange and opaque. The mixture was extracted with two 50 mL portions of ether, each portion being washed with 50 mL of water. The combined ether extracts were dried (Na_2SO_4) and evaporated to a volume of 20 mL. The concentrated ether solution was chilled slowly in a -78°C bath with scratching of the flask side. This procedure gave dimethyl α -diazobenzylphosphonate (**1a** (X=Me)) as orange crystals in 72.6 % yield; mp 44.0-44.5°C; ^1H NMR (CDCl_3) δ 7.30-6.95 (5H, m), 3.70 (6H, d, $J=11.5$ Hz); IR (NaCl neat) 2085 cm^{-1} .

Preparation of Sodium Methyl α -Diazobenzylphosphonate 1a(X=Na). The diazomethane **1a**(X=Na) was prepared by reaction of dimethyl α -diazobenzylphosphonate **1a**(X=Me) with sodium iodide according to the method of Goldstein.³² A solution of **1a**(X=Me) (2.32 g, 10 mmol) and sodium iodide (2.34 g, 16 mmol) in dry acetone (120 mL) was refluxed for 30 min. The resulting solution was cooled to 0°C to precipitate pale yellow crystals of **1a**(X=Na), which were filtered, washed with a small amount of cold dry acetone and dried under reduced pressure (10^{-1} Torr) at room temperature, yield 1.66 g, 70.9%, mp > 250°C; IR (KBr disk) 2080 cm^{-1} .

Preparation of Methyl α -Diazobenzyl(phenyl)phosphinate 1b(X=Me). This compound was prepared analogously to **1a**(X=Me), as orange crystals in 65.5%

yield; mp 65.0-73.0°C; ^1H NMR (CDCl_3) δ 7.90-7.64 (2H, m), 7.50-7.28 (3H, m), 7.25-6.91 (5H, m), 3.86 (3H, d, $J=11.5$ Hz); IR (KBr disk) 2065 cm^{-1} .

Preparation of Sodium α -Diazobenzyl(phenyl)phosphinate 1b(X=Na).

This compound was prepared analogously to 1a(X=Na), as yellow crystals in 43.4% yield; mp > 250°C; IR (KBr disk) 2060 cm^{-1} .

Preparation of Dimethyl (Naphthyl)diazomethylphosphonate 1c(X=Me).

The tosylhydrazone was prepared analogously, as a white solid in 50% yield; mp 112-115°C; ^1H NMR (CDCl_3) δ 7.86-7.70 (4H, m), 7.51-7.20 (7H, m), 3.62 (6H, d, $J=12.0$ Hz), 2.45 (3H, s).

The tosylhydrazone (300 mg, 0.69 mmol) was added in one portion to a solution of sodium (24 mg, 1.0 mM) in ethylene glycol (2.3 ml) at 65°C. The solution was stirred for 13 min at 65°C, cooled rapidly to 30°C and extracted with six portions of ether (5 ml, each). The combined ether extracts were washed with 5% aqueous NaOH and saturated aqueous NaCl, dried (Na_2SO_4) and evaporated to give dimethyl (α -naphthyl)diazomethylphosphonate (α -21c(X=Me)) as yellow crystals in 75.0% yield; mp 51-53°C; ^1H NMR (CCl_4) δ 7.98-7.28 (7H, m), 3.72 (6H, d, $J=11.8$ Hz); IR (KBr disk) 2080 cm^{-1} .

The β -isomer β -1c(X=Me) was prepared by essentially the same procedure as an orange crystals in 89.7% yield; mp < 30°C; ^1H NMR (CCl_4) δ 7.70-7.08 (7H, m), 3.72 (6H, $J=12.0$ Hz); IR (NaCl neat) 2078 cm^{-1} .

Preparation of Sodium Methyl(naphthyl)diazomethylphosphonate 1c(X=Na). These compounds were prepared analogously to 1a(X=Na). α -Isomer α -1c(X=Na); 62.3% yellow crystals; mp > 250°C; IR (KBr disk) 2068 cm^{-1} . β -Isomer β -1c(X=Na); 69.8% pale yellow solid; mp > 250°C; IR (KBr disk) 2070 cm^{-1} .

Preparation of Dimethyl α -Diazophenacylphosphonate 19a(X=Me).

This compound was prepared from dimethyl diazomethylphosphonate³¹ with benzoyl chloride by the procedure of Regitz³³, as a yellow liquid in 50.0% yield; ^1H NMR (CDCl_3) δ 7.70-7.27 (5H, m), 3.80 (6H, d, $J=12.0$ Hz); IR (NaCl neat) 2115 cm^{-1} .

Preparation of Sodium Methyl α -Diazophenacylphosphonate 19a(X=Na). This compound was prepared analogously to 1a(X=Na), as pale yellow crystals in 47.0% yield; mp > 250°C; IR (KBr disk) 2110 cm^{-1} .

Preparation of Dimethyl α -Diazoacetylphosphonate 19b(X=Me). This compound was prepared according to the procedure of Regitz³⁴ by diazo group transfer

of dimethyl acetylphosphonate with tosyl azide as a yellow liquid in 10.0% yield; ^1H NMR (CCl_4) δ 3.80 (6H, d, $J=12.0$ Hz), 2.16 (3H, s); IR (NaCl neat) 2120 cm^{-1} .

Preparation of Sodium Methyl α -Diazoacetylphosphonate 19b(X=Na). This compound was prepared analogously to 1a(X=Na), as white crystals in 35.2% yield; IR (KBr disk) 2100 cm^{-1} .

Preparation of Methyl Diazomethyl(phenyl)phosphinate 1d(X=Me).

This compound was prepared from methyl phthalimidomethyl(phenyl)phosphinate by the procedure of Regitz³⁵, as a yellow liquid in 11.5% yield; ^1H NMR(CCl_4) δ 7.80-7.57 (2H, m), 7.45-7.33 (3H, m), 3.97(1H, d, $J=12.5$ Hz), 3.72 (3H, d, $J=12.0$ Hz); IR (NaCl neat) 2100 cm^{-1} .

Preparation of Sodium Diazomethyl(phenyl)phosphinate 1d(X=Na).

This compound was prepared analogously to 1a(X=Na), as pale yellow crystals in 16.3% yield; mp > 250°C; IR (KBr) 2080 cm^{-1} .

Preparation of Dimethyl Methoxycarbonyldiazomethylphosphonate 1e(X=Me). This compound was prepared by the diazo group transfer of the corresponding phosphonate with tosyl azide according to the slightly modified method of Regitz.³³ To a solution of the phosphonate (1.00 g, 5.5 mmol) and $\text{KF} \cdot \text{Al}_2\text{O}_3$ (2.40 g, 12 mmol), which was prepared according to the method (type A) of Ando³⁶, in anhydrous acetonitrile (20 mL) was added an acetonitrile solution of tosyl azide (1.08 g, 5.5 mmol) at 0-5°C under vigorous stirring in the dark. This solution was stirred for 20 hrs at 20°C, filtered, evaporated and vacuum distilled to give dimethyl methoxycarbonyldiazomethylphosphonate (1e(X=Me)) as a yellow liquid in 75.1% yield; bp 105-130°C/ 8×10^{-4} Torr; ^1H NMR (CCl_4) δ 3.84 (6H, d, $J=12.0$ Hz), 3.82 (2H, s); IR (NaCl neat) 2140 cm^{-1} .

Preparation of Sodium Methyl Methoxycarbonyldiazomethyl phosphonate 1e(X=Na). This compound was prepared analogously to 1a(X=Na), as a pale yellow crystals in 51.0% yield; mp > 250°C; IR (KBr disk) 2120 cm^{-1} .

The Cycloadducts of 2. A solution of the diazo compounds (1, ca. 50mg) in the alkene (3 mL) in a Pyrex tube was irradiated at 10°C. After evaporation of the solvent under reduced pressure, the reaction mixture was separated by preparative TLC to give isomerically pure cyclopropanes. ^1H NMR and MS data are given in Table 9.

Table 9. NMR and MS Data of Cyclopropanes (4-8)

cyclopropanes (syn/anti) ^a	NMR, δ			MS: <i>m/e</i> (rel. intensity)
	Ar	OMe	other	
4a	(syn)	7.32-7.23(5H,m)	3.67(3H,d, $J=10.9$ Hz), 3.55(3H,d, $J=10.9$ Hz)	268(M ⁺ ,95), 143(100)
	(anti)	7.34-7.15(5H,m)	3.57(3H,d, $J=10.9$ Hz), 3.56(3H,d, $J=10.6$ Hz) 0.81(3H,s) 1.97-1.84(1H,m), 1.57(3H,s),1.06(3H,d, $J=6.9$ Hz), 0.82(3H,s)	
4b	(syn)	7.36-7.07(10H,m)	3.58(3H,d, $J=10.6$ Hz)	314(M ⁺ ,60), 143(100), 77(60)
	(anti)	7.36-7.07(10H,m)	3.61(3H,d, $J=10.9$ Hz) 2.21-2.11(1H,m),1.65(3H,s), 0.97(3H,d, $J=6.6$ Hz),0.74(3H,s)	
5a	(syn)	7.39-7.21(5H,m)	3.65(6H,d, $J=10.6$ Hz) 2.02-1.74(2H,m), 1.60-1.24(7H,m), 0.94(3H,t, $J=6.9$ Hz)	282(M ⁺ ,5), 239(25), 200(100), 129(65)
	(anti)	7.36-7.25(5H,m)	3.69(3H,d, $J=10.6$ Hz), 3.64(3H,d, $J=10.6$ Hz) 1.73-1.62(2H,m), 1.44-1.18(5H,m), 0.96-0.91(1H,m), 0.82(3H,t, $J=6.9$ Hz), 0.52-0.47(1H,m)	

^aPhosphonyl group is syn or anti with respect to the alkyl groups. ^bMixture of rotational isomers. ^cDimethyl 1-(β -naphthyl)pent-3-enylphosphonate.

Photolysis of 1, 19 in Methanol. A solution of the diazo compounds (ca. 5mg) in dry methanol (2 mL) in a Pyrex tube was irradiated. The reaction mixture was separated by preparative TLC to afford pure products. ¹H NMR and MS data are given in Table 10.

Photolysis of 1c(X=Me) in Benzene. A solution of 1c(X=Me) (50 mg) in benzene (5 mL) was irradiated and the irradiated mixture was separated by preparative TLC (ether-*n*-hexane 3:2) to give the following benzene adducts. α -10(X=Me) : 22.5% white crystals; ¹H NMR(CCl₄) δ 8.18-7.10 (12H, m), 5.11(1H, d, $J=27.0$ Hz), 3.45 (3H, d, $J=11.0$ Hz) ; MS *m/e* (relative intensity) 326 (M⁺, 20), 217 (100). β -11(X=Me) : 4.6% pale yellow oil; ¹H NMR (CCl₄) δ 7.70-7.10 (7H, m), 6.20-5.98 (2H, m), 5.74-5.64 (2H, m), 3.92-3.83 (1H, m), 3.76-3.68(1H,m), 3.53 (6H, d, $J=11.0$ Hz) ; MS *m/e* (relative intensity) 326 (M⁺, 45), 217 (100). β -37(X=Me) : 11.7% pale yellow oil ; ¹H NMR (CCl₄) δ 7.78-7.20 (7H, m), 6.88-6.77 (2H, m), 6.32-6.20 (2H, m), 5.60-5.40 (2H, m), 3.70 (3H, d, $J=11.0$ Hz), 3.63 (3H, d, $J=11.0$ Hz) ; MS *m/e* (relative intensity) 326 (M⁺, 30), 217 (100).

Table 9. Continued

cyclopropanes (syn/anti) ^a	NMR, δ			MS: <i>m/e</i> (rel. intensity)
	Ar	OMe	other	
α -7c				
(syn)	8.20-7.30(7H,m),	3.55(3H,d, J =11.0Hz), 3.42(3H,d, J =11.0Hz)	1.78-1.55(8H,m),	304(M^+ ,45), 179(100)
(anti)	8.22-8.11(1H,m), 7.79-7.62(2H,m), 7.42-7.32(4H,m)	3.54(3H,d, J =11.0Hz), 3.44(3H,d, J =11.0Hz)	2.23-1.87(2H,m), 1.05(3H,d, J =6.0Hz), 0.96(3H,d, J =6.0Hz)	
β -7c				
(syn)	7.92-7.31(7H,m),	3.64(6H,d, J =11.0Hz)	1.88-1.55(8H,m)	304(M^+ ,55), 179(100)
(anti)	7.90-7.60(4H,m), 7.50-7.20(3H,m)	3.60(6H,d, J =11.0Hz)	2.11-1.70(2H,m), 1.12-0.93(6H,m), 5.42-5.05(2H,m), 1.90-1.43(5H,m)	
β -7c ^c	-	7.87-7.32(7H,m)	3.72(6H,d, J =11.0Hz)	

^aPhosphonyl group is syn or anti with respect to the alkyl groups. ^bMixture of rotational isomers. ^cDimethyl 1-(β -naphthyl)pent-3-enylphosphonate.

Table 9. Continued

cyclopropanes (syn/anti) ^a	NMR, δ			MS: <i>m/e</i> (rel. intensity)
	Ar	OMe	other	
α -5c				
(syn)	8.36(1H,d, J =8.3Hz), 7.85-7.74(2H,m), 7.63-7.37(4H,m)	3.62(3H,d, J =11.2Hz), 3.53(3H,d, J =10.6Hz)	2.33-2.18(1H,m), 2.15-1.28(8H,m), 0.95(3H,t, J =6.9Hz)	332(M^+ ,55), 289(48), 250(69), 179(78), 152(100)
(anti) ^b	8.37-8.32(1H,m), 7.86-7.78(2H,m), 7.55-7.40(4H,m)	3.61,3.60,3.55,3.50, (6H,d, J =10.6Hz)	2.13-0.95(8H,m), 0.82,0.75(3H,t, J =7.1Hz), 0.53-0.10(1H,m)	
β -5c				
(syn)	7.81-7.75(4H,m), 7.53-7.41(3H,m)	3.66(3H,d, J =10.6Hz)	2.08-1.96(1H,m), 1.88-1.78(1H,m), 1.61-1.33(7H,m), 0.96(3H,t, J =7.1Hz)	332(M^+ ,60), 289(56), 250(90), 179(100), 165(54), 152(43)
(anti)	7.83-7.78(4H,m), 7.51-7.45(3H,m)	3.71(3H,d, J =10.6Hz), 3.65(3H,d, J =10.6Hz)	1.80-1.71(2H,m), 1.54-1.15(6H,m), 0.58-0.48(1H,m)	
6a				
(syn)	7.44-7.31(5H,m)	3.76(3H,d, J =10.9Hz), 3.73(3H,d, J =10.9Hz)	2.18-2.08(1H,m), 1.99-1.90(1H,m), 1.75-1.66(1H,m)	251(M^+ ,95), 140(60), 115(90), 109(100)
(anti)	7.47-7.35(5H,m)	3.72(3H,d, J =10.9Hz), 3.67(3H,d, J =10.9Hz)	2.45-2.35(1H,m), 2.08-1.97(1H,m), 1.76-1.67(1H,m)	

^aPhosphonyl group is syn or anti with respect to the alkyl groups. ^bMixture of rotational isomers. ^cDimethyl 1-(β -naphthyl)pent-3-enylphosphonate.

Table 10. Continued

products	NMR, δ		MS: <i>m/e</i> (rel. intensity)
	P-OMe	other	
24e	3.84(3H,d, J =11.6Hz), 3.81(3H,d, J =11.6Hz)	9.07(1H,bs),4.61(1H,d, J =11.2Hz),3.76(3H,s)	198(M^+ ,1),139(25), 124(30),109(100)
25d	3.57(6H,d, J =11.0Hz)	7.42-7.00(5H,m),3.00(2H,d, J =22.0Hz)	200(M^+ ,21),91(100)

Table 10. NMR and MS Data of Irradiation Products of 1,19 in Methanol

products	NMR, δ		MS: <i>m/e</i> (rel. intensity)
	P-OMe	other	
3a	3.60(3H,d, J =11.0Hz), 3.53(3H,d, J =11.0Hz)	7.40-7.10(5H,m),4.30(1H,d, J =15.0Hz),3.30(3H,s)	230(M^+ ,1),121(100)
3b	3.63(1.5H,d, J =11.0Hz), 3.50(1.5H,d, J =11.0Hz)	7.70-7.05(10H,m),3.30(3H,s), 2.50(0.5H,d, J =11.0Hz),2.38(0.5H,d, J =8.0Hz)	276(M^+ ,0.2),155(3), 121(100)
α -3c	3.70(3H,d, J =10.6Hz), 3.54(3H,d, J =10.2Hz)	8.17(1H,d, J =8.3Hz),7.90-7.84(2H,m),7.79-7.75(1H,m), 7.58-7.48(3H,m),5.37(1H,d, J =16.2Hz),3.40(3H,s)	280(M^+ ,3),171(100)
β -3c	3.73(3H,d, J =10.6Hz), 3.62(3H,d, J =10.6Hz)	7.90-7.85(4H,m),7.60-7.39(3H,m), 4.72(1H,d, J =15.5Hz),3.43(3H,s)	280(M^+ ,3),171(100)
3d	3.62(3H,d, J =10.5Hz)	7.78-7.57(2H,m),7.43-7.20(3H,m), 3.68(2H,d, J =11.4Hz),3.36(3H,s)	180(40),179(42), 155(100),77(95)
3e	3.87(3H,d, J =10.9Hz), 3.86(3H,d, J =10.6Hz)	4.28(1H,d, J =18.8Hz),3.86(3H,s),3.54(3H,s)	212(M^+ ,0.5),197(1), 109(45),93(100)
21a	3.64(3H,d, J =11.0Hz), 3.56(3H,d, J =10.0Hz)	7.45-7.15(5H,m),4.10(1H,d, J =23.0Hz),3.39(3H,s)	258(M^+ ,45),132(70), 109(65),93(100)
21b	3.72(6H,d, J =11.0Hz)	3.70(3H,s),3.60-3.22(1H,m), 1.37(3H,dd, J =7.0,18.0Hz)	196(M^+ ,1),109(100), 55(98)
22a	3.70(6H,d, J =11.0Hz)	8.00-7.90(2H,m),7.53-7.20(3H,m), 3.62(2H,d, J =23.0Hz)	228(M^+ ,8),109(6), 105(100),77(60)
22b	3.70(6H,d, J =11.0Hz)	3.00(2H,d, J =23.0Hz),2.25(3H,s)	166(M^+ ,10),109(75),94(100)
23d	3.68(6H,d, J =11.0Hz)	7.81-7.57(2H,m),7.46-7.35(3H,m)	186(M^+ ,50),91(100),77(80)

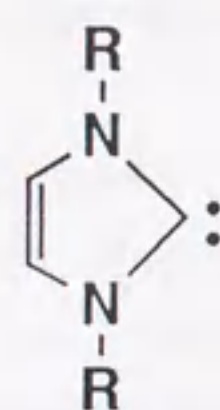
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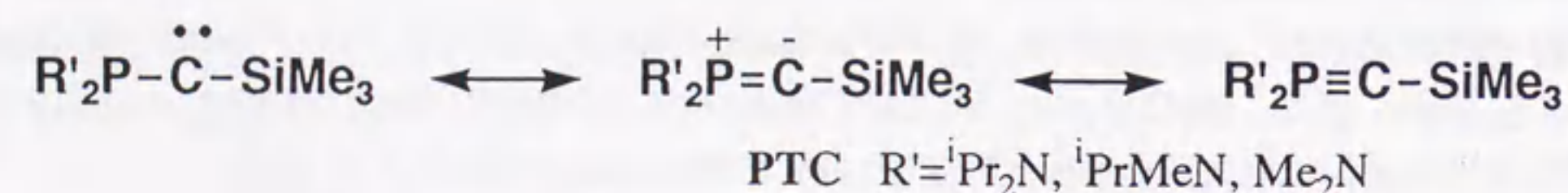
Part 2

Steric Protection in Carbene Chemistry

In contrast to the long history of persistent radicals¹, which started with the work of Moses Gomberg in 1890, that of persistent carbenes is much shorter. Only a few years ago "bottle-able" carbenes i.e., imidazol-2-ylidenes (IDY) and phosphanyl-(trimethylsilyl)carbenes (PTC) were first isolated.^{2,3} These carbenes are stabilized not



IDY R=Ph, Mesityl, Adamantyl etc



only by bulky protecting groups but also by heteroatom substituents directly connected to the carbenic carbon atom. Owing to these substituents, these carbenes have singlet ground states. But their electronic configurations are still a topic of debate.⁴ The next challenge is the stabilization of a carbene hopefully having a triplet ground state by all-carbon substituents.

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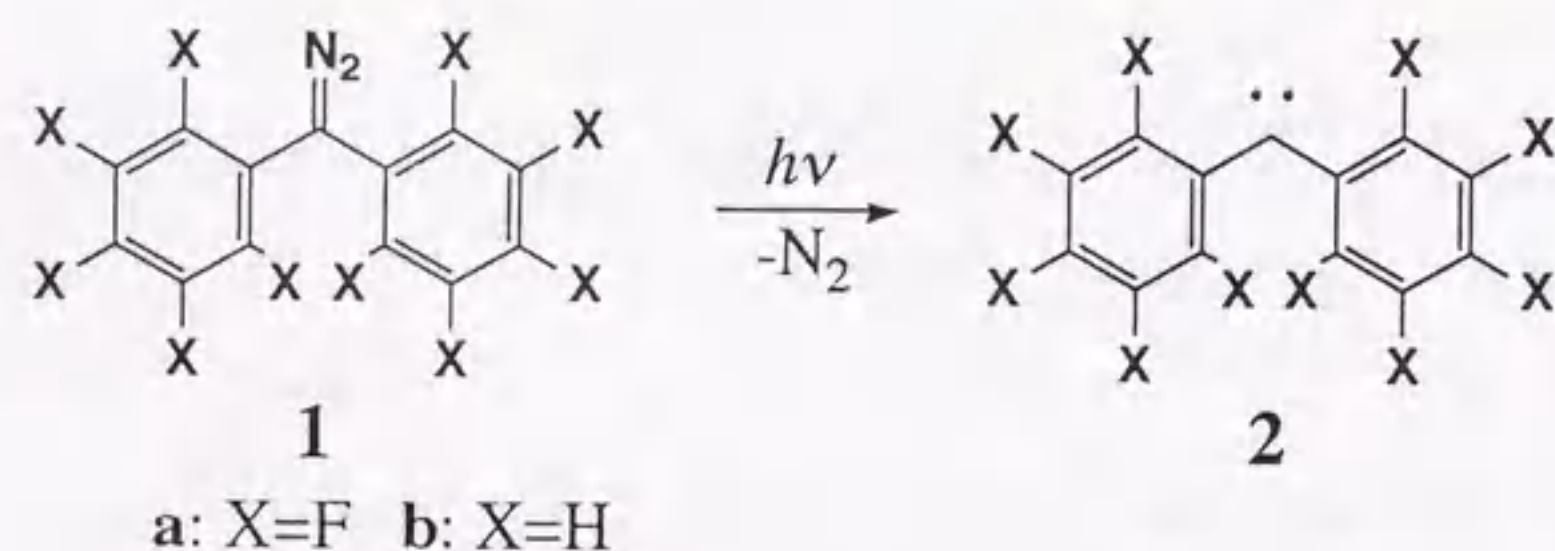
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Chapter 4 Chemistry, Kinetics, and Spectroscopy of Decafluorodiphenylcarbene

4-1 Introduction

Polyfluorinated molecules often display unique reactivity and solubility properties relative to their nonfluorinated analogues and have been the object of considerable interests for many years.¹ This is also true in the field of carbene chemistry.^{2,3} For instance, CF_2 reacts with bicyclo[2.1.0]pentane by two bond cleavage to give 1,1-difluoro-1,5-hexadiene while other simpler carbenes undergo simple insertion.³ Given the expected unusual reactivities, it is somewhat surprising that relatively few perfluorinated carbenes have been investigated.² In this regard, we have prepared and photolyzed decafluorodiphenyldiazomethane (**1a**) and compared the reactivities of decafluorodiphenylcarbene (**2a**) with those of nonfluorinated diphenylcarbene (**2b**) not only in terms of product analysis studies but also by spectroscopic means.



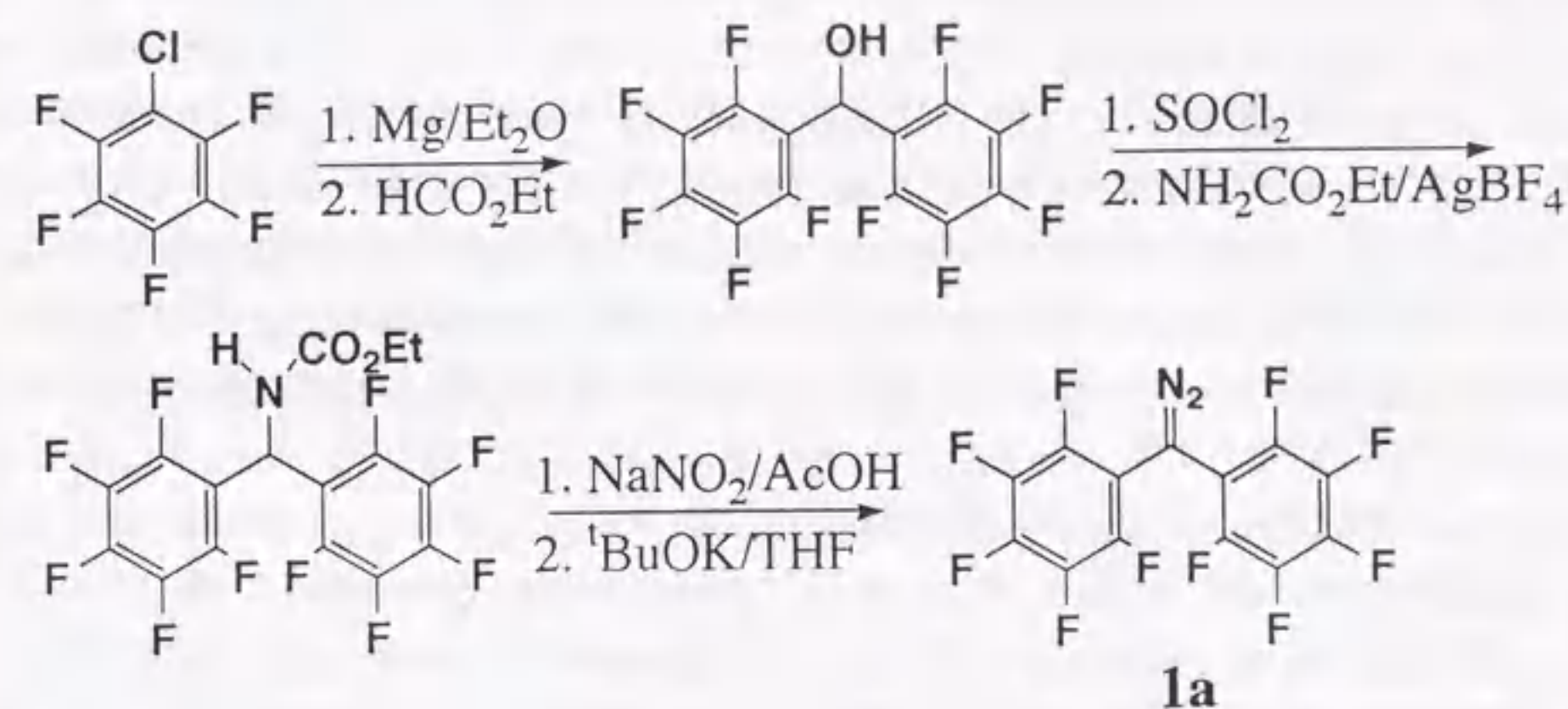
4-2 Preparation of Bis(pentafluorophenyl)diazomethane

The precursory diazomethane (**1a**) was prepared starting from pentafluorochlorobenzene as outlined in Scheme 1 as a rather stable yellow crystals (mp 55-57°C), which can be purified by column chromatography on alumina at -10°C. All attempts to prepare **1a** using other more conventional procedures,⁴ e.g., hydrazone formation followed by oxidation or diazo transfer were unsuccessful.

