Tetrahedron Letters,Vol.30,No.48,pp 6733-6736,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

PHOTODECARBOXYLATION OF UNMODIFIED CARBOXYLIC ACIDS WITH USE OF AZA AROMATIC COMPOUNDS

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Summary: A very simple procedure for photodecarboxylation of intact carboxylic acids leading to alkanes is developed with use of aza aromatic compounds as light absorbers and t-BuSH as a hydrogen donor.

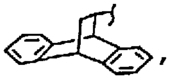
We have recently developed an efficient photosensitized decarboxylation reaction of carboxylic acids via N-acyloxyphthalimides.[1] Although N-acyloxyphthalimides are readily prepared from various carboxylic acids and N-hydroxyphthalimide in high yields with use of DCC, decarboxylation leading to alkanes without such modification is obviously much more convenient. Hitherto, general and efficient methods of this transformation from intact carboxylic acids under mild conditions (at ambient or lower temperature and without use of highly oxidizing reagents) have not been established.[2] In 1967, Nozaki and co-workers reported an interesting photoreaction of decarboxylative alkylation of aza aromatic compounds (acridine or quinoline) with several carboxylic acids.[3] Although the production of alkanes was not observed in their study, the reported reaction might be modified for the alkane synthesis. We have considered that the reaction might proceeds via radical intermediates, although the ionic mechanism via an exciplex formed through π,π^* singlet of acridine was originally suggested to be favorable.[3b] The decarboxylated alkyl radicals must be trapped by suitable hydrogen donors. Here, a highly simple method of alkane synthesis from intact carboxylic acids is reported with its mechanistic aspect.

When a benzene solution (60 ml) containing a carboxylic acid [(**1a**) typically ca. 300 mg], acridine (0.2-1 equivalent), and t-BuSH (1.7-5% of the solvent volume) was irradiated with 100-W high pressure Hg lamp through a pyrex filter for 2 h under nitrogen or air, the decarboxylated alkanes (**2a**) was produced in 51-67% yields. Other aza aromatic compounds such as phenanthridine, phenazine, 1,10-phenanthroline, quinoline, or 4-dimethylaminopyridine (DMAP) are also effective (Table I). This simple method is general and applicable to various primary, secondary, and tertiary aliphatic carboxylic acids (Table I). A small amount of alkylated derivatives of acridine (**4, 5**) or phenanthridine (**6, 7**) were usually obtained in 5-19%

Table I. Photodecarboxylation from unmodified carboxylic acids with use of aza aromatic compounds[a]

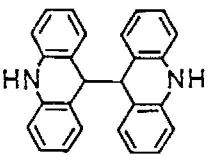
$$\underset{\mathbf{1}}{RCO_2H} \xrightarrow[\text{N-aromatics, t-BuSH in } C_6H_6]{h\nu} \underset{\mathbf{2}}{RH} + CO_2$$

R = a: t-Bu--$(CH_2)_3$-, b: n-$C_{15}H_{31}$, c: (1-naphthoyl)ethyl,

d: $(PhCH_2)_2CH$-, e: , f: 9-triptycyl, g: 1-adamantyl

compd.	N-aromatic compd.	t-BuSH (%)	irr. time (h)	RH (%)	by-products (%)	recovery of N-aromatics (%)
1a	acridine (1 eq)	5	2(N_2)	66	**3**; 51, **4a**; 7	8
1a	acridine (1 eq)	1.7	2(N_2)	67	**3**; 54, **4a**; 8	13
1a	acridine (0.2 eq)	1.7	2(N_2)	51	–[c]	0
1a	acridine (1 eq)	5	4(air)	55	**4a**; 19	40
1a	phenanthridine (0.2 eq)	5	6(N_2)	58	**6a**; 8	4
1a	phenazine (1 eq)	5	10(N_2)	56	–[c]	78
1a	phenanthroline (1 eq)	5	8(N_2)	50	–[c]	–[c]
1a	quinoline (1 eq)	5	8(N_2)	51	–[c]	84
1a	DMAP (1 eq)	5	8(N_2)	43	–[c]	–[c]
1b	acridine (1 eq)	1.7	2(N_2)	72	**3**; 18, **4b**; 13	7
1b	phenanthridine (0.2 eq)	1.7	6(N_2)	66	**6b**; 9	7
1c	acridine (1 eq)	1.7	2(N_2)	70	–[c]	1
1d	acridine (1 eq)	1.7	2(N_2)	69	**3**; 28, **5d**; 14	58
1d	phenanthridine (0.2 eq)	1.7	8(N_2)	70	**6d**; 19	0
1e	acridine (1 eq)	1.7	2(N_2)	65	**3**; 27, **5e**; 19	10
1e	phenanthridine (1 eq)	1.7	5(N_2)	65	**6e**; 14	86
1f[b]	acridine (1 eq)	1.7	2(N_2)	73[b]	–[c]	55
1f[b]	phenanthridine (1 eq)	1.7	6(N_2)	84[b]	**6f**; 13	79
1g	acridine (1 eq)	1.7	2(N_2)	77	**3**; 34, **5g**; 11	19
1g	acridine (1 eq)	1.7	2(air)	64	**5g**; 12	71
1g	phenanthridine (0.2 eq)	1.7	8(N_2)	76	**6g**; 4, **7g**; 5	16

a) Irradiated until starting carboxylic acids almost disappeared (<10%).
b) Irradiated in a suspension. c) Not determined.



