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Aerobic photocatalytic oxidation of activated benzylic and allylic alcohols to carbonyl compounds catalyzed by molecular iodine

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Abstract—An efficient, selective and environmentally benign photocatalytic system in acetonitrile has been developed for aerobic oxidation of activated benzylic and allylic alcohols into their corresponding aldehydes and ketones without the need for a transition metal in moderate to excellent yields with a catalytic amount of iodine. Very high inter- and intramolecular chemoselectivities are observed when benzylic OH groups are oxidized in the presence of aliphatic (nonbenzylic) hydroxyls.

The transformation of alcohols into aldehydes and ketones is important in organic chemistry, both for laboratory-scale experiments and in manufacturing processes.[1] Unfortunately, the vast majority of common oxidants are required in at least stoichiometric amounts. Moreover, they are usually hazardous or toxic and generate large quantities of noxious by-products.[2] From both economic and environmental points of view, there is a need for selective oxidation using molecular oxygen as an oxidant under mild conditions. Although many catalytic methods have been reported for the aerobic oxidation of alcohols to the corresponding carbonyl compounds, expensive and toxic transition metal catalysts, mainly ruthenium,[3] palladium[4] and copper[5] compounds are required to complete the oxidation satisfactorily. Some oxidations are carried out in the presence of reducing agents such as aldehydes which are eventually converted into carboxylic acids.[6] In addition, most of the available transition metal catalytic oxidation processes suffer from severe limitations, being usually only effective with reactive alcohols such as benzylic and allylic alcohols, or require high pressures, high temperatures and high catalyst loadings. The use of metal-free catalysts for the selective oxidation of organic substrates is very appealing.[7] One of the most useful synthetic applications of this approach is the chemoselective oxidation of alcohols promoted by oxoammonium salts.[8] These remarkably active species can be conveniently regenerated through the action of terminal oxidants on stable free nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Efficient methods for the conversion of alcohols to carbonyl derivatives under mild conditions have been thus developed using TEMPO as a catalyst and stoichiometric amounts of inexpensive, safe and easy to handle nonmetallic oxidants including sodium or calcium hypochlorite,[9] sodium chlorite,[10] sodium bromite,[11] *tert*-butyl hypochlorite,[12] Oxone,[13] *N*-chlorosuccinimide,[14] [bis(acetoxy)iodo]benzene,[15] *m*-chloroperbenzoic acid,[16] trichloroisocyanuric acid[17] and or iodine.[18] However, the separation of the products from TEMPO can require lengthy work-up procedures, especially when reactions are run on a large scale.

Despite their obvious economical and ecological benefits, few transition metal-free catalytic systems are available for the transformation of alcohols into aldehydes and ketones using molecular oxygen or air as the ultimate and stoichiometric oxidant.[19] In this context, photochemical processes that take place under mild conditions, that is, room temperature and atmospheric pressure or, more importantly, photocatalytic processes that avoid stoichiometric reagents are particularly

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Keywords: Benzylic alcohols; Photocatalytic; Oxidation; Aerobic; Iodine.

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attractive for synthetic purposes from economic and environmental points of view.[20]

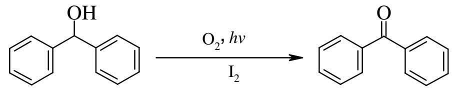
Recently, we reported a photocatalytic oxidation system, where a wide range of alcohols was converted into their carbonyl derivatives in high yields using a catalytic amount of silica-supported polyoxometalate ($H_3PW_{12}O_{40}/SiO_2$) under an oxygen atmosphere.[21] However, that catalytic system required a transition metal. Herein, we report an efficient, highly selective and metal-free photocatalytic method for the oxidation of activated benzylic and allylic alcohols to carbonyl compounds using a catalytic amount of I_2 under an O_2 atmosphere as the stoichiometric reoxidant of the catalyst.

The oxidation of benzhydrol (**1**) was first investigated as a model substrate. In our initial experiments, we found that when a mixture of this alcohol (1 mmol) and I_2 (1 mmol) in acetonitrile was irradiated with a high pressure 400 W mercury lamp as the light source under an O_2 atmosphere, benzophenone (**2**) was formed as the only product in an 88% yield within 3 h at room temperature (Scheme 1).