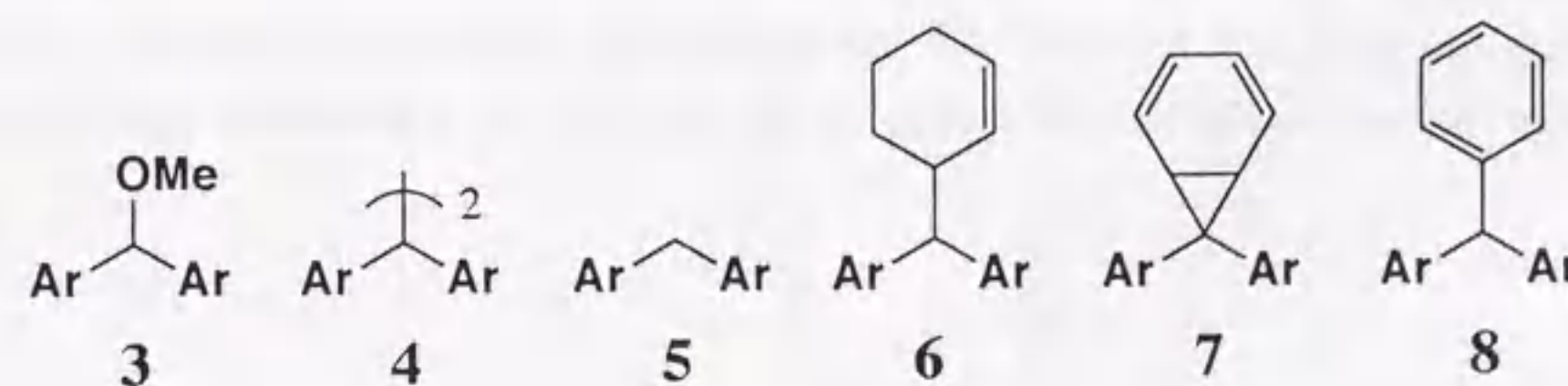
4-3 Product Analysis

Irradiation (>300nm) of **1a** in methanol resulted in the formation of bis(pentafluorophenyl)methyl methyl ether (**3a**) in essentially quantitative yield, while similar irradiation in cyclohexane gave rise to the formation of tetra(perfluorophenyl)ethane (**4a**, 90%) along with a small amount of

Scheme 1



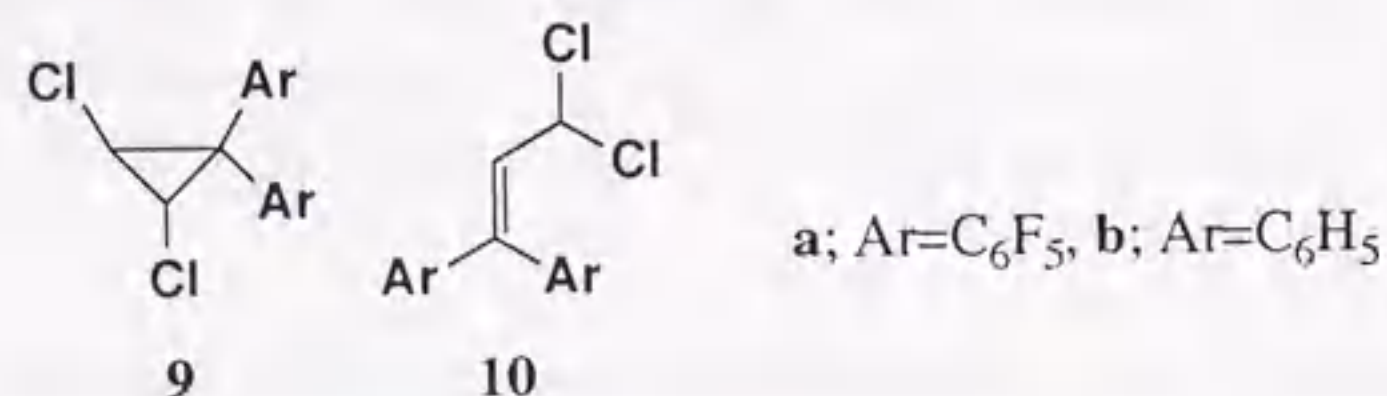
bis(pentafluorophenyl)methane (**5a**, 6%). These behaviors observed for **2a** are essentially similar with that observed for "parent" diphenylcarbene (**2b**) and can be understood as indicating that the carbene generated in methanol is trapped almost exclusively in its singlet state by the solvent O-H bond, which is known to be an efficient trapping reagent for the singlet carbene, while in cyclohexane, the singlet diarylcarbenes are reluctant to undergo insertion into the C-H bonds of alkane and therefore decays to the triplet states which can undergo hydrogen atom abstraction leading to the observed products (**4** and **5**).⁵



Significant changes in the reaction patterns were observed, however, when the carbenes were generated in substrates having moderate reactivities toward diarylcarbenes. Thus, photolysis of **1a** in cyclohexene afforded 3-[bis(pentafluorophenyl)methyl]cyclohexene (**6a**, 44%) along with (**4a**, 16%) and (**5a**, 18%), while similar irradiation of nonfluorinated diazomethane (**1b**) produced

tetraphenylethane (**4a**, 65%) almost exclusively. Furthermore, photolysis of **1a** in benzene gave norcaradiene (**7a**, 79%) along with **4a** (8%), while **2b** generated in benzene produced triphenylmethane (**8b**, 24%) as a solvent adduct, along with (**4b**, 3%) and (**5b**, 6%). Among those products, the norcaradiene (**7**) must be obviously formed from the singlet carbene, whereas the formation of C-H insertion products (**6** and **8**) can be explicable in terms of either of the multiplicities.⁵ However, judging from the amount of products (i.e., **4** and **5**) obviously produced from the triplet side via hydrogen atom abstraction, one may interpret these trends in product distributions as indicating that the perfluorinated carbene (**2a**) tends to react in its singlet state owing to the enhanced electrophilicity caused by fluorine substituents on the aromatic rings compared to the nonfluorinated one (**2b**).

In order to obtain more quantitative insight into the proportion of singlet and triplet carbene undergoing the reaction, the carbenes were generated in trans-1,2-dichloroethylene which is known to yield cyclopropanes from stereospecific addition of singlet carbenes, but a rearranged product from addition of triplet carbenes and therefore is conveniently employed as a substrate allowing inferences to be made concerning the proportion.⁶ Irradiation of **1a** in the dichloroethylene produced two carbene-ethylene adducts which were easily assigned as the dichlorocyclopropane (**9a**, 33%) and the dichloropropene (**10a**, 5%) mainly based on ¹H NMR spectrum, the ratio of **9a** to **10a** being 6.70. This ratio is considerably higher than that reported^{6d} for **2b** (0.25) and even higher than that for fluorenylidene (1.51)^{6e} which is usually considered to be much more electrophilic than diphenylcarbene system. Accepting that the rearrangement product comes entirely from triplet carbene and the cyclopropane principally from the singlet carbene, the results again support the idea advanced above based upon the products distributions in benzene and cyclohexene. In other word, the fluorinated carbene (**2a**) can be regarded as a synthetically useful intermediate to introduce perfluorinated aryl function into the appropriate substrates bearing a carbene-reactive center since it has less opportunity to be "wasted" by abstracting hydrogen from substrates.



4-4 Steady-State Irradiation in Matrix

Irradiation (>350nm) of argon-matrix-isolated **1a** (IR 2082s, 1524s, 1503s, 1248w, 1099w, 1052m, 994m, 989m, 880w, 794w, 740w, and 709w cm⁻¹; UV λ_{max} 420w, 302s and 275s nm) resulted in a rapid decrease in the bands attributable to the starting material and the concurrent appearance of new bands (IR 1506s, 1484s, 1475s, 1050s, 992m, 983m, and 660w cm⁻¹; UV λ_{max} 300nm) (Figure 1). These new absorptions were all assigned to the diphenylcarbene (**2a**) since the strong sharp absorption band characteristic of the diazo group disappeared, while all other major absorption bands due to C-F bonds changed very little during this transformation. This assignment was further supported by trapping experiments. The irradiation of the diazo compound (**1a**) in an argon matrix containing 0.5% O₂ gave essentially the same spectrum as that observed in the photolysis within Ar matrix (Figure 2). Warming the matrix containing **2a** and O₂ from 10 to 35K in dark caused a decrease in band ascribable to **2a** and a simultaneous increase in the absorptions at 1529s, 1514s, 1500s, 1449m, 1365m, 1070s, 998s, 802m, 766m and 720w cm⁻¹ (Figure 2a). The matrix took on a distinct yellow hue upon warming. In the UV-vis spectra, the disappearance of the carbene absorption and the formation of an intense, broad band with a maximum at 400nm was observed.

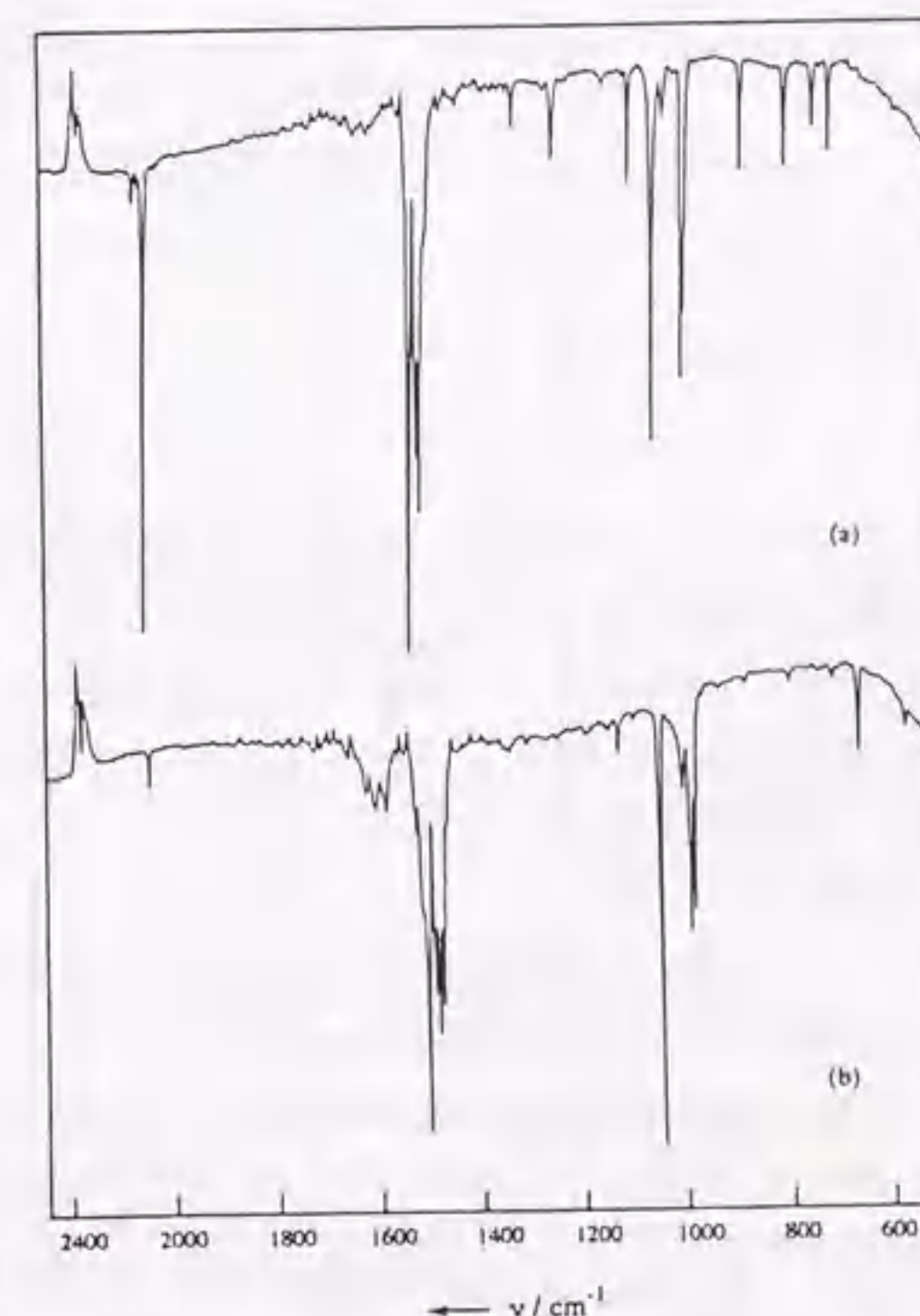


Figure 1. (a) IR spectrum of **1a** matrix-isolated in Ar at 10K. (b) IR spectrum obtained by irradiation of **1a** in Ar at 10K.

This product (A) was remarkably photolabile and completely disappeared upon irradiation with visible light ($>480\text{nm}$) to form an intermediate (B) with absorption bands at 1531m, 1517m, 1337s, 1190s, 1112m, 1048w, 1034m, 1003m, 779w, 700w, and 550w cm^{-1} (Figure 2b). Simultaneously, the color in the matrix was bleached: no new UV-vis maximum corresponding to the secondary product was observed in the region between 400 and 300nm. Subsequent irradiation ($>350\text{nm}$) rapidly converted the

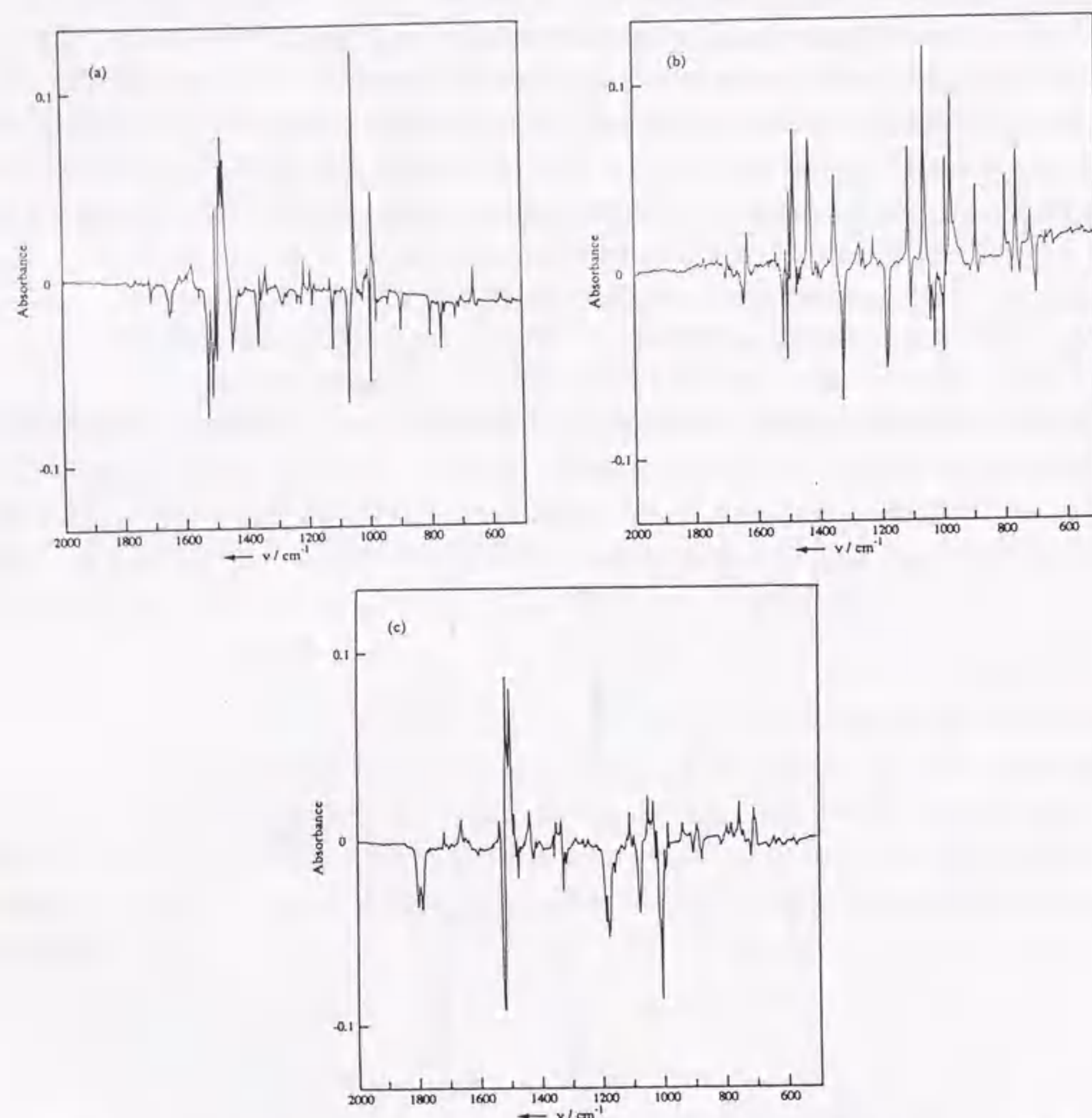
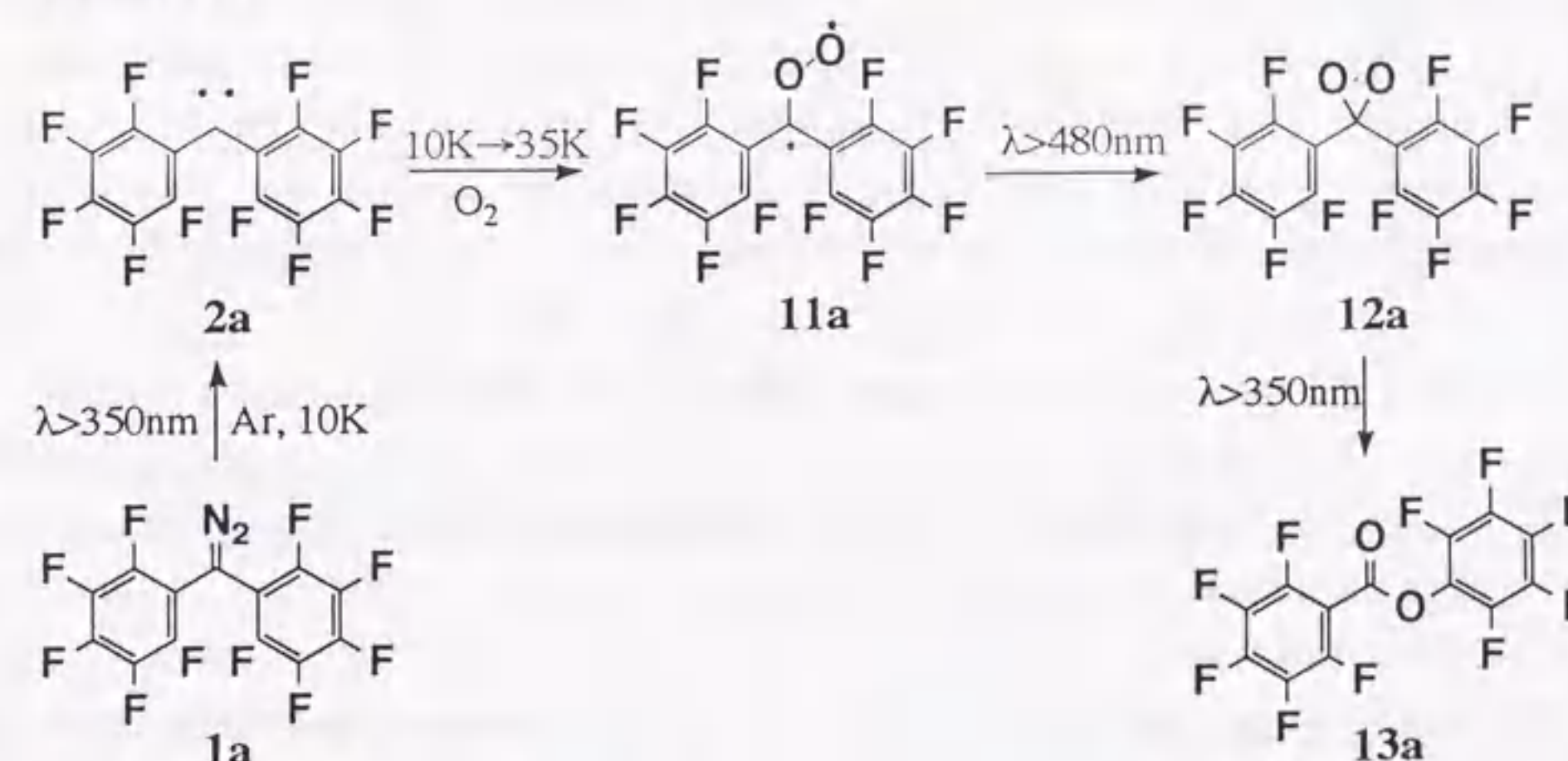


Figure 2. (a) IR difference spectrum obtained by subtracting IR spectra of 10K Ar matrix **2a** and 0.5% O_2 before and after warming to 35K. Positive peaks are assigned to **2a** and negative peaks to **11a**. (b) IR difference spectrum obtained by subtracting IR spectra containing **11a** before and after irradiation at $\lambda > 480\text{nm}$. Negative peaks are assigned to **12a**. (c) IR difference spectrum obtained by subtracting IR spectra containing **12a** before and after irradiation at $\lambda > 350\text{nm}$. Negative peaks are assigned to **13a**.

secondary product into the final product (C) showing the IR absorptions at 1802m, 1788m, 1528s, 1522s, 1331w, 1190m, 1181m, 1078m, 1009m, 905w, 877w, and 718w cm^{-1} (Figure 2c). These observations which are essentially similar with that reported for diphenylcarbene can be reasonably understood as indicating that the carbene (**2a**) presumably in the triplet ground states is trapped by O_2 to generate the carbonyl oxide (**A=11a**) showing $\nu(\text{O-O})$ at 980 cm^{-1} and λ_{max} at 400nm which then undergoes photoisomerization to form the ester (**C=13a**) by way of the dioxirane (**B=12a**) as these transformations are now well-documented (Scheme 2).⁷ Actually the ester (**13a**) was identified by direct comparison with the authentic sample prepared independently.

