Review

Visible Light-Induced Aerobic Oxidative Dehydrogenation of C–N/C–O to C=N/C=O Bonds Using Metal-Free Photocatalysts: Recent Developments

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Abstract: Performing synthetic transformation using visible light as energy source, in the presence of a photocatalyst as a promoter, is currently of high interest, and oxidation reactions carried out under these conditions using oxygen as the final oxidant are particularly convenient from an environmental point of view. This review summarizes the recent developments achieved in the oxidative dehydrogenation of C–N and C–O bonds, leading to C=N and C=O bonds, respectively, using air or pure oxygen as oxidant and metal-free homogeneous or recyclable heterogeneous photocatalysts under visible light irradiation.

Keywords: oxidative dehydrogenation; photocatalysis; metal-free; C–N bond; C–O bond

1. Introduction

Photocatalysis has become one of the most powerful and efficient strategies employed in organic synthesis in recent years, emerging as a sustainable and environmentally friendly alternative methodology in electron transfer-mediated chemical transformations [1–5]. This fact is reflected in the impressive and rapid increase in the number of publications in this field in the last decade. In this context, the use of visible light is singularly attractive due to its renewability and low cost and because organic compounds do not absorb it [6–9]. Therefore, possible side reactions produced in traditional photochemical transformations using UV light, which is absorbed directly by organic molecules, are avoided with the employment of innocuous and less energetic visible light, its use also simplifying the reaction setup. The use of visible light implies the need of using substoichiometric amounts of a photocatalyst [10].

Among all the photocatalysts, transition metal-based compounds [11–14], metal-free molecules [3,15–19] and semiconductors [20,21] are the most utilized. These promoters have been applied successfully to many photochemical transformations, such as oxidations [22–26], cycloadditions [27–30], C–H bond functionalizations [31–34], photoredox reactions [6,16,17,35–43] and even enantioselective reactions [44–51]. In addition, other effective photocatalysts have been widely applied for photocatalysis in energy and environment [52–54].

The oxidation of organic compounds is one of the most performed transformations in organic synthesis, since it is extensively used in the industry to synthesize drugs and fine chemicals [55,56]. Traditional oxidation methodologies use stoichiometric amounts of manganese-, chromium- or hypervalent halogen-based oxidants, which are toxic, have low selectivities, are expensive and generate undesired waste, as well as catalysts based on noble metals. This fact has become unacceptable from an environmental point of view, with the development of new greener and sustainable strategies for carrying out oxidation reactions employing molecular oxygen as an economic and benign oxidant gaining interest [57].
Thus, molecular oxygen present as pure O$_2$ or in atmospheric air is the cheapest, greenest and most readily available oxidant that can be used in oxidative transformations. The combination of O$_2$ with a catalytic system makes the oxidation strategy very attractive for developing environmentally friendly and sustainable protocols, although it is a challenge in organic chemistry [58,59]. Molecular oxygen needs to be activated to generate reactive oxygen species (ROS), photocatalysis then emerging as an attractive way to achieve oxidation reactions [60].

Visible light-induced oxidations for the synthesis of oxygen-containing organic molecules have become an interesting and promising area of research [61]. In particular, the basic selective aerobic oxidative dehydrogenation of alcohols to the corresponding carbonyl compounds is a well-known and very important reaction in the industry [62]. In addition, imines are relevant nitrogen-containing sources in drugs and organic synthesis, the aerobic oxidative dehydrogenation of amines being a sustainable and environmentally friendly strategy to synthesize them [24,25,61].

Several reviews about visible light-induced oxidations have been published up to now, although they are mainly centered on a specific photocatalyst and in metal-catalyzed homogenous or heterogeneous photo-oxidations [7,20,24–26,61–65]. In this review, we summarize the developments in the metal-free photocatalytic aerobic oxidative dehydrogenation of C–N and C–O bonds to achieve C=N and C=O bonds under homogeneous and heterogeneous conditions in the last six years.

2. Oxidative Dehydrogenation of C–N Bonds
2.1. Homogeneous Oxidative Dehydrogenation of C–N Bonds

The homogeneous oxidative dehydrogenation of amines by air or pure O$_2$ is a very interesting strategy for the preparation of imines. The commonly accepted mechanism of this transformation [25,66–68] begins with the formation of the singlet excited state of the photocatalyst (1PC*) by irradiation with visible light (Scheme 1). Next, the triplet excited state (3PC*) is produced by intersystem crossing (ISC), and the singlet oxygen (1O$_2$) is generated by energy transfer (ET) from the triplet oxygen (3O$_2$) [69]. At this point, the starting amine forms an exciplex with the singlet oxygen as an intermediate on which a hydrogen abstraction and a single electron transfer (SET) process occur. After that, hydrogen peroxide is generated leading to an imine. This species can also react with the starting amine to obtain an homocoupled imine and ammonia as a by-product.

![Scheme 1](image)

**Scheme 1.** Commonly accepted mechanism of the oxidative dehydrogenation of amines to imines and subsequent homocoupling, mediated by singlet oxygen.

Based on this transformation, several methodologies have been carried out in recent years. Thus, methylene blue (I), an organic dye, was employed as photocatalyst in the
photo-organocatalytic aerobic oxidative coupling of benzylamines to obtain N-benzylidene benzylamines 2 in good yields (Scheme 2) [70].

![Scheme 2](image.png)

**Scheme 2.** Aerobic photo-oxidative coupling of benzylamines to render N-benzylidene benzylamines 2 catalyzed by 1.

The methodology in Scheme 2 shows the photocatalytic aerobic oxidative coupling of the same primary amine, raising doubt as to which side the oxidation to the imine occurs on if this coupling is carried out between two different primary amines. To solve this question, a theoretical study on what factors influence the oxidation side in the aerobic photo-oxidative coupling of two different primary amines was performed [71]. Thus, tetraphenylporphyrin (TPP) was employed as photocatalyst in the oxidation of non-symmetric aromatic secondary amines, suggesting that the oxidation side depends directly on the bond dissociation energy (BDE) of the C–H bond next to the nitrogen atom. To quantify the selectivity, a theoretically natural bond order analysis (NBO) and an experimental analysis of the $J_{CH}$ coupling constants obtained by NMR spectroscopy, both expressed in terms of hybridization or %s character, were performed, showing a strong inductive effect on hybridization. This means that electronegative groups at the ortho position cause the benzylidene C–H bond to have less p character, increasing the %s character and the regioselectivity to one oxidation side. In addition, one of the aromatic rings was exchanged with an alkyl group with less p character to find out if steric effects influence the oxidation side. Thus, when secondary amines bearing neopentyl residues were submitted to the same oxidation strategy, an inversion in selectivity was observed, favoring the oxidation of the alkyl side.

Apart from the example shown in Scheme 2, other methodologies have been applied in the same transformation. Thus, TPP and methylene blue 1 were used in the aerobic oxidative coupling of benzylamine to N-benzylidene benzylamine using a gas-liquid membrane reactor under homogeneous continuous flow at 90 and 100 °C, respectively, and under white light irradiation, obtaining moderate yields [72]. This strategy is interesting because it enables a safe and accurate mass transport of oxygen, adjusting the gas pressure, the temperature of the membrane and the liquid flow rate, making it possible to maintain reproducible conditions with better control of the process.

Sunlight is a sustainable alternative source of energy that can be employed in photocatalysis. Thus, the aerobic oxidative coupling of benzylamines to render 2 under sunlight irradiation has been carried out using very low loadings of the xanthene-based photocatalyst Eosin Y (3) [73] and a terpyridine-based supramolecular nanoassembly of pyrazine-based donor–acceptor systems, (TETPY, 4) [74], both catalysts showing excellent activity (Figure 1). In the first case, the fact that it could be possible to mimic the solar light environment with a sunlight simulator lamp makes the system very attractive, while in the second case carried out under direct real sunlight irradiation, the nanoassemblies have excellent aggregation-induced emission enhancement (AIEE) and intramolecular charge transfer (ICT), characteristics added to their potential to generate ROS.
Interestingly, an anthraquinone-based photocatalyst (5), which previously showed excellent activity in the oxidative coupling of benzylamines to N-benzylidene benzylamines 2 [75], has also been used to synthesize cis-1,3-diaryl tetrahydroisoquinolines 7 through a photo-organocatalytic aerobic oxidative amine dehydrogenation/super acid-mediated Pictet–Spengler cyclization (Scheme 3) [75]. Thus, α-benzyl dibenzyl-amines were regioselectively converted into the corresponding branched aldimines 6 by aerobic oxidative dehydrogenation under visible light (Scheme 3). Without further purification, these aldimines were submitted to an acid-mediated cyclization using trifluoroacetic acid (TFA) or trifluoroacetic acid (TFA), leading to the respective tetrahydroisoquinolines 7 in moderate to good yields. The diastereoselectivity of 7 could be explained with the chair-like transition state A, in which the aryl groups are in a pseudo equatorial position.

