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Decarboxylative photooxygenation of arylacetic acids by using mercuric oxide

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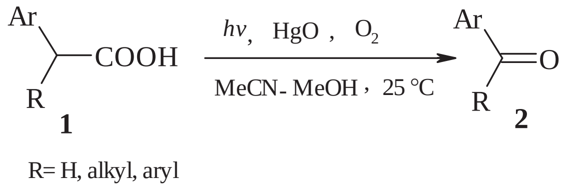
A new method for decarboxylative photooxygenation of arylacetic acids is developed by using light sensitive HgO in MeCN-MeOH which leads to aldehydes and ketones in high yield through trapping of benzylic radical intermediates by dioxygen.

Keywords: decarboxylation, photooxygenation, mercuric oxide, arylacetic acids

One of the best known chemical reactions of carboxylic acids is decarboxylation. In its simplest form, this reaction involves the cleavage of a carbon–carbon bond of carboxylic acids or, more commonly a carboxylate anion, forming carbon dioxide and leaving an organic residue which can be utilised in subsequent reactions. Among various carboxylic acids, much attention has been focused on the decarboxylation of arylacetic acids and their derivatives thermally[1-13] or photochemically[14-21] in the presence of various oxidants, sensitisers and electron acceptors. Such acids provide a benzylic moiety which stabilises an incipient radical or ionic intermediate after loss of carbon dioxide. However, these acids and other carboxylic acids are generally inert toward oxygenation and photooxygenation conditions except for some α-ketocarboxylic acids.[22] In this area, Barton and co-workers reported a mild method for decarboxylative photooxygenation of carboxylic acids.[23] In their method, carboxylic acids must be converted to the ester of N-hydroxypyridine-2-thione. The transformation without such modification is more convenient.[24]

Herein, we report a simple method for decarboxylative photooxygenation of arylacetic acids by using HgO under a dioxygen atmosphere, giving decarboxylated carbonyl compounds in high yields. We observed for the first time that irradiation of a stirred, dioxygen-saturated suspension of HgO and phenylacetic acid or diphenylacetic acid, in MeCN-MeOH solvent, resulted in benzaldehyde and benzophenone respectively as the single major products along with elemental mercury. This observation prompted us to investigate the possibility of a similar behavior for the analogous carboxylic acids containing the aryl group at their α-position. A series of aryl- and diarylacetic acids were irradiated under identical conditions to those used for phenyl- and diphenylacetic acids. It was observed that all of the acids underwent decarboxylative photooxygenation. The results for various arylacetic acids are listed in Table 1. From this, it is apparent that this method is general for primary and secondary arylacetic acids, giving the decarboxylated carbonyl compounds in high yields in agreement with Scheme 1.



Scheme 1

Table 1 Results of decarboxylative photooxygenation of arylacetic acids mediated by HgO

Run	Acid	Product[a]	Yield/%[b]
1	$C_6H_5CH_2CO_2H$	C_6H_5CHO	62
2	$(C_6H_5)_2CHCO_2H$	$(C_6H_5)_2CO$	86
3	$(p\text{-}MeC_6H_4)CH_2CO_2H$	$p\text{-}MeC_6H_5CHO$	76
4	$(o\text{-}MeC_6H_4)CH_2CO_2H$	$o\text{-}MeC_6H_5CHO$	72
5	$CH_3(C_6H_5)CHCO_2H$	$CH_3(C_6H_5)CO$	77
6	$C_2H_5(C_6H_5)CHCO_2H$	$C_2H_5(C_6H_5)CO$	74
7	$(p\text{-}MeOC_6H_4)CH_2CO_2H$	$(p\text{-}MeOC_6H_4)CHO$	78
8	$(o\text{-}MeOC_6H_4)CH_2CO_2H$	$(o\text{-}MeOC_6H_4)CHO$	69
9	$(m\text{-}MeOC_6H_4)CH_2CO_2H$	$(m\text{-}MeOC_6H_4)CHO$	61
10	$(1\text{-}C_{10}H_7)CH_2CO_2H^c$	$(1\text{-}C_{10}H_7)CHO$	70
11	$(2\text{-}C_{10}H_7)CH_2CO_2H^d$	$(2\text{-}C_{10}H_7)CHO$	62
12	$(p\text{-}MeOC_6H_4)_2CHCO_2H$	$(p\text{-}MeOC_6H_4)_2CO$	92
13	$(p\text{-}PhC_6H_4)CH_2CO_2H$	$(p\text{-}PhC_6H_4)CHO$	66
14	$(p\text{-}NO_2C_6H_4)CH_2CO_2H$	$(p\text{-}NO_2C_6H_4)CHO$	57
15	$(C_6H_5)_2COHCOOH$	$(C_6H_5)_2CO$	80
16	$(C_6H_5)CHOHCO2H$	C_6H_5CHO	74
17	$(p\text{-}HOC_6H_4)CH_2CO_2H$	$(p\text{-}HOC_6H_4)CHO$	66
18	$(p\text{-}FC_6H_4)CH_2CO_2H$	$(p\text{-}FC_6H_4)CHO$	60
19	$(p\text{-}ClC_6H_4)CH_2CO_2H$	$(p\text{-}ClC_6H_4)CHO$	76
20	$(o\text{-}ClC_6H_4)CH_2CO_2H$	$(o\text{-}ClC_6H_4)CHO$	68
21	$(2,4\text{-}Cl_2C_6H_3)CH_2CO_2H$	$(2,4\text{-}Cl_2C_6H_3)CHO$	72
22	$(2,6\text{-}Cl_2C_6H_3)CH_2CO_2H$	$(2,6\text{-}Cl_2C_6H_3)CHO$	64
23	$(C_6H_5)_3CCO_2H$	$(C_6H_5)_3CCOH$	88
24	$CH_3(C_6H_5)(CH_3)CCO_2H$	$CH_3(C_6H_5)(CH_3)COH$	77

[a]All products were characterised on the basis of mass, IR and ^1H NMR spectral data. [b]Yields are for isolated products. [c]$1\text{-}C_{10}H_7\text{-}$ =1-naphthyl [d] $2\text{-}C_{10}H_7\text{-}$ =2-naphthyl.