Scheme 2



4-5 Laser Flash Photolysis in Fluid Solution

Flash photolysis of **1a** ($4.0 \times 10^{-4} \text{M}$) in a degassed cyclohexane solution at room temperature with the output of a YAG laser (266nm, pulse width 5ns) produced a transient species showing the maximum at 320nm which appeared with apparent growth rate of $\sim 10^6 \text{s}^{-1}$ (Figure 3). The oscillogram trace of the transient species at 320nm shown in the inset of Figure 3 indicated that the decay was second order ($2k_{\text{el}} = (4.3 \pm 2.8) \times 10^4 \text{M}^{-1} \text{s}^{-1}$, $r = 0.970$). The absorption maximum was apparently different from that observed in matrix at low temperature for **2a**. Moreover, the observed second order decay kinetic was not expected for **2a** since product analysis of the spent solution showed no carbenic dimer of **2a** was formed. The product analysis data indicating the formation of **4a** as major product probably as a result of the dimerization of bis(pentafluorophenyl)methyl radical (**14a**) then suggest that the transient species must be this radical. Support is lent to this assignment by the generation of the radical from different precursor. Thus, laser flash photolysis of bis(pentafluorophenyl)methyl chloride

in acetonitrile resulted in the formation of a transient species showing the absorption at 318nm which also exhibits second order decay kinetics with $2k/\epsilon=3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ($r=0.962$). It is well-documented that flash photolysis of diarylmethyl chlorides produces

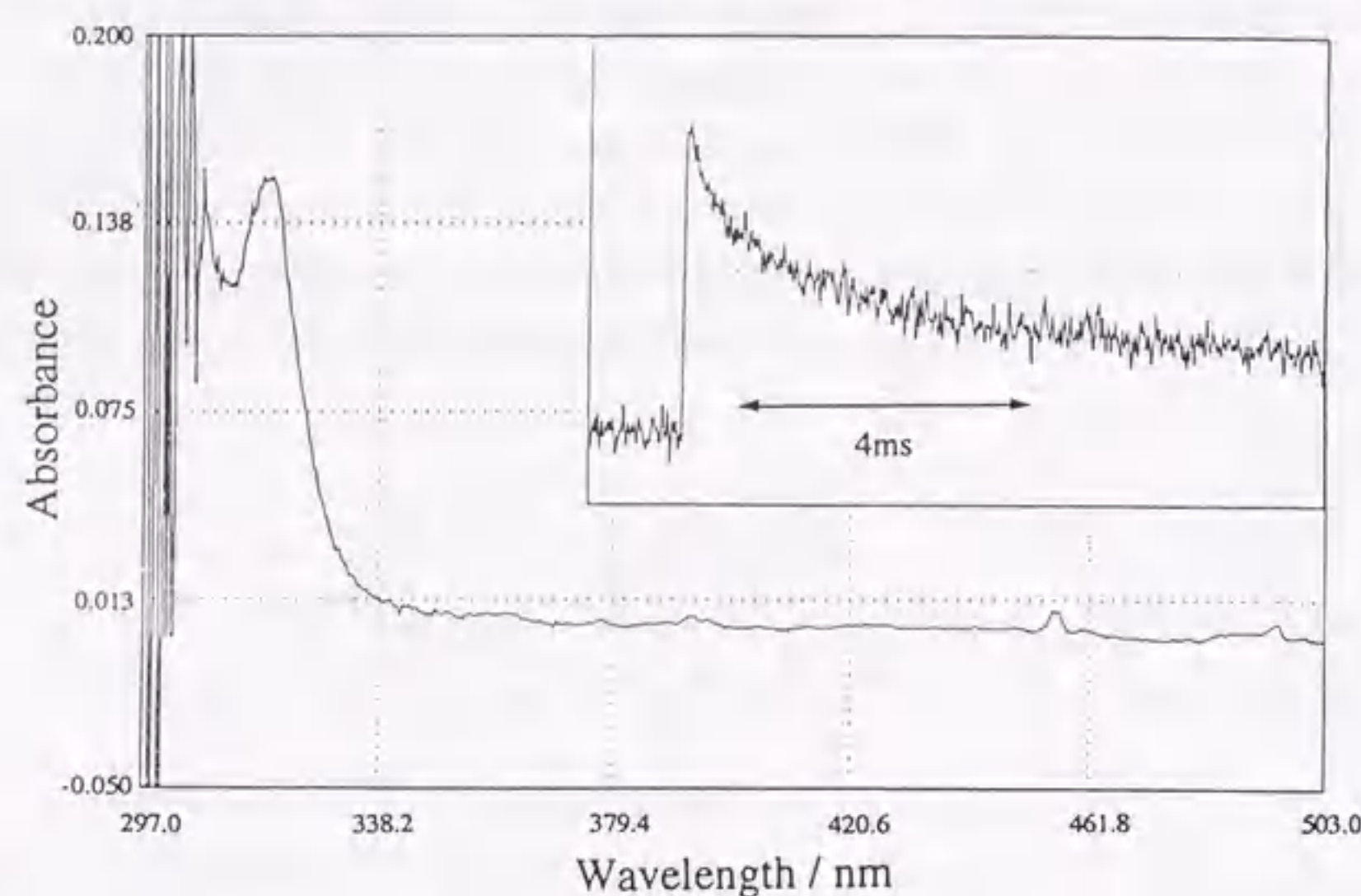
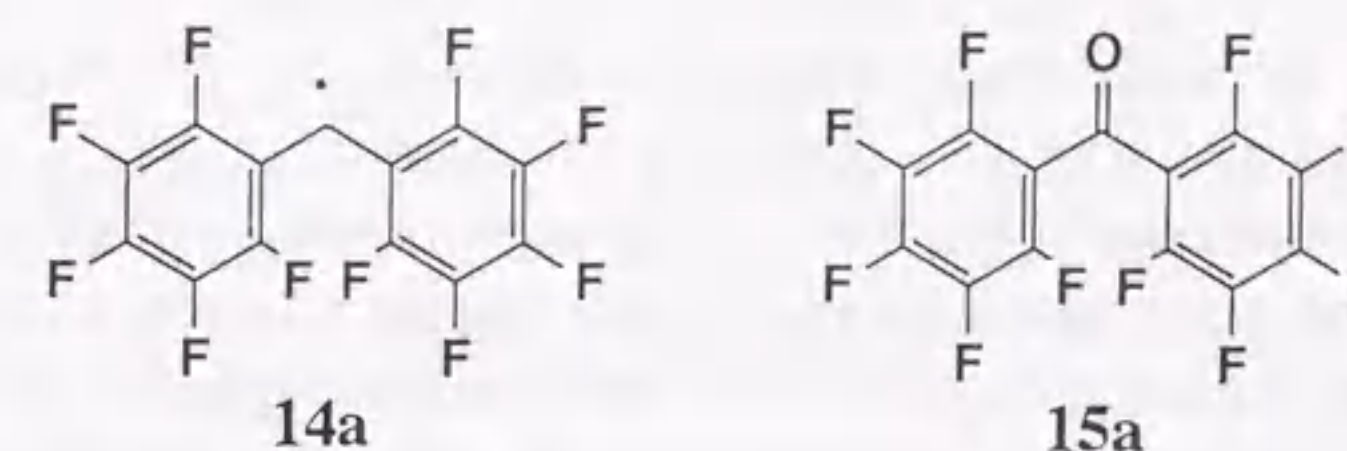


Figure 3. Absorption spectrum of the transient products formed during the irradiation of **1a** in degassed acetonitrile, recorded after 10 μs . Inset shows an oscillogram trace monitored at 320nm.

diarylmethyl radicals as well as diarylmethyl cations.⁸ However, the cations usually exhibit their absorptions at longer wavelength region, usually at 500-600nm, and decay in first order. Moreover, product analysis of the spent solution from the chloride flash photolysis showed the presence of **4a** as a major product. Thus, the transient species at 320nm was unambiguously assigned as the radical, which must be produced from the carbene (**2a**) by abstraction of hydrogen from the solvent. The transient absorption bands ascribable to **2a** was not observed. Indications based on the reported data⁹ for fluorenylidene and diphenylcarbene suggest that the carbenes are usually blue shifted (by ~30nm) with respect to the corresponding radicals. If the same rule of thumb is applied to **2a**, its absorption maxima would be expected in the 290-300nm region, which overlaps that for the diazo precursor. It would therefore be in a region of very difficult detection and where the samples are usually not sufficiently transparent for adequate monitoring. However, intervention of **2a** was shown by the trapping experiment using oxygen. Thus, when the flash photolysis of **1a** was carried out in aerated cyclohexane solution, a broad absorption with a maximum at 400nm appeared at the complete expense of the transient absorption due to the radical **14a**. Analysis of the spent solution showed the presence of large amount (about 80%) of the ketone **15a**. It is now



well-documented that arylcarbenes with the triplet ground state are readily trapped by O_2 to give the corresponding arylketone oxides.^{9,10} The broad absorption observed here is in complete agreement with that observed for the oxide **11a** in matrix. Thus, the observations can be interpreted as indicating that the triplet **2a** is trapped by O_2 to generate the oxide before it undergoes hydrogen atom abstraction. The decay of the carbonyl oxide was found to be first order ($k=1.8 \times 10^2 \text{ s}^{-1}$) and lifetime is estimated to be 5.6ms.

Since we were unable to observe the carbene directly, we have used the probe technique using 1,4-cyclohexadiene in order to know the reactivity.⁹ Thus, when a solution of **1a** in a degassed acetonitrile solution containing the diene was excited, the growth rate for the radical formation (monitored at 320nm) increased with the increase in the diene concentration. The excellent hydrogen donor properties of 1,4-cyclohexadiene have been recognized in its reaction with triplet benzophenone.¹¹ The apparent built-up rate constant, k_{obs} , of the radical is essentially identical with that of the

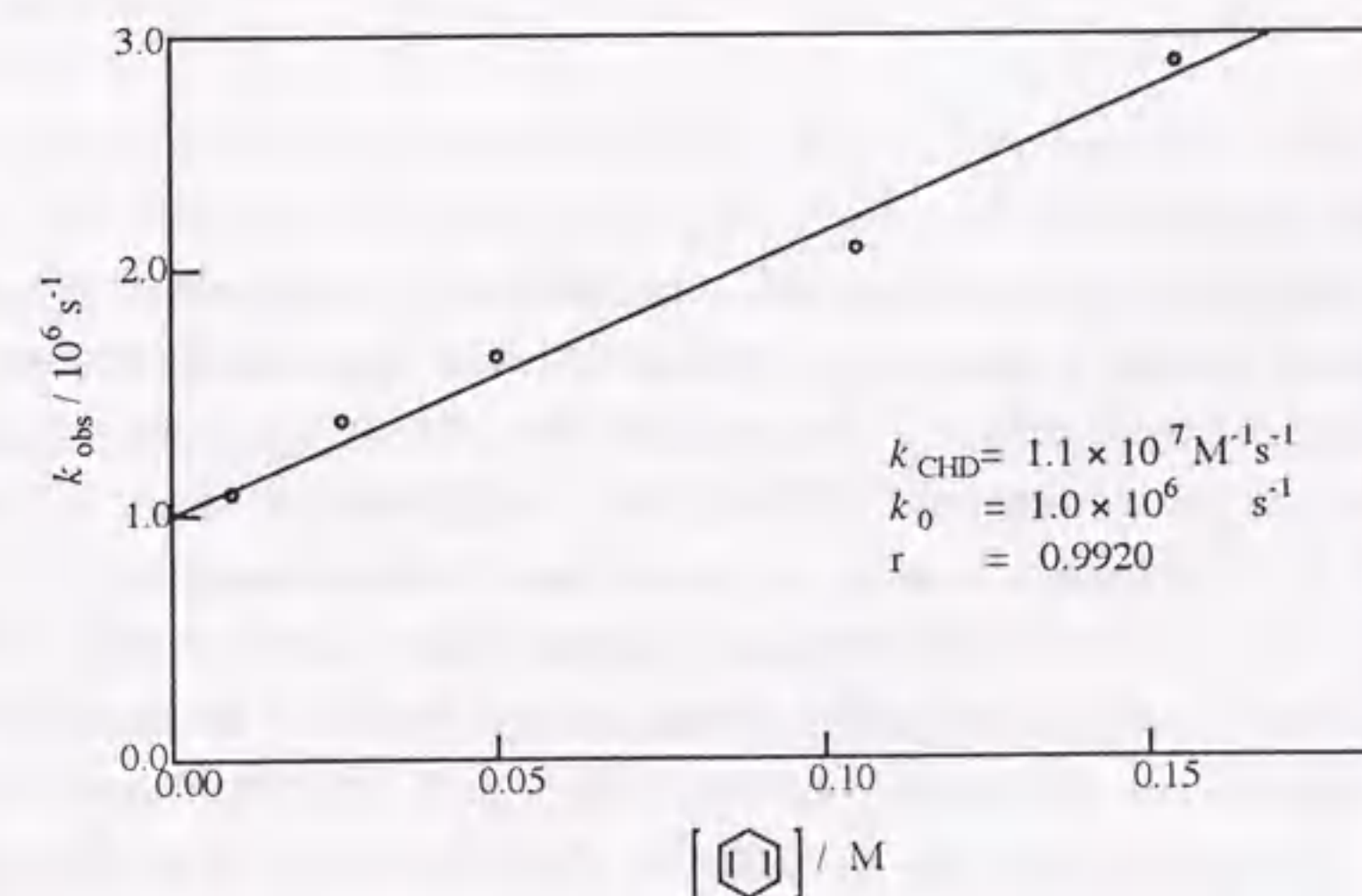


Figure 4. Plots of the growth rate of the perfluorodiphenylmethyl radical in degassed acetonitrile solution containing 1,4-cyclohexadiene.

decay of the carbene, and k_{obs} is expressed as given in eq 1, where k_0 represents the

$$k_{\text{obs}} = k_0 + k_{\text{CHD}} [\text{diene}] \quad (1)$$

decay rate of **2a** in the absence of the diene and k_{CHD} is a quenching rate constant of **2a** by the diene. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] in the range of 0.01–0.16M is linear (Figure 4). The slope of this plot yields the absolute rate constant for reaction of **2a** with the diene, $k_{\text{CHD}} = 1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and the intercept yields $k_0 = 1 \mu\text{s}$.

Table 1. Kinetic Parameters for Perhalogenated Diphenylcarbenes and Their Oxides

Ar in Ar ₂ C:	$\lambda_{\text{max}}/\text{nm}$	$\tau(t_{1/2})/\mu\text{s}$	$k_{\text{CHD}}/\text{M}^{-1} \text{ s}^{-1}$	Ar ₂ CO ₂	
				$\lambda_{\text{max}}/\text{nm}$	$\tau(t_{1/2})$
C ₆ H ₅	315	1.5 ^a	$1.0 \pm 0.1 \times 10^7$ ^b	410	(4ms) ^c
C ₆ F ₅	300	1	$1.1 \pm 0.1 \times 10^7$	400	5.6ms
C ₆ Cl ₅ ^d	525w, 493w, 356s	$(2.8 \pm 0.2 \times 10^4)$	$6.2 \pm 0.1 \times 10^3$	390	(510±9ms)

^a Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488. ^b Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283. ^c Ref 10e. ^d Ref 12.

4-6 Summarizing Discussion

It is conceivable that displacement of all hydrogen atoms on diphenylcarbene with fluorines must result in the enhanced electrophilicity as well as increased steric crowdedness of the carbenic center in the light of the Hammett σ value ($\sigma_{\text{m}} = 0.34$, $\sigma_{\text{p}} = 0.06$) as well as van der Waals radii (1.35) of fluorine substituent. Thus, the carbene (**2a**) reacts with those substrates having moderate reactivities toward carbene, e.g., benzene and dichloroethylene, mostly in the singlet state owing to the increased electrophilicity. However, the electrophilicity of the singlet **2a** is not so increased as to react with σ electrons of the alkane C-H bonds. Moreover, the singlet carbene C-H insertion process is considered to be sensitive to steric factors if one assumes the triangular transition state for this process. Thus, the carbene (**2a**) is forced to undergo intersystem crossing to the triplet which abstracts hydrogen from the solvent with a linear transition state. In this light, it is intriguing to compare the reactivities of **2a** with that of

perchlorodiphenylcarbene (**2c**) which shows essentially no reactivity toward benzene and is reluctant to abstract hydrogen from cyclohexane but dimerizes to the carbenic dimer in benzene.¹² The lifetimes of the triplet states also reflect these electronic as well as steric situations. Thus, triplet state of **2a** has almost similar lifetime with that of diphenylcarbene ($\tau = 1.5 \mu\text{s}$ in cyclohexane), while the chlorinated carbene (**2c**) has a lifetime of some four order of magnitude greater than **2b**. Taking into account electronic ($\sigma_{\text{m}} = 0.34$, $\sigma_{\text{p}} = 0.23$) as well as steric effect (van der Waals radii 1.80) of chlorine substituent, it is rather surprising to note that rather small change in steric factor exerts tremendous effect on the reactivity of triplet diphenylcarbene.

Experimental

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and the mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70eV). ¹H and ¹³C NMR spectra were determined with JEOL JNM-EX 270 spectrometer. UV/vis spectra were determined with a Hitachi 220-S spectrometer. Thin-layer chromatography was done on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was carried out on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral). HPLC and GPC were undertaken with a JASCO 800 chromatography equipped with a UVIDEC-100II UV/vis detector using a Fine pack C18-T5 column (4.6×25cm) and Shodex GPC H-2001 (20mm×50cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using a OV-17 on Diasolid L (5.0mm×50cm).

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard techniques¹⁸ using Iwatani Cryo Mini closed cycle helium cryostat. For IR experiments, CsI window was attached to the copper holder at the bottom of the cold head. Two opposing parts of a vacuum shroud were fitted with KBr windows for spectroscopic viewing, and the remaining parts were fitted with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For the UV experiments, a sapphire cold window and quartz outer window were used. The temperature of the matrix was controlled by Iwatani TCU-1 temperature controller.

Argon (Seitetsu Chemicals, 99.999%), oxygen (Seitetsu Chemicals, 99.9995%) and very volatile organic compounds were mixed in a gas handling system by standard manometric techniques.

Irradiations were carried out using Wacom 500W xenon high pressure arc lamp or Ushio 500W mercury high pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelengths specified).

Laser Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 Flash Spectrometer. The excitation source for the laser flash photolysis was a Quanta-Ray GCR-11 Nd: YAG laser which produced 4-5ns fwhm pulses of up to 30mJ at 266nm. The beam shape and size was controlled by a focal length cylindrical lens.

A Hamamatsu 150W xenon short arc lamp (L2195) was used as the probe source and the monitoring beam guided using an optical fiber scope was arranged in a perpendicular orientation to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing among the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided hard copy graphics capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette, and degassed a minimum of four freeze-degas-thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was sealed and the solution was transferred to the quartz cuvette which was placed in a sample chamber of the flash spectrometer. Concentration of sample was adjusted so that the sample absorbed a significant portion of the laser light. For kinetic measurements a suitable concentration range of trapping reagents were added and rate constant for the decay of the transient was determined by a computer least-squares fit.

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (20mg) in solvents was placed in a Pyrex tube and degassed by subjecting the sample to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} Torr before irradiation. Irradiation was carried out with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The mixture was then concentrated on a rotary evaporator below 10°C . Individual components were isolated by preparative TLC and/or gel permeation chromatography, and identified by NMR and MS.

Irradiation for Analytical Purposes. The irradiations for the quantitative product analysis outlined in the text were carried out in a Pyrex tube of 5.0-mL capacity at below 10°C . In order to avoid ambiguity of the yields due to the oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze degas-thaw cycles at pressure near 10^{-5} Torr before irradiation. Product identifications were established by GC-MS comparisons with authentic sample and product yields were conveniently determined by GC and/or NMR using an internal standard.

Preparation of Bis(pentafluorophenyl)diazomethane (1a).¹³ A solution of decafluorobenzhydrol^{14,15} (4.0g, 11mmol) and SOCl_2 (8.0mL, 11mmol) in anhydrous pyridine (10mL) was refluxed for 2h. After evaporation of the solvent and washing of the residue taken in Et_2O with 0.2N HCl followed by the evaporation of the ether, the brownish residue was chromatographed on silica gel eluted with *n*-hexane to give bis(pentafluorophenyl)chloromethane as a yellowish liquid: 3.5g (83.3%); ^1H NMR (CCl_4) δ 6.58 (s, 1H); MS *m/e* (relative intensity) 382 (M^+ , 1.0), 347 (100), 328 (20.0).

A mixture of 2.7g (13.8mmol) of AgBF_4 , 15g (0.17mol) of ethyl carbamate, and 60mL of dioxane was heated until solution was effected. To this, the chloride (3.5g, 9.2mmol) in dioxane (20mL) was added at once and the mixture was heated at 80°C for 2h. The cooled mixture was extracted with CCl_4 (20mL) and H_2O (30mL). After filtering, the organic layer was washed well with H_2O and then dried (Na_2SO_4). After evaporation of the solvent, the resulting brownish liquid was distilled under reduced pressure ($80^{\circ}\text{C}/1.0\text{Torr}$) using Kugelrohr to remove excess ethyl carbamate. The residue taken in minimum amount of CH_2Cl_2 was chromatographed on silica gel eluted first with *n*-hexane to remove the unreacted chloride and then with CH_2Cl_2 -*n*-hexane (1:1) to obtain 930mg (23%) of ethyl *N*-[bis(pentafluorophenyl)methyl]carbamate as white crystals: mp $60-64^{\circ}\text{C}$; ^1H NMR (CCl_4) δ 6.82 (1H, d, $J=10.3\text{Hz}$), 6.03 (1H, d, $J=10.6\text{Hz}$), 4.16 (2H, q, $J=6.9\text{Hz}$), 1.26 (3H, t, $J=6.9\text{Hz}$).

To a vigorously stirred mixture of the carbamate (930mg, 2.1mmol) in AcOH (2.7mL) and Ac_2O (12mL) at 0°C was added every 20min for 5h a 160mg portion of NaNO_2 (total 3.2g, 46.2mmol). The mixture was stirred overnight at 0°C , poured onto ice-water (60mL), and extracted with Et_2O . The ethereal layer was washed with H_2O , 5% Na_2CO_3 , and H_2O and dried (Na_2SO_4). Evaporation of the solvent afforded crude ethyl *N*-nitroso-*N*-[bis(pentafluorophenyl)methyl]carbamate as a yellow oil (965mg).

To a solution of potassium *tert*-butoxide (700mg, 5.9mmol) in 10mL of anhydrous THF (over benzophenone ketyl) which had been deaerated by repeated cycles of evacuation (10Torr) and purge with argon and then heated at 60°C was added at once under atmosphere of argon a solution of the nitrosocarbamate (950mg, 1.97mmol) in THF (10mL). The mixture was stirred at this temperature for 1min, and poured onto ice-water and extracted with Et_2O . The ethereal layer was washed with H_2O , dried, evaporated to leave reddish viscous oil which was chromatographed on a neutral alumina (deactivated by adding 6% H_2O) at -10°C eluted with *n*-hexane. The diazomethane (**1a**) was eluted as an initial fraction and obtained as yellow crystals in 11.2% (98mg) yield: mp $55-57^{\circ}\text{C}$ dec; IR (KBr disk) 2090, 1160cm^{-1} . ^1H NMR spectra showed no peak.

Pentafluorophenyl Pentafluorobenzoate (13a) was prepared by the treatment of pentafluorobenzoic acid¹⁶ with thionyl chloride to prepare the benzoyl chloride, which was treated with pentafluorophenol¹⁷ and anhydrous pyridine. The desired benzoate was purified by TLC to give a yellowish oil; ¹⁹F NMR (CCl₄) δ 164.0 (2F, t, *J*=3.4 Hz), 162.0 (2F, t, *J*=3.4 Hz), 158.5 (1F, t, *J*=3.4 Hz), 154.8 (2F, d, *J*=3.4 Hz), 147.5 (1F, t, *J*=3.4 Hz), 138.0 (2F, d, *J*=3.4 Hz); MS *m/e* (relative intensity) 378 (M⁺, 0.2), 359 (0.7), 195 (100), 167 (35.0), 117 (30.0).

Bis(pentafluorophenyl)methyl Methyl Ether (3a) was isolated in the photolysis of **1a** in MeOH as a yellowish oil: ¹H NMR (CCl₄) δ 6.02 (1H, s), 3.37 (3H, s); MS *m/e* (relative intensity) 378 (M⁺, 15), 347 (100), 278 (18).

7,7-Bis(pentafluorophenyl)norcaradiene (7a) was obtained in the photolysis of **1a** in benzene as a white oil: ¹H NMR (CCl₄) δ 6.24-6.22 (2H, m), 5.88-5.83 (2H, m), 2.93-2.90 (2H, m); MS *m/e* (relative intensity) 424 (M⁺, 14), 347 (20), 78 (100).

Tetra(pentafluorophenyl)ethane (4a) was isolated in the photolysis of **1a** in cyclohexane as a white solid: mp 200-205°C; ¹H NMR (CCl₄) δ 6.05 (s, 1H); MS *m/e* (relative intensity) 348 (15), 347 (100), 278 (19).

3-Bis(pentafluorophenyl)methylcyclohexene (6a) was isolated in the irradiation of **1a** in cyclohexene as a oil: ¹H NMR (CDCl₃) δ 5.87-5.78 (1H, m), 5.39 (1H, bd, *J*=10.2 Hz), 4.46 (1H, d, *J*=12.2 Hz), 3.36 (1H, bs), 2.04 (2H, bs), 1.80-1.21 (4H, m); MS *m/e* (relative intensity) 425 (M⁺+1, 0.5), 424 (M⁺, 3), 347 (4), 81 (100).

3,3-Bis(pentafluorophenyl)-trans-1,2-dichlorocyclopropane (9a) and 1,1-Bis(pentafluorophenyl)-3,3-dichloropropene (10a) were isolated in the photolysis of **1a** in trans-1,2-dichloroethene both as oil: **9a** ¹H NMR (CDCl₃) δ 4.05 (2H, s); MS *m/e* (relative intensity) 444 (M⁺+2, 1), 443 (M⁺+1, 3), 442 (M⁺, 3), 407 (100). **10a**: ¹H NMR (CDCl₃) δ 6.60 (1H, d, *J*=9.90 Hz), 6.30 (1H, d, *J*=9.90 Hz); MS *m/e* (relative intensity) 442 (M⁺) 407 (100), 215 (50).

References and Notes

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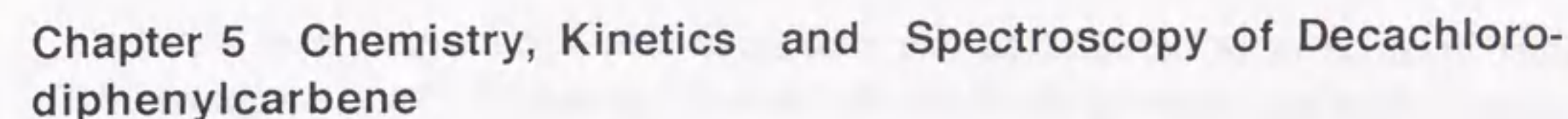
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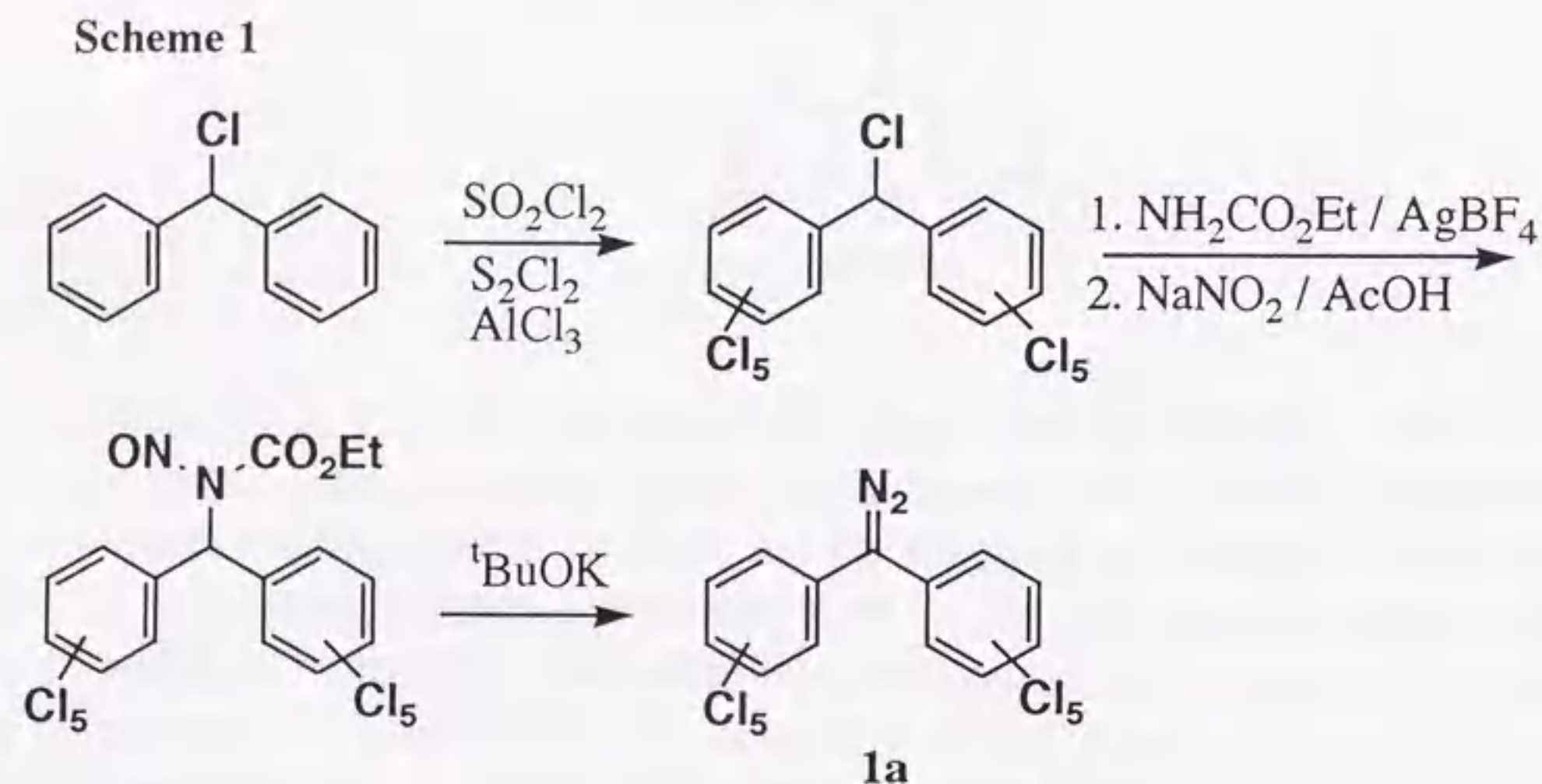
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center must be more crowded as one introduces four chlorine groups at the meta positions which can buttress the four ortho chlorine groups.^{4,5} Thus, we generated decachlorodiphenylcarbene(**2a**) and its reactivities were investigated not only by product analysis but also by using flash photolysis techniques.