It is noteworthy to mention that the dark brown colour of the reaction solution due to iodine did not change during the progress of reaction. Also, titration of the reaction mixture with sodium thiosulfate in the presence of starch indicated that the amount of iodine also did not change during the reaction. These observations confirm that iodine probably plays a catalytic role in the reaction and is regenerated in situ under O_2. To verify this, it was decided to lower the amount of iodine (Table 1). As can be seen in Table 1, decreasing the quantity of iodine did not impair the oxidation of benzhydrol. Although the reaction took longer to reach completion, formation of benzophenone was accomplished in good yield using as little as 0.05 equiv of the catalyst. As a matter of convenience, we settled on 0.25 equiv of I_2 to examine the solvent and substrate scope of oxidation.

We next screened other organic solvents for the aerobic oxidation. Experimental results showed that most of the solvents screened were suitable for this aerobic oxidation (Table 2). The primary difference between the solvents was their ability to solubilize the substrates. Among the solvents examined, we considered acetonitrile as the solvent of choice as it is inert photochemically and all the alcoholic substrates and their products were soluble in this solvent at rt.

Table 1. Oxidation of benzhydrol in the presence of different amounts of I_2[a]



Entry	I_2 (mmol)	Irradiation time (h)	Yield[b] (%)
1	0.05	6	82
2	0.1	5	80
3	0.25	3	90
4	0.5	3	92
5	0.75	3	88
6	1	3	88
7	1.25	3	95
8	1.5	3	90
9	2	3	90
10	3	3	87

[a] Reaction conditions: benzhydrol (1 mmol), CH_3CN (25 mL), O_2 atmosphere, rt.

[b] Yields are for isolated pure benzophenone.

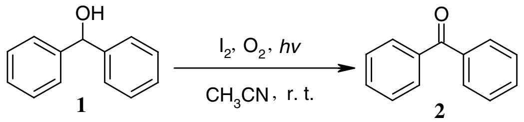
Table 2. Photolysis of benzhydrol in various organic solvents[a]

Entry	Solvent	Irradiation time (h)	Yield[b] (%)
1	*n*-Hexane	2.5	95
2	CH_3CN	3	90
3	$CHCl_3$	2.5	95
4	Et_2O	2	95
5	Toluene	3.5	78
6	CH_2ClCH_2Cl	3	85
7	C_6H_6	3	80
8	Cyclohexane	3	83
9	AcOEt	3	90
10	PhCl	3	87

[a] Reaction conditions: benzhydrol (1 mmol), I_2 (0.25 mmol), solvent (25 mL), O_2 atmosphere, rt.

[b] Yields are for isolated pure benzophenone.

In control experiments, the reaction in the dark or in the absence of I_2 delivered no product thus confirming that I_2 and light were essential for the reaction. Indeed, when the oxidation of benzhydrol was carried out in the presence of air instead of O_2, benzophenone was formed but in a reduced yield (46%). Under an N_2 atmosphere, benzophenone was obtained in only a stoichiometric amount to the iodine catalyst and the brown colour of the reaction mixture almost disappeared.

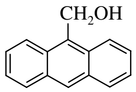
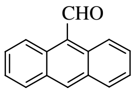
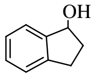
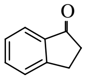
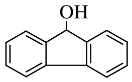
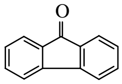


Scheme 1.

We next examined the oxidation of a variety of alcohols under standard conditions. Primary and secondary alcohols such as benzylic, allylic, aliphatic, and even sulfur/nitrogen-containing alcohols were evaluated as substrates for the aerobic oxidation.