Scheme 3. Photo-organocatalytic synthesis of cis-1,3-diaryl tetrahydroisoquinolines 7 by aerobic oxidative amine dehydrogenation/super acid-mediated Pictet–Spengler cyclization.

Imines obtained from the photo-oxidation of amines can also be transformed into aldehydes due to the presence of H₂O in the reaction media. Thus, a cercosporin-bioinspired photocatalyst 8, which is a perylenequinonoid pigment, has been obtained from microbial
fermentation of glucose and employed in the oxidation of amines to aldehydes 9 under irradiation with white light, obtaining good to excellent yields (Scheme 4) [76].

Scheme 4. Aerobic photo-oxidation of amines to aldehydes 9 catalyzed by 8.

The oxidative dehydrogenation of benzylamines protected with a urea moiety was explored, employing 2,4,6-triphenylpyrylium tetrafluoroborate (10) as photocatalyst, leading to the corresponding ketones 11 in moderate to excellent yields (Scheme 5) [77]. The interest in using urea-protected benzylamines resides in avoiding the possible oxidative coupling of the benzylamines.

Scheme 5. Aerobic photo-oxidative dehydrogenation of urea-protected benzylamines leading to ketones 11 catalyzed by 10.

The proposed catalytic pathway begins with the generation of the excited photocatalyst 10* under blue light irradiation, producing the cation radical of the starting urea and the anion radical 10−• by SET (Scheme 6) [77]. Next, another SET process allows the recovery of photocatalyst 10 and the formation of the reduced superoxide radical ion O2−• from the O2. This superoxide radical abstracts a proton and coordinates with the urea moiety, directing the addition to the imine formed in the process. Finally, the elimination of H2O leads to the formation of ketone 11 and a N-aryl urea.
Scheme 6. Proposed mechanism for the aerobic photo-oxidative dehydrogenation of urea-protected benzylamines to ketones 11.

The photocatalytic oxidative dehydrogenation of N-heterocycles is another interesting reaction that has been explored due to the biological interest in the obtained products [78]. Hence, an attractive synthetic methodology under green light irradiation using the xanthene-based organic dye Rose Bengal disodium salt (12) as photocatalyst was developed for the oxidative dehydrogenation of tetrahydroquinolines under base- and additive-free conditions in N,N-dimethylacetamide (DMA) as solvent, rendering the corresponding quinolines 13 in moderate to excellent yields (Scheme 7a) [79]. In order to expand the scope of the reaction using this direct synthetic route, other N-heteroaromatics 14, such as acridines, benzofused-quinolines, quinoxalines and quinazolines, were synthesized in high yields from the corresponding starting compounds (Scheme 7b) [79].

Scheme 7. Aerobic photo-oxidative dehydrogenation of (a) tetrahydroisoquinolines and (b) other N-heterocycles to render 13/14 catalyzed by 12.

The proposed mechanism is the same for 13 and 14 (Scheme 8) [79]. Thus, Rose Bengal disodium salt (12) is excited by green light irradiation to render it its singlet state 12\(^*\),
which oxidizes the amine by a SET process generating an amine radical cation while the triplet state of Rose Bengal $12^T$ is formed (Scheme 8). At the same time, $O_2$ is reduced to the superoxide radical ion that transforms the amine radical cation to an imine by a hydrogen atom transfer process (HAT), recovering the photocatalyst and generating hydrogen peroxide. The final step consists of the isomerization of the imine, after which a second catalytic cycle is produced to yield the desired product 13.

![Scheme 8. Proposed mechanism for the photo-organocatalytic oxidative dehydrogenation of tetrahydroquinolines to quinolines 13.](image)

Recently, an aminoquinolate diarylboron compound 15, which demonstrated good activity in the dehydrogenation of tetrahydroquinolines and other $N$-heterocycles leading to 13/14 [80], was used as a photocatalyst in the dehydrogenation of the products B generated from the cyclization of 2-substituted anilines with benzaldehydes to the intermediates A. Final 16/17 were obtained in moderate to excellent yields in $N$-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), CH$_2$CN or DMA as solvent (Scheme 9) [80].

![Scheme 9. Aerobic photo-oxidative dehydrogenation of in situ generated $N$-heterocycles B catalyzed by 15.](image)

Other $N$-heterocyclic compounds oxidized under aerobic conditions and irradiation with visible light were 1,2- and 1,4-dihydropyridines (Scheme 10a,b), hexahydroacridinediones (Scheme 10c) and polyhydroquinolines (Scheme 10d), employing a 1,8-dimethoxy-substituted
acridinium ion 18 as catalyst, leading to the corresponding aromatic N-heterocycles 19–22 in excellent yields [81].

Scheme 10. Aerobic photo-oxidative aromatization of: (a,b) dihydropyridines, (c) hexahydroacridinediones and (d) polyhydroquinolines, catalyzed by 18.

The proposed mechanism for these transformations, exemplified in the case of dihydropyridine, is shown in Scheme 11. First, photocatalyst 18 is excited to its singlet state 18* by irradiation with visible light. Subsequently, a cation radical is generated in the nitrogen of the heterocyclic compound by a SET process, while the triplet state of the catalyst 18T is formed. Finally, the cation radical reacts with the superoxide anion radical from the O2,
recovering the starting photocatalyst and generating the corresponding cation, which is oxidized into the corresponding aromatic compound.

![Scheme 11. Proposed mechanism for the aerobic photo-oxidative aromatization of 1,4-dihydropyridines.](image)

From all these results, it can be observed that, as supposed, lower photocatalyst loadings generally result in slower reactions. However, photocatalysts 8, 15 and 18 yielded very good results in much shorter reaction times, despite low catalyst loading. These differences can be attributed to a higher photoabsorptivity of the photocatalysts and their ability to generate ROS, final yields materializing particularly well when using 8 and 18.

2.2. Heterogeneous Oxidative Dehydrogenation of C–N Bonds

The aerobic dehydrogenation of amines to imines has also been carried out using metal-free heterogeneous photocatalysts under environmentally friendly conditions. These methodologies are very attractive, the catalysts being suitable for recycling using several procedures. For example, conjugated microporous polymers (CMPs) can present photoactive structures and high thermal stability and can be applied to several photocatalytic processes [82–84]. Thus, a carbazole-based CMP with a fluorene moiety (MFC-CMP, 23) was recently employed in the aerobic dehydrogenation of secondary amines, leading to imines 24 in good to excellent yields (Scheme 12) [85]. The catalyst was reused in four cycles without losing its activity, although the recycling procedure was not described.

![Scheme 12. Aerobic photo-oxidative dehydrogenation of secondary amines to imines 24 catalyzed by 23.](image)

The proposed mechanism of transformation is the same as shown in previous homogeneous C–N bond oxidation (Scheme 1). The authors suggest that the formation of electrons at the electron donor moiety of carbazole and holes at the electron acceptor moiety of fluorine generates the superoxide anion radical and the amine cation radical.

Another CMP with a thiazolo [5,4-d]thiazole base structure (Tz-Tz-CMP-2, 25) has been used in the same transformation, achieving excellent conversions to imines 24...
In addition, other heterogeneous catalysts, such as C\textsubscript{70} fullerene (26) \cite{87} and a 2D porphyrin-based sp\textsuperscript{2} carbon-conjugated covalent organic framework (Por-sp\textsuperscript{2} c-COF, 27) \cite{88} have demonstrated excellent activity towards the photocatalytic aerobic dehydrogenation of secondary amines to imines 24 (Figure 2). In the case of 27, the authors published a later work in which the same heterogeneous photocatalyst was applied in a cooperative photocatalysis with TEMPO, also obtaining excellent results (Figure 2) \cite{89}. Regarding the recyclability of these catalysts, the recycling of 25 was not mentioned by the authors, whereas 26 could be recovered and reused by precipitation from MeOH, obtaining a C\textsubscript{70} fraction that contains C\textsubscript{70} epoxides, which are then thermally treated to recover the underivatized C\textsubscript{70}. In the case of 27, it could be recovered by centrifugation.