5-2 Preparation of Bis(pentachlorophenyl)diazomethane

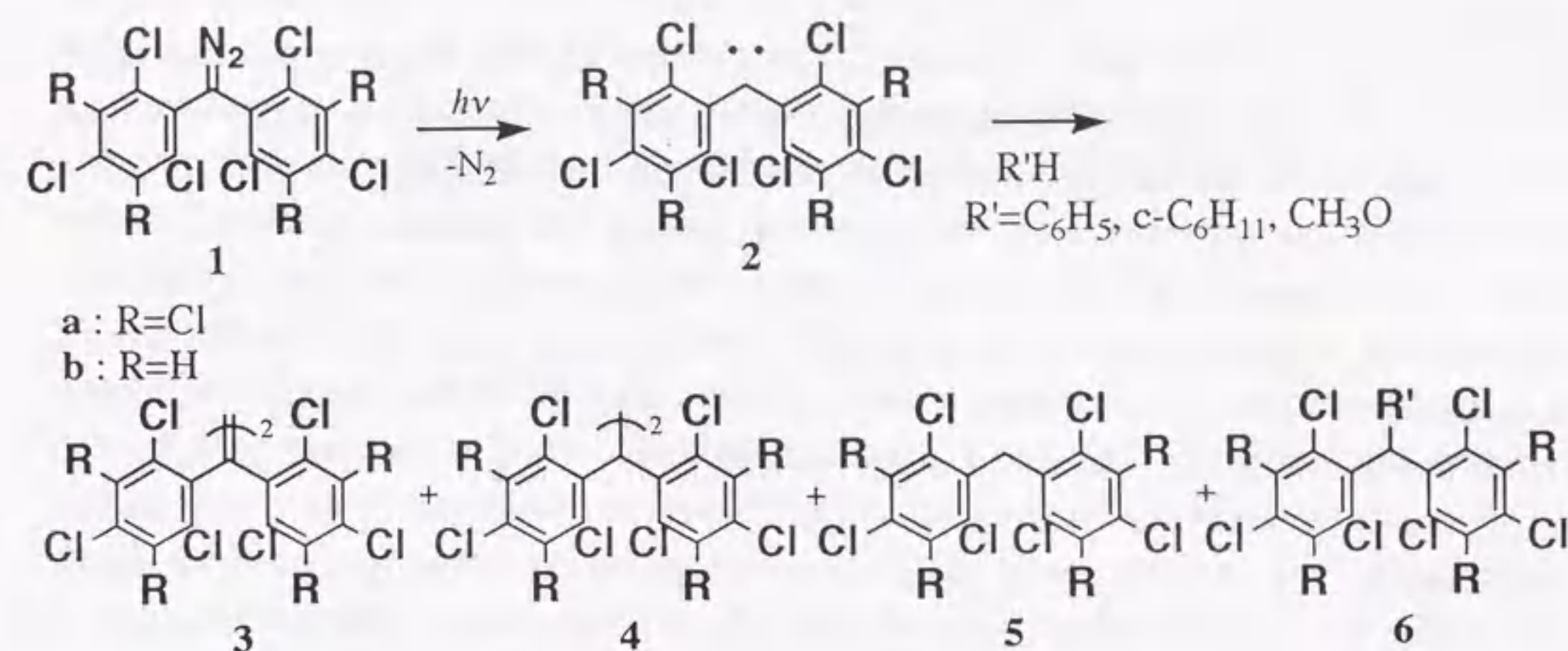
The diazomethane (**1a**) was prepared by essentially the same procedure reported by Zimmerman² for the preparation of the corresponding hexachloro analogues (**1b**) as very stable red crystals (Scheme 1), although the overall yield of **1a** was considerably lower than that of **1b**. The crude **1a** containing a small amount of partially chlorinated diphenyldiazomethanes was purified by the repeated chromatograph on a Shodex GPL H-2001 column.



5-3 Product Analysis

Irradiation ($> 350 \text{ nm}$) of **1** in various solvents at room temperature produced products apparently derived from the photolytically generated perchlorodiphenylcarbene (**2a**) (Scheme 2). Thus, photolysis in benzene afforded perchlorotetraphenylethylene (**3a**) almost exclusively, while irradiation in cyclohexane results in the formation of a small amount of perchlorodiphenylmethane (**5a**) and perchlorotetraphenylethane (**4a**) although the carbenic dimer (**3a**) was still the major product. Photolysis in methanol-benzene, on the other hand, produced the OH insertion product (**6a**, $\text{R}'=\text{OMe}$) along with

Scheme 2



4a, **5a** and **3a**, **3a** being a major product. Product distributions are listed in Table 1 which includes the data for **2b** for comparison purposes. Inspection of the data indicates that, although the reactions observed with **2a** were essentially similar to those

Table 1. Photolysis of Chlorinated Diphenyldiazomethane in Fluid Solution at Room Temperature^a

solvent	precursor	yield, ^b %			
		3	4	5	6
PhH	1a	>99	trace	trace	0
	1b	>99	trace	trace	0
c-C ₆ H ₁₂	1a	80	3	17	0
	1b	26	17	29	28
MeOH/PhH ^c	1a	50	9	20	21
	1b	14	1	24	61

^a Irradiations were carried out on 5 mL degassed solution with light of $\lambda > 350 \text{ nm}$ from 300-W high-pressure mercury lamp equipped with a Corning CS-052 filter. ^b Determined by combination of GC and ¹H NMR (270 MHz). ^c Benzene was used as cosolvent due to poor solubility of **1** to methanol.

observed with hexachlorodiphenylcarbene (**2b**), the product distributions from **2a** were significantly different from those obtained from **2b** (see Table 1). A key difference is found in the formation of the dimer **3**. Thus, as more reactive solvents were employed, the yield of **3** was decreased. However, **3a** was always formed as major product, while the formation of **3b** was sharply decreased and the solvent adducts, i.e., **6**, was formed. The difference in reactivities between **2a** and **2b** can be interpreted as reflecting the difference in the extent of steric crowdedness around the carbenic centers between these two carbenes. It is well known^{5,6} that, in 1,2-disubstituted benzene derivatives, introduction of substituents in the 3 position exerts a very large effect on the rate of appropriate reactions and the data are considered in the light of the importance of bond bending; the 3-substituents buttress the 2- substituents. Thus, in **2a**, each of four ortho chlorine groups around carbene center are buttressed by that of four meta-chloro groups and therefore the carbene center in **2a** is surrounded by the chloro groups more rigidly than that in **2b**. In other words, **2a** is more effectively blocked from external reagents.

5-4 Steady-State Irradiation in Frozen Media

Irradiation (> 350 nm) of **1a** (0.95×10^{-3} M) in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of new absorption bands at the expense of the original absorption due to **1a**. As is shown in Figure 1, the new spectrum consisted of two identifiable features. There was a sharp, intense UV band at 356 nm, and the visible portion of the spectrum showed two weak and broad bands with apparent maxima at 493 and 525 nm. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming it up to room temperature and refreezing at 77 K led to disappearance of the characteristic absorption bands. Product analysis of the spent solution showed the presence of the dimer **3a** as a nearly exclusive product. The optical absorption spectra of several diarylcarbenes in frozen media have been assigned.⁷ Typically they consist of an intense UV band and a weak visible transition. These features are present in the spectrum obtained from the photolysis of **1a**. In these circumstances, the transient absorption is attributable to the triplet decachlorodiphenylcarbene (**2a**) generated by the photodissociation of **1a**. Hexachlorodiphenylcarbene (**2b**) also shows an intense absorption at 338 nm along with a broad, weak absorption with apparent maximum at 482 and 495 nm.

5-5 Flash Photolysis in Fluid Solution

Irradiation of a degassed benzene solution of **1** (1.24×10^{-4} M) at room temperature with the output of a xenon flash lamp (pulse width of 10 μ s) produced a

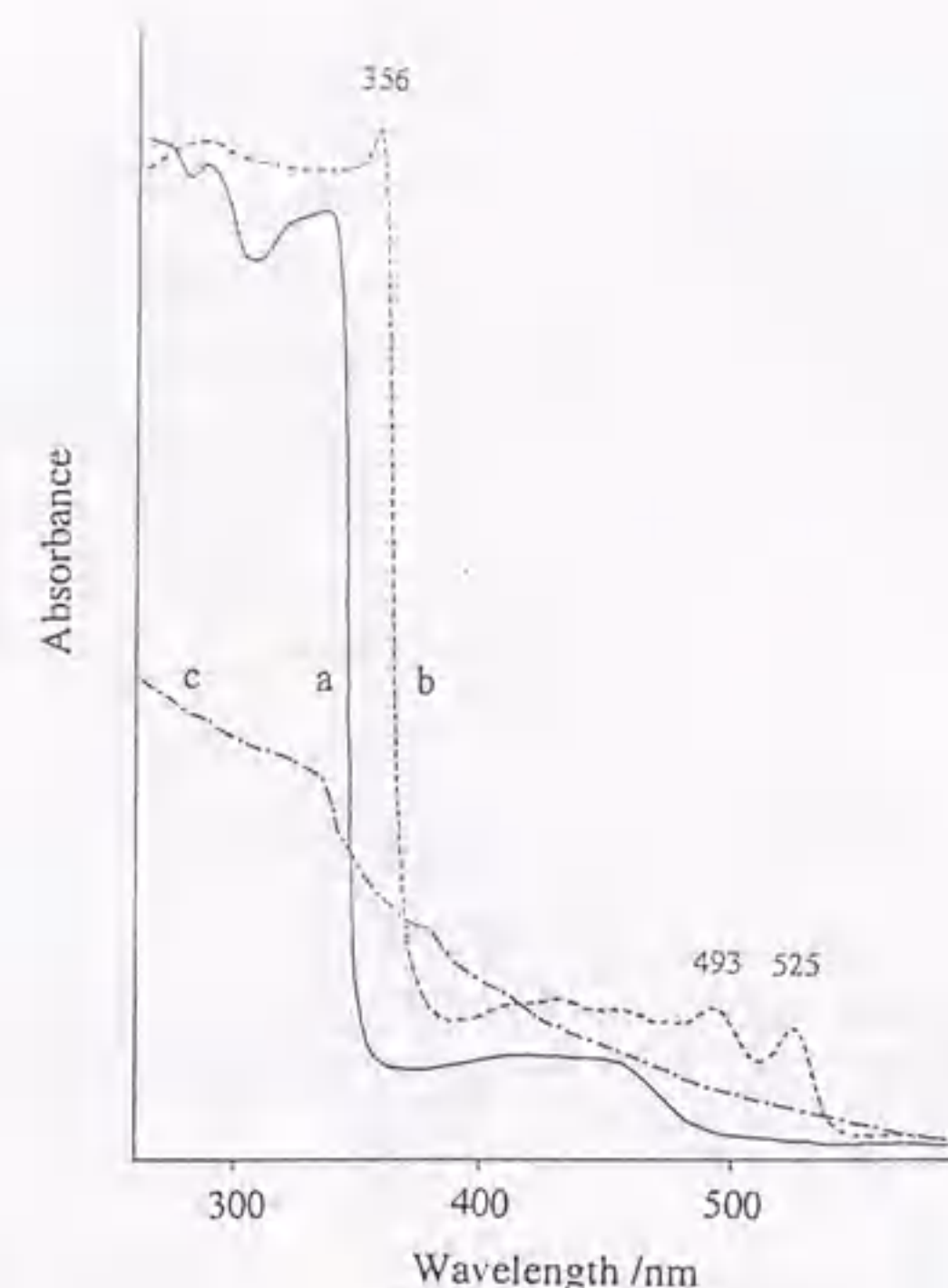


Figure 1. (a) UV/vis spectrum of **1a** in MTHF at 77K. (b) Same sample after 40min irradiation ($\lambda > 350$ nm). (c) Same sample after thawing the matrix.

transient species showing a strong absorption at 357 nm and a weak absorption extending from 410 to 520 nm which appeared coincident with the xenon pulse and disappeared within ca. 100 ms (Figure 2). The final stable products formed from irradiation of **1a** under these conditions again consist almost exclusively of carbenic dimer (**3a**). On the basis of the low-temperature spectrum coupled with chemical analysis, we assign the transient product from the photolysis of **1a** in benzene at room temperature to triplet decachlorodiphenylcarbene (**2a**). The oscillogram trace of the transient absorption due to **2a** monitored at 357 nm is shown in the inset of Figure 2. The decay was found to be second order in accordance with the product analysis data, showing that dimerization to form **3a** is the main pathway for **2a** under these conditions. Support is lent to this assignment by trapping experiments using oxygen. When flash photolysis measurements were carried out on a non-degassed benzene solution of **1a** ($\sim 10^{-4}$ M), the half-life of triplet **2a** was decreased by about one-third, and a broad absorption band with a maximum at 390 nm appeared. The rate of increase in the absorbance at 390 nm was practically the same as that of the decay of the peak at 357 nm, showing that triplet **2a** was quenched with oxygen to form a new species. Analysis

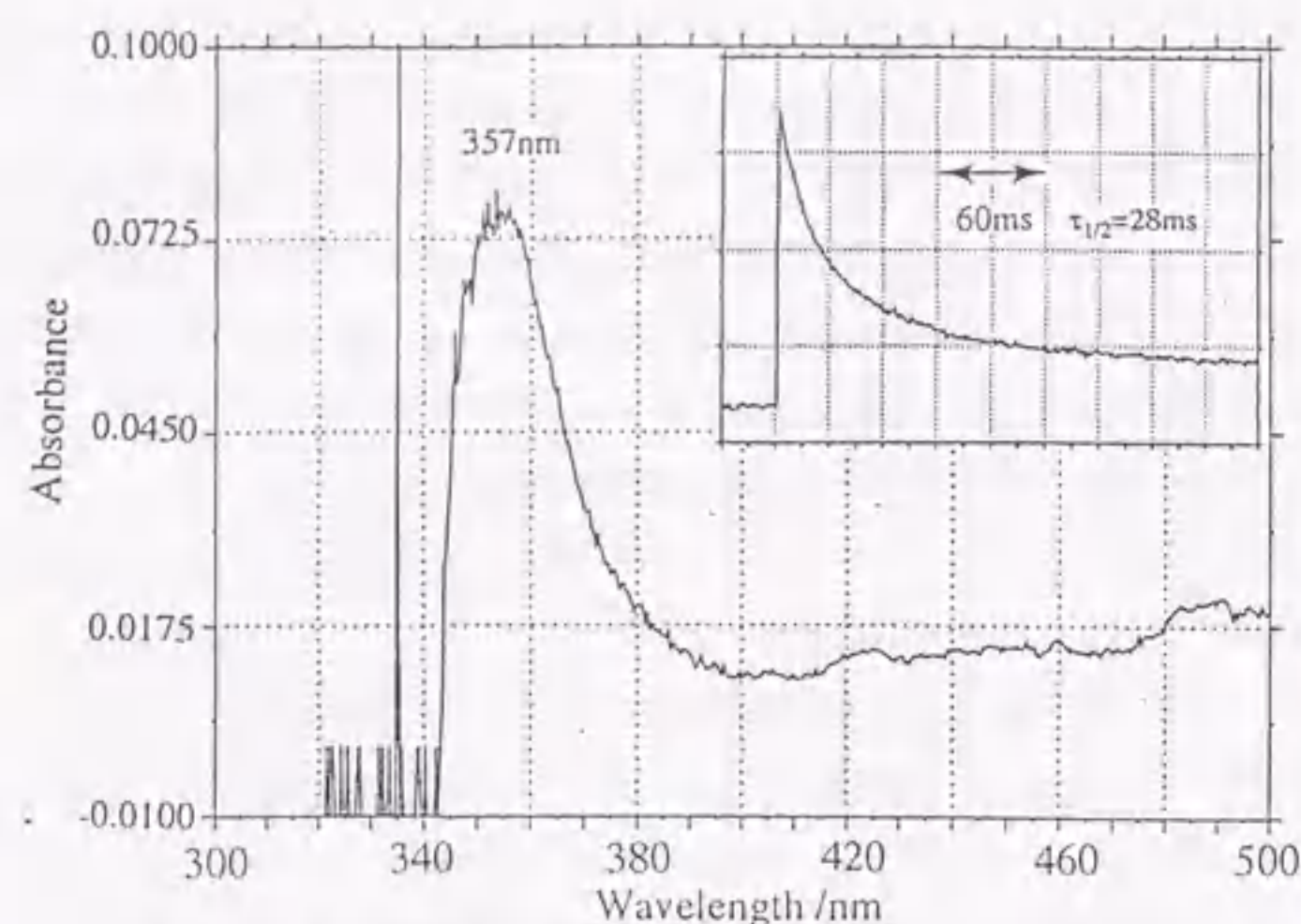
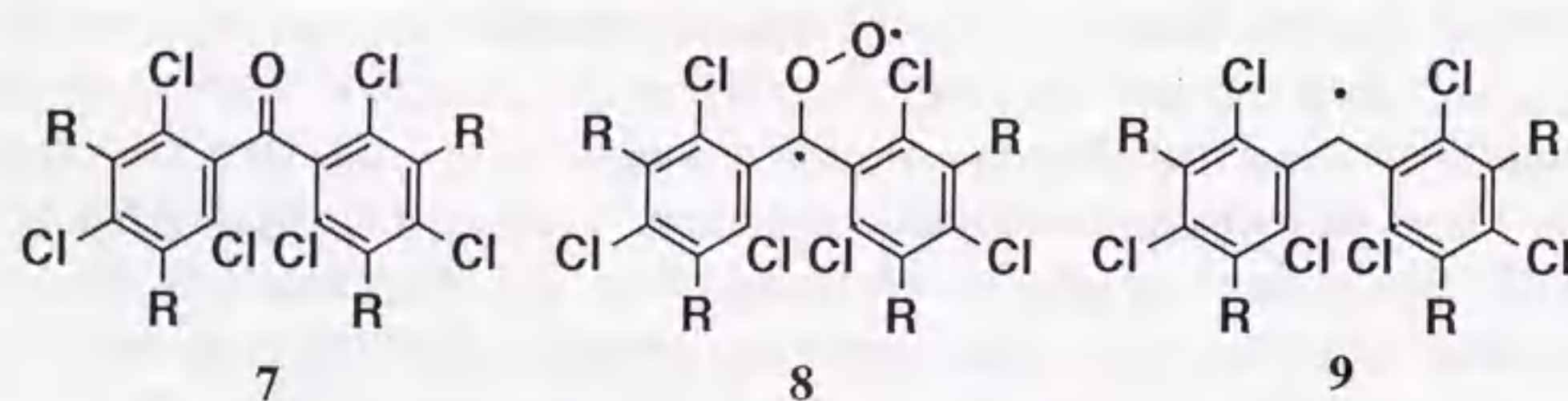


Figure 2. Absorption spectra of the transient products formed during the irradiation of **1a** in degassed benzene, recorded after 50 μ s. Inset shows oscillogram trace monitored at 357 nm.

of the spent solution showed the presence of a large amount of perchlorobenzophenone (**7a**) at the expense of the carbenic dimer (**3a**). It is now well-documented⁸ that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diarylketone oxides, which are observed directly either by matrix isolation techniques or by flash photolysis. These carbonyl oxides usually show a rather broad absorption band centered at around 390-450 nm. Thus, the observation can be interpreted as indicating that the triplet **2a** is trapped with oxygen to generate carbonyl oxide (**8a**), thus, confirming that the transient absorption quenched by oxygen is due to **2a**.



Second-order fitting of transient absorption data for **2a** yields $2k_d/\epsilon l$ values, where $2k_d$ is the dimerization reaction rate constant, ϵ the extinction coefficient, and l the optical

path.^{8b} The extinction coefficient of **2a** at 357 nm was conveniently determined in the matrix photolysis in MTHF to be $11749 \pm 160 \text{ M}^{-1}\text{cm}^{-1}$ based on the assumption that **1a** is completely decomposed and **2a** is not consumed under these conditions. This is shown to be valid by the observations that almost no **1a** was left in the spent solution and that the absorption due to **2a** was not decreased at all if kept at 77 K and even under prolonged irradiation. Thus, k_d was determined to be $(2.5 \pm 0.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. The decay of the carbonyl oxide **8a** was, on the other hand, found to be somewhat difficult to fit with a single exponential presumably due to self-reactions of carbonyl oxides, or reactions with other transients likely to be present or generated in the system.^{8,9} Therefore the rough lifetime of **8a** is estimated in the form of half-life, $t_{1/2}$, to be $510 \pm 9 \text{ ms}$.

When a solution of **1a** in a degassed benzene solution containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing a strong absorption with $\lambda_{\text{max}} = 376 \text{ nm}$, as the 357 nm signals of **2a** decayed. Figure 3 shows the transient spectrum obtained 50 μ s after the photoexcitation where decay of **2a** was not complete; the inserts show the decay of **2a** at 357 nm and the formation of the new

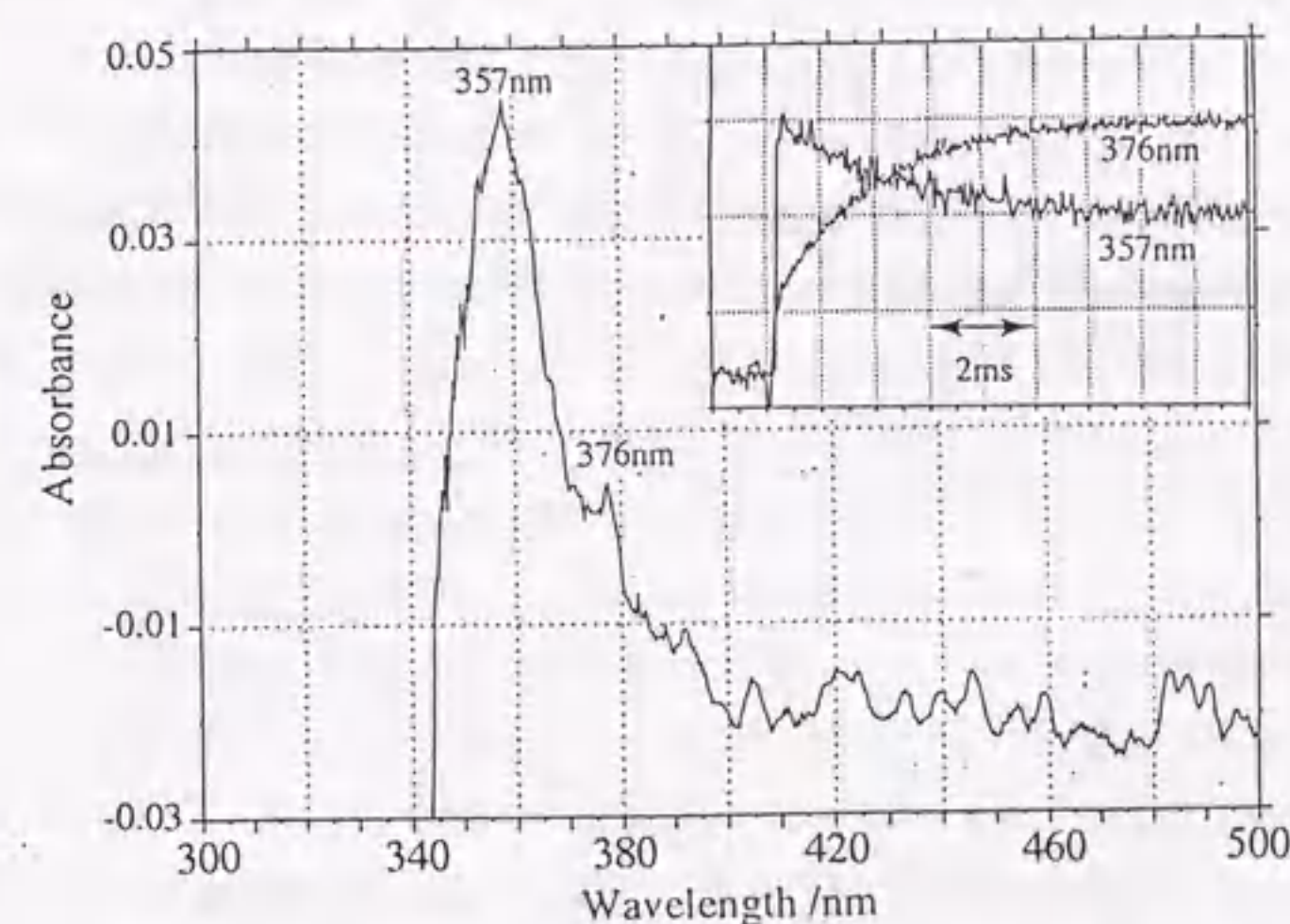


Figure 3. Absorption spectra of the transient products formed during the irradiation of **1a** in degassed benzene containing 1,4-cyclohexadiene, recorded after 50 μ s. Insets show oscillogram traces monitored at 357 nm and 376 nm.

species at 376 nm, indicating that the decay of **2a** is kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the perchlorodiphenylmethyl radical (**9a**) formed as a result of H abstraction of **2a** from the diene, since it is now well-documented¹¹ that triplet arylcarbenes generated in good

hydrogen donor solvents undergo H abstraction leading to the corresponding radical showing transient absorption at longer wavelength than that of the precursor carbene. The excellent hydrogen donor properties of 1,4-cyclohexadiene have been recognized in its reaction with triplet benzophenone.¹² The formation of perchlorodiphenylmethane (**5a**) at the expense of **3a** under these conditions also supports this assignment. The apparent build-up rate constant, k_{obs} , of the radical is essentially identical with that of the decay of the carbene, and k_{obs} is expressed as given in equation 1,

$$k_{\text{obs}} = k_0 + k_{\text{CHD}} [\text{diene}] \quad (1)$$

where k_0 represents the rate of decay of **2a** in the absence of the diene and k_{CHD} is a quenching rate constant of **2a** by the diene. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [cyclohexadiene] in the range 0.05–0.14M is linear (Figure 4). The slope of this plot yields the absolute rate constant for reaction of **2a** with the diene, $k_{\text{CHD}} = (6.2 \pm 0.1) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, and the intercept yields $k_0 = 24.1 \pm 8.2 \text{ s}^{-1}$. Since the product analysis study clearly indicates that dimerization forming **3a** is the sole decay pathway for **2a**, k_0 must be represented as $k_d [\text{2a}]$. The concentration of triplet carbene **2a** generated by a pulse of the xenon flash lamp was adequately approximated by using ϵ for **2a** as well as absorbance at 357 nm after photoexcitation in benzene without quencher to be $(8.3 \pm 0.1) \times 10^{-6} \text{ M}$. This leads to $k_d \sim 2.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, in excellent agreement with that determined by the direct monitoring of **2a** (vide supra).