All the primary benzylic alcohols were converted into their corresponding aldehydes and no over-oxidation to acids was observed (Table 3, entries 1–21). Primary benzylic alcohols possessing electron-donating substituents such as methyl, *iso*-propyl, *tert*-butyl and methoxy on the aromatic ring, and also halogen-substituted benzyl alcohols were oxidized to the corresponding aldehydes in high yields (Table 3, entries 2–13). On the other hand, benzylic alcohols containing electron-withdrawing groups required longer reaction times and gave the corresponding benzaldehydes in lower yields (Table 3, entries 14–18). Most of the reactions of these substrates did not reach completion and increasing the

Table 3. Photocatalytic oxidation of various activated alcohols with O_2 catalyzed by I_2

Entry	Substrate	Product[a]	Irradiation time (h)	Yield[b] (%)
1	$C_6H_5CH_2OH$	C_6H_5CHO	5	88
2	p-$MeC_6H_4CH_2OH$	p-MeC_6H_4CHO	2.5	94
3	o-$MeC_6H_4CH_2OH$	o-MeC_6H_4CHO	3	92
4	p-$Pr^iC_6H_4CH_2OH$	p-$Pr^iC_6H_4CHO$	3	75
5	p-$Bu^tC_6H_4CH_2OH$	p-$Bu^tC_6H_4CHO$	3.5	80
6	p-$MeOC_6H_4CH_2OH$	p-$MeOC_6H_4CHO$	3	92
7	o-$MeOC_6H_4CH_2OH$	o-$MeOC_6H_4CHO$	3	90
8	m-$MeOC_6H_4CH_2OH$	m-$MeOC_6H_4CHO$	3	88
9	2,4-$(MeO)_2C_6H_3CH_2OH$	2,4-$(MeO)_2C_6H_3CHO$	2	96
10	3,4,5-$(MeO)_3C_6H_2CH_2OH$	3,4,5-$(MeO)_3C_6H_2CHO$	2	95
11	p-$ClC_6H_4CH_2OH$	p-ClC_6H_4CHO	6	85
12	2,4-$Cl_2C_6H_3CH_2OH$	2,4-$Cl_2C_6H_3CHO$	6	85
13	p-$BrC_6H_4CH_2OH$	p-BrC_6H_4CHO	5	87
14	p-$PhC_6H_4CH_2OH$	p-PhC_6H_4CHO	6	45
15	p-$CF_3C_6H_4CH_2OH$	p-$CF_3C_6H_4CHO$	8	60
16	p-$NO_2C_6H_4CH_2OH$	p-$NO_2C_6H_4CHO$	8	55
17	o-$NO_2C_6H_4CH_2OH$	o-$NO_2C_6H_4CHO$	8	45
18	m-$NO_2C_6H_4CH_2OH$	m-$NO_2C_6H_4CHO$	8	35
19	1-$C_{10}H_7CH_2OH$[c]	1-$C_{10}H_7CHO$	5	78
20	2-$C_{10}H_7CH_2OH$[d]	2-$C_{10}H_7CHO$	6	70
21			4	75
22	$C_6H_5CHOHCH_3$	$C_6H_5COCH_3$	3	90
23	p-$MeC_6H_4CHOHCH_3$	p-$MeC_6H_4COCH_3$	2	94
24	p-$NO_2C_6H_4CHOHCH_3$	p-$NO_2C_6H_4COCH_3$	5	80
25	$C_6H_5CHOHC_2H_5$	$C_6H_5COC_2H_5$	4	84
26	$C_6H_5CHOH(n\text{-}C_3H_7)$	$C_6H_5CO(n\text{-}C_3H_7)$	4	82
27	$C_6H_5CHOH(cyclo\text{-}C_3H_5)$	$C_6H_5CO(cyclo\text{-}C_3H_5)$	3	80
28	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CO$	3	90
29	p-$ClC_6H_4CHOHC_6H_5$	p-$ClC_6H_4COC_6H_5$	3.5	84
30	$(p\text{-}ClC_6H_4)_2CHOH$	$(p\text{-}ClC_6H_4)_2CO$	3.5	87
31	p-$MeOC_6H_4CHOHC_6H_5$	p-$MeOC_6H_4COC_6H_5$	2.5	92
32	$(p\text{-}MeOC_6H_4)_2CHOH$	$(p\text{-}MeOC_6H_4)_2CO$	2.5	95
33	p-$NO_2C_6H_4CHOHC_6H_5$	p-$NO_2C_6H_4COC_6H_5$	4.5	77
34	$(p\text{-}FC_6H_4)_2CHOH$	$(p\text{-}FC_6H_4)_2CO$	7	78
35	$C_6H_5CHOHCOC_6H_5$	$C_6H_5COCOC_6H_5$	8	75
36			2.5	95
37			3	90
38	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	6	85
39	$C_6H_5CH{=}C(CH_3)CH_2OH$	$C_6H_5CH{=}C(CH_3)CHO$	6	82
40	$C_6H_5CHOHCH_2OH$	$C_6H_5COCH_2OH$	8	55
41	p-$MeC_6H_4CHOHCH_2OH$	p-$MeC_6H_4COCH_2OH$	6	78
42	p-$MeOC_6H_4CHOHCH_2OH$	p-$MeOC_6H_4COCH_2OH$	6	84
43	p-$ClC_6H_4CHOHCH_2OH$	p-$ClC_6H_4COCH_2OH$	6	75
44	p-$NO_2C_6H_4CHOHCH_2OH$	p-$NO_2C_6H_4COCH_2OH$	8	50

