J. Chem. Research (S), 1998, 776–777†

Photoinduced Decarboxylation of Aryl-substituted Carboxylic Acids Using HgO. A New Photo-Kolbe Reaction Pathway†

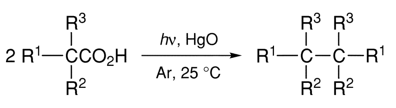
Mohammad H. Habibi* **and Saeid Farhadi**

Department of Chemistry, University of Esfahan, Esfahan 81745, Iran

Photoassisted decarboxylation of several arylcarboxylic acids using HgO in argon-saturated organic solvents at 25 °C gives dimeric products in good yield *via* homocoupling of arylalkyl intermediates.

Thermal oxidative decarboxylation of saturated as well as aryl-substituted carboxylic acids by high-valent metal ions has been extensively studied. Many of the oxidants used for this purpose are metallic ions such as Pb^{IV},[1–3] Co^{III},[4,5] Ag^{II},[6–8] Mn^{III},[9] Ce^{IV},[10] and Tl^{III},[11] but non-metallic oxidants[12,13] have also been used. In addition, oxidative decarboxylations have been effected by electrochemical means (Kolbe reaction).[14–16] The mechanism generally proposed for these decarboxylations has involved homolytic decomposition of the carboxylate anion into carbon dioxide, and alkyl or arylalkyl radicals, and the reduced form of the metal oxidant. The heterogeneous photochemical decarboxylation of saturated carboxylic acids on TiO_2 powder (photo-Kolbe reaction) has been reported.[17,18] Photolysis of phenylacetic acid, sodium phenylacetate, phenylacetate esters and benzyl esters have also been investigated.[19,20] However, in comparison with thermal decarboxylation, relatively little work has been reported on photochemical decarboxylation of carboxylic acids by metallic oxidants.[21,22]

During our initial experimental studies on the effect of light-sensitive compounds of mercury on photolysis of arylcarboxylic acids we found that these acids are readily decarboxylated when treated with HgO under illumination in organic solvents. This light-sensitive reagent, which is a very poor decarboxylating agent in the absence of light, can be activated photochemically, affording selectively decarboxylated products in good yields. In this paper we report our results on photoassisted decarboxylation of arylacetic acids by light-sensitive HgO. The results of decarboxylation are summarised in Table 1. In the cases of **1**–**6**, photolysis of acids led to decarboxylative dimerization and gave 1,2-diarylethanes. The formation of coupled products is in full accord with Scheme 1.



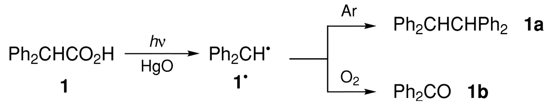
	R^1	R^2	R^3
1	Ph	Ph	H
2	Ph	Ph	Me
3	Ph	Et	H
4	$C_{10}H_7$	H	H
5	Ph	H	H
6	*p*-MeC_6H_4	H	H

$C_{10}H_7$ = 1-naphthyl

Scheme 1

A proposed reasonable mechanism for the present decarboxylation is outlined in Scheme 2 using diphenylacetic acid **1** as a prototype. The HgO photodecarboxylation of **1** generated diphenylmethyl radical **1**$^{\bullet}$ which dimerized to tetraphenylethane **1a** or would react directly with molecular oxygen to afford a diphenylmethylperoxyl radical. The peroxyl radical would finally give benzophenone **1b**.[19,20,23]

Therefore, the formation of these dimeric products is attributed to homocoupling of arylalkyl radicals *via* carbon–carbon bond formation. Evidence for the formation of the arylalkyl radical as an intermediate was obtained from oxygen-trapping experiments. In the presence of oxygen, the major decarboxylation products of diphenylacetic acid and phenylacetic acid were benzophenone and benzaldehyde respectively. The formation of these products is consistent with the trapping of diphenylmethyl **1**$^{\bullet}$ and benzyl radicals with oxygen. It is noted that in protic solvents (methanol or ethanol) and under argon, a small amount of diphenylmethane was observed from **1**, probably *via* reaction of **1**$^{\bullet}$ with the solvent. Irradiation of 2-hydroxy-2-phenylacetic acid (entry 7) and 2-hydroxy-2,2-diphenylacetic acid (entry 8) in the presence of HgO was also investigated and it was found that the principal products were benzaldehyde and benzophenone respectively. In all of these reactions, carbon dioxide and mercury were formed in high yields. Control



Scheme 2

Table 1 Photodecarboxylation of arylcarboxylic acids using HgO[a]

Entry	Acid	Product	Yield (%)[b]
1	$(C_6H_5)_2CH{-}COOH$	$(C_6H_5)_2CH{-}CH(C_6H_5)_2$	84
2	$(C_6H_5)_2C(CH_3){-}COOH$	$(C_6H_5)_2C(CH_3){-}C(CH_3)(C_6H_5)_2$	78
3	$(C_6H_5)CH(C_2H_5){-}COOH$	$(C_6H_5)CH(C_2H_5){-}CH(C_2H_5)(C_6H_5)$	75
4	$(C_{10}H_7)CH_2{-}COOH$[c]	$(C_{10}H_7)CH_2{-}CH_2(C_{10}H_7)$	57
5	$(C_6H_5)CH_2{-}COOH$	$(C_6H_5)CH_2{-}CH_2(C_6H_5)$	68
6	(*p*-$CH_3C_6H_4$)CH_2COOH	(*p*-$CH_3C_6H_4CH_2$)$-CH_2$(*p*-$CH_3C_6H_4$)	78
7	$(C_6H_5)CHOH{-}COOH$	$(C_6H_5)CHO$	82
8	$(C_6H_5)_2COH{-}COOH$	$(C_6H_5)_2CO$	88
9	$(C_6H_5){-}COOH$	No decarboxylation	—

