

# Pd/TiO<sub>2</sub>-Photocatalyzed Self-Condensation of Primary Amines to Afford Secondary Amines at Ambient Temperature

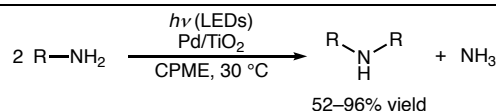
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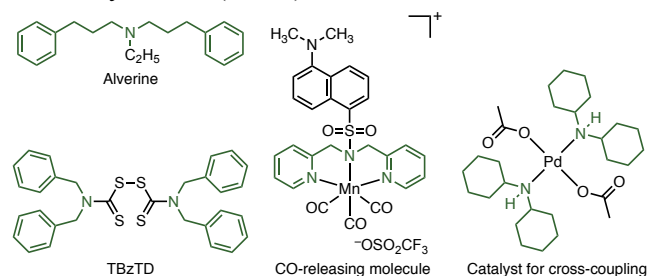
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Supporting Information Placeholder



**ABSTRACT:** Symmetric secondary amines were synthesized by the self-condensation of primary amines over a palladium-loaded titanium dioxide (Pd/TiO<sub>2</sub>) photocatalyst. The reactions afforded a series of secondary amines in moderate to excellent isolated yields at ambient temperature (30 °C, in cyclopentyl methyl ether). Applicability for one-pot pharmaceutical synthesis was demonstrated by a photocatalytic reaction sequence of self-condensation of an amine followed by N-alkylation of the resulting secondary amine with an alcohol.

Symmetric secondary amino groups (R<sub>2</sub>N) are fundamental structures present in various pharmaceuticals, agrochemicals, and molecular catalysts.<sup>1</sup> Figure 1 illustrates selected examples of such functional molecules bearing symmetric secondary amino groups. These molecules have most frequently been synthesized from the parent secondary amines (R<sub>2</sub>NH).<sup>2,3</sup>



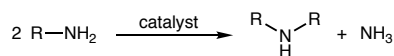
**Figure 1.** Functional molecules with symmetric secondary amino moieties.

Intermolecular self-condensation of primary amines (RNH<sub>2</sub>) is one of the most efficient methods for the synthesis of symmetric secondary amines (R<sub>2</sub>NH, Scheme 1a).<sup>4–10</sup> The beauty of this clean reaction scheme is illustrated by the highly atom-economical and selective production of the target secondary amine and the coproduction of ammonia as the only by-product. The self-condensation process is free from the problem of organic waste formation involved in the conventional N,N-dialkylation of primary carboxamides or sulfonamides followed by

cleavage of the amide moieties.<sup>11</sup> Moreover, the selectivity for secondary amine over tertiary amine is generally higher than in the analogous alkylation of primary amines using alkyl halides<sup>12</sup> or alcohols.<sup>2,13–16</sup>