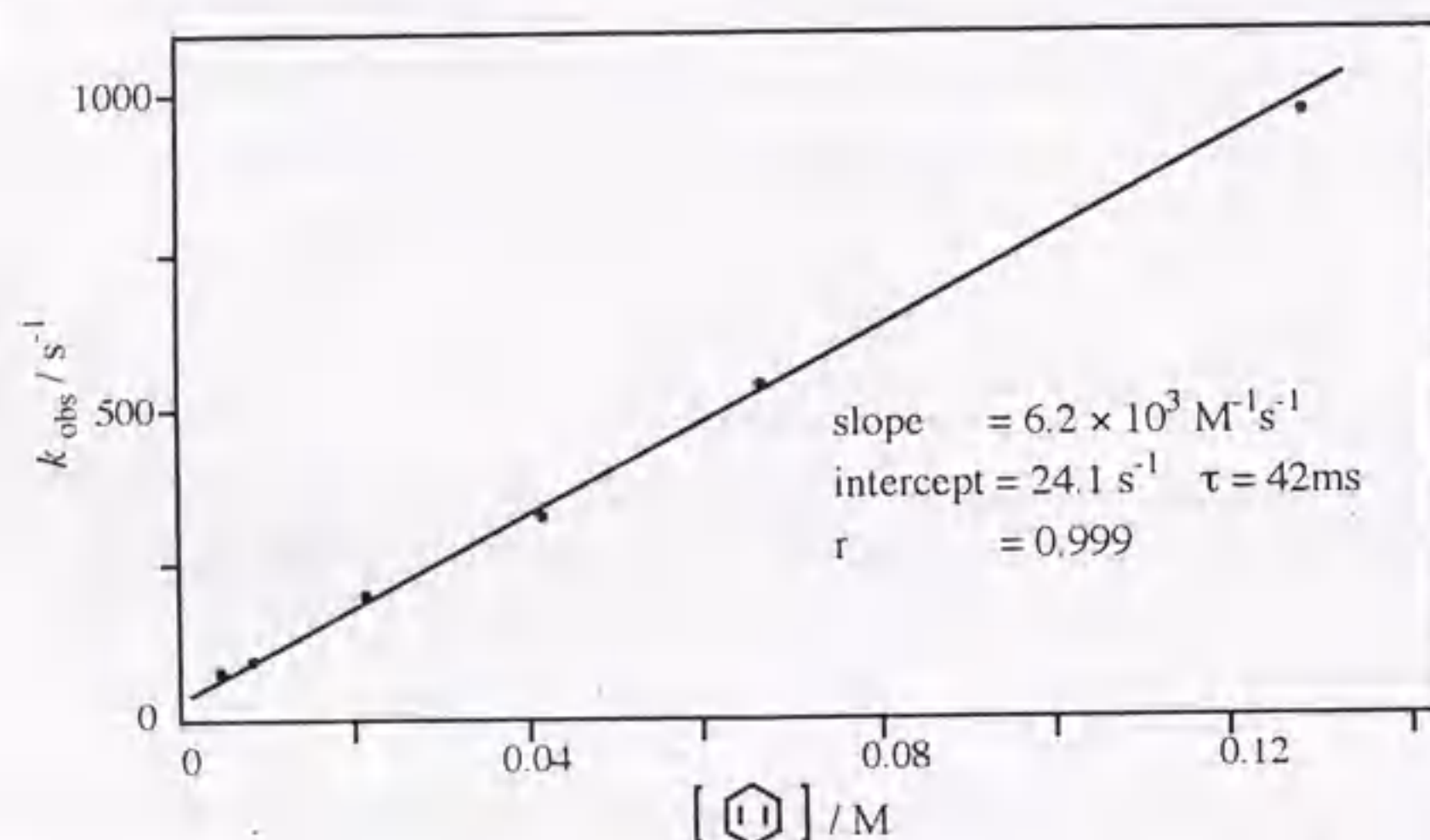


Figure 4 Plots of the growth rate of the decachlorodiphenylmethyl radical in degassed benzene containing 1,4-cyclohexadiene.

Essentially similar results were obtained in the flash photolysis of **1b** in benzene, where the absorption due to the carbonyl oxide (**8b**) appeared at 390 nm ($t_{1/2} = 370 \pm 0.3$ ms) in the presence of oxygen and that ascribable to the hexachlorodiphenylmethyl **9b** at 365 nm in the presence of the diene, as the 344 nm triplet **2b** signals decayed. Kinetic data obtained for **2a** as well as **2b** are summarized in Table 2 which also includes the data¹¹ for unsubstituted diphenylcarbene for comparison purposes.

Table 2. Bimolecular Rate Constants for the Reaction of Diarylcarbenes

diarylcarbenes	$k_d / \text{M}^{-1}\text{s}^{-1}$	$k_{\text{CHD}} / \text{M}^{-1}\text{s}^{-1}$
diphenylcarbene	$(5.4 \pm 1.6) \times 10^9$ ^a	$(1.0 \pm 0.1) \times 10^7$ ^b
2b	$(1.2 \pm 0.1) \times 10^7$	$(3.5 \pm 0.1) \times 10^3$
2a	$(2.5 \pm 0.1) \times 10^6$	$(6.2 \pm 0.1) \times 10^3$

^a Ref 11f. ^b Ref 11b.

5-6 Summarizing Discussion

It is conceivable that displacement of all hydrogen atoms on diphenylcarbene with chlorides must result in the increased steric crowdedness of the carbenic center in the light of van der Waals radii (1.80) of chloride substituent. Thus, although the major reaction found for **2a** is dimerization forming **3a** and is essentially similar to that observed for the hexachlorodiphenylcarbene (**2b**), product distribution clearly indicates that the carbenic center in **2a** is more rigidly protected than that in **2b**. Furthermore, inspection of the kinetic data immediately indicates that the dimerization rate is sharply decreased as one simply introduces four chlorine atoms at the *ortho* positions but is further decreased by 1 order of magnitude as four additional chloro groups are introduced at the meta positions, obviously due to the buttressing effect. This confirms the explanation based on the product analysis (vide supra) and supports the idea that the buttressing effect should play an important "buttressing" role in protecting the reactive center. On the other hand, k_{CHD} is also decreased dramatically in going from $\text{Ph}_2\text{C:}$ to **2b**, but it increases albeit slightly as one introduces the four more chlorine atoms. This is somewhat surprising in the light of a marked decrease in the dimerization rate by the four meta buttressing chloro substituents as noted above and is explicable as indicating that electrophilicity of the carbenic center is increased as one introduces more chlorine groups on the phenyl rings. Thus, as more chloro groups are introduced, the carbenic center is more rigidly protected and, on the other hand, becomes more reactive. Thus,

the attack of a bulky substrate, e.g., chlorinated diphenylcarbene (2), on the carbenic center must be severely restricted while the rate of abstraction of a very small hydrogen atom from a very efficient hydrogen donor is still controlled by electrophilicity of the carbenic center even in these highly hindered carbenes.

Experimental

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and the mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ^1H and ^{13}C NMR spectra were determined with JEOL JNM-EX 270 or JNM-MH 100 spectrometer. UV/vis spectra were measured on a Hitachi 220-S spectrophotometer. Thin-layer chromatography was done on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was carried out on silica gel (ICN for dry column chromatography). HPLC and GPC were undertaken with a JASCO 800 chromatograph equipped with a UVDEC-100-II UV/VIS detector using a Fine pack C18-T5 column (4.6 \times 25 cm) and Shodex GPC H-2001 (20 mm \times 50 cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using a OV-17 on Diasolid L (5.0 mm \times 50 cm).

Low Temperature UV/vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford Variable Temperature liquid Nitrogen Cryostat (DN1704) equipped with quartz outer windows and sapphire inner windows. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked quartz cuvette of 1 mm path length and degassed by repeated freeze-degas-thaw cycles at pressure near 10^{-5} Torr. The cuvette was placed in the cryostat and cooled to 77 K. After a base line had been recorded, the sample was irradiated for several minutes in the spectrophotometer with a Halos 300-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with Oxford Instrument Intelligent Temperature Controller (ITC4).

Flash Photolysis. All flash measurements were made on a Unisoku Flash Spectrometer. The sample was dissolved in dry benzene (over benzophenone ketyl), placed in a long-necked 10 \times 10 or 20 \times 10 mm (3-5 mL) quartz fluorescence cuvette, and degassed by minimum of four freeze-degas-thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. An energy input of 100 J/flash was discharged through a cylindrical 150-W Xe flash lamp, which was parallel to the long axis of the

photolysis cell. The excitation flash lamp had a half-life of 10 μs . The absorption spectra of the transients were obtained after a predetermined delay. Light from the monitoring flash was dispersed in multichannel detector and then transferred to a PC9801 RX2 computer which provides data processing, storage and hard copy graphics capabilities. Decay of the transient absorption was followed quantitatively by photomultiplier.

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (ca. 30 mg) in solvents was placed in Pyrex tube and irradiated with a high pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The irradiation mixture were then concentrated on a rotary evaporator below 20°C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS.

Irradiation for Analytical Purpose. Irradiation outlined in Table I were carried out in a Pyrex tube of 5.0-mL capacity at below 10°C. In order to avoid ambiguity of the yields due to the oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} Torr before irradiation. Irradiation was carried out with filtered light ($\lambda > 350$ nm) through Corning CS-052 filter from the 300 W mercury lamp and was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC-MS as well as NMR comparisons with authentic samples and product yields were conveniently determined by GC and/or NMR using internal standard.

Preparation of Decachlorodiphenyldiazomethane (1a). αH -Undeca-chlorodiphenylmethane.¹³ To a boiling solution of anhydrous AlCl_3 (0.75 g, 5.7 mmol) in SO_2Cl_2 (225 mL), a solution of diphenylchloromethane (2.64 mL, 14.9 mmol) and S_2Cl_2 (0.90 mL, 11.1 mmol) in SO_2Cl_2 (75 mL) was added gradually (20 min). The resulting mixture was then distilled gently until the total volume was down to ca. 60 ml and then it was refluxed for 2 hr to obtain pure green solution. The solvent was evaporated under reduced pressure to leave a greenish solid, which was added to 5 % NaHCO_3 aqueous solution (50 mL). The mixture was refluxed for 1 h to give a white precipitate which was filtered and dried: 9.28 g (99 %); mp 230-232°C; ^1H NMR (CDCl_3) δ 7.10 (s, 1H); ^{13}C NMR (CDCl_3) δ 134.5, 134.4, 133.7, 133.4, 58.4; IR (KBr disk) 1520, 1360, 1340, 1225, 1110 cm^{-1} .

Ethyl *N*-Bis(pentachlorophenyl)methylcarbamate. A mixture of 1.44 g (7.4 mmol) of AgBF₄, 1.92 g (0.22 mmol) of ethyl carbamate, and 60 ml of dioxane was heated until solution was effected. To this the chloride (3.0 g, 5.48 mmol) in dioxane (240 ml) was added at once at 100°C. The mixture was refluxed until TLC monitoring showed almost all of the chloride was consumed (18 h). The cooled reaction mixture was extracted with CCl₄ (50 mL) and H₂O (100 mL). After filtering, the organic layer was washed well with water and then dried (Na₂SO₄). After evaporation of the solvent, the resulting white solid was distilled under reduced pressure (60°C / 1.0 Torr) using Kugelrohr to remove excess ethyl carbamate. The residue was chromatographed on silica gel eluted with ethyl ether-*n*-hexane (5:95) to give 950 mg (28.8 %) of white crystals; mp 240-245°C; ¹H NMR (CDCl₃) δ 7.09 (1H, d, *J* = 10.0 Hz), 5.46 (1H, d, *J* = 10.0 Hz), 4.20 (2H, q, *J* = 7.0 Hz), 1.28 (3H, t, *J* = 7.0 Hz); IR (KBr disk) 1750, 1520, 1370, 1340 1130, 1080 cm⁻¹.

Bis(pentachlorophenyl)diazomethane (1a). To a vigorously stirred mixture of the carbamate (0.95 g, 1.58 mmol) in AcOH (30 mL) and Ac₂O (200 mL) at 0°C, 100 mg portion of NaNO₂ (total 3.0 g, 43.5 mmol) was added every 20 min for 5 h. The mixture was stirred overnight at 0°C, poured onto ice-water (100 mL), and extracted with ether. The ethereal layer was washed with water, 5 % Na₂CO₃, water and dried. Evaporation of the solvent afforded *N*-nitroso-*N*-bis(pentachlorophenyl)carbamate as a white solid (663 mg, 66.8 %); mp 242-245°C; ¹H NMR (CDCl₃) δ 7.17 (1H, s), 3.47 (2H, q, *J* = 13.0 Hz), 1.38 (3H, t, *J* = 13.0 Hz); IR (KBr disk) 1770, 1595, 1530, 1340, 1250, 1130 cm⁻¹.

To a heated solution of potassium *tert*-butoxide (85.3 mg, 0.76 mmol) in *tert*-butyl alcohol (5.0 mL) at 60°C, a solution of the nitroso-carbamate (160 mg, 0.25 mmol) in *tert*-butyl alcohol (100 mL) was added at once under the atmosphere of argon. The mixture was stirred for 2 h at 60°C and poured onto ice-water to produce an orange solid. The solid was dissolved into ether and chromatographed on alumina column at -10°C eluted with ether to produce yellowish crystal. Since ¹H NMR spectra of this crystalline product indicated the presence of small amount of partially chlorinated products, it was further purified by recycling the sample on a gel permeation chromatograph with CHCl₃ elution to leave pure sample. 18 mg (3.5 %); mp 178-180°C (dec); ¹³C NMR (CDCl₃) δ 133.5, 133.0, 132.8, 128.7, 29.7; IR (KBr disk) 2080, 1350 cm⁻¹. ¹H NMR spectra showed no peak.

Bis(2,4,6-trichlorophenyl)diazomethane was prepared by the procedure by Zimmerman.² ***αH*, *αH*-Decachlorodiphenylmethane (5a)** was prepared¹³ by the reduction of *αH*-undecachlorodiphenylmethane in diglyme and ***syn*-**

tetrakis(pentachlorophenyl)ethane (4a) was obtained² by the treatment of *αH*-undecachlorodiphenylmethane with phenyl lithium.

***αH*-Undecachlorodiphenylmethyl methyl ether (6a, R'=OMe)** was isolated in the photolysis of **1a** in MeOH / PhH as a yellowish oil. ¹H NMR (CDCl₃) δ 6.32 (1H, s), 3.49 (3H, s); MS *m/e* (relative intensity) 548 (M⁺+10, 4.5), 546 (M⁺+8, 10.1), 544 (M⁺+6, 21.1), 542 (M⁺+4, 24.5), 540 (M⁺+2, 18.9), 538 (M⁺, 5.7), 513 (25.1), 511 (49.0), 509 (81.9), 507 (100), 505 (74.7), 503 (27.6), 297 (16.1), 295 (46.2), 293 (72.4), 291 (49.3).

***syn*-Tetrakis(pentachlorophenyl)ethene (3a)** was isolated in the photolysis of **1a** in benzene as yellowish solid. mp > 340°C; MS *m/e* (relative intensity obs / calcd), 1031.0 (M⁺+20, 5.8/5.7), 1029.0 (M⁺+18, 14.1/16.8), 1027.2 (M⁺+16, 28.8/28.2), 1025.0 (M⁺+14, 38.3/53.1), 1023.4 (M⁺+12, 68.8/81.5), 1021.1 (M⁺+10, 100/100), 1019.3 (M⁺+8, 77.3/95.9), 1017.4 (M⁺+6, 60.1/69.2), 1015.4 (M⁺+4, 21.6/35.4), 1012.9 (M⁺+2, 12.0/11.4), 1011.4 (M⁺, 3.2/1.8).

Bis(2,4,6-trichlorophenyl)cyclohexylmethane (6b, R'=c-C₆H₁₁) was isolated in the photolysis of **1b** in cyclohexane in 15 % yield as yellow oil. ¹H NMR (CCl₄) δ 7.24 (4H, s), 5.32 (1H, bs), 3.72 (1H, bs), 1.58-1.04 (10H, m); MS *m/e* (relative intensity) 423 (6), 421 (2.3), 4.19 (1.1), 364 (5.3), 193 (2.2), 83 (100).

Bis(2,4,6-trichlorophenyl)methyl methyl ether (6b, R'=OMe) was isolated in the photolysis of **1b** in methanol as an oil. ¹H NMR (CCl₄) δ 7.24 (4H, bs), 6.04 (1H, s), 3.44 (3H, s); MS *m/e* (relative intensity) 406 (M⁺+4, 4.5), 404 (M⁺+2, 5.7), 402 (M⁺, 2.1), 369 (57), 335 (9.6), 207 (100).

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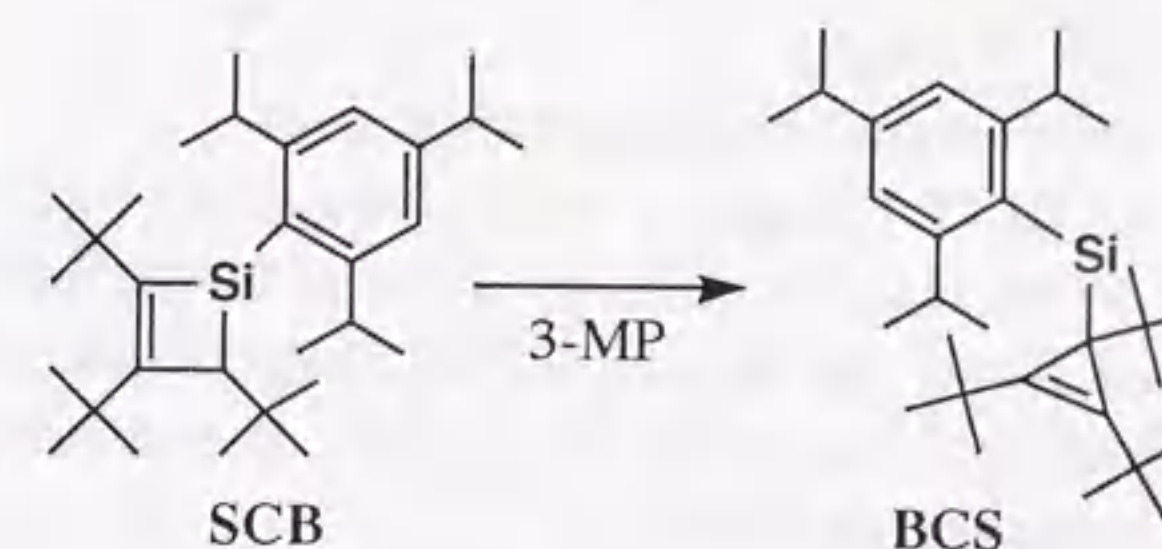
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Chapter 6 Chemistry, Kinetics, and Spectroscopy of Polyalkyl-diphenylcarbene

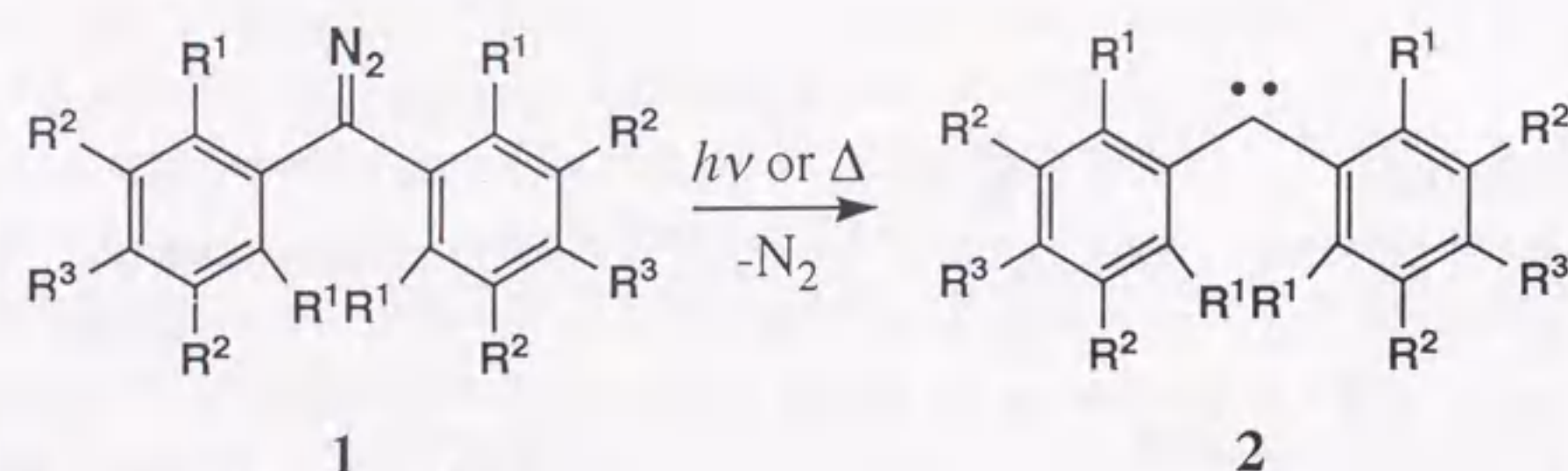
6-1 Introduction

The most persistent triplet carbene known so far is dimesitylcarbene (**2a**), which was first generated by Zimmerman and Paskovich¹ in 1964. The congestion at the carbene center in **2a** is reflected in its unique behavior. For example, its proclivity to dimerize and reluctance to attack secondary carbon-hydrogen bonds. Carbene **2a** was not stable enough to be isolated, and systematic kinetics studies were also not conducted for further characterization. If four additional methyl groups are introduced at the *meta* positions, the carbenic center would be more crowded, because of the "buttressing effect" on the four *ortho* methyl groups.²

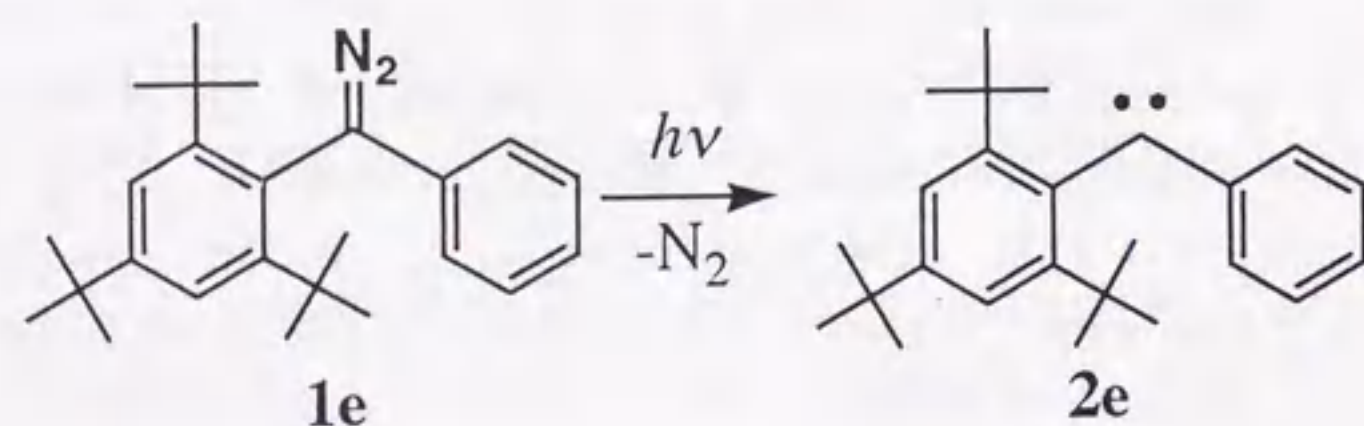
On the other hand, *tert*-butyl group has been recognized as one of the most effective protecting groups and successfully used to protect many reactive centers in organic molecules.³ For example, Fink et al. reported^{3a} that the photogenerated 1-(2,4,6-triisopropylphenyl)-2,3,4-tri-*tert*-butyl-1-silacyclobutadiene (SCB) underwent a clean isomerization to the thermodynamically more stable (2,4,6-triisopropylphenyl)(1,2,3-tri-*tert*-butylcyclopropenyl)silylene (BCS) in 3-methylpentane solution. The extreme stability of BCS can be attributed to steric protection by its two bulky substituents i.e., *tert*-butyl and the triisopropylphenyl groups.



In view of the scarcity of the data in this field despite recent growing interest in triplet carbenes as potential organic ferromagnets,⁸ we became interested in designing and generating persistent triplet carbenes. Thus, we have generated a series of poly methylated diphenylcarbenes **2a-d** and (2,4,6-tri-*tert*-butylphenyl)phenylcarbene **2e**, and their reactivities were investigated not only by product analysis but also by using flash photolysis techniques.