[a] Reaction conditions: aryl carboxylic acid (1 mmol), HgO (2 mmol), ethanol (30 ml), under argon gas; light source was a 400 W high pressure Hg lamp. [b] Yields are based on isolated products. [c] $C_{10}H_7$ = 1-naphthyl.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Yield of 1,1,2,2-tetraphenylethane from photolysis of diphenylacetic acid using HgO in various organic solvents[a]

Solvent	Irradiation time/h[b]	Yield (%)[c]
CH_3CN	28	74
CH_3OH	18	78
C_2H_5OH	18	84
Pr^nOH	12	88
Pr^iOH	14	85
Bu^nOH	14	92
Bu^iOH	20	65
Bu^tOH	20	60
Tetrahydrofuran	36	76

[a]Reaction conditions: diphenylacetic acid (1 mmol), HgO (2 mmol), solvent (30 ml) and under argon gas; light source was a 400 W high pressure Hg lamp. [b]In all reactions, irradiation was stopped when the mixture had darkened completely. [c]Yields are based on isolated product.

experiments established that HgO and light were essential components for the decarboxylation reaction, while the use of Hg, $HgCl_2$ and or $HgBr_2$ instead of HgO did not initiate the reaction. Under our reaction conditions, no decarboxylated products were observed from benzoic and aliphatic acids.

The photodecarboxylation of diphenylacetic acid was explored in several organic solvents to test for the possibility of expanding this reaction to other organic media. In all solvents the major product was 1,1,2,2-tetraphenylethane which is attributed to dimerization of diphenylmethyl radical **1**•. The results are shown in Table 2.

This efficient decarboxylation of arylcarboxylic acids at room temperature provides a new technique in synthetic organic methodology. Moreover, it represents a new reaction pathway in the sequence of the Kolbe reaction. Extending this reaction to other carboxylic acids should clarify the mechanistic and synthetic scope of this alternative photo-Kolbe reaction. Work on the photolysis of aryl-substituted carboxylic acids in the presence of other light-sensitive mercury compounds, such as HgF_2 and Hg_2F_2, is currently being investigated in our laboratory.

Experimental

In a typical experiment, arylcarboxylic acid (1 mmol) was dissolved in 30 ml of ethanol and poured into a 20 mm diameter Pyrex cell. To this solution was added HgO (434 mg, 2 mmol). The reaction cell was deaerated with argon and sealed. It was then placed in a Pyrex water bath, with temperature regulated at 25 °C. The mixture was stirred magnetically and illuminated with light from a 400 W high-pressure Hg lamp until it was darkened completely. During the course of the reaction a dark-grey precipitate of mercury was formed. After an irradiation time of 12 to 24 h, depending on the nature of the acid, mercury was separated by centrifuging. The residue was concentrated on a rotary evaporator at reduced pressure and chromatographed over a silica-gel plate using CCl_4–Et_2O as eluent to give products in 57–88% yield (Table 1). The products were identified by IR, ^1H NMR and MS spectral data and melting point determination.

This work was supported by Special Grant (No. 750934) from the University of Esfahan.

Received, 23rd March 1998; Accepted, 5th August 1998
Paper E/8/02256I

References

1 J. D. Bacha and J. K. Kochi, *Tetrahedron*, 1968, **24**, 2215.
2 J. K. Kochi, R. A. Sheldon and S. S. Lande, *Tetrahedron*, 1969, **25**, 1197.
3 T. Shono, I. Nishiguchi and R. Oda, *Tetrahedron Lett.*, 1970, 373.
4 S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, 1968, **90**, 5196.
5 R. M. Dessau and E. I. Heiba, *J. Org. Chem.*, 1975, **40**, 3647.
6 J. M. Anderson and J. K. Kochi, *J. Org. Chem.*, 1970, **35**, 986.
7 J. M. Anderson and J. K. Kochi, *J. Am. Chem. Soc.*, 1970, **92**, 1651.
8 W. E. Fristad and J. A. Klang, *Tetrahedron Lett.*, 1983, **24**, 2219.
9 J. M. Anderson and J. K. Kochi, *J. Am. Chem. Soc.*, 1970, **92**, 2450.
10 W. S. Trahanovsky, J. Cramer and D. W. Brixius, *J. Am. Chem. Soc.*, 1974, **96**, 1077.
11 J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1968, **33**, 83.
12 D. D. Tanner and S. A. A. Osman, *J. Am. Chem. Soc.*, 1968, **90**, 6572.
13 R. O. C. Norman, P. M. Storey and P. R. West, *J. Chem. Soc. B*, 1970, 1087.
14 L. Eberson, in *Organic Electrochemistry*, ed. M. M. Baizer, Marcel Dekker, New York, NY, 1973.
15 J. P. Coleman and L. Eberson, *Chem. Commun.*, 1971, 1300.
16 I. H. P. Utley, in *Technique of Electroorganic Synthesis*, ed. N. L. Weissberger, Wiley-Interscience, New York, NY, vol. 1, 1974.
17 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1977, **99**, 7729.
18 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 2239 and 5985.
19 T. O. Meiggs and S. I. Miller, *J. Am. Chem. Soc.*, 1972, **94**, 1989.
20 T. O. Meiggs, L. I. Grossweiner and S. I. Miller, *J. Am. Chem. Soc.*, 1972, **94**, 7981 and 7986.
21 R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, 1968, **90**, 6688.
22 J. Barluenga and M. Yus, *Chem. Rev.*, 1988, **88**, 487.
23 R. Akaba, T. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Kuragami, A. Negishi, M. Kamata, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc.*, 1992, **114**, 4460.