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Unprecedented selective synthesis of imines by photocatalytic oxidative coupling of primary amines under N₂O atmosphere

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Abstract: In a climate change context, N₂O contributes to global warming with CO₂ and CH₄. As an inert molecule, its upgrading as oxidant still constitutes a challenge in chemical synthesis. Here, the synthesis of imines was unprecedentedly performed using nitrous oxide (N₂O) as a novel and highly selective oxidative agent for the photocatalytic homo-coupling of amines. In a similar way, unsymmetric imines were produced through cross-coupling of amines with alcohols. Promisingly, this greenhouse gas showed excellent performances towards the target reactions when photocatalytically activated at atmospheric pressure, with silver photodeposited on titanium dioxide as catalyst. Relevantly, reactions under N₂O atmosphere exhibited high conversion rates and turn-over frequencies, and higher selectivities than the ones carried out under a dioxygen atmosphere. Mechanisms for both reactions were detailed, showing the release of nitrogen and water as benign by-products.

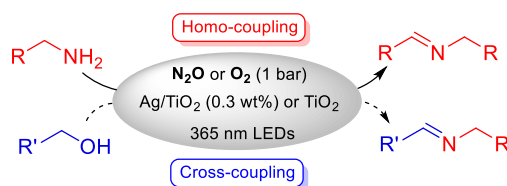
Introduction

To face contemporary concerns about increasing emissions of greenhouse gases, the design of eco-friendly chemical transformations that beyond the usual elimination reconsider these by-products as relevant synthons to produce valuable chemical intermediates, is a timely topic. Although the reuse of carbon sources such as carbon dioxide or methane are well documented,^[1,2] the upgrading of nitrous oxide (N₂O), another major contributor to the global warming,^[3,4] is a research field of prime importance considering the fact that the emissions are steeply increasing, with an estimated rate of 2% per decade, owing to human activities (for instance agriculture, biomass burning, production of nitric and adipic acids^[5]). This compound effectively constitutes an available and cheap oxygen source, only releasing benign dinitrogen (N₂),^[6] but with quite limited applications as oxidant in organic synthesis owing to the high temperatures (140-350°C) and pressures (50-200 bar) required for its activation.^[7] Moreover, nitrous oxide (N₂O) has already proved to be a more selective oxidative agent than dioxygen (O₂) in the catalytic oxidation of methane into methanol under high temperature activation,^[8] or for the synthesis of air sensitive compounds.^[9] Consequently, the quest for mild methodologies to

efficiently use this oxidant and access value added chemical compounds renders this emerging research area very appealing and photocatalytic processes sound as a relevant approach to activate nitrous oxide.

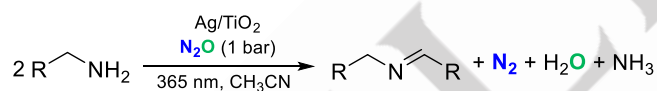
Imines stand as an important class of N-containing organic intermediates, widely used in the manufacture of pharmaceuticals, agrochemicals^[10,11] as well as the latest anticancer drugs,^[12] that are traditionally prepared by condensation of carbonyl compounds with amines.^[10] Other pathways for one-pot synthesis of imines have largely been developed through oxidation reactions under oxygen atmosphere, so as to reduce energy consumption and waste emission,^[10] like self-coupling of primary amines^[11,13-15] or cross-coupling of alcohols with amines.^[16-18] More recently, photocatalytic alternative processes have been described with TiO₂,^[19-21] carbon nitride based catalysts,^[22,23] Ru on polyoxometalate,^[24] porphyrinic covalent organic framework,^[25] or a mixed-phase MoS₂^[26] as photocatalysts, under air or oxygen atmosphere. Controlling the selectivity remains a crucial challenge for such photocatalytic reactions to avoid usual over-oxidation of the organic compounds and even mineralization into carbon dioxide. Indeed, photocatalytic systems with semiconductor materials as catalyst such as titanium dioxide (TiO₂) generate radical oxygen species, with a reactivity that can be difficult to control. Thus, more selective photocatalytic systems for applications in organic synthesis is still a research hotspot.^[27] In this area, alternative oxidative agents avoiding the formation of reactive radical oxygen species, as well as uncontrolled autooxidation products, could be a pertinent target.

N₂O constitutes a cheap and eco-friendly oxidative agent that is efficiently activated under mild photocatalytic conditions, thus reusing this industrial waste for the synthesis of high-value added compounds. In this work, we disclose the unprecedented highly selective photocatalytic oxidative homo-coupling of amines into imines, upgrading the undervalued nitrous oxide gas as an O-atom source and only releasing benign N₂, with silver on titanium dioxide (Ag/TiO₂) as active and recyclable heterogeneous catalyst (Scheme 1). This process was further extended to the cross-coupling of alcohols and amines into unsymmetric imines. To our knowledge, the use of nitrous oxide as oxidative agent for the synthesis of imines by photocatalysis has never been described in the literature.