## Scheme 1. Approaches for Self-Condensation of Primary Amines to Secondary Amines

### a) Intermolecular self-condensation of primary amines



- atom-economical
- high selectivity for 2° amines

homogeneous cat.: Ru, Ir or Co complexes, > 120 °C

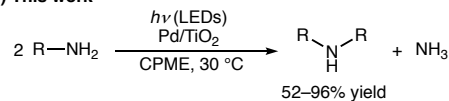
heterogeneous cat.: Raney Ni, > 140 °C

supported metal catalyst, 120–145 °C

Pd@porous graphene oxide, H<sub>2</sub>, 90 °C

TiO<sub>2</sub>-Pt + hν(Hg), rt, 20–33% yield

### b) This work



- ambient temperature
- no reducing reagent needed

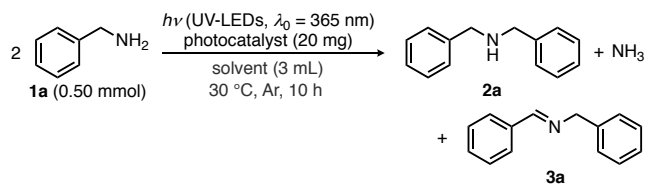
The self-condensation of primary amines could be effectively catalyzed by both molecular and heterogeneous catalysts. Ru and Ir complexes have frequently been used to achieve the self-condensation of amines at 150–185 °C, affording the desired products in moderate to good yields.<sup>5,6</sup> A cobalt complex catalyzes this reaction at 120 °C.<sup>7</sup> Heterogeneous catalysts such as Raney Ni, Pt–Sn/γ-Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, NiCuFeO<sub>x</sub>, and Pd<sub>3</sub>Pb/Al<sub>2</sub>O<sub>3</sub> effectively promote this transformation at 120–145 °C.<sup>8</sup> The self-condensation can be carried out at 90 °C with Pd

on a porous graphene oxide catalyst under an H<sub>2</sub> atmosphere.<sup>9</sup> These methods provide efficient access to various symmetric secondary amines. However, the development of self-condensation of primary amines at ambient temperature has remained elusive.

During the course of our studies on the photocatalytic conversion of amines and alcohols by metal-loaded titania-based photocatalysts,<sup>2,14c,17</sup> we noticed that the self-condensation of benzylamines competes with alkylation with alcohols. In addition, it was reported that the self-condensation of primary amines proceeds under light irradiation in the presence of a Pt-modified TiO<sub>2</sub> photocatalyst<sup>10a</sup> or a polycrystalline CdS photocatalyst<sup>10b</sup>, albeit the substrate scope of the intermolecular condensation was limited to three substrates (ethylamine, propylamine, and benzylamine) and the yields were poor (20–33%). Inspired by our observations and these preceding reports, we herein report the first photocatalytic self-condensation of primary amines at ambient temperature that enables scalable synthesis of symmetric secondary amines (Scheme 1b).

We selected benzylamine (**1a**) as a model substrate (Table 1). Cyclopentyl methyl ether (CPME) was used as a solvent because of its favorable properties in sustainable chemistry.<sup>18</sup> Among the tested photocatalysts, Pd/TiO<sub>2</sub> proved to be the best, affording dibenzylamine (**2a**) in 98% GC yield and 96% isolated yield under light irradiation (UV-LEDs, λ<sub>0</sub> = 365 nm) for 10 h (entry 1). The Pd/TiO<sub>2</sub> photocatalyst was prepared as previously described using PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, TiO<sub>2</sub> (Aeroxide® P25), and NaBH<sub>4</sub> [see Supporting Information (SI) for details].<sup>2b,17c</sup> The presence of palladium nanoparticles ([Pd]<sub>n</sub>, mean particle size = 3.3 nm ± 0.6 nm [based on the analysis of 100 [Pd]<sub>n</sub> nanoparticles]) on TiO<sub>2</sub> was also established.<sup>2b</sup> GC monitoring of the reaction progress every hour indicated the clean formation of **2a** from **1a** (Figure S1 in SI). We could not detect any side products such as imine **3a** throughout the reaction. This preliminary kinetic study indicated that the reaction is subjected to a zero order with respect to the concentration of **1a** (Figure S1). The reaction hardly proceeded in the dark, indicating that it is driven by light irradiation (entry 2). Platinum is a privileged co-catalyst on heterogeneous photocatalysts for hydrogen evolution from water and alcohols.<sup>19</sup> In fact, Pt/TiO<sub>2</sub> showed good reactivity for the formation of imine **3a**, but almost no catalytic ability for further hydrogenation to the desired secondary amine **2a** (entry 3). Other photocatalysts such as Au/TiO<sub>2</sub>,<sup>17c</sup> Ag/TiO<sub>2</sub>,<sup>14c</sup> Cu/TiO<sub>2</sub>,<sup>2a</sup> a Cu/TiO<sub>2</sub>–Au/TiO<sub>2</sub> mixture,<sup>2a</sup> and pristine TiO<sub>2</sub> poorly promoted the reaction leading to **2a** and **3a** (entries 4–8). The Pd/TiO<sub>2</sub>-mediated photocatalytic self-condensation also proceeded selectively in THF (entry 9). Other solvents such as acetonitrile, ethyl acetate, and toluene could be used, but a small amount of **3a** was formed (entries 10–12).