[a] Product identification was accomplished by the comparison of physical and spectral data (TLC, mp, IR, ^1H NMR and or MS) with known compounds.

[b] Yields are for isolated pure products.

[c] 1-Naphthyl methanol.

[d] 2-Naphthyl methanol.

irradiation time did not improve the yields. Other arylmethyl alcohols gave the corresponding benzaldehydes in good yields (Table 3, entries 19–21).

Secondary benzylic substrates generally gave very clean, high-yielding reactions (Table 3, entries 22–37). The electronic effect observed for the primary benzylic systems also seems to be prevalent in the case of secondary benzylic systems. For example, 1-(p-nitrophenyl)ethanol (Table 3, entry 24) required a longer reaction time and gave a decreased yield compared to more electron-rich secondary benzylic substrates.

Allylic alcohols, such as cinnamyl alcohol, were also good substrates for this reaction and were converted into the corresponding carbonyl compounds in high yields (Table 3, entries 38 and 39). In these cases, no oxidation of the carbon–carbon double bond was observed.

Unfortunately, this photocatalytic system is restricted to benzylic and allylic alcohols. A number of unreactive substrates included heterocyclic alcohols such as furfuryl alcohol, pyridine-4-methanol and thiophene-2-methanol which probably coordinate to iodine via their heteroatoms (O, N and or S), thereby inactivating the catalyst. Also, aliphatic and aryl-substituted nonbenzylic alcohols such as 3-phenyl-1-propanol were inert and were recovered unchanged even after very long irradiation times (10 h).

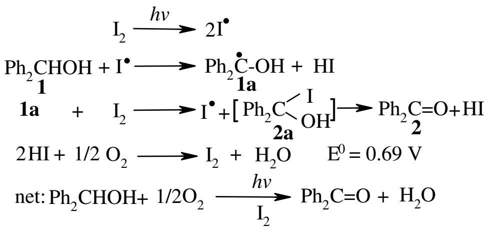
To study the chemoselectivity, a mixture of 1-phenylethanol and 2-phenylethanol was subjected to 3 h irradiation in the presence of I_2 under O_2. GC analysis indicated that the former was oxidized to acetophenone in 92% yield while the latter was unchanged. These findings prompted us to investigate the oxidation of 1,2-diols containing benzylic and nonbenzylic hydroxy groups (Table 3, entries 40–44). These diols were cleanly oxidized to α-ketols without the cleavage of the 1,2-diol bond.

The experiments, usually performed on 1 mmol scale, could be scaled up to 100 mmol without difficulties. A 50 mmol reaction of 4-methoxybenzyl alcohol gave 4-methoxybenzaldehyde in 92% isolated yield and a 100 mmol reaction of benzhydrol using the present procedure provided the corresponding ketone in 95% isolated yield.

From the above observations, it seems that this reaction requires the removal of one hydrogen from the benzylic position of the substrate. Further evidence that supports this statement was drawn from the fact that when tertiary benzylic alcohols such as 2-phenyl-2-propanol and triphenylmethanol which lack this structural feature, were examined as the substrate, no oxidation occurred and the starting materials were recovered unchanged.