- 1
 a: $R^1=R^3=CH_3, R^2=H$
 b: $R^1=CH_3, R^2=H, R^3=tBu$
 c: $R^1=R^2=CH_3, R^3=H$
 d: $R^1=R^2=R^3=CH_3$



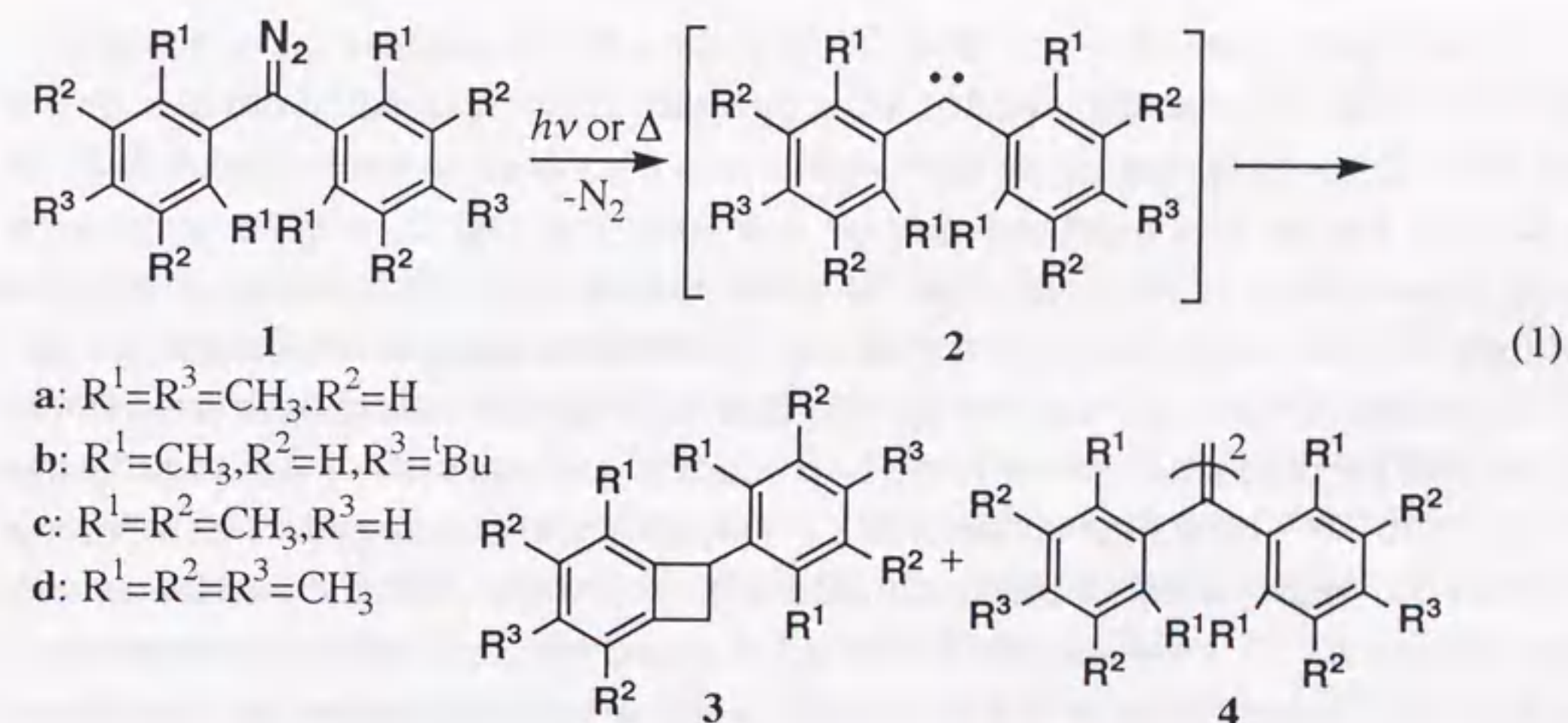
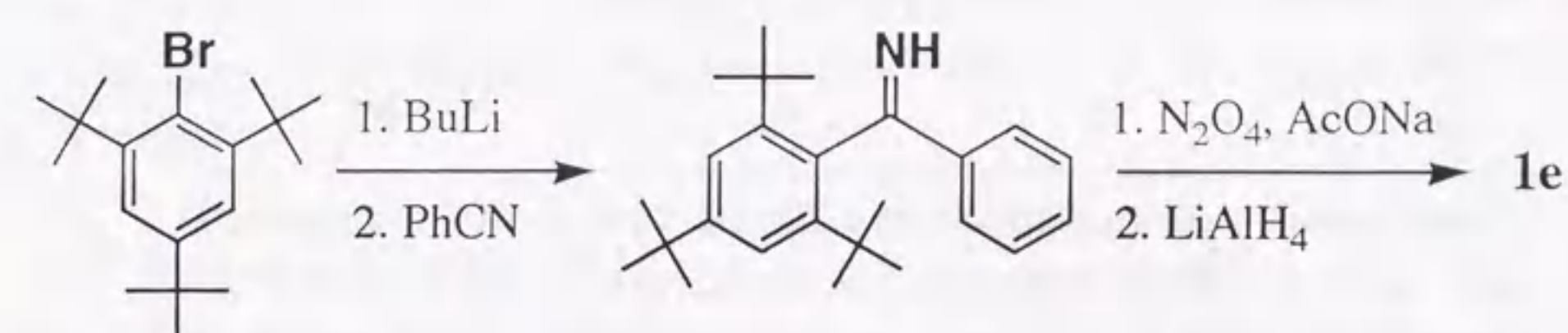
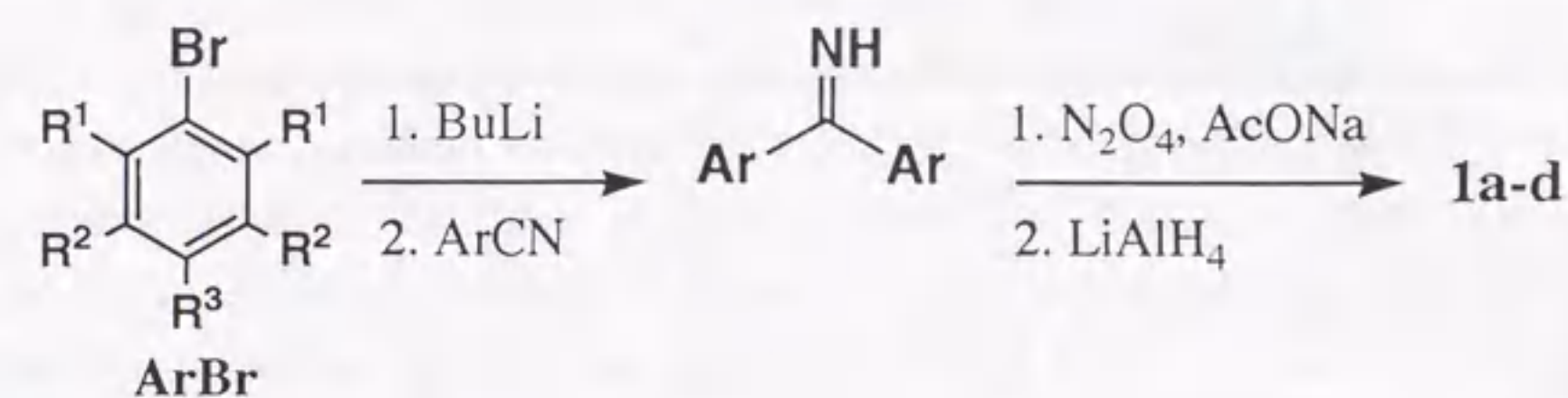
6-2 Preparation of Polyalkyldiphenyldiazomethanes

The diazomethanes **1b**, **1c**, **1d**, and **1e** were prepared by essentially the same procedure reported by Zimmerman¹ for the preparation of the corresponding dimesityl analogues (**1a**) and were purified by repeated chromatograph on a Shodez GPC H-2001 column (Scheme 1). **1b** was obtained as a red oil and **1c**, **1d**, and **1e** were obtained as very stable orange or red crystals.

6-3 Product Analysis

(1) *Thermolysis in Benzene* Thermolysis (140°C) of dimesityldiazomethane (**1a**) in benzene afforded 1,2-dihydrocyclobutabenzene ("benzocyclobutene") **3a** again in accord with earlier observations (eq 1, Table 1). Thermolysis of diduryldiazomethane (**1c**) or decamethyldiphenyldiazomethane (**1d**) under the same conditions also resulted in the formation of an essentially similar product. These products are apparently derived from thermolytically generated carbene **2** which must undergo insertion into the C-H bond of the *o*-methyl group.

Scheme 1



(2) *Photolysis in Fluid Media* Irradiation (>300 nm) of **1a** in benzene afforded **3a** and 1,1,2,2-tetramesitylethylene (**4a**) in 11 and 61% yield, respectively (Table 1). When **1b-d** were irradiated under the same conditions, however, the formation of the benzocyclobutene **3** was reduced and 1,1,2,2-tetraarylethylene **4** was increased. These

Table 1. Conditions and Product Distribution for the Decomposition of Diazo Compounds **1**^a

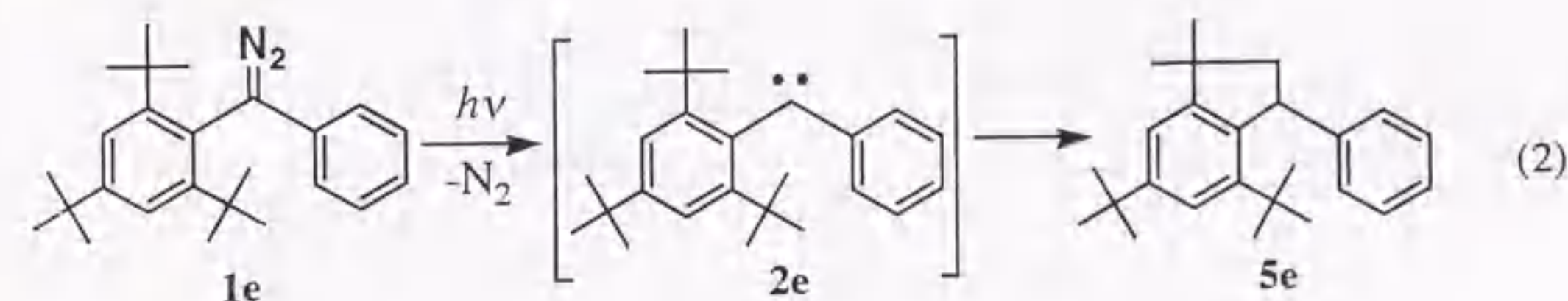
carbenes	conditions	yield, ^b %		
		3	4	5
2a	C ₆ H ₆ /140°C	73	0	-
2c		96	0	-
2d		90	0	-
2a	hν/C ₆ H ₆ /10°C	11	61	-
2b		10	80	-
2c		41	29	-
2d		79	5	-
2e		-	0	97

^aIrradiations were carried out on a 20mM solution of **1** in degassed benzene with a 300W high-pressure mercury lamp and a Pyrex filter. Thermolysis were performed in degassed benzene and in a sealed Pyrex tube. ^bDetermined by GC and NMR spectroscopy.

photolitically generated carbenes **2b-d** did not react with the diazomethane precursors to give ketazines. Instead they reacted either by attack at an ortho methyl group to give **3** or by dimerization to form **4**. A key difference is found, however, in the formation of **3**. In the case of **2a**, **3a** was produced only by thermolysis at 140°C, and **2a** underwent mainly dimerization when photolyzed at room temperature. Photolysis of **2b** also produced **4b** along with a small amount of **3b**. On the other hand, in the case of **2c**, **3c** was produced not only by thermolysis but also by photolysis along with the dimer. Compound **2d** produced **3d** as a major product at the expense of **4d** even in the photolytic run. The difference in reactivities among **2a-d** can be interpreted as reflecting the difference in the extent of steric crowdedness around the carbenic centers among these carbenes. It is well-known^{2b} that, in 1,2-disubstituted benzene derivatives, introduction of substituents in the 3 position exerts a very large effect on the rate of appropriate reactions and the data are considered in the light of the importance of bond bending; the 3-substituents buttress the 2-substituent. Thus, in **2c**, each of four ortho methyl groups around the carbene center is buttressed by one of four meta methyl groups, and therefore the carbene center in **2c** is surrounded by the methyl groups more rigidly than that in **2a**. In other words, **2c** is more effectively blocked from external reagents. In the case of **2d**, further, since two more methyl groups are introduced at the para positions, the carbenic center is forced to react with the ortho methyl groups, which are brought much closer to the carbene. The effect of two *tert*-butyl group at the para

positions in **2b** also was interpreted as a similar "buttressing effect", although the extent of the effect is very smaller than that of **2c** since in **2b** hydrogen, which is a smallest substituent, is introduced at the all meta positions.

On the other hand, irradiation of **1e** in benzene afforded 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan (**5e**) almost quantitatively. It is probable that the indan **5e** must be produced from the photolitically generated 2,4,6-tri-*tert*-butyldiphenylcarbene (**2e**), which underwent insertion into the CH bond of *tert*-butyl groups at the ortho positions. Similar irradiation of **1e** either in cyclohexane or in methanol also gave only **5e**, no solvent adducts being detected. It is rather surprising to note that the carbene was not trapped even by methanol since methanol is well-known as an particularly excellent scavenger for most of carbene, and this indicates that the carbenic center in **2e** is not only almost completely blocked toward external reagents but also trapped by the butyl group instantaneously.



6-4 Detection of Triplet Carbenes by ESR Spectroscopy⁵

Irradiation of diduryldiazomethane (**1c**) in 2-methyltetrahydrofuran (MTHF) at 40 K with Pyrex-filtered UV light produced signals characteristic of the carbene in the triplet states, together with the intense signal at 0.34 T due to radicals formed by reactions of the carbene with matrices. The signals of the triplet species, which were assigned to H_z, H_x, H_y, and H_z transition, appeared (Figure 1). The zero-field splitting (zfs) parameters are calculated to be $D=0.3848\text{ cm}^{-1}$, $E=0.0128\text{ cm}^{-1}$. The zfs parameters of dimesitylcarbene are reported to be $D=0.3849\text{ cm}^{-1}$, $E=0.0083\text{ cm}^{-1}$ in MTHF at 77 K.⁶

In order to determine the spin multiplicity of the ground states of carbene **2c**, the temperature dependence of the intensities of their ESR signals was examined. The ESR spectra were recorded in the range from 1.7 to 110 K. The temperature dependence of ESR spectra of randomly oriented **2c** in trans-decalin/methylcyclohexane (2:1) glass after annealing indicated the absence of molecular conformation changes of **2c** during the process of increasing temperature. The temperature dependence of the ESR signal intensity of the z transition (low magnetic field) after annealing is shown in Figure 2. The

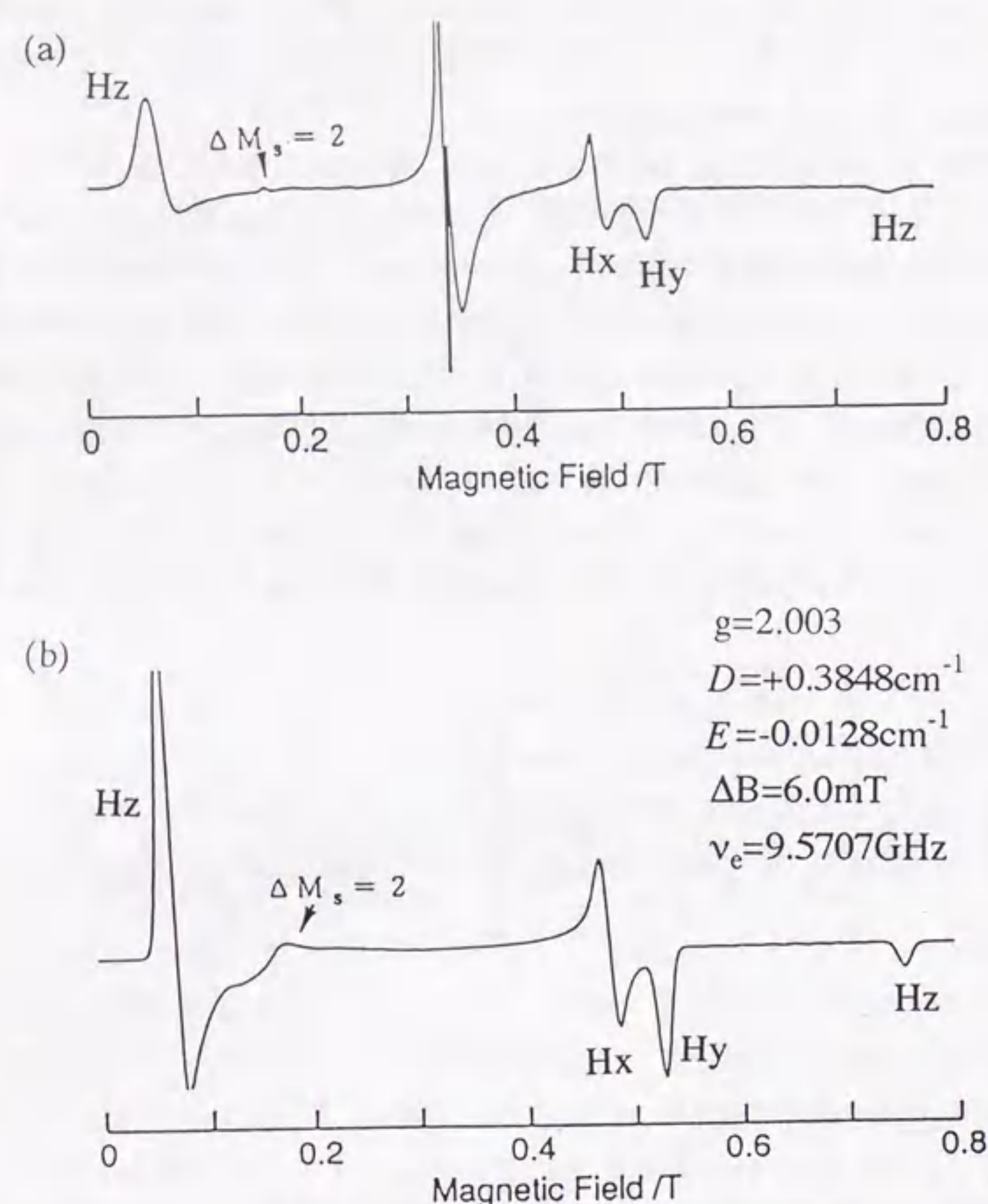


Figure 1. The X-band ESR spectra from the triplet state of **2c** in MTHF glass before annealing. (a) the observed spectrum at 40 K, $\nu_e=9.5707$ GHz (b) the simulated spectrum.

signal intensity vs. the reciprocal of temperature in the range from 40 to 80 K indicates that it follows Curie law dependence over that temperature range. The points denote the observed values, and the solid curve represents the following expression

$$I = \frac{A}{T} \cdot \frac{1}{3 + \exp(\Delta E/kT)}$$

where A stands for the normalization constant and ΔE the energy gap between the singlet and triplet states. From these results it is concluded that the observed triplet is the electronic ground state and the singlet state is located far above the triplet state.

When the MTHF glass was warmed to 130 K for 10 seconds, there was a striking shift in the positions of the x and y lines, which moved closer to each other. This is due to

the reduction in E value of **2c** by annealing. On the other hand, the position of the z line slightly shifted to lower magnetic field, indicating a small amount of the reduction in D value. Re-cooling the sample did not reverse this change. As can be seen in Table 2, the annealing process decreased the zfs parameters (especially E value) by about 50%. It means that a structural irreversible change of **2c** occurred in MTHF glass by annealing.

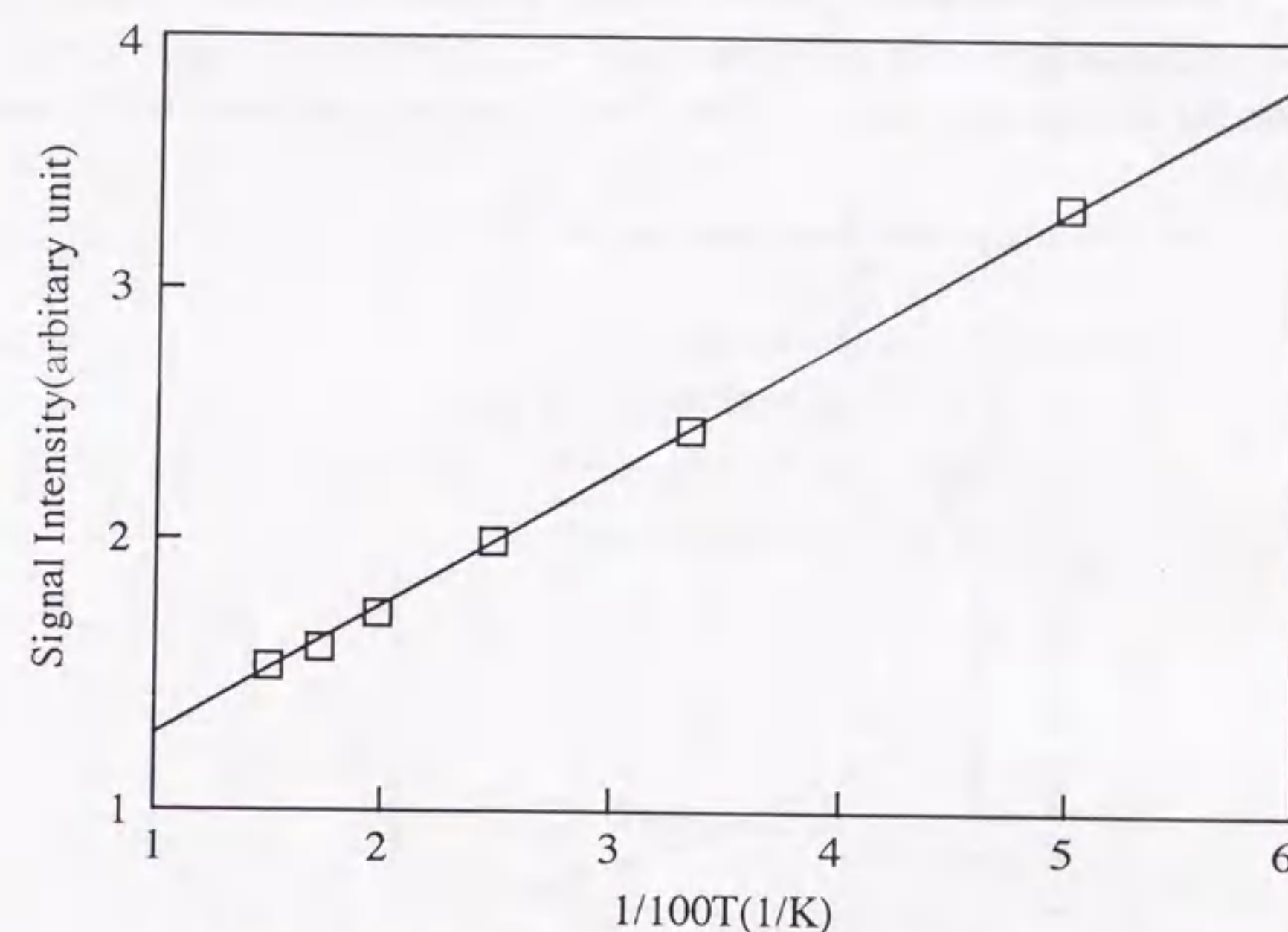


Figure 2. Temperature dependence of the signal intensity of the Z-transition (low magnetic field) of **2c** in trans-decalin/methylcyclohexane(2:1) glass after annealing.

Table 2. Zero-Field Splitting Parameters of **2c**

matrix	temp, K	D, cm^{-1}	E, cm^{-1}
before annealing			
MTHF	40	+0.3848	-0.0128
after annealing ($T_a=130$ K)			
MTHF	40	+0.3520	-0.0060
decalin/methylcyclohexane	40	+0.3508	-0.0067

The reduction in D value shows an increase in the delocalization of the spin density from the divalent carbon atom, and the reduction in E value an increase of axial symmetry of **2c**.

In 1971 Higuchi predicted the relation between the zfs parameters and molecular conformations of diphenylcarbene on the basis of LCAO-MO calculations.⁷ Figure 3 shows the calculated D and E values of diphenylcarbene as a function of the carbene bond angle (θ) assuming the planar structure ($\alpha=0^\circ$) and the structure with the two phenyl groups perpendicular to the observed values of $D=0.4050\text{ cm}^{-1}$, $E=0.01918\text{ cm}^{-1}$. Because molecular conformation changes affect the zfs parameters more than functional

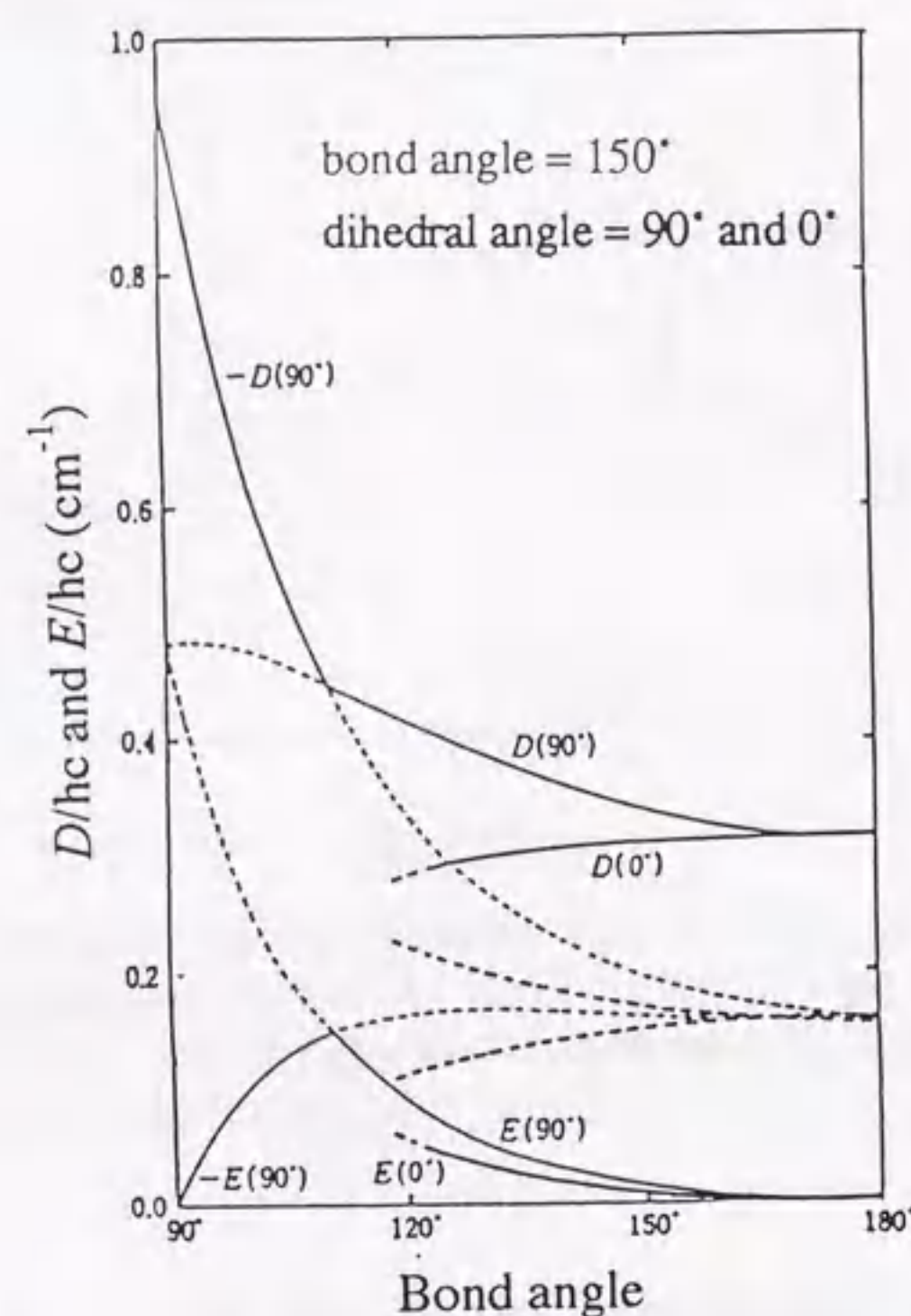


Figure 3. The relation between the fine-structure constants and molecular conformations.

group substitutions do, it is reasonable that the relation shown in Figure 3 applies to the case of **2c**. Broken lines in Figure 3 are for the observed D and E values of **2c** in MTHF glass after annealing. According to Higuchi's model, θ and α of **2c** are 148.6° and 90° , respectively. This result indicates that the phenyl rings of **2c** were perpendicular to each other and that the carbene center was protected by the four methyl groups of the two phenyl rings.