The mentioned metal-free photocatalyzed oxidative dehydrogenation of N-heterocycles is another C–N bond oxidation reaction that has been performed under heterogeneous conditions. Thus, an environmentally friendly protocol, using a perylene diimide organic semiconductor covalently immobilized to SiO\textsubscript{2} nanospheres (PDI-SN, 28) as catalyst and DMA as solvent, was developed to carry out the oxidative dehydrogenation of tetrahydroquinolines and other N-heterocycles to render 13/14, under violet light irradiation, in good to excellent yields (Figure 3) \cite{90}. The photocatalyst 28 could be recycled up to six cycles, by washing the crude reaction mixture with acetone three times and drying the filtrate at 60 °C for 6 h, and reused without observing a significant decrease in its activity.
Recently, an imidazole-linked porphyrin-based CMP was employed in the aerobic oxidative dehydrogenation of N-heterocycles to render 13/14 in high yields [91]. The recyclability of the photocatalyst was carried out, and it was reused up to six cycles without remarkable changes in its activity.

Additionally, C70 fullerene (26) was also used for the partial aerobic oxidation of 1,2,3,4-tetrahydroisoquinoline under irradiation with white light and chloroform as solvent, which was previously saturated with oxygen, rendering the corresponding oxidized product 29 in quantitative yield (NMR) (Scheme 13) [87]. Furthermore, the same imidazole-linked CMP used in the dehydrogenation of N-heterocycles to 13/14 was used in the partial oxidation of 1,2,3,4-tetrahydroisoquinolines, leading to the corresponding isoquinolines in high yields [91]. The photocatalyst 26 was recycled by precipitation, whereas the CMP was recovered by centrifugation and reused in up to 10 cycles, both maintaining the activity.

Carbazolic CMP (C-CMP, 30, 15 wt.%), which was also used in the photo-oxidation of a secondary amine shown in Scheme 12 (Ar = Ph, R = Bn, 10 wt.%, 76% yield), was employed in the former partial aerobic photo-oxidation of tetrahydroisoquinoline, working in acetonitrile under irradiation with a 150 W Xe lamp at 10 °C, obtaining 29 in 72% yield [92]. In the same work, this photocatalyst was also employed in the aerobic oxidation of tetrahydroquinazolines to quinazolines 31 in moderate to good yields (Scheme 14). The catalyst 30 was reused, but not for this particular transformation.

Two efficient and mild protocols using a polymeric carbon nitride with terephthalic acid monomers in its structure (P-CN, 32) (Figure 4) [93] and a melamine-based carbon nitride 33 (Figure 4) [94] as photocatalysts, were developed for the aerobic photo-oxidative aromatization of a 1,4-dihydropyridine (Hantzsch ester), leading to the corresponding aromatic pyridine 20 (R1 = H, R2 = OEt) in quantitative yield. The catalyst 32 could be recycled three times without any change in its activity, while the reusability of 33 was not reported.
Scheme 14. Aerobic photo-oxidation of tetrahydroquinazolines to quinazolines 31 catalyzed by 30.

The aerobic oxidative coupling of benzylamines under irradiation with visible light (Scheme 2) has been widely explored using polymeric photocatalysts. CMPs are one of those polymer-based catalysts studied for this transformation. Thus, a benzothiadiazole-based CMP (B-BT, 34a) and a benzooxadiazole-based CMP (B-BO-1,3,5; 34b) were used in the mentioned reaction, obtaining good results (Figure 5) [95,96]. In both cases, the catalyst was recovered for up to five cycles with only a slight decrease on the activity of 34b, the authors not reporting the recycling procedure.
Other CMPs employed as photocatalysts in the same reaction leading to 2 are a truxene-based polymer (Tx-CMP, 35) under natural sunlight irradiation [97], a carbazolyl porphyrin-based CMP (TCP-P-CMP, 36), also employed in the aerobic dehydrogenation of amines to imines shown in Scheme 12 (Ar = Ph, R = iPr, Bn, CH₂-(4-MeOC₆H₄), ca. 19 wt.%, CH₃CN, O₂ (1 atm), 25 °C, 16 h, 100 W white LED, 3 examples, 99% conv.) [98], a triphenylamine-based CMPs functionalized with anthracene moieties (PAA-CMP, 37) [99] (Figure 5) and with β-diketone boron difluoride motifs (TPA-B-CMP, 38) [100], a boranil-based polymeric material (TDFB-TEB, 39) [101] and a pyrene-based polymeric promoter (CMP-A, 40) [102] (Figure 6). In all cases, excellent results were obtained. It should be noted that all the catalysts could be recovered by centrifugation, washing and drying (35, 38 and 39), by simple centrifugation (36 and 37) or by filtration (40), maintaining their activity for five/six cycles without any noticeable change in performance.
Figure 6. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 38–40.
Other conjugated polymers have also been used in this transformation leading to 2. Thus, a conjugated trithienyl triazine-based polymer (P4-1, 41) [103], conjugated polyhexylthiophene nanofibers (PHT, 42) [104], an emeraldine salt of a conjugated HCl-doped polyaniline (PANI-ES, 43) [105] and two conjugated imide-based polymers, an oxygen vacancies-rich polyimide (R-PI, 44) [106] and ultrathin nanosheets containing imide motifs (PTCDI-H, 45) [107], have been successfully employed as heterogeneous photocatalysts (Figure 7). In the case of the reactions promoted by 43 and 44, butylamine was also tried, albeit without success. All photocatalysts could be recycled five times (for 41, 44 and 45) and six times (for 42 and 43) by centrifugation without observing significant variations in their activity in most cases, although polyaniline 43 needed to be regenerated with HCl, with photocatalytic performance dropping between cycles due to leaching.

![Figure 7. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 41–45.](image-url)
Porous organic polymers (POPs), which have different applications in photocatalysis [108], have also been used as heterogeneous photocatalysts in the same oxidative coupling of benzylamines. In this sense, two carbazole-based POPs were recently used in the aforementioned reaction, the fluorenone-based (CF-HCP, 46) [109] and the BODIPY-based (CzBDP, 47) [110], successfully obtaining the corresponding N-benzylidene benzylamines 2 (Figure 8). It is worth mentioning that 46 was also employed in the aerobic dehydrogenation of secondary amines to the imines 47 (HMP-TAPA, 46) [110], while the use of an anthracene ionic polymer (AN-POP, 48) [112] and two heptazine-based polymeric promoters, presenting tris-aminoethylamine units (HP-AA, 47) [113] and tris(4-aminophenyl)amine moieties (HMP-TAPA, 50) [114], allowed for the obtention of 2 in quantitative conversions (Figure 9). In the case of the hyper-cross-linked polymer, it was also tested in the aerobic dehydrogenation of secondary amines to the imines 47 (1 atm), 25 °C, 6–10 h, 30 W green LED, 2 examples, 81–93% yield), as well as in the partial aerobic oxidation of the 1,2,3,4-tetrahydroisoquinoline shown in Scheme 12 (Ar = Ph, R = Bn, 3Bu, ca. 23 wt.%, CH3CN, O2 (1 atm), 25 °C, 10 h, 30 W green LED, >99% yield) [109]. The recycling of 46 was not carried out for this particular transformation, while 47 was not reused.

Figure 8. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 46 and 47.

In addition, a hyper-cross-linked polymeric material, synthesized via the AlCl3-catalyzed coupling reaction of hexaphenylbenzene monomers, was used with irradiation with a 210 W Xe lamp under air, obtaining moderate conversions to 2 [111], while the use of an anthracene ionic polymer (AN-POP, 48) [112] and two heptazine-based polymeric promoters, presenting tris-aminoethylamine units (HP-AA, 49) [113] and tris(4-aminophenyl)amine moieties (HMP-TAPA, 50) [114], allowed for the obtention of 2 in quantitative conversions (Figure 9). In the case of the hyper-cross-linked polymer, it was also tested in the aerobic dehydrogenation of secondary amines to the imines 24 shown in Scheme 12 (Ar = Ph, R = Bn, ca. 19 wt.%, CH3CN, O2 (1 atm), 25 °C, 4 h, 210 W Xe lamp, 75% yield) [111]. The reusability of the photocatalysts was studied by filtration and washing with CH3CN (for 48), and centrifugation (for 49 and 50), without observing remarkable changes in their activity.
Figure 9. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 48–50.