Table 1. O₂ vs. N₂O for photocatalytic homo-coupling of amines and cross-coupling of amines with alcohols into imines. ^[a]

Entry	Amine	Alcohol	Catalyst	Time (min)	N ₂ O or O ₂	Conv. (%) ^[b]	Yield (%) ^[c]	Sel. (%) ^[d]	CO ₂ formed (mol) ^[e]
1		-	Ag/TiO ₂	15	N ₂ O	>99	87	87	<3.0·10 ⁻⁸
2		-	Ag/TiO ₂	15	O ₂	>99	64	64	1.32·10 ⁻⁵
3		-	TiO ₂	15	O ₂	>99	59	59	1.94·10 ⁻⁵
4 ^[f]		-	Ag/TiO ₂	30	N ₂ O	80	74	93	5.10·10 ⁻⁷
5 ^[f]		-	Ag/TiO ₂	15	O ₂	>99	31	31	2.38·10 ⁻⁵
6 ^[f]		-	TiO ₂	5	O ₂	>99	28	28	5.20·10 ⁻⁵
7		-	Ag/TiO ₂	15	N ₂ O	96 ^[g]	70 ^[h]	73	1.34·10 ⁻⁶
8			Ag/TiO ₂	15	O ₂	45 ^[g]	23 ^[h]	41	1.76·10 ⁻⁵
9			TiO ₂	15	O ₂	50 ^[g]	32 ^[h]	64	1.01·10 ⁻⁵

[a] Reaction conditions: amine (0.24 mmol, 1 eq.); alcohol (0.24 mmol, 1 eq.); 3 mL MeCN; 365 nm irradiation (two LEDs, 160 mW/cm²); under N₂O atmosphere (0.29 mmol in gas phase, 7 mL, 1.2 eq.), or under O₂ atmosphere; 100 mg of Ag/TiO₂ (0.3 wt%, TiO₂ Aeroxide P25), i.e. substrate/metal = 100, or 100 mg of TiO₂ Aeroxide P25. [b] Amine conversion determined by Gas Chromatography analyses using chlorobenzene as internal standard. [c] Imine yield compared with the initial amine quantity and determined by Gas Chromatography analyses using chlorobenzene as internal standard. [d] Selectivity in imine product = yield/conversion. [e] Carbon dioxide in the gas phase of the vessel quantified by GC-BID. [f] 10 mg of catalyst instead of 100 mg. [g] Alcohol conversion determined by Gas Chromatography analyses using chlorobenzene as internal standard for a complete conversion of the amine. [h] Relative proportion of the peak area obtained by Gas Chromatography.

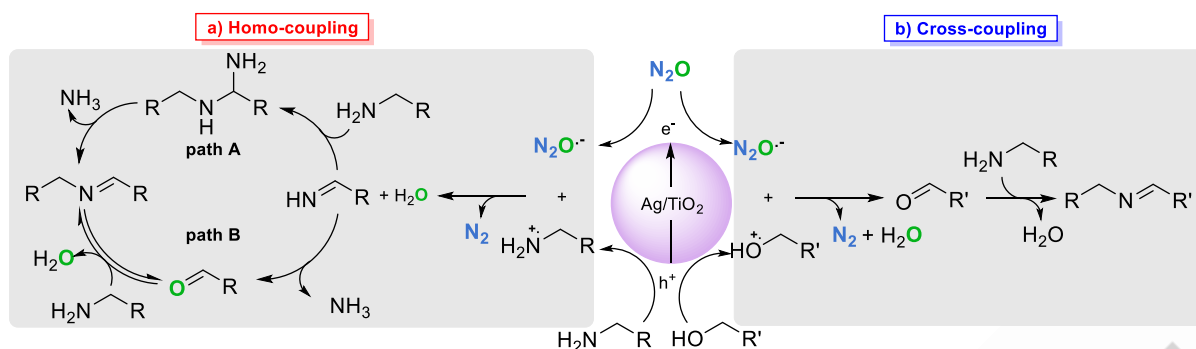
**Scheme 1.** Photocatalytic homo-coupling of amines into imines under N₂O atmosphere.