**Table 1. Photocatalytic Self-Condensation of 1a to 2a<sup>a</sup>**

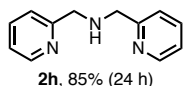
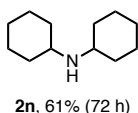
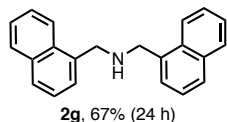
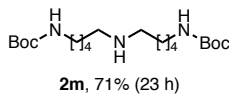
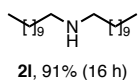
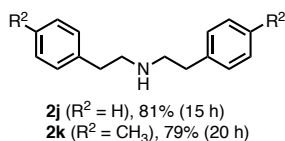
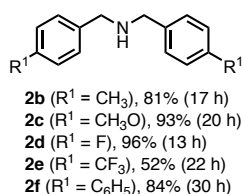
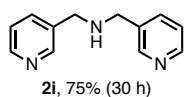
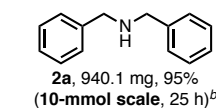
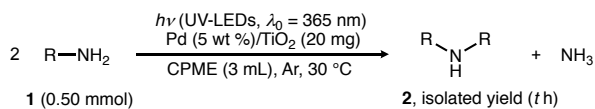


entry	photocatalyst		yield (%) <sup>b</sup>	
	[metal (mol %)]	solvent	<b>2a</b>	<b>3a</b>
1	Pd/TiO <sub>2</sub> [Pd (1.7)]	CPME	98 (96)	< 1
2 <sup>c</sup>	Pd/TiO <sub>2</sub> [Pd (1.7)]	CPME	< 1	< 1
3	Pt/TiO <sub>2</sub> [Pt (1.0)]	CPME	< 1	78
4	Au/TiO <sub>2</sub> [Au (0.9)]	CPME	< 1	22
5	Ag/TiO <sub>2</sub> [Ag (1.5)]	CPME	< 1	< 1
6	Cu/TiO <sub>2</sub> [Cu (2.9)]	CPME	< 1	20
7 <sup>d</sup>	Au/TiO <sub>2</sub> + Cu/TiO <sub>2</sub>	CPME	1	26
8	TiO <sub>2</sub>	CPME	< 1	< 1
9	Pd/TiO <sub>2</sub> [Pd (1.7)]	THF	75	< 1
10	Pd/TiO <sub>2</sub> [Pd (1.7)]	CH <sub>3</sub> CN	88	9
11	Pd/TiO <sub>2</sub> [Pd (1.7)]	AcOC <sub>2</sub> H <sub>5</sub>	88	4
12	Pd/TiO <sub>2</sub> [Pd (1.7)]	toluene	90	3

<sup>a</sup>32 W UV-LEDs λ<sub>0</sub> = 365 nm. Metal content (Pd: 5 wt %; Pt: 5 wt %; Cu: 5 wt %; Ag: 4 wt %; Au: 5 wt %) was determined by ICP-AES. <sup>b</sup>GC/MS yields using *n*-decane as an internal standard, isolated yield in parenthesis. <sup>c</sup>In the dark. <sup>d</sup>10 mg each of photocatalyst [Au (0.5 mol %), Cu (1.5 mol %)].