Other polymers recently employed in the same reaction leading to 2 were a melamine-based material (SC-HM, 51) [115], a nanogel composed of poly(N-isopropylacrylamide), N-(4-(7-(phenylbenzo[c][1,2,5]thiadiazol-4-yl)phenyl)acrylamide and polyethylene glycol.
dimethylacrylate monomers 52 [116] and an organic polymer based on 1,3,5-triformylphloroglucinol and a terephthalohydrazide (TFG-BPTH, 53) [117]. These promoters enabled the preparation of N-benzylidene benzylamines 2 (for 52: Ar = Ph) in moderate to good conversions in all cases (Figure 10). The recyclability was tested in another photo-oxidation reaction (for 51 and 52) and by filtration (for 53), without any loss in their catalytic activity.

Figure 10. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 51–53.

Polymeric carbon nitride as a metal-free promoter has been used in many photoredox processes [118]. Thus, the former carbon nitride 33 obtained from cytosine and urea units [119] and a cyanated modified carbon nitride (TCNS, 54) (Figure 11) [120] were
employed in the aerobic oxidative homocoupling of benzylamines leading to 2, achieving moderate to excellent conversions. This latter catalyst was recovered and reused up to four times without loss of performance, but the recycling procedure was not specified. In another work leading to 2, acetone was needed as co-catalyst to promote the spin relaxation and cancel non-radiative energy losses, using 33 as photocatalyst (ca. 4 wt.%, 10 µL acetone, CH$_3$CN, O$_2$ (1 atm), 20 °C, 3 h, Xe lamp, 8 examples, 90–99% conv.) [121]. Additionally, a polymeric carbon nitride (93.5 wt.%), organized in layers and synthesized by a self-assembly approach, introducing hydroxyl and carboxyl groups, was employed in the aerobic oxidative coupling of benzylamine leading to N-benzylidene benzylamine in 58% yield [122].

![Scheme 13](image)

**Figure 11.** Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 54.

The mentioned carbon nitride 33 packed in a flow reactor, which was also used in the photo-oxidative aerobic dehydrogenation of secondary amines shown in Scheme 12 (Ar = Ph, R = Bn) with a conversion to 24 of 78%, allowed for the obtention of 2 in excellent conversions (ca. 4 wt.%, CH$_3$CN, air, 55 °C, τ = 60 min, 14.4 W blue LED, 5 examples, 95–100% conv.) [123].

Graphitic carbon nitrides, which have been extensively applied in many photocatalytic processes related to energy and environment [124–126], have been recently used in the mentioned oxidative coupling leading to 2. Recently reported examples of the use of this type of metal-free photocatalysts include a ketone-group modified graphitic carbon nitride 55, which successfully catalyzed this transformation (Figure 12) [127], also showing excellent activity in the partial photo-oxidation of 1,2,3,4-tetrahydroisoquinoline in Scheme 13, as well as 54 in its graphitic form (ca. 234 wt.%, CH$_3$CN, air, 1 atm), 25 °C, 4 h, 300 W Xe lamp, 9 examples, 94–99% conv.) [128]. In addition, a garland-like interconnected graphitic carbon nitride, synthesized via an oxalic acid-mediated assembly strategy, was also employed, obtaining good results (ca. 47 wt.%, CH$_3$CN, O$_2$ (1 atm), 20 °C, 8–33 h, 300 W Xe lamp, 9 examples, 82–99% conv.) [129], while a perylenetetracarboxylic diimide covalently connected in a graphitic carbon nitride (PDI/mpgCN, 56) promoted the reaction in excellent conversions (Figure 12) [130]. Concerning recovery, the performance of 55 was maintained with a slight decrease in the third reaction cycle, which was overturned by washing the catalyst with a 0.1M solution of NaOH. The graphitic form of 54 was reused by centrifugation, while 56 was recycled by filtration without a noticeable drop in their activity. The recyclability of the garland-like graphitic carbon nitride was not tested for this transformation.
Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines catalyzed by 55 and 56.

In addition, a porous few-layer carbon nitride obtained from melamine and cyanuric acid by molecular self-assembly was used to render N-benzyldiene benzylamines 2 in moderate to excellent conversions (ca. 4 wt.%, CH\textsubscript{3}CN, O\textsubscript{2} (0.1 MPa), 25 °C, 1 h, 300 W Xe lamp, 7 examples, 82–99% conv.) [131]. The catalyst could be recovered and reused for up to five cycles without decreasing its activity.

Porous organic frameworks (POFs) have also been employed in the aerobic oxidative coupling of benzylamines leading to 2, a few examples being recently published. In this sense, a nanoporous graphene-like POF synthesized from hexahydroxytriphenylene and hexaazatrinaphthylene monomers (HOTT-HATN, 57) [132], a carbazole-triazine based donor–acceptor POF (pTCT-2P, 58) [133] (Figure 13) and a supramolecular microporous porphyrin-based POF (PTC-1(2H), 59) [134] (Figure 14) were used as photocatalysts in the mentioned transformation, obtaining excellent conversions and working under flow conditions in the first case. All these catalysts were recovered by filtration and reused for five cycles, maintaining their catalytic activity.

In Figure 12, the results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines are shown. In Figure 13, the results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines are shown.
Figure 13. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines 2 catalyzed by 57 and 58.

Figure 14. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines 2 catalyzed by 59.

Figure 15. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzyldiene benzylamines 2 catalyzed by 60.

Covalent organic frameworks (COFs) have also been used in the aforementioned reaction. Thus, a hydrophilic hydrazone-based COF with 2-methoxyethoxy groups (TFPT-BMTH, 60) has been employed as photocatalyst, yielding 2 in moderate to excellent conversions (Figure 15) [135]. The promoter was recovered by filtration without any change in its activity.

Other COFs used successfully in the same transformation were a pyrene-benzothiadiazole conjugated donor-acceptor (Py-BSZ-COF, 61) [136] and a pyrene-thiazolo[5,4-d]thiazole donor-acceptor (PyTz-COF, 62) [137] (Figure 16). The recyclability of these photocatalysts was achieved by centrifugation in both cases, being able to perform the reaction four and six times, respectively, maintaining their performance.
Graphene-based composites have been recently employed in many photocatalytic processes, such as those related to the environmental area [138–140]. Metal-free graphene quantum dots (GQDs) and carbon quantum dots (CQDs) are interesting materials due to their unique physical and chemical properties, demonstrated to have various photocatalytic applications [141,142]. Thus, the aerobic oxidative coupling of benzylamines for the preparation of benzylidene benzylamines has been successfully carried out with nitrogen- and sulfur-codoped GQDs synthesized from a catecholamine derivative (NS-GQDs, 63) [143], oxygen-rich CQDs (O-CQDs, 64) [144] and dimethylamino-functionalized GQDs (GQD-DMA, 65).
CQDs (O-CQDs, 64) [144] and dimethylamino-functionalized GQDs (GQD-DMA, 65) [145] (Figure 17). Recycling experiments were performed by precipitation (for 63), vacuum distillation of the reactants, products and solvents (for 64), and by CO$_2$ bubbling for 10 min (for 65), without observing significant changes in the results.

Figure 17. Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 63–65.

Remarkably, catalysts 63 and 64 were also able to effectively promote the amine aerobic photo-oxidative heterocoupling, yielding imines 66 in good yields (Scheme 15) [143,144].

Scheme 15. Aerobic photo-oxidative heterocoupling of amines catalyzed by 63 or 64.
Another different type of photocatalyst employed in the aerobic photo-oxidative coupling of benzylamines was a hollow microporous organic network obtained from tris(4-ethylphenyl)amine and 2,6-diido-9,10-anthraquinone (MTAN, 67), rendering 2 in moderate to excellent yields (Figure 18) [146]. Besides this reaction, 67 was also employed in the aerobic photo-oxidative dehydrogenation of secondary amines shown in Scheme 12 (Ar = Ph, R = Bn, ca. 9 wt.%, toluene, O$_2$ (balloon), rt, 24 h, blue LED, 55% yield) [146]. The photocatalyst was not reused.

![Figure 18](image_url)

**Figure 18.** Results obtained in the aerobic photo-oxidative coupling of benzylamines to N-benzylidene benzylamines 2 catalyzed by 67.