Results and discussion

Selectivity of N₂O vs. O₂

In a first set of experiments, benzylamine was used as a model substrate to optimize the parameters, as the system proved to be very active for the synthesis of *N*-benzyl-1-phenylmethanimine. According to preliminary investigations about oxidation with N₂O,^[28] blank tests (Table S1) confirmed the crucial role of silver (Ag) photodeposited preferentially on commercially available P25 titanium dioxide (Table S2), for photocatalytic oxidative coupling of benzylamine. On one hand, this amine was completely converted with a 87 % yield in *N*-benzyl-1-phenylmethanimine under N₂O atmosphere after only 15 minutes of irradiation (Table 1, Entry 1; Figure S8). On the other hand, and remarkably, under these conditions the homocoupling of benzylamine was more

selective compared with the reaction performed under O₂ atmosphere (Table 1, Entry 2); in fact, in that case, over-oxidation until mineralization into carbon dioxide occurred, corroborated by the production of CO₂ measured. It is noteworthy to underline that under an O₂ atmosphere, TiO₂ alone catalyzes the homocoupling with complete conversion, but a decreased selectivity, compared to Ag/TiO₂ material (Table 1, Entry 2 vs. 3). Similarly, N₂O was also very selective in the homocoupling of an alkylated amine such as hexylamine into the corresponding imine (Table 1, Entry 4; Figure S9), with a 74 % yield for a 80 % conversion after 30 minutes of irradiation. Under O₂ atmosphere, although a complete conversion is observed in 15 or 5 minutes according to the presence of Ag, the selectivity is uncontrolled with only 31 % of the targeted compound and a significant formation of CO₂ (Table 1, Entries 5 & 6). In the cross-coupling of hexylamine and benzyl alcohol into the corresponding imine (Table 1, Entries 7-9), N₂O proved once more a higher selectivity than O₂ as oxidative agent, but also a higher conversion rate of the starting alcohol. Indeed, under a dioxygen atmosphere, the cross- and homo-coupling products are observed, respectively in 23% (vs. 70% with N₂O) and 15% (vs. < 5% with N₂O), due to the competition between both reactions (Figure S10), alongside with over-oxidation until mineralization into CO₂. To resume, these preliminary investigations demonstrate the remarkable potential of nitrous oxide over dioxygen for the homo- and cross-coupling of amines, undoubtedly being more selective under usual conditions and



Scheme 2. Proposed mechanisms for photocatalytic homo-coupling of amines (a) and cross-coupling of amines with alcohols (b) by nitrous oxide with Ag/TiO₂.

providing complete conversion into imines. This higher selectivity observed with N₂O is favored by an oxygen atom transfer mechanism, *via* the corresponding adsorbed radical anionic species,^[28] while under O₂ atmosphere various reactive oxygen species (O₂^{•-}, ¹O₂, etc.) can lead to over-oxidation into CO₂.

Original mechanistic investigations

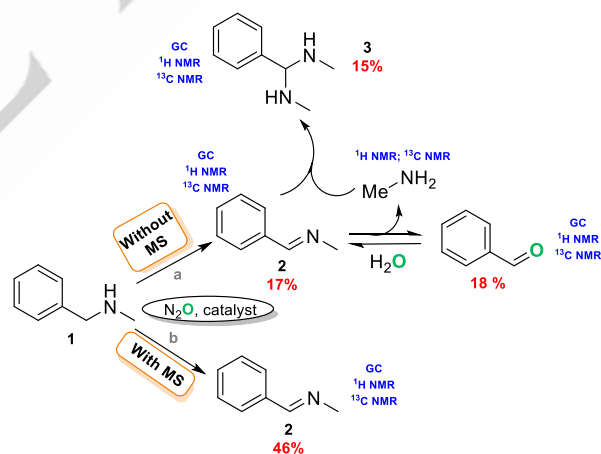
For the homo-coupling of amines (Scheme 2 a), the radical form of N₂O, produced by photocatalysis with the electron/hole pairs at the catalyst's surface, as previously described,^[28] allows the oxidative dehydrogenation of the amine into the imine, thus releasing nitrogen and water from the decomposition of N₂O.

For the formation of the final homocoupling product, two routes are possible, in accordance with mechanisms described under O₂ atmosphere.^[11,13,26,29,30] On one hand, the imine is hydrolysed into ammonia and aldehyde (Scheme 2 a, path B), which is then coupled to a second equivalent of the starting amine to produce the targeted imine (reversible step). On the other hand, the imine is condensed with the amine (Scheme 2a, path A). In both routes, valuable ammonia as raw material, with application in fertilizers or as hydrogen carrier compound for instance,^[31] is concomitantly released. For the cross-coupling reactions between alcohols and amines (Scheme 2 b), the proposed mechanism is based on the formation of the aldehyde from the dehydrogenation of the alcohol,^[23,32] with release of water and N₂ from N₂O activation,^[28] before a condensation step with the amine to form the final unsymmetric imine.