Having established the optimized conditions, the scope of this Pd/TiO<sub>2</sub>-mediated photocatalytic self-condensation of primary amines was clarified (Scheme 2). This reaction could be operated on a 10-mmol scale using a Xe lamp (λ = 300–470 nm), affording **2a** in 95% yield (940.1 mg) after 25-h irradiation. Benzylamines with electron-donating groups, such as methyl and methoxy groups, gave the corresponding secondary amines (**2b** and **2c**) in good to excellent yields. The presence of a fluoro group on the aromatic ring was well tolerated, and the desired secondary amine **2d** was obtained in 96% yield. The reactions of benzylamines bearing more reducible chloro-, bromo-, or nitro groups on the aromatic rings were sluggish (see Scheme S1 in SI). A substrate with a strongly electron-withdrawing CF<sub>3</sub> group was less reactive than **2a–d**, yet still gave the product **2e** in a fair yield. Moreover, the present method for the first time offers salt-free access to amines with biphenyl, 1-naphthyl, and 2-/3-pyridyl functionalities (**2f–2i**), which are frequently used in the metal ligands of molecular catalysts (**2f** and **2h**).<sup>3b,20</sup> 2-Phenethylamines and a long-chain alkyl amine also underwent the self-condensation reaction, affording the secondary amines **2j–l** in high yields. The condensation of a Boc-protected amine took place selectively at the free amino moiety and gave the desired Boc-diprotected triamine **2m** in 71% yield. Cyclohexanamine was considerably less reactive than primary amines, but the sterically congested dicyclohexylamine (**2n**) was obtained in an acceptable yield after prolonged irradiation.

**Scheme 2. Self-Condensation of Primary Amines to Secondary Amines Catalyzed by a Pd/TiO<sub>2</sub><sup>a</sup>**



<sup>a</sup>Conditions were similar to those in Table 1, entry 1. <sup>b</sup>**1a** (10 mmol), Pd/TiO<sub>2</sub> (300 mg, 1.3 mol % Pd), CPME (20 mL), 300 W Xe lamp with a UV-cold mirror ( $\lambda = 300\text{--}470 \text{ nm}$ ).

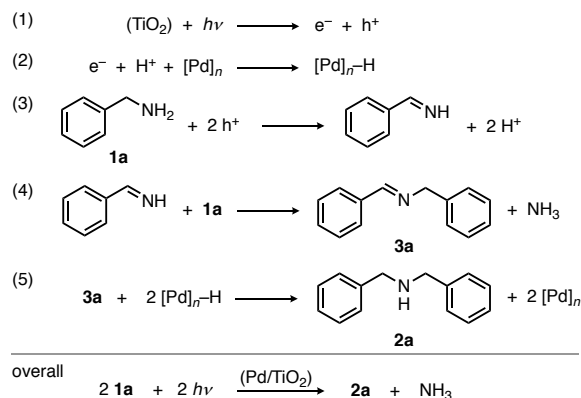
Furthermore, the Pd/TiO<sub>2</sub> photocatalyst was found to be recyclable at least for 4 times without losing its photocatalytic activity (96–98% yields, Table S1).

Co-production of ammonia (0.19 mmol, 75%) was detected by <sup>1</sup>H NMR analysis in dimethylsulfoxide-*d*<sub>6</sub> on self-condensation of **1l** after trapping with HCl in methanol (see SI for details).<sup>21</sup> This result confirms that the light-induced conversion of **1** to **2** involves formation of ammonia as a stoichiometric byproduct (Scheme 1b).