Although the details of the reaction mechanism are unknown and intermediates were not observed directly, the results presented in Table 3, together with literature data,[22] indicate that benzylic radicals are possible intermediates. The fundamental steps of the proposed oxidation mechanism are shown in Scheme 2 using benzhydrol (Ph_2CHOH; **1**) as a prototype substrate. Formation, assisted by irradiation, of the iodine radical ($I^\bullet$) from molecular iodine initiates a free-radical chain reaction. Abstraction of a benzylic hydrogen atom from the substrate by $I^\bullet$ leads to an α-hydroxyl benzyl radical (**1a**). It is possible that **1a** reacts with I_2 to give an iodohydrin (**2a**), which can easily lose HI to form carbonyl product (**2**). Then, generated HI is oxidized to I_2 via reaction with dioxygen.[23]

However, it seems more likely that the oxidation proceeds through the reaction of **1a** with O_2 instead of I_2, under aerobic conditions (Scheme 3).[24] The reaction of **1a** with O_2 forms an α-hydroxy peroxyl radical (**1b**). The latter species abstracts hydrogen from the original alcohol giving hydroperoxide (**2b**), a precursor of the carbonyl product, and regenerating I_2.



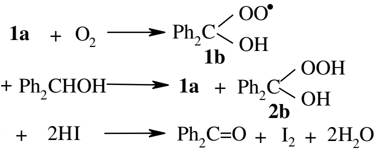
Scheme 2. A plausible path for aerobic photocatalytic oxidation of benzhydrol by I_2 under irradiation.

In fact, I_2 acts as a hydrogen transfer mediator and is either regenerated by oxygen under catalytic aerobic conditions according to the above mechanism, or is converted to HI under stoichiometric anaerobic conditions. Such a simple mechanistic proposal accommodated the observation that highly activated benzylic alcohols were good substrates due to the enhanced lability of their α-hydrogen atoms. In contrast, aliphatic alcohols are far less reactive towards H-radical abstraction, and accordingly, very poor conversions should ensue.

According to the mechanism, since iodine radicals have a low reactivity and a high selectivity, the species with a high reactivity for oxidation are those that have easily removable or abstractable H-atoms. Therefore, primary and secondary alcohols with benzylic activated C–H bonds in the present work act as good substrates. Also, the observed selectivity for the oxidation of *vic*-diols at benzylic positions can be attributed to the ease of H-abstraction by iodine radicals.

In conclusion, we have successfully developed an efficient and environmentally benign transition metal-free photocatalytic process for the aerobic oxidation of activated alcohols to aldehydes and ketones using a catalytic amount of I_2 under O_2. Benzylic hydroxy groups can be efficiently converted into the corresponding carbonyl in the presence of nonbenzylic hydroxy groups. A study on the detailed mechanism and also photocatalytic applications of I_2 for the oxidation of other organic substrates is now in progress in our laboratory.

General procedure for the oxidation of alcohols: A solution of activated alcohol (1 mmol) in acetonitrile



Scheme 3. A second plausible path for reaction of an α-hydroxyl benzyl radical (**1a**) under an O_2 atmosphere.

(25 mL) was added to a Pyrex flask containing a Teflon-coated stirring bar. To this solution was added iodine (I_2, 0.25 mmol, 63.5 mg). Oxygen was bubbled through, and the reaction mixture was kept under an oxygen atmosphere (using an O_2 balloon). The mixture was vigorously stirred and irradiated with a high pressure 400 W mercury lamp using a cut-off Pyrex filter ($\lambda \geqslant 320$ nm) at room temperature. The reaction was monitored by TLC and/or GC and after an appropriate irradiation time, as shown in Table 3, the irradiation was stopped. A saturated solution of sodium thiosulfate was added until the brown colour of the reaction mixture disappeared. The mixture was extracted with dichloromethane. After evaporation of the solvent, the products were purified by silica gel plate or column chromatography with the appropriate solvent. All the products are known and were characterized by the comparison of melting points and IR, ^{1}H NMR and/or MS spectra with those of authentic samples or literature data.[25]

Acknowledgement

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