To deepen the mechanism of the homocoupling reactions and verify the favored path (Scheme 2 a, path A vs. B), formation of ammonia was first checked in an original way using *N*-methylbenzylamine (**1**) as a less reactive secondary amine and thus producing methylamine (instead of ammonia), which is easier to detect. Thus, performing the reaction with **1** in standard conditions allows evidencing the formation of benzaldehyde and methylamine by NMR analysis (Scheme 3, route a, Figure S13-14), as proof of the first step of path B (Scheme 2 a). Besides, release of methylamine was also confirmed with the formation of *N,N'*-dimethyl-1-phenylmethanediimine (**3**) with a 15% yield, from its coupling with *N*-methyl-1-phenylmethanimine (**2**) (Scheme 3, a). Moreover, experiments under dry conditions were carried out adding activated molecular sieves as a water trap.^[33] In this case

(Scheme 3, route b), the first hydrolysis step of path B did not occur as no benzaldehyde was detected in the reaction media, and only **2** was observed with a 46% yield. In both conditions (standard or anhydrous), the direct homocoupling of the starting secondary amine **1** was disfavored due to an increased steric hindrance, so only **2** was produced by oxidative dehydrogenation. The same hydrolysis step was also avoided in the homocoupling of benzylamine under dry conditions (Figure S11). Thus, mechanistically, for photocatalytic homocoupling of amines, the proposed path B seems favored compared to path A (Scheme 2, a).

Finally, kinetic experiments were performed in the photocatalytic homocoupling of benzylamine under N₂O atmosphere (Figure 1), and allowed to correlate the amine consumption with the amounts of *N*-benzyl-1-phenylmethanimine **1**, water, and N₂ formed.



Scheme 3. Original mechanistic investigations with photocatalytic oxidation of *N*-methylbenzylamine, under N₂O atmosphere without molecular sieves (MS) (a), and with molecular sieves (b). Reaction conditions: amine (0.24 mmol, 1 eq.); 3 mL MeCN; 365 nm irradiation (two LEDs, 160 mW/cm²); under N₂O atmosphere (0.29 mmol in gas phase, 7 mL, 1.2 eq.); 100 mg of Ag/TiO₂ (0.3 wt%, TiO₂ Aeroxide P25), *i.e.* substrate/metal = 100; reaction time 30 min (not optimized for complete conversion). Route (b) performed with 150 mg of activated 3Å molecular sieves. Indicated yields in red: relative proportion of the peak area obtained by Gas chromatography. Characterizations of the detected compounds indicated in blue.

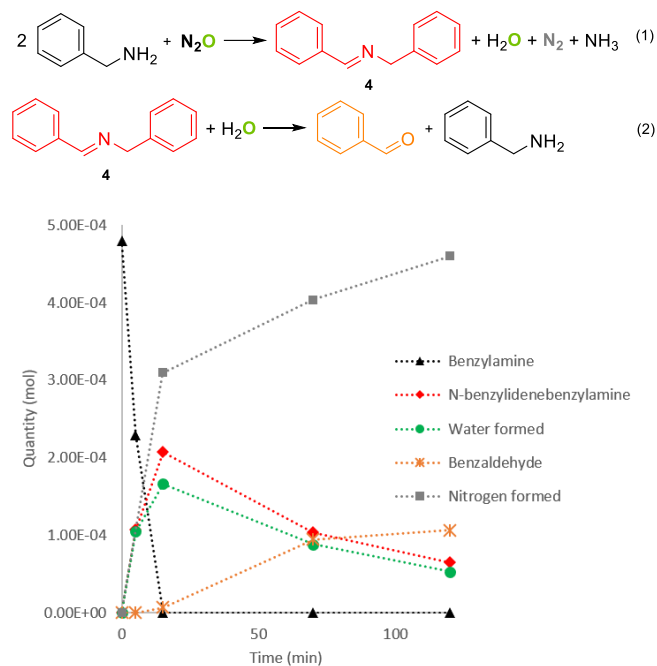


Figure 1. Evolution of benzylamine, *N*-benzyl-1-phenylmethanimine, benzaldehyde quantities, and water and dinitrogen quantities formed during the reaction, with time. Reaction conditions: benzylamine (0.48 mmol, 1 eq.), 6 mL MeCN, N_2O (0.78 mmol in gas phase, 19 mL, 1.6 eq.), 200 mg Ag/TiO_2 (0.3 wt.%), i.e. amine/silver = 100, 365 nm irradiation (two LEDs, 160 mW/cm²). Benzylamine (black triangles), *N*-benzyl-1-phenylmethanimine (red diamonds), and benzaldehyde (orange crosses) quantities determined by Gas Chromatography analyses using chlorobenzene as internal standard. N_2 (grey squares) quantified by GC-BID detector. H_2O content (green circles) quantified with a Karl Fischer titrator.