In order to obtain further mechanistic insight, the self-condensation of **1a** to **2a** in the presence of impurities was examined (Table S2). The desired reaction proceeded well (**2a**, 82%) in the presence of chlorobenzene, but 17% of imine **3a** formed (Table S2, entry 1). This tendency was stronger in the case of bromobenzene, and **3a** (80%) was obtained as a major product, together with **2a** (18%) and recovered bromobenzene (60%, Table S2, entry 2). More reducible iodobenzene or nitrobenzene stopped the reaction at the imine stage without formation of any desired **2a**, yet the **3a** was formed in 39% and 77% yields and the impurities were recovered in 87% and 70% yields, respectively (Table S2, entries 3 and 4). These results imply the participation of the borrowing hydrogen mechanism<sup>13</sup> promoted by light-irradiation of photocatalyst (Scheme 3).<sup>10a</sup> The proposed mechanism involves (1) formation of an electron–hole pair on Pd/TiO<sub>2</sub> by irradiation and their separation ( $e^- + h^+$ ); (2) production of [Pd]<sub>n</sub>-H species on the photocatalyst surface from electrons, protons, and Pd nanoparticles ([Pd]<sub>n</sub>); (3) dehydrogenation of primary amine **1a** to benzaldimine and protons by holes on the photocatalyst surface; (4) amine–imine exchange (transamination) between **1a** and benzaldimine to give imine **3a** and ammonia, and (5) reduction of imine **3a** to secondary

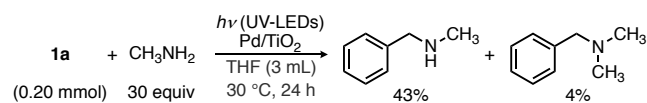
amine **2a** by the [Pd]<sub>n</sub>-H species. The overall reaction is summarized in the bottom of Scheme 3. The presence of reducible impurities lowered the yield of **2a** and increased the yield of **3a** (Table S2) by retarding the reduction of **3a**. High reactivity of [Pd]<sub>n</sub>-H for the reduction of **3a** to **2a** account for the higher selectivity of Pd/TiO<sub>2</sub> for producing **2a** over **3a**, compared with other metal/TiO<sub>2</sub> analogues (Table 1, entry 1 vs entries 3–7). Hydrogenation of **3a** in the presence of Pd/TiO<sub>2</sub> under H<sub>2</sub> (1 atm) proceeded both under light irradiation and in the dark (Scheme S2).

### Scheme 3. Proposed Mechanism

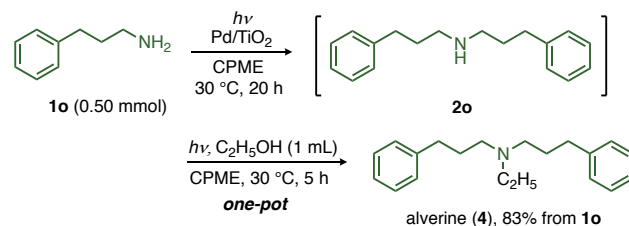


Next, we tested the cross-condensation of two different amines.<sup>4</sup> Whereas reactions of **1a** with *n*-butyl or *n*-octylamine gave complex mixtures, reasonable amounts of cross-condensation products were obtained in the reaction of methylamine with **1a**; *N*-methylbenzylamine formed in 43% yield together with *N,N*-dimethylbenzylamine (4%, Scheme 4).

### Scheme 4. Cross-Condensation



### Scheme 5. One-Pot Photocatalytic Synthesis of Alverine at Ambient Temperature



Finally, the current protocol was extended to a one-pot photocatalytic pharmaceutical synthesis (Scheme 5). Alverine (**4**), a drug used for irritable bowel syndrome, was synthesized through sequential photocatalytic amine self-condensation of **1o** to **2o** followed by photocatalytic *N*-ethylation of **2o** with ethanol.<sup>2</sup> These two photocatalytic reactions were both promoted by Pd/TiO<sub>2</sub> and coproduce only ammonia and water as by-products, respectively. Thus, the present method for the first time enabled the synthesis of alverine in high yield without stoichiometric salt-waste formation.

In summary, we have developed an efficient photocatalytic method for the self-condensation of primary amines to symmetric secondary amines at room temperature. We expect this method will serve as an economical and environmentally friendly complement to existing methods for secondary amine synthesis.

## ASSOCIATED CONTENT

### Supporting Information

Supplementary Tables, Figure, and Schemes; experimental procedures, spectroscopic data, and NMR charts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing interest.

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