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Photoinduced Oxidative Dehydrogenation of Benzylic Alcohols Using Mercury(II) Oxide

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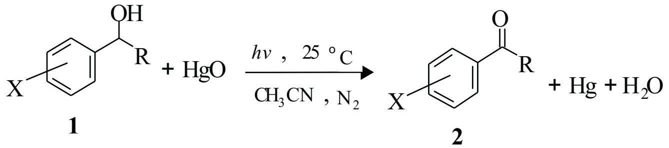
The discovery of new methods for selective partial oxidation of benzylic alcohols to their respective carbonyl compounds is an important goal for chemical synthesis [1]. In this framework, several authors have recently focused their research interest on the development of modern oxidation methods for oxidation of benzylic alcohols and a wide variety metallic and non-metallic oxidants, such as Ce^{IV}, Oxone, $Zn(BiO_3)_2$, Ag_2O, MnO_2, $Q_2Cr_2O_7$, $Q_2S_2O_8$, $QMnO_4$, $QCrO_3Cl$, *etc.* (Q = various large cations) under different conditions including non-aqueous solvent, solvent-free, microwave irradiation and on solid supports have been used for this purpose [2–10]. Moreover, development of new improved methods continues to attract attention [11–16]. However, in comparison with these thermal oxidation methods, little works have been reported on photochemical oxidation of benzylic alcohols [17–19].

Recently, we reported a convenient method for selective photodecarboxylation of arylacetic acids by use of light-sensitive mercury(II) oxide (red, HgO) reagent, which acts as the photo-oxidant in conjunction with light [20]. As a part of our continuing works in this field, we report here results on photochemical oxidation of benzylic alcohols with this reagent, which led to elaboration of a new method for selective oxidation of these substrates to the corresponding aldehydes and ketones. In initial experimental studies we observed that when a heterogeneous mixture of benzyl alcohol and HgO in acetonitrile was irradiated with a 400 W high pressure mercury lamp, it was darkening gradually and the benzaldehyde separated as the only photoproduct. The above observation prompted us to investigate the photolysis of a series of ring-substituted primary and secondary benzylic alcohols (**1**) in the presence of HgO under similar conditions as with benzyl alcohol. We found, that these substrates are cleanly oxidized to the corresponding carbonyl compounds **2** in a high yield without overoxidation of the benzaldehydes to the carboxylic acids. The results, summarized in Table 1, can be explained on the basis of the reaction in Scheme 1.

Blank irradiation experiments in the absence of HgO did not result in any oxidation of benzylic alcohols. Indeed, the photodehydrogenation of **1** leading to **2** did not take place by use of non- or less light-sensitive mercury compounds, such as $HgCl_2$, $HgBr_2$, HgI_2 and $Hg(NO_3)_2$. Therefore, it seems verified that high sensitivity of HgO to light plays an important role in this process. This reagent, which is not a dehydro-

Scheme 1



X = H, alkyl, aryl, halogen, OMe and NO_2
R = H, alkyl and aryl

genating agent of benzylic alcohols in the dark, probably can be activated under illumination, affording selectively dehydrogenation product.

Although the details of the reaction mechanism are unknown, the nature of the photoproduct **2** and the formation of elemental Hg during the irradiation supports a hypothesis that the conversion of **1** to **2** proceeds through a photoinduced two electron transfer. This reagent only oxidizes benzylic alcohols and cannot oxidize aliphatic and non-benzylic aryl-substituted alcohols such as 2-phenylethanol and 2- or 3-phenylpropanol, revealing that only the hydroxyl group at the benzylic position is reactive, and it was converted efficiently to the carbonyl group. Also, photolysis of α-hydroxyphenylacetic and α-hydroxydiphenylacetic acids in the presence of HgO gave benzaldehyde and benzophenone respectively *via* an oxidative decarboxylation (entries 12 and 13). It seems that this reaction requires removal of hydrogen at benzylic position from the alcohol. To test this requirement, triphenylmethanol and 2-phenyl-2-propanol, which lack this structural feature, were examined as the substrate for the oxidation. We observed that these species were inert as may have been expected, due to the absence of hydrogen at α-position. Therefore, the above facts and the results, presented in Table 1, confirm that this photochemical reaction is characteristic of α-aryl and α,α-diarylalcohols. Further evidence that supports this statement can be drawn from the observation that oxidation of 1-phenyl-1,2-ethanediol resulted in α-hydroxyacetophenone exclusively (entry 9).

Table 1. Photooxidation of benzylic alcohols using HgO in CH_3CN.

Entry	Alcohol	Product[a]	Yield (%)[b]
1	Benzyl alcohol	Benzaldehyde	75
2	Benzhydrol	Benzophenone	80
3	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	88
4	4-Isopropylbenzyl alcohol	4-Isopropylbenzaldehyde	85
5	4-*t*-Butylbenzyl alcohol	4-*t*-Butylbenzaldehyde	85
6	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	88
7	2-Methoxybenzyl alcohol	2-Methoxybenzaldehyde	84
8	2,4-Dimethoxybenzyl alcohol	2,4-Dimethoxybenzaldehyde	92
9	1-Phenyl-1,2-ethanediol	α-Hydroxyacetophenone	86
10	Benzoin	Benzyl	81
11	4,4′-Dimethoxybenzhydrol	4,4′-Dimethoxybenzophenone	94
12	Mandelic acid	Benzaldehyde	74
13	Benzylic acid	Benzophenone	82

Table 1 (continuation)

14	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	86
15	1-Phenylethanol	Acetophenone	75
16	1-Phenylpropanol	1-Phenylethanone	75
17	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	54
18	9-Anthracenemethanol	9-Anthraldehyde	70
19	4-Biphenylylmethanol	Biphenyl-4-carbaldehyde	62
20	1-Naphthylmethanol	1-Naphthaldehyde	77
21	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	84
22	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	82

[a]Identification of the products were accomplished by comparison of their physical and spectral data (TLC, IR, ^{1}H-NMR and m.p.) with authentic samples.
[b]Yields are for isolated and chromatographically pure products.

In conclusion, we have introduced for the first time a novel, efficient and selective photochemical method by using an inexpensive, available and light-sensitive inorganic oxide, which acts as the photo-oxidant. Further research is under way in our laboratory in order to decipher the mechanism of these and similar reactions.

General procedure for photooxidation of benzylic alcohols in the presence of HgO: In a Pyrex cell equipped with a magnetic stirrer, a solution of benzylic alcohol (1 mmol) in acetonitrile (25 mL) was prepared. To this solution was added HgO (red, 1 mmol), deaerated 10 min with N_2 gas to exclude any influence of autooxidation and sealed. The reaction cell was irradiated with a 400 W high pressure Hg lamp in a Pyrex water bath thermostated at 25 ± 2°C, which was darkening during irradiation. The progress of the reaction can easily be followed by TLC. After an irradiation time of 6–10 h, depending on the nature of benzylic alcohol, the irradiation was stopped and the dark precipitate of mercury separated by filtration. The residue was concentrated and chromatographed on a silica-gel plate with CCl_4–Et_2O as an eluent to give the carbonyl compound. Yields are shown in Table 1. The all products are known compounds and were characterized by comparison of their physical and spectral data (TLC, IR, ^{1}H-NMR and m.p.) with authentic samples.

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