In addition, the C$_{70}$ fullerene 26 was also employed in the photo-oxidative homocoupling of benzylamines leading to 2 in excellent yields (0.05 mol%, CH$_3$CN, O$_2$, rt, 24 h, 34 W blue LED, 17 examples, 67–98% yield) [147], and also in the aerobic oxidative dehydrogenation of amines to yield aldehydes 9 (0.05 mol%, CHCl$_3$, O$_2$, rt, 24 h, 34 W blue LED, 14 examples, 37–96% yield) [147]. The recyclability of the photocatalyst was not tested.

From the above-presented results, it can be observed that the structural variety of the recently employed heterogeneous photocatalysts scores higher than in the case of their homogenous counterparts. When polymeric-based heterogeneous photocatalysts are employed, the reaction times are generally shorter, while the reaction yields or conversions are usually high, showing their good photoabsorptivity and capacity to generate ROS. In contrast, the reaction times are usually higher when POFs, COFs and graphene-based photocatalysts are used, while the yields and conversions are excellent. Nevertheless, the results can be considered excellent in almost all oxidative dehydrogenations shown. Considering the crucial point of recyclability, polymeric-based photocatalysts could generally be recycled more easily and in more catalytic cycles than other heterogeneous photocatalyst types, although good results were also obtained with other heterogeneous systems.

3. Oxidative Dehydrogenation of C–O Bonds
3.1. Homogeneous Oxidative Dehydrogenation of C–O Bonds

The selective oxidative dehydrogenation of alcohols to the corresponding carbonyl compounds (ketones, aldehydes, carboxylic acids, etc.) is one of the most important reactions in organic chemistry and has become a very active research area in recent years. To perform this transformation, the use of air or pure O$_2$ as the terminal oxidant, non-toxic metal-free compounds as catalysts and mild conditions under visible light, is interesting from an environmental point of view, the development of effective, versatile and sustainable methodologies being desirable.
The commonly accepted mechanism for the aerobic photocatalytic oxidative dehydrogenation of alcohols is shown in Scheme 16 [148]. Firstly, the photocatalyst (PC) is excited by irradiation with visible light to form its excited state (PC*), which is converted to its free radical state (PC•) by an electron transfer process, and the cation radical of the alcohol is formed. At the same time, an ET process is developed to produce the singlet oxygen ($^1$O$_2$) from the triple oxygen ($^3$O$_2$). The photocatalyst is recovered by another electron transfer process between the PC• and the O$_2$, obtaining the corresponding superoxide radical ion (O$_2$•−) that can oxidize the cation radical of the alcohol to the final carbonyl compound [149]. The singlet oxygen generated before could follow two pathways: the first one consists of a HAT process and radical recombination to form a peroxo hemiacetal intermediate that collapses to the final oxidized product, while in the second one, the singlet oxygen is directly inserted on the carbon bearing the hydroxyl group to form the mentioned peroxo hemiacetal that also collapses to the carbonyl compound [150]. In all the pathways, hydrogen peroxide is generated.

Scheme 16. Commonly accepted mechanism of the aerobic photocatalytic oxidation of alcohols to carbonyl compounds.

Flavin-based promoters are a promising type of photocatalyst that have been employed in different visible light-mediated transformations in recent years [151–155]. In this context, riboflavin tetraacetate (RFTA, 68), derived from riboflavin (vitamin B2), could successfully catalyze the oxidation of different aromatic primary and secondary alcohols to the corresponding aldehydes and ketones 69 in the presence of molecular oxygen under visible light and solvent-free conditions (Scheme 17) [156].

Other flavin-related compounds used as photocatalysts in the oxidation dehydrogenation of alcohols to 69 were 70, which oxidized the benzyl alcohol in more than 95% yield using thiourea as electron mediator (Figure 19) [157], and the flavinium salt 71, which could catalyze the oxidation of para-substituted aromatic alcohols to the corresponding carboxylic acids (69: $R^1$ = Ph, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$; $R^2$ = OH), aldehydes (69: $R^1$ = 4-NO$_2$C$_6$H$_4$; $R^2$ = H) and ketones (69: $R^1$ = 4-ClC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$; $R^2$ = Me) in good yields using trifluoroacetic acid (CF$_3$CO$_2$H) as additive (Figure 19) [158].
Results obtained in the aerobic photo-oxidation of aliphatic alcohols to ketones corresponding ketones obtaining good yields [159]. In the same work, the authors reported another flavin-based photocatalyst (CsCO\(_3\)) for the aerobic photo-oxidation of aromatic secondary alcohols to render ketones using cesium carbonate (CsCO\(_3\), 70 mol%) as additive, O\(_2\) (balloon) as oxidant and under blue light irradiation, obtaining good yields [159]. The flavinium salt 71 (5 mol%) was also recently employed in the oxidative dehydrogenation of aromatic secondary alcohols to render ketones using cesium carbonate (CsCO\(_3\), 70 mol%) as additive, O\(_2\) (balloon) as oxidant and under blue light irradiation, obtaining good yields [159]. In the same work, the authors reported another flavin-based photocatalyst 72 for the oxidation of cyclohexanol, 2-cyclohexenol and decan-2-ol to the corresponding ketones 69 under the same reaction conditions, although in low yields (Figure 20) [159].

The flavinium salt 71 (5 mol%) was also recently employed in the oxidative dehydrogenation of aromatic secondary alcohols to render ketones using cesium carbonate (CsCO\(_3\), 70 mol%) as additive, O\(_2\) (balloon) as oxidant and under blue light irradiation, obtaining good yields [159]. In the same work, the authors reported another flavin-based photocatalyst 72 for the oxidation of cyclohexanol, 2-cyclohexenol and decan-2-ol to the corresponding ketones 69 under the same reaction conditions, although in low yields (Figure 20) [159].
Xanthene-based catalysts have been used in many photoredox reactions in recent years [160–162]. Recently, a neutral form of Rose Bengal 12 (5 mol%), in cooperation with NH₄SCN (3 equiv.), could successfully catalyze the oxidative dehydrogenation of aromatic alcohols, including (9-ethyl-carbazol-3-yl)methanol, (indol-3-yl)methanol and cinnamyl alcohol to the corresponding aldehydes 69 in good to excellent yields [163].

Additionally, other xanthene-related photocatalysts used were Eosin Y (3, 1 mol%), which promoted the oxidation of aromatic and long-chain aliphatic primary alcohols to aldehydes 69 in moderate to good yields under O₂ atmosphere (balloon) and irradiated with a 50 W Xe lamp [164]. Thioxanthone (5–20 mol%) also successfully catalyzed the oxidation of aromatic and aliphatic primary and secondary alcohols (including cinnamyl alcohol, 1,3-diphenylpropargylalcohol, xanthenol, cyclohexanol, borneol, menthol and cholesterol) to aldehydes or ketones 69, obtaining excellent results [160]. The last approach was also applied, in the same work, to the synthesis of quinazolinones by oxidation of alcohols to aldehydes, imine formation using ortho-aminobenzamides, cyclization and final oxidative dehydrogenation of a C–N bond.

Other simple molecules have been employed as photocatalysts to carry out the aforementioned oxidation. Thus, metal-free TPP (0.005 mol%) promoted the oxidative dehydrogenation of aromatic and aliphatic alcohols to aldehydes and ketones 69 in low yields under solvent-free and ambient conditions [165]. In this reported strategy, epoxides of cinnamyl alcohol and cinnamaldehyde, and the hydroperoxide of the cycloheptanol, were generated as byproducts in the corresponding reactions. In addition, the use of 9-fluorenone as photocatalyst (3–6 mol%) allowed for the obtention of aldehydes or ketones 69 from alcohols (including xanthenol, cyclohexanol and heteroaromatic substrates) in moderate to excellent yields under blue light irradiation [149]. Moreover, tetrabutylammonium tribromide (TBATB, 13 mol%) promoted the formation of aldehydes and ketones 69 from alcohols in excellent isolated yields under violet or blue light irradiation [166], a low amount of the corresponding carboxylic acid being observed. Furthermore, sodium trifluoromethanesulfinate (5 mol%) catalyzed the oxidation of secondary alcohols to ketones 69 under violet light, obtaining very good results [167].