The ESR spectra observed from a single crystal of **2c** at 3 K and 250 K were shown in Figure 4. The observation of two similar spectra indicates the remarkable chemical stability of **2c** in comparison with the other diphenylcarbene derivatives. It can be concluded that the chemical stability is due to the perpendicular conformation of **2c**, which is caused by the steric hindrance of the substituted methyl groups. This conformation prevents other molecules from approaching the reactive center.

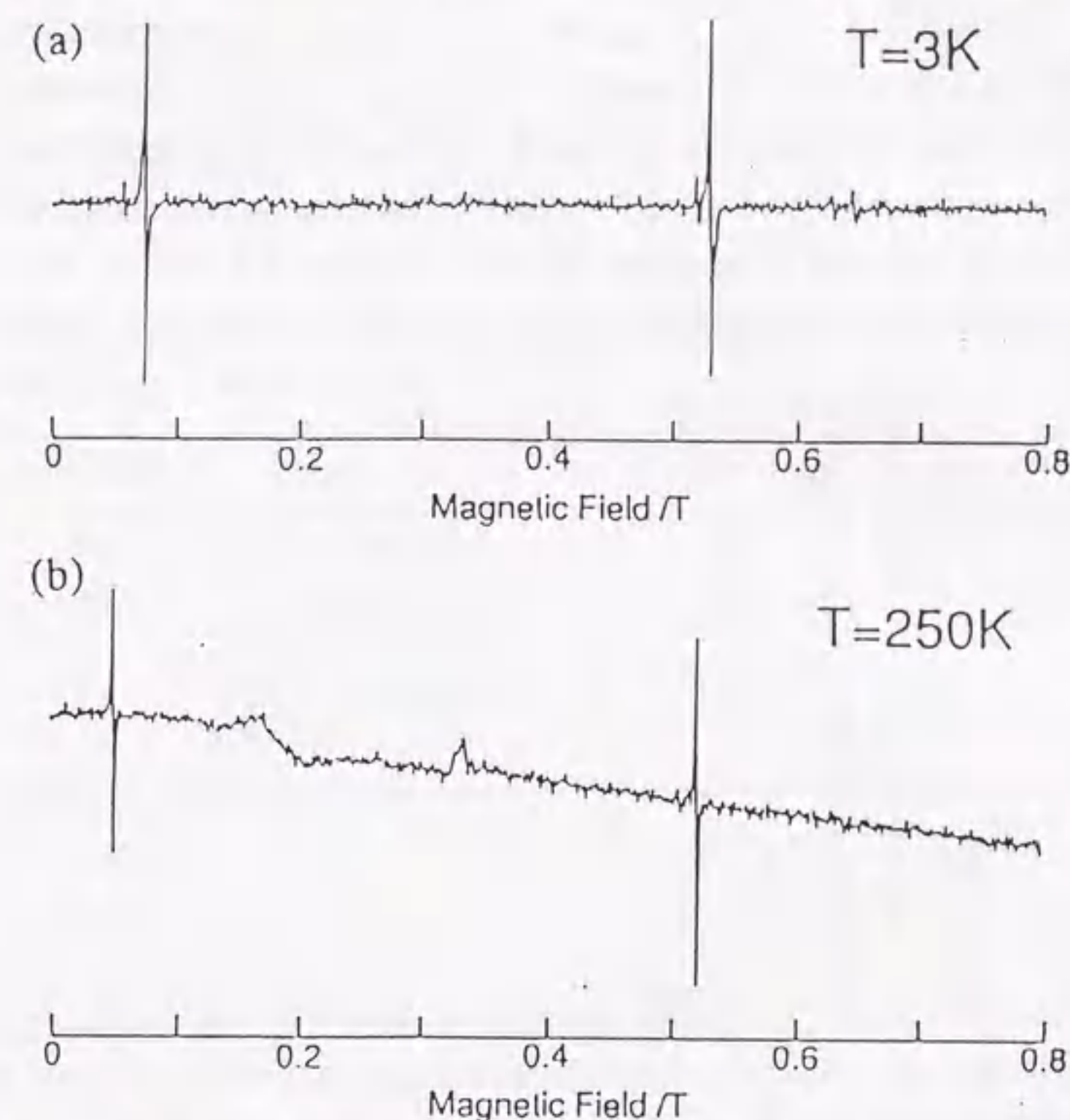


Figure 4. The ESR spectra observed from a single crystal of **2c** (a) at 3K and (b) at 250K.

6-5 Steady-state Irradiation in Frozen Media

(1) *Detection of Triplet Carbenes by UV/vis Spectroscopy* Irradiation ($>300\text{ nm}$) of **1c** ($1.0 \times 10^{-4}\text{ M}$) in a MTHF glass at 77 K resulted in the appearance of new absorption bands as the absorption due to **1c** was consumed, as is shown in Figure 5a. The spectrum displays two distinct features: two sharp, intense UV bands with maxima at 321 and 335 nm, and in the visible portion of the spectrum two weak, broad, overlapping bands with apparent maxima at 466 and 495 nm. The glassy solution did not exhibit any changes in its absorption spectrum for several hours when kept at 77 K. However, when it was allowed to warm to room temperature and then cooled to 77 K, the characteristic

absorption bands disappeared (vide infra). The absorption spectra of several arylcarbenes in frozen media have been reported⁸. Typically, they display an intense UV band and a weak visible transition. These features are present in the spectrum obtained in the photolysis of **1c**. Moreover, the product analysis of the reaction solution showed the presence of dimer **4c** as well as benzocyclobutene **3c**. Thus, the absorption spectrum can be attributed to didurylcarbene (**2c**) generated by the photodissociation of **1c**. The spectral changes of the matrix were carefully monitored as a function of temperature as the matrix thawed. At higher temperatures a new broad absorption at 375 nm appeared and increased as carbene absorption bands decreased (Figure 5c). The species responsible for this new absorption showed appreciable thermal stability; even at room temperature it persisted a few seconds before decaying. These observations suggest that the absorption at 375 nm must be due to an intermediate formed from the initially generated triplet carbene that leads to the final products.

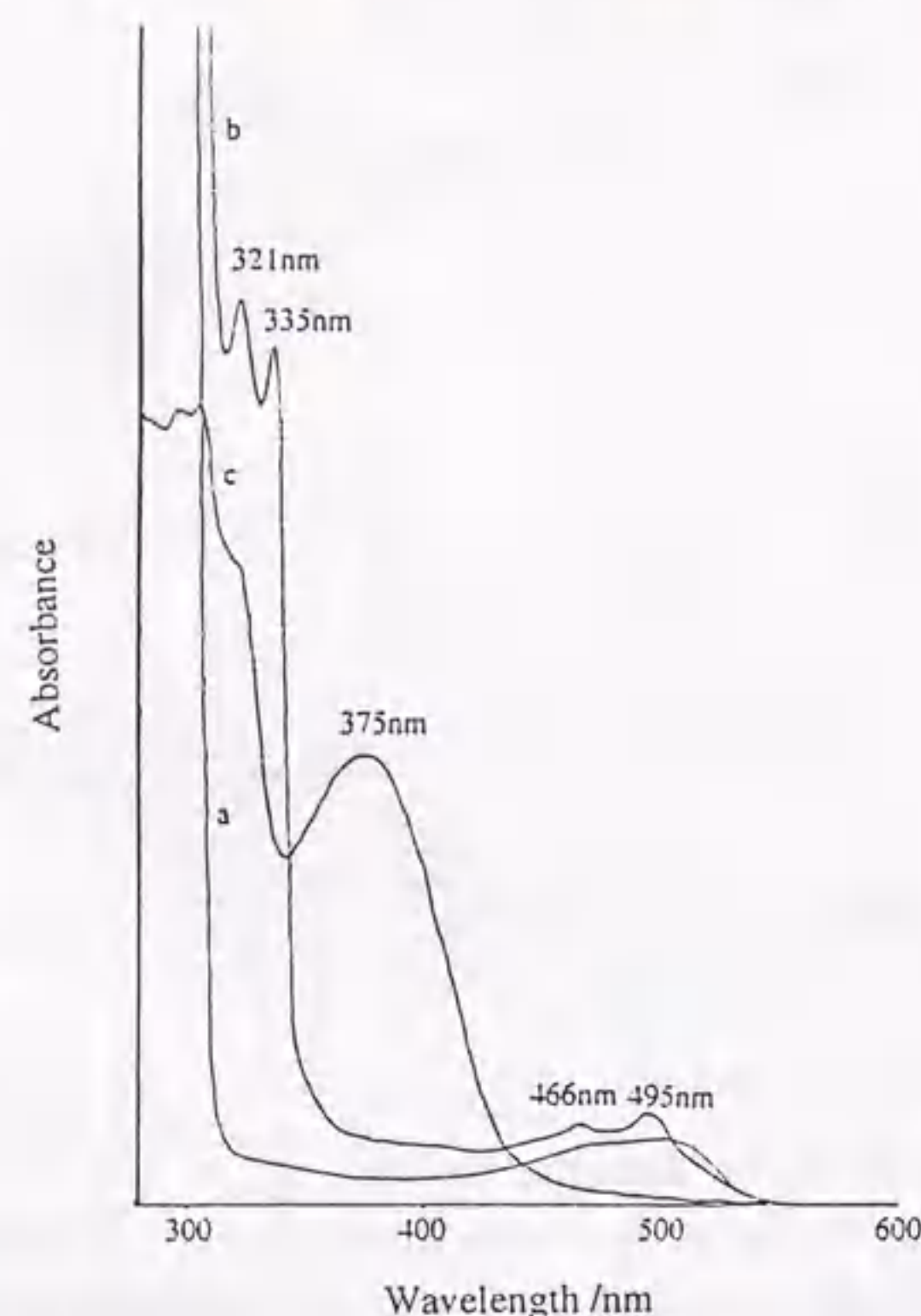


Figure 5. (a) UV/vis spectrum of **1c** in MTHF at 77K. (b) Same sample after 6min irradiation ($\lambda > 300\text{nm}$). (c) Same sample after the matrix was warmed to 100K.

A plausible candidate for the intermediate, which also explains the formation of benzocyclobutene, is *o*-xylylene **6c**, formed by intramolecular 1,4-H shift from an ortho-

methyl group to the carbenic center of **2c**. Coincidentally, the formation of *o*-xylylene from *o*-tolylmethylene and its subsequent cyclization was demonstrated by matrix isolation spectroscopy in inert gas matrices at low temperature both upon photolysis and upon thawing the matrix.⁹ Moreover, several *o*-xylylenes have been reported to exhibit a broad absorption band centered at around 350 to 460 nm depending on the substituents.¹⁰

Essentially similar absorptions were observed with the carbenes **2** and the *o*-xylylenes **6** and the absorption maxima are summarized in Table 3. However, only the absorption spectra of carbene **2e** displays a very weak UV band. It is probable that an amount of the ground triplet carbene generated by photolysis of **1e** was smaller than that of other present carbenes.

Table 3. Spectra of Carbenes **2** and *o*-Xylylenes **6** in 2-Methyltetrahydrofuran Matrix at 77K

carbenes	$\lambda_{\text{max}}/\text{nm}$	<i>o</i> -xylylenes	$\lambda_{\text{max}}/\text{nm}$
2a	318,330,449,461	6a	390
2b	318,330,458,468	6b	390
2c	321,335,466,495	6c	375
2d	325,338,458,485	6d	380
2e	320,331	-	

(2) *Flash Photolysis of Polymethyldiphenyldiazomethane in Fluid Solution* Flash photolysis of **1c** (1.0×10^{-4} M) in a degassed benzene solution at room temperature with a xenon flash lamp (pulse width of 10 μs) produced a transient species absorbing at 310-350 nm; the apparent maximum at around 335 nm was coincident with the xenon pulse (Figure 6). The decay kinetics of the transients indicates that the absorption at 335 nm decays within 1 s and a new species with an absorption maximum at around 370 nm arises, which is too long-lived to be monitored by our system. Product analysis of the spent solution showed the presence of **3c** and **4c**. Thus, on the basis of the low-temperature spectrum coupled with chemical analysis, we assigned the initially formed transient with a maximum at 335 nm to carbene **2c** and the second to *o*-quinodimethane **6c**. This interpretation is supported by the trapping experiments using oxygen. In the flash photolysis of an oxygen-saturated benzene solution of **1c** a broad absorption band with a maximum at 390 nm appeared at the expense of the absorption due to the carbene. The reaction mixture was found to contain octamethylbenzophenone as the main product. It is well documented that diarylcarbenes with triplet ground states are

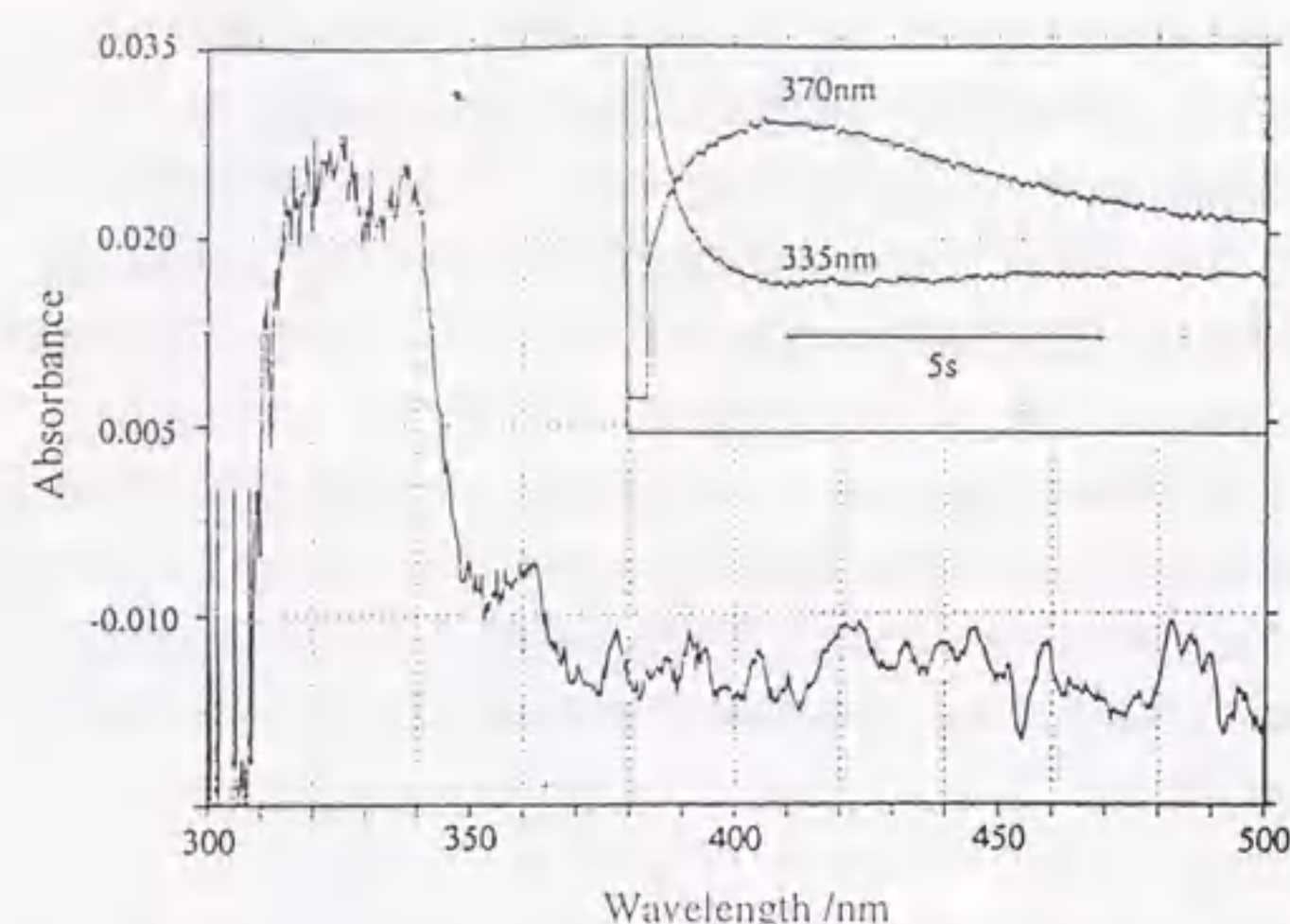
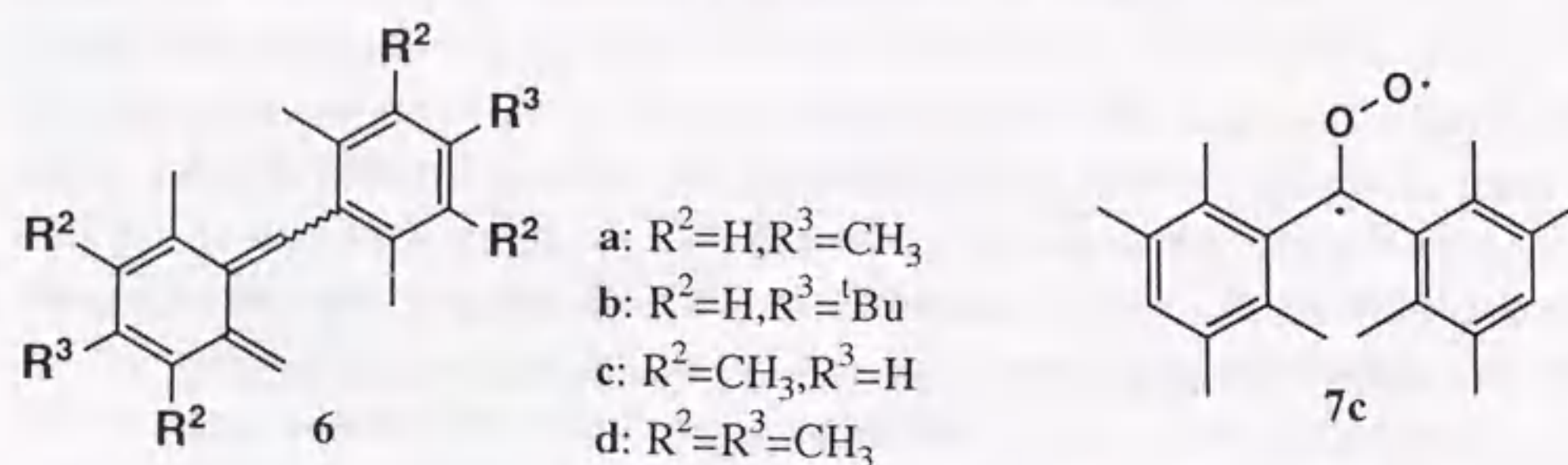


Figure 6. Absorption spectra of the transient products formed during the irradiation of **1c** in degassed benzene, recorded after 50 μ s. Insets show oscillogram traces at 335 and 370 nm.

readily trapped by oxygen to generate the corresponding diarylketone oxides.¹¹ Thus, our observation can be interpreted as indicating that the triplet carbene **2c** is trapped by oxygen to form the carbonyl oxide (**7c**), which confirms that the transient absorption quenched by oxygen is due to **2c**. The bimolecular rate constant for the quenching of **2c** by oxygen, k_{O_2} , was readily determined to be $7.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ by monitoring the pseudo-first-order growth rate of **7c**, k_{obs} , at various oxygen concentrations by using equation 1,

$$k_{obs} = k_0 + k_{O_2} [\text{oxygen}] \quad (1)$$

where k_0 represents the rate of decay of **2c** in the absence of oxygen.



The inset in Figure 6 shows the decay of **2c** and the formation of **6c** over time and indicates that the decay of **2c** is kinetically correlated with the growth of **6c**. The decay rate constant was determined to be $2.1 \pm 0.1 \text{ s}^{-1}$, while the growth rate constant was

$1.8 \pm 0.2 \text{ s}^{-1}$. Since the product analysis shows that carbene **2c** decays not only by intramolecular H abstraction but also by dimerization, the difference in the rate constants can be ascribed to the dimerization rate constant (k_d) under the assumption that the rate constant for the formation of **6c** is identical with that for H abstraction (k_i). If the dimerization rate constant (k_d) is deduced on the basis of the assumption that the product ratio produced by the flash photolysis is similar to that of the product analysis, k_d is determined to be $8.4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. A half-life ($t_{1/2}$) of roughly 310 ms was determined for **2c** from the decay curve, while the lifetime based on k_i was estimated to be $555 \pm 62 \text{ ms}$. Similar measurements for the carbenes **2a**, **2b**, and **2d** gave values of k_d , k_i , and $t_{1/2}$ (τ) (Table 4).

These results indicate that when four methyl groups are introduced at the meta positions of the ortho-methylated diphenylcarbene, the carbenic center is more effectively blocked by the four ortho methyl groups presumably owing to the buttressing

Table 4. Spectra and Kinetic Parameters of Carbenes **2**

carbenes	λ_{max}/nm	$k_d/\text{M}^{-1}\text{s}^{-1}$	k_i/s^{-1}	τ/ms	$t_{1/2}/\text{ms}$
2a	330	1.1×10^5	1.5 ± 0.1	667 ± 44	210
2b	328	2.5×10^4	0.62 ± 0.10	1610 ± 160	500
2c	335	8.4×10^3	1.8 ± 0.2	555 ± 62	310
2d	340	1.5×10^3	3.8 ± 0.2	263 ± 14	-
2e	340	0	$8.2 \pm 0.5 \times 10^3$	0.12 ± 0.01	-

effect exerted by the meta substituents. Didurylcarbene is found to be some five orders of magnitude longer lived than the parent diphenylcarbene (2 μ s in cyclohexane)¹². However, when two more methyl groups are introduced at the para positions, the carbenic center is forced to react with the ortho methyl groups, which are brought much closer to the carbene, and the carbene is shorter lived.

The difference of k_i and k_d for **2a** and **2b** is rather surprising. The replacement of methyl group by *tert*-butyl group at the para positions decreased both the rate of the intramolecular hydrogen shift and the dimerization. For the present it is not clear why *tert*-butyl groups at the para positions has decreased the reactivities of the carbene dramatically.

6-6 Laser Flash Photolysis of (2,4,6-Tri-*tert*-butylphenyl)phenyl-diazomethane in Fluid Solution

Laser flash photolysis (LFP) of a degassed cyclohexane or acetonitrile solution of **1e** (2.8×10^{-4} M) at room temperature with the forth harmonic (266nm) of a Nd:YAG laser produced no transient species to the limit of time resolution of our LFP system (5nsec). Similar LFP of **1e** in the presence of 1,4-cyclohexadiene also produced no transient absorption. Since the cyclohexadiene is known as an excellent hydrogen donor and often used to trap triplet carbenes generating the corresponding radicals,¹³ the observation again suggests that the carbenic center is not only sterically blocked toward external reagents but also internally trapped by the butyl group. However, when LFP measurements were carried out in an oxygen saturated acetonitrile solution of **1e**, a weak and broad absorption band with a maximum at 400nm appeared, and the growth rate of this transient absorption was increased as the concentration of oxygen was increased. The observation can be interpreted as indicating that the triplet carbene (**2e-t**) is trapped with oxygen to generate carbonyl oxide (**7e**). The bimolecular rate constant for the reaction of **2e-t** with oxygen, k_{O_2} , was determined to be $(1.2 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The above observations indicate that the nascent and therefore singlet carbene (**2e-s**) generated by direct irradiation of **1e** is trapped almost instantaneously by the *tert*-butyl group before it undergoes intersystem crossing to an extent that the triplet state can be observed directly. In order to generate the triplet state more effectively, triplet sensitized photolysis of **1e** was carried out.