According to the stoichiometry, 0.5 equivalent of imine as well as water and nitrogen were produced after complete conversion (Eq. 1), thus proving the oxidation of the starting amine by N_2O . Then, the reversible hydrolysis of the imine (Eq. 2) occurs, corroborated with the amounts of water consumed and benzaldehyde formed. Noteworthy, the amine is not detected since it still undergoes oxidation into imine, with formation of N_2 and H_2O (Eq. 1), thus justifying that the N_2 amount kept increasing after 20 minutes.

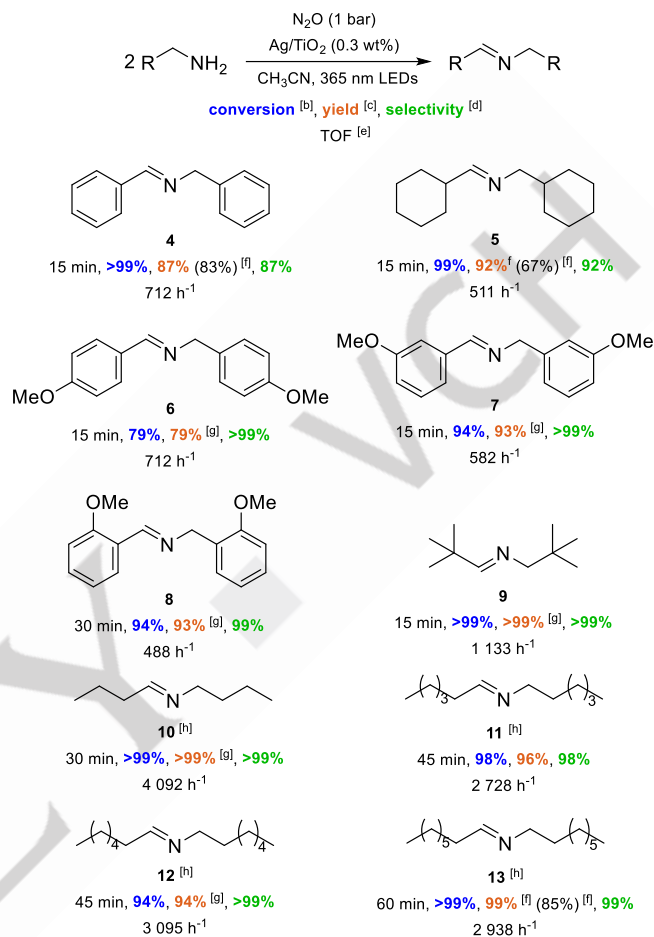
Scope of amines for homo-coupling reactions

The homocoupling process was successfully extended to benzylamine derivatives (Table 2, 4-8) as well as aliphatic amines (Table 2, 9-13) with good to excellent performances in terms of conversions, yields and selectivities. High turnover activities (TOF) up to 4000 h⁻¹ were achieved according to the nature of amines (aryl or aliphatic skeletons).

For benzylamine derivatives, the presence of a methoxy electron-donating group on the different positions of the aromatic ring had no influence on the selectivity (Table 2, 6-8), just a longer reaction time required for the *ortho* derivative (8) owing to a steric effect. These observations are in accordance with results from the literature under O_2 atmosphere.^[22,25,30,33] Homocoupling of aliphatic amines showed such relevant activities that it allowed decreasing the metal loading to 0.1 mol% (i.e. amine/silver = 1000), with excellent TOF up to 4 000 h⁻¹ for the synthesis of *N*-butylbutan-1-imine (10). As the length of the carbon chain was

extended from butylamine to octylamine (10-13), longer reaction times were needed to reach complete conversion.

Table 2. Substrate scope for photocatalytic oxidative coupling of amines into imines under N_2O atmosphere. [a]



[a] Reaction conditions: substrate (0.24 mmol, 1 eq.), 3 mL MeCN, N_2O (0.29 mmol in gas phase, 7 mL, 1.2 eq.), 100 mg Ag/TiO_2 (0.3 wt%), i.e. amine/silver = 100, 365 nm irradiation (two LEDs, 160 mW/cm²), optimized time to control the selectivity. [b] Amine conversion determined by Gas Chromatography analyses using chlorobenzene as internal standard. [c] Imine yield compared with the initial amine quantity and determined by Gas Chromatography analyses using chlorobenzene as internal standard. [d] Selectivity in imine product = yield/conversion. [e] Turnover frequency, equal to the molar quantity of amine transformed over surface silver molar quantity over time unit. [f] Isolated yield. [g] Relative proportion of the peak area obtained by Gas Chromatography. [h] 10 mg Ag/TiO_2 (0.3 wt%), i.e. amine/silver = 1000.

