

PHOTODECARBOXYLATION OF ARYLACETIC ACIDS INDUCED BY LIGHT-SENSITIVE Hg_2F_2

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Received 16 December 1998; accepted 3 February 1999

Abstract:

Photolysis of arylacetic acids in argon-saturated acetonitrile in the presence of Hg_2F_2 gives the corresponding 1,2-diarylethanes as the major product via a radical pathway. This reaction offers an interesting procedure for selective decarboxylation of arylacetic acids with the assistance of a light-sensitive compound. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Carboxylic acids and derivatives; Decarboxylation; Mercury and compounds; Photochemistry

Considerable attention has been focused recently on the decarboxylation of arylacetic acids since these simple systems provide a benzyl moiety which is capable of stabilizing an incipient carbanion or radical intermediate. Although the oxidative decarboxylation of arylacetic acids has been achieved with various oxidizing agents, including cerium(IV) ammonium nitrate,¹ cobalt(III) acetate,² sodium hypochlorite,³ tetrabutylammonium periodate,⁴ sulfate anion radical,⁵⁻⁸ copper(I)- O_2 ,⁹ iron(III) porphyrin-iodosylbenzene,¹⁰ sodium periodate-crown ethers,^{11,12} manganese(III) acetate¹³ and 2-nitrobenzenesulfonyl peroxy radical generated by the reaction of 2-nitrobenzenesulfonyl chloride with potassium superoxide,¹⁴ these methods are not selective. Selective decarboxylation of arylacetic acids to 1,2-diarylethanes has only been reported with sodium persulfate-silver nitrate system.¹⁵ In addition, direct photodecarboxylation of arylacetic acids has been investigated.¹⁶⁻²⁰ However, since the yield of the decarboxylated product is usually low, the direct photodecarboxylation has been considered to be of no synthetic value. Nevertheless, there are ample precedents for photochemical decarboxylation of arylacetic acids in the presence of various electron acceptors, including heterocyclic compounds, via photo-induced single-electron transfer followed by decarboxylation to give the corresponding arylmethanes, 1,2-diarylethanes and adducts with the electron acceptors employed.²¹⁻²⁴

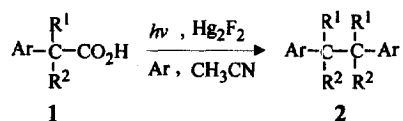
In this paper we wish to report that arylacetic acids are selectively decarboxylated via a radical mechanism when irradiated in the presence of light-sensitive mercury(I) fluoride (Hg_2F_2) in argon-saturated acetonitrile as solvent to afford the 1,2-diarylethanes. The present procedure provides a useful and convenient method for

selective decarboxylation of arylacetic acids in the presence of a light-sensitive compound. To the best of our knowledge, this type of reaction is novel for photochemical decarboxylation of arylacetic acids.

General experimental procedure: To a solution of arylacetic acid (1 mmol) in acetonitrile (25 ml) in a Pyrex cell was added Hg_2F_2 (440 mg, 2 mmol). The reaction cell was deaerated with argon and sealed. It was then placed in a Pyrex water bath at room temperature. The mixture was stirred magnetically and irradiated with a 400 W high-pressure Hg lamp for 2-3 days, depending on the nature of the acid, until it was darkened. The dark-gray precipitate of mercury was separated by filtration. The solvent was evaporated and the resulting crude material was purified on a silica-gel plate (eluent: $\text{CCl}_4/\text{Et}_2\text{O}$) affording the pure product. (Table 1)

As shown in Table 1, this photodecarboxylation is characteristic of arylacetic acids. In contrast to the arylacetic acids, α -hydroxyarylacetic acids such as benzylic and mandelic acids gave benzophenone and benzaldehyde respectively under the same reaction conditions. (Runs 11 and 12)

Table 1 Photodecarboxylative dimerization of arylacetic acids using Hg_2F_2 .



Run	Ar	R ¹	R ²	Product ^a	Yield (%) ^b
1	Ph	Ph	H	2a	83
2	Ph	Ph	CH ₃	2b	73
3	Ph	CH ₃	H	2c	66
4	Ph	C ₂ H ₅	H	2d	72
5	Ph	H	H	2e	63
6	<i>p</i> -tolyl	H	H	2f	78
7	<i>o</i> -tolyl	H	H	2g	73
8	<i>m</i> -tolyl	H	H	2h	68
9	1-naphthyl	H	H	2i	58
10	2-naphthyl	H	H	2k	52
11	Ph	Ph	OH	benzophenone	85
12	Ph	H	OH	benzaldehyde	78

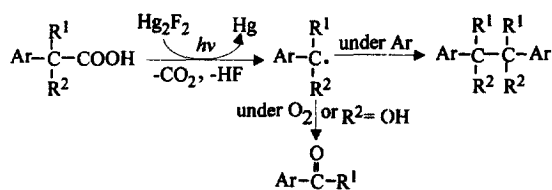
^a All products exhibited spectral data (IR, ¹H-NMR and MS) consistent with their structures.

^b Yields refer to isolated and chromatographically pure products.

In control experiments, these reactions did not occur in the dark (e.g. reflux for 48 h) or in the absence of Hg_2F_2 . On the other hand, the use of non- or less-photosensitive mercury salts such as Hg_2Cl_2 , HgCl_2 , HgBr_2 ,

$\text{Hg}(\text{NO}_3)_2$ instead of Hg_2F_2 did not initiate the reaction. Therefore, the light sensitivity of Hg_2F_2 plays an important role in this selective photodecarboxylation. The photosensitive Hg_2F_2 which is not a decarboxylating agent in the dark, can be activated photochemically, affording decarboxylated product selectively. The carboxylic acids in which the α -carbon atoms are attached to aryl groups, exhibit good reactivity. However, aliphatic acids, benzoic acid and arylcarboxylic acids with no aryl group at their α -position (e.g. 3-phenylpropionic and 3,3,3-triphenylpropionic acids) were not decarboxylated under these reaction conditions.

Unfortunately the exact mechanism of the reaction is not clear to us. However, the formation of coupled photoproducts most likely supports the generation of the corresponding benzylic radicals in the course of the reaction. Moreover, the formation of benzophenone as the major product from photodecarboxylation of diphenylacetic acid with Hg_2F_2 under O_2 , provides evidence for the diphenylmethyl radical intermediates which are highly reactive toward O_2 .^{14,16,25} A possible reaction mechanism of photodecarboxylation with Hg_2F_2 can be postulated as shown in Scheme 1.



Scheme 1

It is possible that the formation of the radical intermediate proceeds *via* the photodecomposition of an organomercurial, generated *in situ*, by the reaction of the corresponding acid with Hg_2F_2 on irradiation.²⁶ It is worthwhile noting from mechanistic point of view that the photodecarboxylation of diphenylacetic acid under conditions employed in MeOH resulted in diphenylmethane (20 %), in addition to dimerized product. The formation of this minor product is thought to support the generation of the corresponding benzylic radical as the intermediate which is trapped by the solvent.

In summary, we have introduced a novel and efficient procedure for selective photodecarboxylation of arylacetic acids with the use of Hg_2F_2 . This reaction offers an interesting example of the use of light-sensitive inorganic compounds for photochemical reactions and it is also useful for synthetic organic chemistry. The details of reaction mechanism and the use of other light-sensitive mercury compounds are being studied in our laboratory.

Acknowledgement:

We are grateful to the University of Esfahan Research Council for the partial support of this work.

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