TBATB has also been used as catalyst for the photo-oxidation of silyl ethers to aldehydes and ketones 69, obtaining low to excellent yields (Scheme 18) [167].

\[
\text{OTBDMS} \quad \xrightarrow{\text{TBATB (25 mol%)}} \quad \text{R}^1\text{R}^2 \quad \xrightarrow{\text{CH}_3\text{CN, air, rt, 5–20 h, 3 W blue LEDs}} \quad \text{R}^1\text{R}^2
\]

\[\text{R}^1 = \text{Ar}, \text{CH}_3\text{CH} = \text{CH} \text{CH}_3; \quad \text{R}^2 = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3\]

Scheme 18. Aerobic photo-oxidation of primary and secondary tert-butylidemethylsilyl ethers catalyzed by TBATB.

Anthracene-based promoters have also been employed to photocatalyze the oxidative dehydrogenation of alcohols to carbonyl compounds 69. Thus, the water-soluble sodium anthraquinone-2-sulfonate (SAS, 73, ca. 34 mol%) allowed for the obtention of aldehydes and ketones 69 from aromatic and aliphatic alcohols (including cyclohexanol, 1,2,3,4-tetrahydronaphthol and pentanol) under O₂ atmosphere, although obtaining conversions below 20% [168]. This anthraquinone 73 was recently used in another reported strategy for the cascade transformation of racemic alcohols to enantiopure amines 74 in moderate to excellent yields, using different ω-transaminases as chiral inducers, sodium phosphate (NaPi), pyridoxal-5-phosphate (PLP) and isopropylamine (IPA), the carbonyl compounds 69 being the intermediates of the reaction (Scheme 19) [169].
lammonium phosphate (TBAP) as additives [174] and a pyridinium derivative (TETPY)
aldehydes and ketones

Results obtained in the aerobic photo-oxidation of aromatic and aliphatic alcohols to
def hydes and ketones

Figure 21.
cascade transformation of racemic alcohols into enantiopure amines 74 by oxidative dehydrogenation catalyzed by 73 and enantioselective transamination.

9,10-dihydroanthracene (10 mol%) promoted the photo-oxidation of the benzyl alcohol, hexanol, cyclohexanol and furfuryl alcohol to their respective aldehydes and ketones in very good yields, using pure O2 and irradiated with a tungsten-bromine lamp [170]. Another observed product from primary alcohols was the corresponding carboxylic acid.

Apart from the catalysts shown, a group of metal-free nitrogen-containing photocatalysts has been employed to synthesize carboxylic compounds by the aerobic oxidative dehydrogenation of alcohols. This group includes a tetrazine-based catalyst (pytz, 75) using two methodologies [171], a dicyanopyrazine-derived chromophore (DPZ, 76) used in cooperation with N-hydroxysuccinimide (NHS) and dibenzyl phosphoric acid (DBPA) [172], and an iminoquinone-based catalyst (PA, 77) [173], enabling all of them to obtain aldehydes and ketones 69 from alcohols in moderate to excellent yields (Figure 21).

Figure 21. Results obtained in the aerobic photo-oxidation of aromatic and aliphatic alcohols to aldehydes and ketones 69 catalyzed by 75–77.

In addition, a carbazole-based promoter (4CzIPN, 78) with quinuclidine and tetrabutylammonium phosphate (TBAP) as additives [174] and a pyridinium derivative (TETPY 3Br, 79) [148] were successfully used in the same mentioned transformation (Figure 22). The carbazole photocatalyst 78 has also been employed in a novel strategy of oxidizing alco-
hols to aldehydes and coupling them in situ with amines to generate the corresponding amides [175].

In addition, a carbazole-based promoter (4CzIPN, 78) with quinuclidine and tetrabutyrammonium phosphate (TBAP) as additives [174] and a pyridinium derivative (TETPY·3Br, 79) [148] were successfully used in the same mentioned transformation (Figure 22). The carbazole photocatalyst 78 has also been employed in a novel strategy of oxidizing alcohols to aldehydes and coupling them in situ with amines to generate the corresponding amides [175].

Figure 22. Results obtained in the aerobic photo-oxidation of aromatic and aliphatic alcohols catalyzed by 78 and 79.

An attractive and selective aerobic oxidative dehydrogenation of carbohydrates achieved after irradiation with visible light under aerobic conditions was recently developed, employing an acridinium salt 80 as catalyst and quinuclidine as HAT mediator, obtaining the corresponding ketosugars 81 in moderate yields (Scheme 20) [176].

Scheme 20. Aerobic photo-oxidation of carbohydrates to ketosugars 81 catalyzed by 80.

An approach to the oxidation of different β-O-4 lignin models was developed, employing 4,4′-bis(diphenylamino)benzophenone (DPA-BP, 82) as photocatalyst and N-hydroxyphthalimide (NHPI) as co-catalyst, leading to the corresponding carbonyl...
An approach to the oxidation of different β-O-4 lignin models was developed, employing 4,4′-bis(diphenylamino)benzophenone (DPA-BP, 2.5 mol%), 82 (1.5 mol%), and NHPI (25 mol%) as photocatalyst and co-catalyst, leading to the corresponding carbonyl compounds 83 in very good yields (Scheme 21) [177]. In the same work, 82 (1.5 mol%) was also used in combination with NHPI (15 mol%) in the aerobic photo-oxidation of 4-methoxyphenethyl alcohol to its acetophenone in 97% yield.

![Scheme 21.](image)

Scheme 21. Aerobic photo-oxidation of β-O-4 lignin models catalyzed by 82.

The proposed reaction mechanism leading to 83 is shown in Scheme 22. Thus, visible light excites the catalyst 82 to the corresponding excited state 82*. This excited state generates a phthalimide-N-oxyl radical (PINO) from NHPI through a proton-coupled electron transfer process (PCET). Then, a hydrogen atom from the alcohol is abstracted by the PINO radical through a HAT process, generating an α-hydroxybenzylic radical and recovering NHPI. This radical reacts with O₂ to form a peroxy radical and evolves to the final ketone, abstracting a hydrogen atom from NHPI. The same process occurs to recover the catalyst from ketyl 82-H [177].

![Scheme 22.](image)

Scheme 22. Proposed mechanism for the photo-oxidation of β-O-4 lignin models catalyzed by 82 and NHPI.

Continuing with lignin models, 78 has been employed as catalyst, in combination with a phosphate and a thiol, in the photo-oxidative fragmentation of lignin model derivatives to obtain the corresponding carbonyl products 84 and the corresponding phenol in moderate...
to good yields (Scheme 23) [178]. In the same work, the methodology was also applied to diol derivatives presenting several backbones and leaving groups, obtaining good results.

\[
\begin{align*}
\text{R}^1 &= \text{H}, 4\text{-MeO}, 3.4\text{-}(\text{MeO})_2, \\
\text{R}^2 &= \text{H}, \text{CH}_2\text{OH}, \\
\text{R}^3 &= \text{H}, 2\text{-MeO}, 2.6\text{-}(\text{MeO})_2, \\
\text{R}^4 &= 3.5\text{-}(\text{MeO})_2, 4\text{-Me}
\end{align*}
\]

Scheme 23. Aerobic photo-oxidative cleavage of lignin model derivatives catalyzed by 78.

This oxidative cleavage occurs through a similar mechanism to the one shown in Scheme 22 to generate the ketone (in this case the thiol is the co-catalyst). Then, a SET process occurs reducing it to a ketyl radical anion, and the photocatalyst is regenerated. This radical suffers a $\beta$ C(sp$^3$)-O bond cleavage due to its very poor stability, generating a carbonyl radical and an anion from the leaving group. Finally, the radical and the anion are transformed into the corresponding fragmentation products [178].

The aerobic oxidative dehydrogenation of phenols or naphthols to quinones or naphthoquinones, important in some biochemical transformations [179], is another reaction carried out with metal-free catalysts. Thus, TPP was used as photocatalyst in the photo-oxidation of naphthols to naphthoquinones 85 under continuous-flow conditions, obtaining low to good yields (Scheme 24) [180].

\[
\begin{align*}
\text{R}^1 &= \text{H}, \text{Me}, \text{OH}, \text{NO}_2, \text{Ac}, \\
\text{NHA}c, \text{CH(OH)}/\text{CH}_3, \\
\text{R}^2 &= \text{H}, \text{NHA}c, \\
\text{R}^3 &= \text{H}, \text{Cl}, \text{Br}, \text{NHA}c, \\
\text{R}^4 &= \text{H}, \text{NH}_2, \text{OH}, \\
\text{R}^5 &= \text{H}, \text{OH}
\end{align*}
\]

Scheme 24. Aerobic oxidative dehydrogenation of naphthols to naphthoquinones 85 catalyzed by TPP.