Productivity



The productivity of the process was also investigated to assess the performances of Ag/TiO_2 catalyst to fit in with economical and environmental industrial concerns. First, a four-fold scaling-up of the reaction, starting from 104 μ L of benzylamine instead of 26 μ L (Table S1, entry 6), leads to the formation of the imine with a 83% isolated yield in 15 minutes. The reusability of the catalyst was studied afterwards (Figure S12; recycling procedure in the SI). After the first recycling experiment, conversion was complete with an adapted reaction time, while maintaining both yield and selectivity. However, a decrease in the catalytic performances

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was observed for the next run, likely due to a catalyst deactivation by a potential modification of the Ag^+/Ag^0 ratio. As explained in our previous work,^[28] the presence of both Ag^0 and Ag^+ is essential to maintain a good activity of the catalyst.

Thirdly, the decrease in the metal loading was also investigated (Table 3) on both benzylamine (Entries 1-3) and hexylamine (Entries 4-6). For the aromatic substrate, complete conversion was achieved in only 15 minutes with both substrate/metal ratio of 100 and 200 (Table 3, entries 1-2). The catalyst was still active at a substrate/metal ratio as high as 1000, with a TOF value higher than 4000 h^{-1} (Table 3, entry 3). A similar tendency was observed with hexylamine, with an optimal Turnover Frequency of 2730 h^{-1} achieved with a substrate/metal ratio of 1000 (Table 3, entry 6). Besides, with a very high substrate/metal ratio of 10 000, a longer irradiation time of 14h is required to reach complete conversion of the amine (Table 3, entry 7), but with an excellent isolated yield of 93%.

Table 3. Impact of the metal loading for photocatalytic oxidative coupling of benzylamine and hexylamine. ^[a]

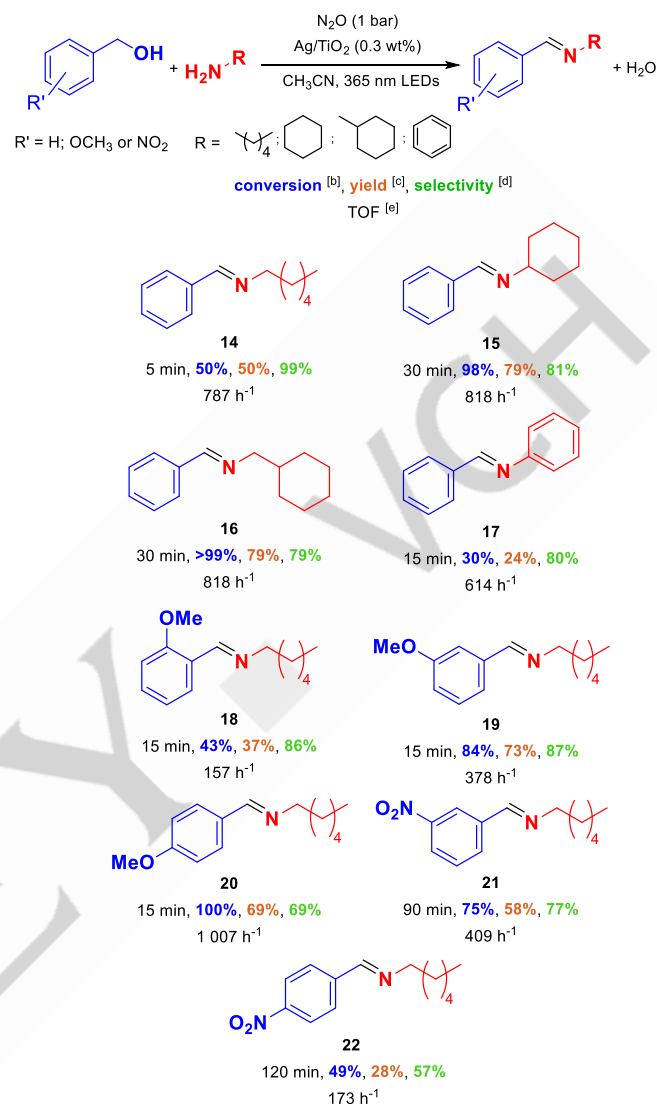
Entry	Amine	Substrate /metal	Time (min)	Conv. (%) ^[b]	Yield (%) ^[b]	Sel. (%) ^[c]	TOF (h ⁻¹) ^[d]
1		100	15	>99	87	87	712
2		200	15	>99	85	85	1 549
3		1 000	25	>99	82	82	4 407
4 ^[f]		100	15	>99	86	86	525
5 ^[f]		200	15	>99	82	82	1 353
6 ^[f]		1 000	45	98	96	98	2 728
7		10 000	840	>99	93 ^[e]	93	1 049