In addition, when the tertiary arylacetic acids *e.g.* triphenylacetic acid and 2-methy-2-phenylpropionic acid were photooxygenated under similar conditions, the corresponding decarboxylated alcohols formed in high yields (Runs 23 and 24). Control experiments have shown that no decarboxylation occurs when HgO or light is omitted from the system. Also, the photooxygenation of **1** leading to **2** did not take place if $Hg(NO_3)_2$ replaces HgO, revealing that the light-sensitivity of HgO plays a provital role in this process. Indeed, photolysis of phenyl-, *p*-tolyl- and diphenylacetic acids under the conditions outlined above, except with argon- rather than dioxygen-saturated solution, resulted in 1,2-diphenylethane (70 %) and 1,2-di(*p*-tolyl)ethane (85 %), and 1,1,2,2-tetraphenylethane (80 %), respectively, as the major products. Obviously, the formation of these dimeric products is attributed to homocoupling of the corresponding benzylic radicals. Moreover, photolysis of triphenylacetic acid under an argon atmosphere in MeCN–MeOH and also MeCN–EtOH gave methyl trityl ether (88 %) and ethyl trityl ether (82 %), respectvely. Clearly, the formation of these ethers is related to the reaction of photogenerated trityl cation (Ph_3C^+) with the alcohol. It is possible that this acid, in a similar way to other arylacetic acids, initially produces the trityl radical ($Ph_3C\cdot$) which is then oxidised to the trityl cation.[25] These observations and the generation of appreciable amounts of elemental Hg and carbon dioxide (limewater test) in the course of the irradiation confirm that the present

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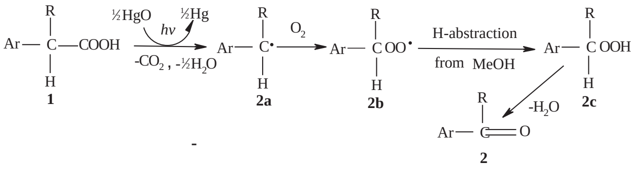

Scheme 2

photoreaction initially involves a photoinduced, one-electron transfer from arylacetate anion to the photo-oxidant HgO.

Therefore, although the details of the reaction mechanism are unknown, the above facts most likely support the intermediate generation of benzylic radicals in the reaction course from **1** to **2** (Scheme 2). Under the O_2 atmosphere, the photogenerated benzylic radical intermediates (**2a**) are trapped by molecular oxygen, initially forming the corresponding hydroperoxide (**2c**). The hydroperoxides (**2c**) were probably formed by H-abstraction by the peroxy radical (**2b**) from methanol. The intermediacy of **2c** was evidenced by a positive KI-starch test of the photolysate. The hydroperoxides (**2c**) are known to readily eliminate H_2O to yield the corresponding aldehydes or ketones (**2**).[11,17,26] A plausible reaction mechanism can therefore be postulated as shown below (Scheme 2).

For the possible extension of the reaction to other carboxylic acid salts, we investigated the photochemical behaviour of arylcarboxylic acids with aryl groups in the β-position such as 3-phenylpropanoic and 3-phenylbutanoic acids. These acids did not undergo photodecarboxylation by HgO under our reaction conditions, revealing that only the carboxyl group at the benzylic position is reactive and it was eliminated efficiently. Therefore, the above facts and the results summarised in Table 1, indicate that this decarboxylative photooxygenation to the corresponding carbonyl compounds is characteristic of α-aryl and α,α-diarylacetic acids.

In conclusion, we have reported a novel and efficient method for photooxygenation of arylacetic acids to the corresponding decarboxylated carbonyl compounds with dioxygen in the presence of light-sensitive HgO, a reaction of general interest for photochemists. Further details of the mechanism are currently under investigation in our laboratory.

Experimental

General procedure: A solution of arylacetic acid **1** (1 mmol) in MeCN-MeOH (1:1v/v; 25 ml) was placed in a Pyrex cell equipped with a magnetic stirrer bar. To this solution was added HgO (red, 1 mmol). The stirred red suspension was irradiated under a continuous stream of dioxygen with a 400 W high pressure Hg lamp in a Pyrex water bath, thermostated at 25 °C. Samples of the reaction mixture were taken out at appropriate time intervals to monitor the reaction by TLC. During the irradiation the initially red suspension turns into a black one that appears to be elemental Hg. After an irradiation time of 3 to 6 h, during which the mixture had darkened completely, the irradiation was stopped and the dark precipitate separated by centrifuging. The residue was concentrated *in vacuo* and chromatogrphed on a silica-gel plate with CCl_4–Et_2O as an eluent to give the decarboxylated product. Yields are shown in Table 1. All isolated reaction products were characterised by TLC, m.p., IR, MS, IR, and ^1H NMR and compared with data obtained from authentic samples.

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