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DECARBOXYLATIVE PHOTOOXYGENATION OF CARBOXYLIC ACIDS BY THE USE OF ACRIDINE

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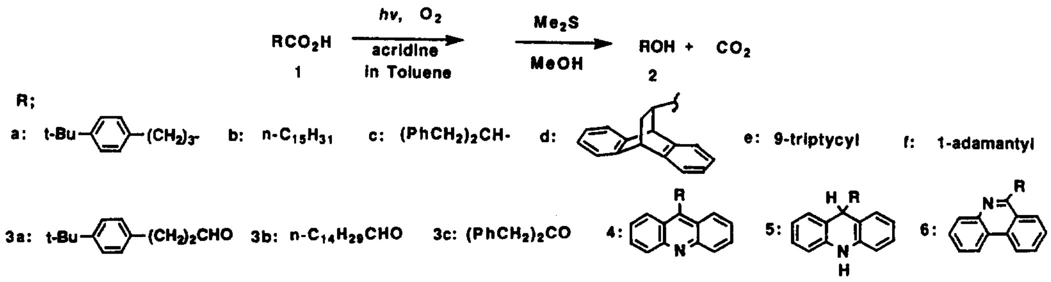
Abstract: A new method of decarboxylative photooxygenation of free carboxylic acids is developed by the use of acridine as a light absorber, leading to alcohols after reductive treatment of the photolysate.

The transformation of carboxylic acids to alcohols with concomitant loss of carbon dioxide is usually carried out in multi-steps including oxidative decarboxylation with strongly oxidizing metal salts. Hunsdiecker type halogenation or acetoxylation with lead tetraacetate is a typical reaction involved for this conversion. Recently, Barton and co-workers reported a mild method for this transformation. In their method, carboxylic acids must be converted to the ester of N-hydroxypyridine-2-thione.[1] The transformation without such modification is more convenient. However, carboxylic acids are generally inert toward photooxygenation conditions except for some α−ketocarboxylic acids.[2] We have recently reported that carboxylic acids are easily decarboxylated via radical mechanism when irradiated with aza aromatic compounds in nonpolar solvents.[3] This method may be applied to the above transformation. We now report a simple method of decarboxylative photooxygenation of carboxylic acids, giving alcohols after reductive treatment of the photolysate.

Irradiation was carried out using a 100-W mercury lamp through a Pyrex filter with continuous bubbling of molecular oxygen into a toluene solution (60 ml) of carboxylic acid **1** (ca. 300 mg) and acridine (0.2-1.0 eq) until starting carboxylic acid was almost consumed (2-4 h). After evaporation of toluene, the reaction mixture was treated with dimethyl sulfide (1 ml) in methanol (10 ml) for 1 h. The results for various carboxylic acids **1a-1f** are summarized in Table 1. Run 1 and 2 show the results when benzene was used as a solvent in the presence or absence of t-butyl mercaptan, respectively. Although alcohol **2a** is formed even in the absence of hydrogen donor (run 2), the higher yield of **2a** is obtained by the use of toluene as a solvent. From the table, it is apparent that this simple method is general for primary, secondary, and tertiary carboxylic acids, giving the decarboxylated alcohols in moderate to good yields (38-82%) along with a small amount of alkylated products **4-6** of aza aromatic compounds. When primary and secondary carboxylic acids are photooxygenated, the decarboxylated carbonyl compounds **3** are usually produced in small amounts (6-15%).[4] Interestingly from mechanistic and synthetic points of view, the reaction proceeds even when a small amount of acridine (0.2-0.3 eq) was used. Phenanthridine is also effective for this conversion as exemplified in run 8 and 10.

We envision the reaction mechanism shown in Scheme 1. The decarboxylated free alkyl radical produced according to our previous studies reacts with molecular oxygen to give alkyl peroxy radical **7**, which undergoes electron transfer reaction with acridanyl radical to give ion pair **8** and in turn to afford an alkyl hydroperoxide and acridine via proton transfer. The alkyl hydroperoxide may also be formed by hydrogen abstraction of the peroxy radical from toluene. The intermediacy of alkyl hydroperoxide was evidenced by positive KI-starch test of the photolysate. The reduction of alkylhydroperoxides to alcohols by dimethyl sulfide is well established reaction.[5]

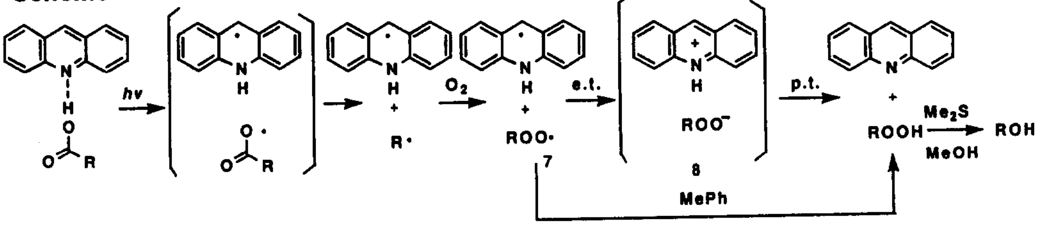
Table 1. Decarboxylative photooxygenation of carboxylic acids by the use of acridine[a]



run	compound	acridine (eq)	irradiation time (h)	alcohol (%)	carbonyl compound (%)	by-products (%)	recovery of acridine
1[b,c]	1a	1	2	49[b]	15	4a; 13	53
2[c]	1a	0.2	2	44	0	4a; 5	0
3	1a	0.2	2	60	10	4a; 6	0
4	1b	0.5	4	38	14	4b;11	2
5	1c	0.3	4	54[d]	6[d]	5c;7d	0
6	1d	1	2	48	0	5d; 18	74
7	1e	1	4	68	-	-[e,f]	21
8[g]	1e	1[g]	10[g]	74	-	6e; 8[f]	45
9	1f	0.3	4	82	-	5f; 3	0
10[g]	1f	0.2[g]	10[g]	66	-	6f; 7	13

[a] Photolysis was carried out in tolene if otherwise noted. [b] In the presence of t-BuSH (2eq). [c] Benzene was used as a solvent. [d] 1c was recovered (20%); the product yields were calculated without consideration of the recovery. [e] Not determined. [f] Triptycene was formed in 12-16%. [g] Phenanthridine was used as a sensitizer.

Scheme 1



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4 The mechanism of formation of carbonyl compounds is not clear. It may involve the secondary reaction of alkylhydroperoxides under the conditions.
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