[a] Reaction conditions: amine (0.24 mmol, 1 eq.), 3 mL MeCN, N_2O (0.29 mmol in gas phase, 7 mL, 1.2 eq.), catalyst Ag/TiO_2 (0.3 wt%), 365 nm irradiation (two LEDs, $160\text{ mW}/\text{cm}^2$). [b] Determined by Gas Chromatography analyses using chlorobenzene as internal standard. [c] Selectivity in imine product = yield/conversion. [d] Turnover frequency, equal to the molar quantity of amine transformed over surface silver molar quantity over time unit. [e] Isolated yield.

Cross-coupling of amines

Unsymmetric imines can be obtained from the cross-coupling of two amines or of amines with alcohols under oxygen atmosphere and thermal activation with excellent selectivities.^[32] Here under photocatalytic activation with N_2O as oxidative agent, the Ag/TiO_2 material proved to be very efficient in the cross-coupling of different alkyl and aryl amines with benzyl alcohol or some substituted derivatives (Table 4).

Table 4. Substrate scope for photocatalytic oxidative cross-coupling of amines with alcohols into imines under N_2O atmosphere. ^[a]



[a] Reaction conditions: alcohol (0.24 mmol, 1 eq.), amine (0.24 mmol, 1 eq.), 3 mL MeCN, N_2O (0.29 mmol in gas phase, 7 mL, 1.2 eq.), 100 mg Ag/TiO_2 (0.3 wt%), i.e. substrate/silver = 100, 365 nm irradiation (two LEDs, $160\text{ mW}/\text{cm}^2$), optimized time to favored the selectivity. [b] Alcohol conversion determined by Gas Chromatography analyses using chlorobenzene as internal standard. [c] Relative proportion of the peak area obtained by Gas Chromatography. [d] Selectivity in imine product = yield/conversion. [e] Turn over frequency, equal to the molar quantity of alcohol transformed over surface silver molar quantity over time unit.

Once again, these photo-oxidative coupling reactions were more selective under N_2O than O_2 atmosphere (Figure S10). In the synthesis of **14**, stopping the conversion of benzyl alcohol at 50% allows a good selectivity control around 99%; otherwise, the homo-coupling product was formed, thus decreasing the selectivity e.g. to 70% for **14**, for a 96% conversion of the alcohol, after 15 min of irradiation. This reaction was also performed with a substrate/metal ratio of 1000 (i.e. 0.1 mol% loading); however, the homo-coupling product formed quicker than the cross-coupling one (Figure S7). The synthesis of **14** could be also performed through the cross-coupling of two different amines, benzylamine and cyclohexylamine. However, the targeted imine

14 was produced with a selectivity of only 58 % for a 49 % conversion of the benzylamine, alongside with the three other products arising from homo- and cross-coupling reactions. Thus, as already reported in the literature,^[34,35] the cross-coupling of amines with alcohols is a more pertinent and straightforward strategy for the synthesis of unsymmetric imines. Coupling benzyl alcohol with cyclohexylamine or cyclohexanemethylamine (Table 4, **15-16**) was also achieved with efficient selectivities into imines (up to 81%) and higher conversion rates than with hexylamine due to a less favorable homo-coupling. Reaction with aniline (Table 4, **17**) was less efficient due to a less nucleophilic character. The influence of the substituents on the phenyl ring on the catalytic performances was also studied with hexylamine (Table 4, **18-22**). The presence of the methoxy electron-donating group showed again a steric effect in *ortho* and *meta* position, and no significant impact on the activity in *para* position. On the other hand, the presence of a nitro electron-withdrawing group provides lower activities owing to both steric and electronic effects (Table 4, **21-22**), thus requiring longer reaction times. Indeed, the nitro substituent decreases the electron density of the phenyl ring, especially in *para* position, disfavoring the oxidation of the alcohol into aldehyde. Coupling of *o*-nitrobenzyl alcohol and hexylamine was not representative as formation of an indazolone compound was observed without N₂ formation (*i.e.* without oxidation by N₂O), as already described in the literature with these substrates upon UV irradiation.^[36] For cross-coupling reactions, that afford lower selectivities compared with the homo-coupling reactions (Table 2), formation of traces of amides was possible,^[37] but was not evidenced.