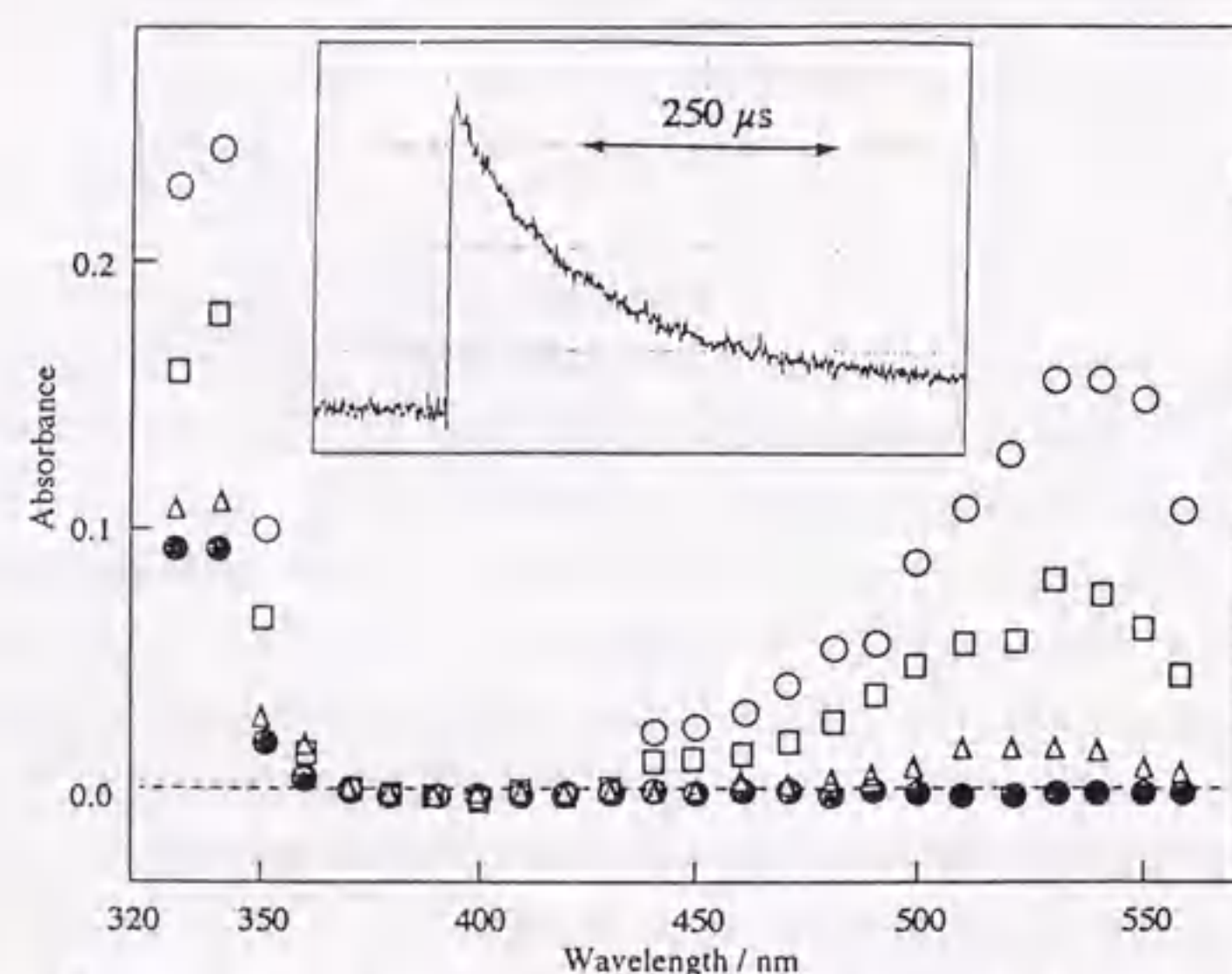
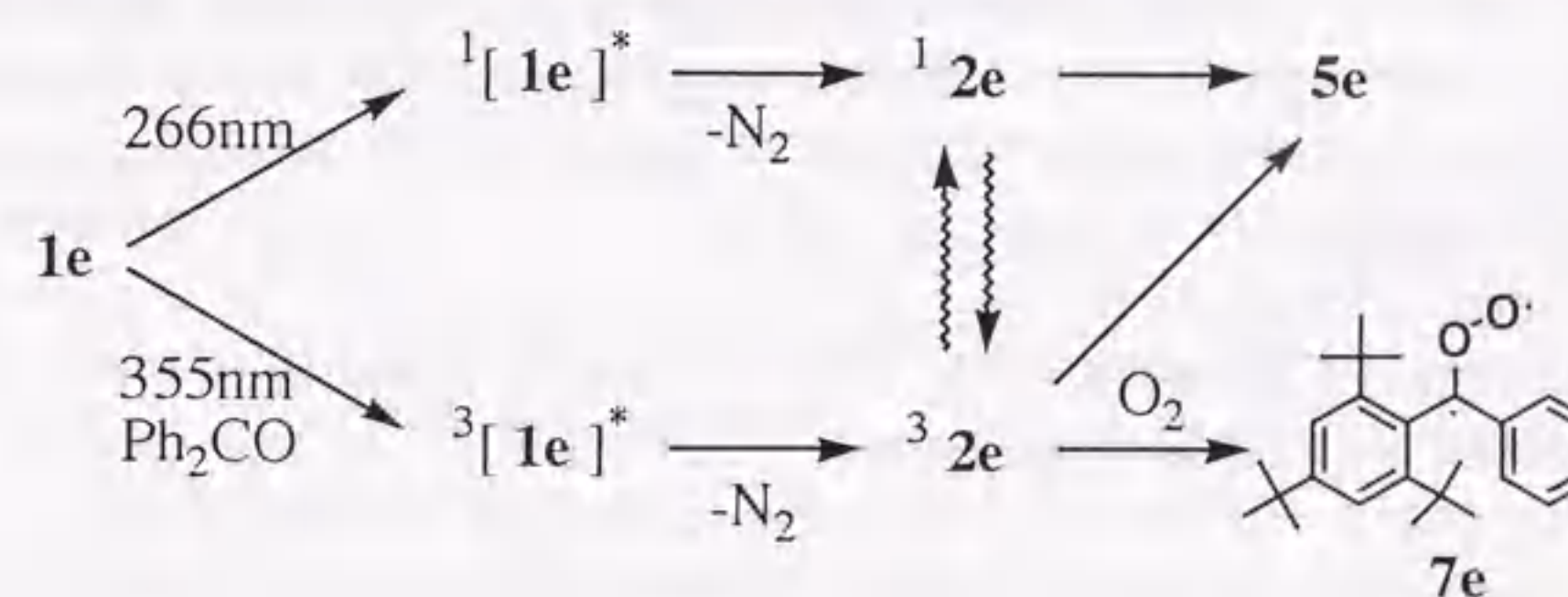


Figure 7. Absorption spectra observed on excitation of benzophenone (1.1×10^{-3} M) with a 355nm laser pulse in the presence of **1e**. Key is as follows: O, 0.2 μ s; \square , 0.4 μ s; Δ , 1.0 μ s; \bullet , 3.0 μ s after pulse. Inset shows an oscillogram trace monitored at 340nm.

LFP of a degassed benzene solution of benzophenone (BP, 1.1×10^{-3} M) as a triplet sensitizer at room temperature with the third harmonic (355nm) of a Nd:YAG laser produced transient species showing maxima at 340 and 530nm apparently due to triplet BP.^{11,14} When LFP of BP was carried out in the presence of **1e**, the essentially similar absorption was observed (Figure 7). However, the absorption band at 530nm disappeared much faster than that at 340nm and the rate of the 530nm decay increased with increasing the concentration of **1e**. This suggests that triplet BP is quenched by **1e**. The bimolecular rate constant for triplet BP quenching by **1e** was obtained from a plot of the rate of decay for triplet BP monitored at 530nm vs. concentration of **1e** to be $k_{BP} = (4.7 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is nearly diffusion controlled, indicating that energy transfer from triplet BP to **1e** occurs. The residual spectrum at 340nm is similar to that obtained during the photolysis of **1e** in MTHF glass at 77K. This absorption band was stable for hours at 77K, but warming the sample to 110K let to the disappearance. The product analysis of the spent solution showed the presence of the indan **5e**. On the basis of the low-temperature spectrum,¹⁵ the room temperature transient spectrum and the chemical analysis, we assigned the transient product, showing the absorption maximum at 340nm from the sensitized photolysis of **1e** in benzene, to triplet carbene **2e-t** generated from triplet excited state of **1e**. The oscillogram trace of the transient absorption due to **2e-t** monitored at 340nm is shown in the inset of Figure 7. The decay was found to be first order, in accordance with the product analysis data, showing that intramolecular CH insertion to form **5e** is the main decay pathway for triplet carbene **2e-t** under these conditions, and the lifetime was determined to be ca. 120 μ s, which is some 60 times longer than that observed for diphenylcarbene.¹²



6-7 Theoretical Calculations for Didurylcarbene

The structural optimization of **2c** were carried out by AMI UHF MO calculations. The calculations were performed for the carbene bond angle (θ) and the dihedral angle

(α). The energy-optimized conformation of **2c** is shown in Figure 8, indicating $\theta=151.4^\circ$ and $\alpha=89.4^\circ$. This result agrees with one obtained in terms of the comparison with Higuchi's work. Both calculations indicated that the phenyl rings of **2c** were perpendicular to each other and that the reactive center (the divalent carbon atom) was protected by the four methyl groups of the two phenyl rings.

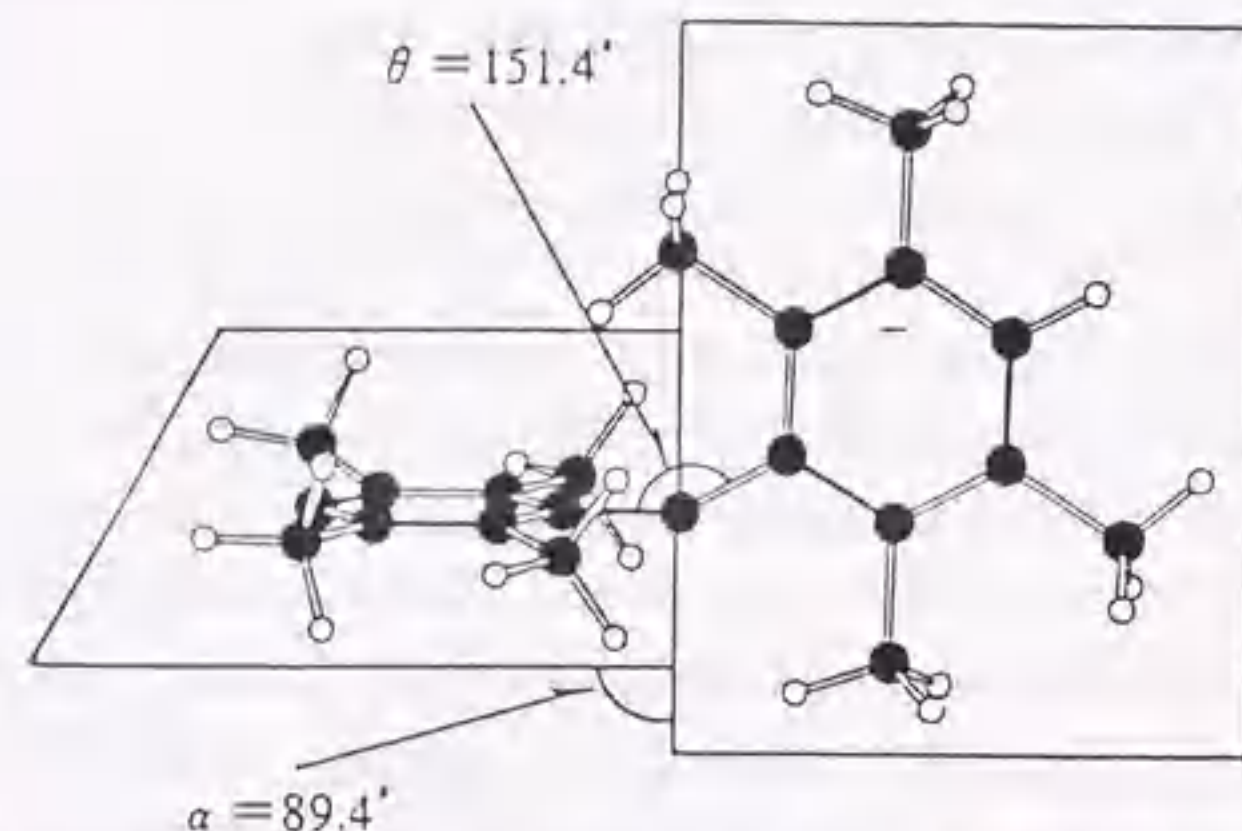


Figure 8. The energy-optimized conformation of **2c** by AM1 UHF MO calculations (the optimization was carried out for θ and α).

6-8 Summarizing Discussion

The present results demonstrate that polymethylated diphenylcarbenes are exceptionally long-lived for diarylcarbenes, although they are not persistent enough to be isolable. The buttressing effects effectively strengthen the *ortho* effect that protects the reactive center. However, these effects also accelerate the intramolecular hydrogen shift. Thus, the formation of benzocyclobutene **3** increased as increasing methyl group on the phenyl rings.

tert-Butyl group at the *para* position of **2b** obviously increases the stability of the divalent center relative to methyl group at the *para* position of **2a**.

On the other hand, in the light of the fact that half-lives of dimesitylcarbene **2a** and 2,2',4,4',6,6'-hexachlorodiphenylcarbene¹⁶ are determined to be 210 and 18ms, respectively, life-time of **2e** suggests that *tert*-butyl group at the *ortho* position is much less effective in stabilizing the divalent center than methyl and even chloro groups. This is obviously due to a voracious appetite of carbenes for electrons by which they react even with very weak sources of electrons, e.g., C-H bond σ electrons.

The electronic structure and the chemical stability of **2c** were investigated by ESR spectroscopy, and the molecular conformation responsible for this stability was shown by AM1 UHF MO calculations and LCAO-MO calculations of zero-field splitting parameters.

All the resonance fields were well interpreted by an effective spin Hamiltonian. The temperature dependence of the signal intensity proved the ground state to be a triplet state. The single-crystal ESR experiment showed that **2c** survived up to 250 K in the neat crystal. The AM1 UHF MO calculations and LCAO-MO calculations indicated that the stability of **2c** was due to the perpendicular conformation.

Experimental

General Methods. UV spectra were recorded on a Hitachi 220-s spectrophotometer. IR spectra were measured on a JASCO IR-700 spectrophotometer, and ¹H-NMR spectra were determined with a JEOL JNM-EX 270 NMR spectrometer in CDCl₃ with Me₄Si as an internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). The GC analyses were performed on a Yanagimoto instrument, Model G-180. The GC column was prepared from OV-17 on Diasolid L (5.0 mm \times 50 cm). Thin-layer chromatography was done on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was carried out on silica gel (Fuji Davison for column chromatography). Gel permeation chromatography (GPC) was performed on a JASCO, Model HLC-01 instrument. The GPC column was a shodex H-2001.

ESR Measurements. The diazo compounds were dissolved in MTHF or trans-decalin/methylcyclohexane (volume ratio 2:1) mixed solvent and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The solution yielded a dark red glass at 77 K. The glassy sample was irradiated with light of 405 nm wavelength. The irradiated sample was transferred to the sample site of a cryostat at cryogenic temperature. ESR measurements were carried out at X band microwave frequencies by use of magnetic field modulation of 100 kHz. The temperature dependence of the ESR spectral intensity was observed in the range of 1.7 to 110 K. The temperature was controlled by an Oxford ESR 910 helium gas flow system. Numerical calculations were carried out with a HITAC M680 and HITAC M660/180E.

Low Temperature UV-vis Spectra. Low-temperature spectra (77 K) were obtained by using an Oxford variable temperature liquid nitrogen cryostat (DN 1704) equipped with quartz outer windows and sapphire inner windows. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long necked quartz cuvette of 1 mm path length and degassed by repeated freeze-degas-thaw cycles at ca. 10⁻⁵ Torr. The cuvette was placed in the cryostat and cooled to 77 K. After a baseline had been recorded, the sample were irradiated for several minutes in the spectrophotometer with a Halos 300 W high pressure lamp using a Pyrex filter, and the spectral changes were

recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instruments intelligent temperature controller (ITC 4).

Flash Photolysis. All flash measurements were made on a Unisoku Flash Spectrometer. The sample ($\sim 10^{-4}$ mol dm $^{-3}$) was dissolved in dry benzene (over benzophenone ketyl), placed in a long-necked 10×10 mm or 5×10 mm (1-2 mL) quartz fluorescence cuvette, and degassed by a minimum of four freeze-degas-thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. An energy input of 100 J/flash was discharged through a cylindrical 150-W Xe flash lamp had a half-life of 10 μ s. The absorption spectra of the transients were obtained after a predetermined delay. Light from the monitoring flash was dispersed in a multichannel detector and then transferred to a NEC PC9801 RX2 computer which provides data processing, storage, and hard copy graphics capabilities. Decay of the transient absorption was followed quantitatively by a photomultiplier.

Laser Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolysis was a Quanta-Ray GSR-11 Nd:YAG laser which produced 4-5 ns fwhm pulses of up to 30 mJ at 266 nm and 5-6 ns fwhm pulses of up to 40 mJ at 355 nm. The beam shape and size was controlled by focal length cylindrical lens.

A Hamamatsu 150-W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in a perpendicular orientation to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing among the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope which was interfaced to a NEC PC9801 RX2 computer. This allowed for rapid processing and storage of the data and provided hard copy graphic capabilities.

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (ca. 20 mg) in solvents was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20°C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS.

Irradiation for Analytical Purposes. The irradiations for the quantitative product analysis outlined in the text were carried out in a Pyrex tube of 5.0-mL capacity at below 20°C. In order to avoid ambiguity of the yields due to the oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} Torr before irradiation. Product identifications were established by GC-MS comparisons with authentic sample, and product yields were conveniently determined by GC and/or NMR using an internal standard.

Preparation of Dimesityldiazomethane 1a. This compound was prepared from dimesityl ketimine by the procedure of Zimmerman¹ as a red crystals in 16.9% yield; mp 130-131°C. Spectral data are given in Table 5.

Preparation of 5-*tert*-Butyl-*m*-xylene. A solution of *m*-xylene (10 mL, 0.082 mol) and *tert*-butylchloride (25 mL) was cooled to -40°C and anhydrous aluminum chloride (5.6 g, 0.042 mol) was added to the stirred solution in portions over a 10 min interval. Upon completion of addition the temperature was allowed to rise to between -15 and -10°C and maintained with an ice salt bath for a period of 2 hrs. The mixture was then carefully poured into a crushed ice and water and agitated vigorously for about 10 min. Following the separation of layers, the organic phase was washed well with water, dried (Na₂SO₄) and evaporated to give 5-*tert*-butyl-*m*-xylene as a yellow liquid in quantitative yield; ¹H NMR (CDCl₃) δ 6.93 (2H, s), 6.82 (1H, s), 2.31 (6H, s), 1.30 (9H, s).

Preparation of 2-Bromo-5-*tert*-butyl-*m*-xylene. To a solution of 5-*tert*-butyl-*m*-xylene (14 g, 0.082 mol) in carbon tetrachloride (50 mL), was added dropwise a solution of bromine (4.4 mL, 0.085 mol) in carbon tetrachloride (10 mL) at 0°C during 1 hr. The solution was stirred at the same temperature for an additional 2 hrs and then at room temperature for 1 hr. The mixture was washed with water, 20% NaOH, and water, dried (Na₂SO₄), evaporated and vacuum distilled to give 2-bromo-5-*tert*-butyl-*m*-xylene (15.9 g) as white needles in 80% yield; mp <30°C; bp 94-98°C/0.8 mmHg; ¹H NMR (CDCl₃) δ 7.08 (2H, s), 2.40 (6H, s), 1.24 (9H, s).

Preparation of 4-*tert*-Butyl-2,6-dimethylbenzonitrile. A mixture of 2-bromo-5-*tert*-butyl-*m*-xylene (6.4 g, 0.027 mol) and 98% cuprous cyanide (7.2 g, 0.079 mol) in N,N-dimethylformamide (40 mL) was heated at 150°C for 13 hrs. After cooling, to the mixture were added nitric acid and water and the resulting mixture was extracted with ether. The ethereal layer was washed with water, 10% NaHCO₃, and water, dried (Na₂SO₄), evaporated and vacuum distilled to afford the benzonitrile as white needles in 95% yield; bp 108-112°C/0.8 mmHg; ¹H NMR (CDCl₃) δ 7.12 (2H, s), 2.52 (6H, s), 1.30 (9H, s).

Preparation of Bis(4-*tert*-butyl-2,6-dimethylphenyl)ketimine. To a solution of 2-bromo-5-*tert*-butyl-*m*-xylene (2.0 g, 8.3 mmol) in absolute ether (10 mL) 1.66 M butyllithium solution (5.0 mL, 8.3 mmol) was added dropwise under an atmosphere of argon during 10 min and the mixture was refluxed for 3 hrs. To the refluxed mixture a solution of 4-*tert*-butyl-2,6-dimethylbenzonitrile (1.6 g, 8.5 mmol) in absolute ether (5 mL) was added at once and the mixture was refluxed over night. After addition of aqueous NH_4Cl , the resulting mixture was extracted with three portions of ether (10 mL each). The combined ether extracts were washed with saturated aqueous NaCl , dried (Na_2SO_4) and evaporated to leave a brown residue, which was chromatographed on silica gel eluted with chloroform to give the ketimine as a pale yellow oil in 36.9% yield; ^1H NMR (CDCl_3) δ 7.02 (4H, s), 2.18 (12H, s), 1.29 (18H, s).

Preparation of Bis(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane 1b. This compound was prepared from the corresponding ketimine according to the slightly modified method of Zimmerman. A solution of the ketimine (1.0 mg, 2.9 mmol) in carbon tetrachloride (10 mL) was added dropwise during 15 min to a slurry of 30 mL of carbon tetrachloride containing dinitrogen tetroxide (1.4 g, 15 mmol) and anhydrous sodium acetate (2.5 g, 30 mmol) at -5 - -10°C and the reaction mixture was stirred for an additional 2 hrs at the same temperature. The mixture was poured into ice and saturated sodium carbonate solution, extracted with three portions of carbon tetrachloride (20 mL each), dried (Na_2SO_4), and evaporated at 20 - 25°C . The crude *N*-nitrosoketimine was dissolved in absolute ether (30 mL) and placed in a 100 mL flask equipped with addition funnel, stirrer, and thermometer. After cooling to -50°C , the slow addition of a suspension of lithium aluminum hydride (0.57 g, 15 mmol) in absolute ether (10 mL) was started. Several times during the addition the temperature was allowed to rise to -10°C for a few minutes. The mixture was cooled to -50°C and ethyl acetate slowly added until in excess. After warming above 0°C , the resulting mixture was poured into ice, extracted with three portions of ether (10 mL each), dried (Na_2SO_4), and evaporated. The crude product was chromatographed on neutral alumina (deactivated by adding 6% H_2O) at -15°C eluted with *n*-hexane. The diazomethane **1b** was eluted as an initial fraction and obtained as a red oil in 20.7% (215 mg) yield.

Preparation of Diduryl ketimine. This compound was prepared analogously to bis(4-*tert*-butyl-2,6-dimethylphenyl) ketimine, as an orange solid in 27.6% yield; mp 186 - 189°C ; ^1H NMR (CDCl_3) δ 6.97 (2H, s), 2.21 (12H, s), 2.08 (12H, s).

Preparation of Diduryldiazomethane 1c. This compound was prepared analogously to **1b** as orange crystals in 10.6% yield; mp 158 - 160°C .

Preparation of Bis(pentamethylphenyl)ketimine. This compound was prepared analogously, as a yellow solid in 25.9% yield; mp 187 - 189°C ; ^1H NMR (CDCl_3) δ 2.25 (6H, s), 2.19 (12H, s), 2.14 (12H, s).

Preparation of Bis(pentamethylphenyl)diazomethane 1d. This compound was prepared analogously, as an orange crystals in 15.7% yield; mp 156 - 159°C .

Preparation of (2,4,6-Tri-*tert*-butylphenyl)phenyl ketimine. This compound was prepared analogously, as a yellow oil in 49.9% yield; ^1H NMR (CDCl_3) δ 7.40-6.80 (7H, m), 1.36 (9H, s), 1.20 (18H, s).

Preparation of (2,4,6-Tri-*tert*-butylphenyl)phenyldiazomethane 1e. This compound was prepared analogously, as a red crystals in 36.1% yield; mp 80 - 85°C .

4,6-Dimethyl-1-mesitylbenzocyclobutene 3a. This compound was obtained in the thermolysis of **1a** in dry benzene as a pale yellow oil in 68% yield. NMR and mass spectral data are given in Table 6.

3,5,6-Trimethyl-1-durylbenzocyclobutene 3c. This compound was isolated in the thermolysis of **1c** in dry benzene as a white crystals in 75% yield; mp 129 - 130° .

3,4,5,6-Tetramethyl-1-(pentamethylphenyl)benzocyclobutene 3d. This compound was obtained in the photolysis of **1d** in dry benzene as a white solid in 80% yield.

1,1,2,2-Tetramesitylethylene 4a. This compound was isolated in the irradiation of **1a** in dry benzene as a yellow viscous oil in 43% yield. NMR spectral data are given in Table 7.

1,1,2,2-Tetrakis(4-*tert*-butyl-2,6-dimethylphenyl)ethylene 4b. This compound was obtained in the photolysis of **1b** in dry benzene as a white oil in 75% yield.

1,1,2,2-Tetradurylethylene 4c. This compound was isolated in the photolysis of **1c** in dry benzene as a white solid in 46% yield.

1,1,2,2-Tetrakis(pentamethylphenyl)ethylene 4d. This compound was obtained in the irradiation of **1d** in dry benzene as a white solid in 7.0% yield.

4,6-Di-tert-butyl-1,1-dimethyl-3-phenylindan 5e. This compound was isolated in the photolysis of **1e** in dry benzene as a pale yellow oil in 95% yield.

Table 5. Physical Data of Diaryldiazomethanes **1a-e**

1	mp, °C	IR, cm ⁻¹	NMR, δ
a	129-130	2038	6.74(4H,s), 2.24(6H,s), 2.03(12H,s)
b	^a	2040	7.08(4H,s), 2.11(12H,s), 1.30(18H,s)
c	168-169	2038	6.78(2H,s), 2.10(12H,s), 1.98(12H,s)
d	156-159	2032	2.26(6H,s), 2.22(12H,s), 2.10(12H,s)
e	80-85	2050	7.60-6.88(7H,m), 1.40(9H,s), 1.34(18H,s)

^aOil.

Table 6. NMR and MS Data of 3-Arylbenzocyclobutenes **3a-d** and Arylindan **5**

		NMR, δ	MS: m/e(rel intensity)
3 or 5			
3a	6.65(4H,bs), 4.98(1H,bs), 3.45-3.08(2H,m), 2.30(3H,s), 2.20(3H,s), 2.03(6H,s), 1.93(3H,s)		250(M ⁺ , 1), 235(94), 220(100), 205(13)
3c	6.74(1H,bs), 6.70(1H,bs), 5.04-4.94(1H,m), 3.55-2.98(2H,m), 2.32(3H,bs), 2.24(3H,bs), 2.18(3H,s), 2.14(3H,s), 2.08(3H,s), 1.82(3H,s), 1.76(3H,bs)		278(M ⁺ , 4), 264(94), 248(100)
3d	5.03(1H,bs), 3.51(1H,dd, J=6.0, 13.5Hz), 3.12(1H,d, J=13.5Hz), 2.40(3H,bs), 2.27(3H,bs), 2.25(3H,s), 2.21(3H,s), 2.19(3H,s), 2.16(3H,s), 2.13(3H,s), 1.90(3H,bs)		306(M ⁺ , 2), 292(90), 276(100)
5e	7.37(1H,d, J=1.98Hz), 7.21-7.10(3H,m), 7.09(1H,d, J=1.98Hz), 6.88(2H,d, J=7.26Hz), 4.83(1H,dd, J=1.32, 9.24Hz), 2.48(1H,dd, J=9.24, 12.54Hz), 1.98(1H,dd, J=1.32, 12.54Hz), 1.37(9H,s), 1.27(3H,s), 1.19(9H,s), 1.04(3H,s)		334(M ⁺ , 24), 320(26), 319(96), 57(100)

Table 7. NMR Data of Tetraarylethylenes **4a-d**

4	NMR, δ
a	6.46(4H,s), 6.51(4H,s), 2.16(12H,s), 1.84(12H,s), 1.64(12H,s)
b	6.74(4H,s), 6.64(4H,s), 1.84(12H,s), 1.75(12H,s), 1.21(36H,s)
c	6.64(4H,s), 2.08(12H,s), 1.87(12H,s), 1.64(12H,s), 1.62(12H,s)
d	2.15(12H,s), 2.04(12H,s), 1.81(12H,s), 1.69(12H,s), 1.66(12H,s)

References and Notes

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Acknowledgment

This thesis presents the studies that the author carried out from 1985 to 1995 at the Department of Industrial Chemistry and the Chemistry Department for Materials, Faculty of Engineering, Mie University under the direction of Professor Hideo Tomioka.

The author would like to express his grateful acknowledgment to Professor Hideo Tomioka whose encouragements and helpful suggestion have been indispensable to the completion of the present thesis.

Grateful acknowledgment is also made to Assistant Professor Shigeru Murata for his helpful advices and discussions.

The author is also grateful to Professor Satoshi Inagaki of Gifu University, who was a co-worker of the author in the studies described in chapter 2, for his helpful suggestions, encouragement and the theoretical calculations.

The author is also grateful to Professor Yoshifumi Tanimoto of Hiroshima University, who was a co-worker of the author in the studies described in chapter 3, for his helpful suggestions, encouragement and advices on experimental techniques.

The author is very grateful to all members of professor Tomioka's laboratory for their warm encouragement.

Finally, the author would like to express special thanks to Professor Yasuhiko Sawaki, Shoji Eguchi, Kenji Itoh, Katsuhiko Takagi, and Masatomi Ohno for serving on his dissertation committee.