The proposed mechanism of this reaction is shown in Scheme 25. Firstly, the photocatalyst (TPP) is excited to its singlet excited state ($^1\text{TPP}^*$) by irradiation with visible light. Next, an ISC process is produced to generate the triplet excited state of the catalyst ($^3\text{TPP}^*$) from the singlet one. To recover the promoter, triplet oxygen ($^3\text{O}_2$) is converted to singlet oxygen ($^1\text{O}_2$), which reacts with the starting naphthol by a [4+2] cycloaddition. Then, the formed cycle is opened by an H transposition, and, finally, a molecule of H$_2$O is lost to generate the final product.
was also applied to a multistep formation of 1,2,4-trioxanes from para-quinones (85).

Results obtained in the aerobic oxidative dehydrogenation of 1,5-dihydroxynaphthalene to Juglone (85: R₁ = R₂ = R₅ = H, R₄ = OH) catalyzed by 86. In addition, it has also been employed in the photo-oxidation of para-substituted phenols in a continuous-flow and high-pressure system on a multigram scale using supercritical CO₂, leading to para-hydroperoxy quinones in moderate to excellent yields [182]. This system was also applied to a multistep formation of 1,2,4-trioxanes from para-phenol derivatives and alkyl or aromatic aldehydes in very good yields [182].

Other catalysts used in the photo-oxidation of 1,5-dihydroxynaphthalene to Juglone (85: R₁ = R₂ = R₅ = H, R₄ = OH) were two perylenebisimide-[60]fullerene systems dissolved in CH₂Cl₂/MeOH (9:1) (86a,b) (Figure 23) [183], although only the quantum yield of the transformation was reported.

![Scheme 25. Proposed mechanism of the aerobic oxidative dehydrogenation of naphthols to naphthoquinones 85.](image)

The same photocatalyst (TPP) was used in the oxidative dehydrogenation of 1,5-dihydroxynaphthalene working under flow conditions, obtaining the corresponding naphthoquinone (Juglone, 85: R₁ = R₂ = R₅ = H, R₄ = OH) in very good yield [181]. In addition, it was also employed in the photo-oxidation of para-substituted phenols and alkyl or aromatic aldehydes in very good yields [182].

In addition, a mixture of two 1,7-phenanthroline based bis-BODIPYs with Cl- or SMesubstituents (87a,b) [184] and two BODIPY-carbazole derivatives (88a,b) [185] photocatalyzed the same oxidation of 1,5-dihydroxynaphthalene to Juglone (85: R₁ = R₂ = R₅ = H, R₄ = OH), only reporting the obtained quantum yield in the first case (Figure 24). Furthermore, methylene blue 1 has been employed in the photo-oxidation of different phenols and...
naphthols to quinones or naphthoquinones under continuous-flow conditions, obtaining good results [186].

![Figure 24. Results obtained in the aerobic oxidative dehydrogenation of 1,5-dihydroxynaphthalene to Juglone (85: R₁ = R² = R₃ = H, R₄ = OH) catalyzed by 87 and 88.](image)

In all these results, it is shown that the oxidative dehydrogenation of C–O bonds to the corresponding carbonyls has been successfully carried out using almost all the recently employed homogeneous photocatalysts, except in the case of some promising flavins. Xanthene-based and nitrogen-containing photocatalysts, such as tetrazines or pyrazines, demonstrated remarkable activity in the mentioned transformation in short reaction times, showing a high capacity to generate ROS. It is worth mentioning that some simple photocatalysts, for instance, 78, 80 and 82, as well as TPP, were able to successfully catalyze the photo-oxidation of several alcohols present in sugars, lignin model derivatives and naphthols, resulting in interesting compounds for the pharmacological industry.

3.2. Heterogeneous Oxidative Dehydrogenation of C–O Bond

The aerobic photo-oxidation of C–O bonds under heterogeneous conditions has been carried out extensively in recent years, using several photocatalysts [7,20,62]. One of the reactions included in this group is the oxidation of primary and secondary alcohols to their carbonyl products. This transformation was performed, for instance, using polymer-based materials as photocatalysts. Thus, the melamine-based polymer 51 promoted the photo-oxidation of benzyl alcohols to the corresponding aldehydes 69 in moderate yields [115]. Other polymers used in this transformation were a trithiocyanuric acid-based material composed of disulfide units 89 (Figure 25) [187], an heptazine-based porous material with ethane-1,1,2,2-tetrayl tetraaniline units (POP-HE, 90) (Figure 25) [188], a flavin-based mesoporous polymeric network with ethylene glycol dimethacrylate units (RFITMA-co-EGDMA, 91) (Figure 25) [189], and the same hyper-cross-linked material was used in the aerobic oxidative coupling of amines and the dehydrogenation of dibenzylamine [111]. The recyclability of these photocatalysts was successfully carried out by filtration and washing with ethanol and acetone (for 90) and through a filter-equipped glass reactor (for 91), while 89 was not reused.
As in heterogeneous C–N bond oxidative dehydrogenation, carbon nitrides have been used frequently in heterogeneous C–O bond photo-oxidations. In particular, the aerobic oxidation of aliphatic and aromatic alcohols under visible light irradiation has been promoted by several polymeric carbon nitrides. Thus, a melamine-based polymeric promoter [190], a hydrazine-linked heptazine carbon nitride 92 (Figure 26) [191] and a coral-like melamine-based polymeric material [192] were employed in the mentioned transformation (92 only being employed in the oxidation of the benzyl alcohol to benzaldehyde), obtaining the corresponding aldehydes 69 in moderate to excellent conversions in all cases. The coral-like material was reused by centrifugation and washed with acetonitrile and ethanol, observing similar conversions in all the catalytic cycles. The recycling of the other two photocatalysts was not reported.

Several graphitic carbon nitrides were also employed as photocatalysts in the transformation of alcohols to aldehydes or ketones. Thus, a carbon-nanodot-doped material derived from 33 [193], a few-layered phosphorene nanostructure graphitic material [194], the basic unmodified graphitic carbon nitride 33 [119,195,196] and several 33 modified by thermal, chemical and mechanical processes [197], with N vacancies [198] and doped with P [199], O [200] and S atoms [201], could successfully catalyze the mentioned reaction under visible light irradiation. The photocatalysts were able to be reused after centrifugation or filtration without decreasing their catalytical activity.

Other carbon nitride-based photocatalysts used in the same process were a mesoporous material combined with N-hydroxyphthalimide [202], a porous carbon nitride packed in a reactor [123], a boron carbon nitride (BCN-500, 93) (Figure 27) [203,204], which is a carbon nitride-based photocatalyst applied in energy and environmental areas [205–207], and an aerogel composed of carbon nitride nanolayers [208], obtaining the corresponding aldehydes and ketones (only in the first case) from benzyl alcohols in low to excellent conversions. The recyclability of the catalysts was carried out by filtration and washing (for the mesoporous material) and by centrifugation (for 93), maintaining their activity. The recycling of the other photocatalysts was not reported.

Figure 25. Results obtained in the aerobic photo-oxidation of benzyl alcohol to benzaldehyde catalyzed by 89–91.
Figure 26. Result obtained in the aerobic photo-oxidation of benzyl alcohol to benzaldehyde catalyzed by 92.

Figure 27. Results obtained in the aerobic photo-oxidation of benzylic alcohols to aldehydes catalyzed by 93.
CQDs have also been employed to catalyze the aerobic photo-oxidation of alcohols to carbonyl derivatives. Thus, the use of the oxygen-rich CQDs (O-CQDs, 64) [144], also successfully employed in the aerobic photo-oxidative coupling of benzylamines (Schemes 2 and 15), and a polyethylene-based material [209], resulted in the preparation of aldehydes in low or high conversions, respectively. The photocatalysts were recycled by filtration and rinsing in CH$_2$CN (for 64) and by extraction with ethyl acetate (for the polyethylene-based promoter) without any change in their activity.