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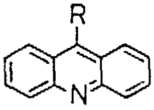

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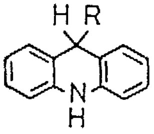

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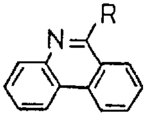

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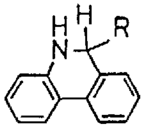

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yields. A considerable amount of biacridane (**3**) was formed (18-54%) when the solution containing an equimolar amount of acridine was irradiated under nitrogen atmosphere; the formation of biacridane was considerably diminished under the aerated conditions and acridine was recovered (>40%). The reaction proceeds effectively even when a small amount (0.2 eq) of acridine or phenanthridine was used. 9-Triptycyl derivative (**1f**) which has low solubility in benzene can also be decarboxylated by irradiation in a suspension. The limiting quantum yields at infinite concentration of carboxylic acids under inert atmosphere for the selected compounds (**1a**, **1d**, and **1g**) are 0.089 for **1a**, 0.085 for **1d**, and 0.059 for **1g**.[4] In practical concentration region (5.5×10^{-3}-2.2×10^{-2} M) used for these carboxylic acids, the quantum yields are roughly in the range of 0.015-0.065.

Several mechanistic investigations have been reported on Nozaki's decarboxylative alkylation reaction; ionic mechanism through an exciplex formed via π,π^* singlet state by Nozaki,[3b] an electron transfer mechanism by Davidson,[5] and a radical pair mechanism by Libman.[6] We have also made some mechanistic studies for the decarboxylation of **1a** with use of acridine. Our results are consistent with the mechanism proposed by Libman. As reported by Nozaki and by Libman, acridine is not protonated but chelated with carboxylic acids (confirmed by uv spectroscopy). This chelation plays a very important role in the photodecarboxylation, because the breaking the chelation by addition of photochemically inert t-BuOH[7] dramatically decreases the quantum yield [Φ = 0.051 in C_6H_6, 0.0043 in C_6H_6-t-BuOH (7:3 v/v) at [**1a**] = 2.25×10^{-2} M]. The reaction efficiency is rather insensitive to dissolved oxygen [Φ = 0.051 (0.016) under argon, 0.042 (0.015) under air at [**1a**] = 2.25×10^{-2} M (2.82×10^{-3} M)], indicating that the long lived triplet (π,π^*) is not the reactive state.[8] Although acridine has been reported to be very nearly nonfluorescent in benzene,[7] it does emit weak fluorescence (π,π^*) in the same solvent. Figure 1 compares the fluorescence spectra of acridine measured in the absence and in the presence of **1a**. Although the shape of the spectrum slightly changes in the longer wavelength region by addition of **1a**,[9] very little quenching is observed, indicating that the π,π^* singlet state is not likely to be a reactive state. A plausible reaction mechanism is shown in Scheme 1. The excitation of the chelated complex of acridine-carboxylic acid produces the chelated excited states. The chelated n,π^* singlet or the second triplet (n,π^*)[8] directly abstracts the chelated hydrogen (path a) to produce the carboxyl radical which in turn undergoes decarboxylation and abstracts hydrogen from t-BuSH to give the alkane. Alternatively, adiabatic protonation through the chelated complex gives the excited ion pair (path b), which undergoes the electron transfer reaction to produce the carboxyl radical. The discrimination of the two mechanisms is difficult at present.

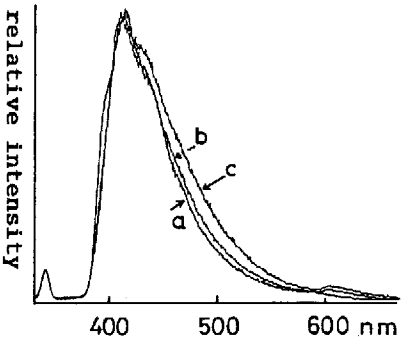
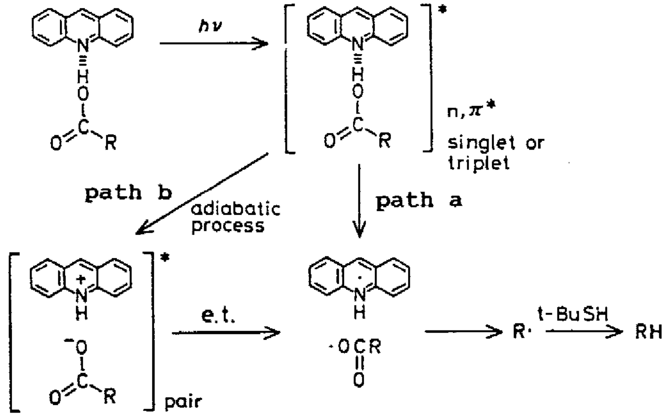


Figure 1. Fluorescence spectra of acridine (8.36 x 10^{-4} M) in benzene, a: in the absence of **1a**, b: [**1a**] = 1.00 x 10^{-2} M, c: [**1a**] = 3.00 x 10^{-2} M.

Scheme 1



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9. A new emission appeared in 420-600 nm might be due to the formation of a very small amount of protonated acridine; the protonated acridine has an emission maximum at 480 nm.

(Received in Japan 31 July 1989)