Conclusion

In summary, we have developed for the first time the direct synthesis of imines through the catalytic oxidative homo-coupling of amines by upgrading the most potent ozone-depleting and greenhouse nitrous oxide as a suitable and efficient oxidative agent. Upon photocatalytic irradiation, good to excellent yields were achieved for a variety of imines, using an Ag/TiO₂ catalyst, which was easily prepared by photodeposition. Remarkably, nitrous oxide allows achieving, under photocatalytic conditions, higher selectivity than dioxygen, avoiding the over-oxidation reactions. This highly attractive protocol was further extended to the cross-coupling of amines with alcohols to produce unsymmetric imines which are highly demanded synthons. These results provide an economical and practical way to produce imines, that shows good green chemistry metrics. This study is ongoing to extend to other challenging substrates, for the synthesis of benzoxazole derivatives from oxidative cross-coupling.

Experimental section

Materials

All the organic compounds were purchased from Acros Organics (Illkirch, France), TCI Europe N.V. (France), or Sigma-Aldrich-Fluka (Saint-Quentin-Fallavier, France). Silver nitrate (AgNO₃)

was purchased from Acros Organics (Illkirch, France). The titanium dioxide, either anatase or rutile allotropic forms, as well as the P25 mix were obtained from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Nitrous oxide 99.99% purity was purchased from Air Liquide (Paris, France). All these starting materials were used without further purification. Water was distilled twice before use by conventional method. Organic solvents were all HPLC grade.

The LED lamps were purchased from HepatoChem (EvoluChem™ LED; wavelength: 365 nm; 18W). UV intensity, or surface power density, in mW/cm² unit at 365 nm was measured with a radiometer VLX-3W (Vilber) with a 365 nm sensor. The UVA lamp was a Philips high-pressure Hg lamp (reference PL-L 24W/10/4P; 350-400 nm with λ_{max} around 360 nm).

Synthesis of Ag/TiO₂ by photodeposition

In a round bottom flask, an adequate amount of TiO₂ (3-4g) was added to 80 mL of an aqueous AgNO₃ solution (9.42.10⁻⁵ – 1.24.10⁻⁴ mol, depending on the amount of TiO₂ to have a metal loading of 0.3 wt%), under stirring. The pH was adjusted to approximately 6.3 by addition of a few drops of a potassium hydroxide solution (0.1 mol.L⁻¹). After 15 min under stirring, 4 mL of methanol were added and the suspension was irradiated by a UVA lamp (Philips) for 4 hours, under continuous argon bubbling flow and vigorous stirring. The solid product was recovered by filtration of the suspension, washed several times with re-distilled water under air atmosphere, and dried under vacuum at 100 °C for 1h30. The obtained photocatalyst was grinded manually, and stored away from the light.

Photocatalytic experiments

Photocatalytic experiments were performed at room temperature under nitrous oxide atmosphere (1 bar). A 10 mL schlenk tube, closed by a septum and containing the right amount of photocatalyst, is filled with nitrous oxide (three vacuum-nitrous oxide cycles) while stirring with a cross-shape magnetic stirrer. 3 mL of a solution of the amine (1 equivalent) in acetonitrile (containing also 1 equivalent of the alcohol for the cross-coupling reactions), that has been previously bubbled and stored under nitrous oxide atmosphere, was added with a syringe. The volume of the gas phase in the vessel was 1.2 equivalent of nitrous oxide (7 mL, 0.29 mmol). After stirring for 30 min in the dark to reach adsorption equilibrium conditions, the reactor was irradiated by two LED lamps at 365 nm with an average intensity around the reactor of 160 mW/cm². Due to the light irradiation, the temperature of the media reached 38 °C after 15 min and remained stable afterwards. Before and after the reaction, gas phase samples were collected with a 100 μL (*i.e.* 1% of the total volume of the vessel) Hamilton Gastight SampleLock syringe, equipped with a syringe guide, and analyzed by GC for quantification. The syringe was left open and purged three times with air between each sampling. After the reaction, the reactor was opened to air and the solution was filtered through a 0.20 μm syringe filter to remove the catalyst. The solution was then analyzed by GC for quantification with chlorobenzene as internal standard.

Supporting Information

The authors have cited additional references within the Supporting Information.^[38,39]

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Symmetric and unsymmetric imines were successfully synthesized using nitrous oxide (N₂O) as an oxidative agent through the Ag-TiO₂-photocatalyzed couplings of amines. In this unprecedented and mild strategy, not only N₂O proves to be more selective than O₂, but this problematic industrial waste known as a potent greenhouse gas was successfully upgraded, only releasing dinitrogen as a benign co-product.

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