Similarly, graphene oxide-based promoters have demonstrated good activity in the oxidation of aromatic and aliphatic alcohols leading to the corresponding carbonyl products when irradiated with visible light. In this sense, this reaction was performed well using a graphene oxide/carbon nitride hybrid material [210] and a surface-modified graphene oxide with TPP (GO-TPP40, 94) (Figure 28) [211], being able to recycle the last one by dispersion in H$_2$O and sonication for 1 h with a decrease in its activity in the fourth cycle.

Figure 28. Results obtained in the aerobic photo-oxidation of alcohols to aldehydes catalyzed by 94.

Immobilizing an organic molecule on mesoporous silica is a good strategy for preparing heterogeneous photocatalysts. In this manner, a covalent triazine framework supported on mesoporous silica (CTF-Th@SBA-15, 95) [212] and two riboflavin derivatives (96a,b) anchored to mesoporous silica MCM-41 [213] enabled the process of aerobic photo-oxidation of several aromatic alcohols to render aldehydes or ketones in low to excellent conversions (Figure 29). The catalyst 95 was recovered by centrifugation, its activity slightly decreasing along with cycles. In the case of 96, recycling was not reported.

The photocatalytic transformation of biomass-derived chemicals has been explored in recent years [214–216], and there are some recently reported examples in which metal-free photocatalysts are employed. Starting with polymer-based promoters, the CMP 41 catalyzed the aerobic oxidative dehydrogenation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfurfural (DFF, 97) in 25% yield under visible light irradiation (Scheme 26) [217]. The recyclability of 41 was studied, but on a different reaction.

Other metal-free catalysts used in this transformation included a melamine-based polymeric carbon nitride, also employed in the photo-oxidation of two benzyl alcohols to the corresponding aldehydes shown in Scheme 17 [218], the basic graphitic carbon nitride [219,220], a mesoporous carbon nitride [221] and the covalent triazine framework supported on mesoporous silica [222]. In all cases, moderate conversions to 97 were obtained when irradiated with visible light or using solar light. The photocatalytic materials were recycled by decantation (for the melamine-based polymeric carbon nitride), by decantation and washing with water or centrifugation (for 33), by washing with water and ethanol (for the mesoporous carbon nitride) and by filtration and washing with water and acetone (for 95) with no remarkable changes in the results.
Similarly, graphene oxide-based promoters have demonstrated good...98, R² = R³ = H, R⁴ = OH) in 75% conversion [224]. Other photocatalysts used in the same photo-oxidation of 1,5-dihydroxynaphthalene were a benzoquinone-functionalized carbon nitride (CN-T, 98) [225] and two perylenebisimide-fullerene dyads (99a,b) [226], obtaining Juglone (85, R¹ = R² = R³ = H, R⁴ = OH) in high yields (Figure 30). Recycling of the methylene blue-dyed polyester fabrics and 99 was not carried out, while 98 was recovered and reused three times, with a slight decrease in its activity at the third catalytic cycle.
In addition, two C_{60}-BODIPY photosensitizers (C_{60}-B1/C_{60}-B2, 100a,b) [227], a C_{70}-BODIPY-triphenylamine triad (C_{70}-B-T, 101) [228] and a meso-tetakis(N-methylpyridinium-4-yl)porphyrin supported on the sodium salt of Amberlyst 15 nanoparticles and complexed with formic acid (nanoAmbSO_{3}@H_{2}TYMPyP(HCO_{2}H)_{2}, 102a) [229] and BF_{3} (nanoAmbSO_{3}@H_{2}TYMPyP(BF_{3})_{2}, 102b) [230] were employed in the mentioned transformation, obtaining Juglone (85, R^{1} = R^{2} = R^{3} = H, R^{4} = OH) in high yield (only quantum yield was given in the case of using 100 and 101) (Figure 31). The recyclability of 100 and 101 was not tested, while 102a and 102b were recycled but in a different photo-oxidation reaction.

Furthermore, non-complexed 102 in a continuous flow photoreactor [231] and a gigantic porphyrin-based organic cage with 12 units of tetra(4-aminophenyl)porphyrin and 24 moieties of 2-hydroxy-5-octyloxy-1,3-benzenedicarboxaldehyde [232] were used as photocatalysts in the preparation of Juglone (85, R^{1} = R^{2} = R^{3} = H, R^{4} = OH) from 1,5-dihydroxynaphthalene in good to excellent yields. However, those catalysts were not recycled.

An oxidative photocatalytic cleavage of the C–C bond of lignin models was recently reported using a mesoporous carbon nitride as photocatalyst, leading to 84 in excellent conversions and moderate yields [233]. In the reaction, the corresponding carboxylic acid from 84 could also be obtained in low to moderate yields. The reusability of the carbon nitride was studied, and the cleavage could be performed again for up to five cycles.

Another recent aerobic oxidative C–C bond cleavage, in this case in vicinal diols, has been reported in two works using the carbon nitride 33 in a micellar medium with cetyltrimethyl ammonium bromide (CTAB) as surfactant [234] and the graphitic form of 33 [235], rendering the corresponding aldehydes or ketones 69 in moderate to good yields and also performing a broad scope of internal and monosubstituted diols (Scheme 27). In the first case, the catalyst was recycled 10 times by extracting the product and adding more starting reagent to the water phase that contained the catalyst. In the case of the graphitic form of 33, it was recovered by filtration and washing with dichloromethane, being reused for up to five cycles.
The proposed mechanism for this aerobic photo-oxidative cleavage of diols is shown in Scheme 28. Firstly, the photocatalyst (PC) is excited, producing electrons (e\(^{-}\)) and holes (h\(^{+}\)). Then, one hydroxyl of the 1,2-diols is oxidized by a hole, generating the radical A.

Scheme 27. Aerobic photo-oxidative C–C bond cleavage of 1,2-diols catalyzed by 33 or graphitic 33.
a proton, while \( \text{O}_2 \) is reduced to the superoxide radical by an electron. At this moment, two pathways are possible depending on whether aldehydes or ketones are generated: pathway 1, in which the corresponding aldehyde or ketone and an \( \alpha \)-hydroxy radical are generated through a \( \beta \)-scission of the radical A, the \( \alpha \)-hydroxy radical being transformed subsequently to a second aldehyde or ketone by a HAT process; and pathway 2, in which an intermediate B and \( \text{H}_2\text{O} \) are produced from the reaction between the radical A and the superoxide radical, the intermediate B being hydrolyzed immediately to generate an aldehyde and a germinal diol that suffers dehydration to render two other aldehydes [235].

![Scheme 28. Proposed mechanism for the aerobic photo-oxidative C–C bond cleavage of 1,2-diols.](image)

Observing the previous examples, it can be deduced that, in terms of reaction yields and conversions, the best photocatalysts for the heterogeneous oxidative dehydrogenation of alcohols to the corresponding carbonyl derivatives were the boron carbon nitride 93, the graphene oxide/carbon nitride hybrid material 94 and the immobilized ones in silica, while polymer-based photocatalysts promoted transformation in lower yields. In terms of reaction time, the mentioned catalyst types added to BODIPY-based ones promoted different photo-oxidation reactions faster than the other ones. These differences are probably related to different photoabsorptivities and ROS generation abilities. The recyclability of all the photocatalysts was carried out generally simply and conveniently, and all materials were able to be reused for several catalytic cycles, maintaining their activity.

4. Conclusions

The oxidative dehydrogenation of C–N and C–O bonds leading to C=N and C=O bonds, catalyzed by metal-free molecules under visible light irradiation and using atmospheric air or pure \( \text{O}_2 \) as readily available and cheap oxidant, is a powerful strategy for preparing compounds, such as imines and carbonyl derivatives from amines and alcohols, being also interesting due to the use of environmentally friendly and sustainable reaction conditions. In this review, the recent advances and activities in this field have been shown, a broad variety of metal-free homogeneous and heterogeneous photocatalysts being employed, achieving excellent results. For instance, cheap organic dyes, such as methylene blue or Rose Bengal, are examples of homogeneous promoters used successfully, while polymeric- or carbon nitride-based materials have been used as heterogeneous catalysts among others, showing very good performance and being able to be recovered in most cases without losing their activity, which adds additional value to the methodology. However, some oxidations of biomass-derived chemicals, such as lignin models and 5-hydroxymethylfurfural, are less explored, and the development of more methodologies...
in this field is necessary. Undoubtedly, the oxidative dehydrogenation of C–N and C–O bonds under these convenient reaction conditions will be explored and improved in the nearest future, particularly in the case of recoverable photocatalysts devoted to their use in flow conditions and applicable to industrial processes.

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