Novel Photochemical Coupling of Hindered Phenols in the Presence of Acridine Mechanistically Probed by CIDEP

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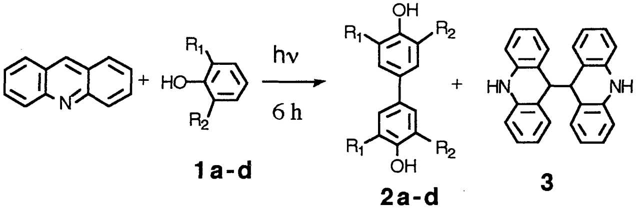
Irradiation of hindered phenols in the presence of acridine as a light absorber gives bisphenols and biacridane. CIDEP study establishes the path of hydrogen abstraction by the triplet acridine. The overall mechanism is proposed by the product analysis and the CIDEP studies.

We have previously reported the photochemical reductive decarboxylation of carboxylic acids with use of acridine as a light absorber.[1] The key step of the reaction was shown to be hydrogen abstraction in the excited state of the hydrogen bonding complex of acridine-carboxylic acid. In this connection, photochemical reaction of phenols with acridine may be interesting. However, the reaction with phenol itself is very sluggish as described later. This may indicate that the produced radical pair is converted to the starting materials by electron transfer and proton transfer cascades. If that is the case, phenols having relatively bulky substituents in *o*-position may decrease the rate of deactivation and consequently increase the probability of free radical generation. We report the product analysis and CIDEP studies in the reaction of acridine with phenols having relatively bulky substituent(s) at *o*-position(s).

When a benzene solution (60 ml) of 2,6-di-*tert*-butylphenol (**1a**, 212 mg) was irradiated by a 100-W Hg lamp though a Pyrex filter in the presence of acridine (1 equiv., 184 mg) for 6 h, bis[(2,6-di-*tert*-butyl)phenol] (**2a**) and biacridane was produced in 32 (with 45% recovery) and 37% (with 48% recovery) yields, respectively. The reaction proceeds in higher yields in acetonitrile (Table 1), although the reason of this solvent effect is not clear at present.[2] As shown in the table, similar reactions were observed for 2,6-di-*iso*-propylphenol (**1b**), 2,6-dimethylphenol (**1c**), 2-*tert*-butylphenol (**1d**). Interestingly, the yield of bisphenol is higher in the phenol with more crowded substituents (**1d** ≈ **1c** < **1b** < **1a**) and phenol itself is unreactive under the conditions. The cross coupling product of acridanyl and phenoxy radicals was not observed in all cases.

Table 1. Photoreactions of acridine with hindered phenols



a: $R_1 = R_2 =$ *t*-Bu; b: $R_1 = R_2 =$ *i*-Pr; c: $R_1 = R_2 =$ Me, d: $R_1 =$ H, $R_2 =$ *t*-Bu; e: $R_1 = R_2 =$ H

1	Solvent	Irr. Time (h)	Product (%)[a] 2	Product (%)[a] 3[b]	Recovery (%)[a] 1	Recovery (%)[a] acridine
a	C_6H_6	6	32[c]	37	45	48
a	C_6H_6-*t*-BuOH[d]	6	35[c]	47	47	47
a	CH_3CN	6	75	50	21	–[e]
b	CH_3CN	6	64	52	34	38
c	C_6H_6	6	11	9	62[f]	81
c	CH_3CN	6	42	32	43	34
d	C_6H_6	6	16	15	62[f]	77
d	CH_3CN	6	47	37	–[e]	–[e]
e	CH_3CN	20	0	0	54[f]	77

[a]Isolated yields. [b]Biacridane **3** was isolated by filtration of photolysate. The poorer yields of **3** than those of **2** in acetonitrile would be due to this isolation method. [c]The oxidized quinone is also produced in ca. 5% yield. [d]In a mixed solvent of C_6H_6-*t*-BuOH (9:1). [e]Not determined. [f]The poorer recovery of the phenol than that of acridine is due to the volatality of the phenol.

In order to obtain an insight into the mechanism of this reaction, the chemically induced dynamic electron polarization (CIDEP) experiments were carried out. CIDEP has been known to occur typically by either triplet mechanism (TM) or radical pair mechanism (RPM) and the rules on the phase pattern can be briefly summarized as follows: TM gives polarization of all emissive (E) (in many cases) or absorptive (A) pattern, whereas RPM affords E/A (triplet precursor) or A/E (singlet precursor) pattern depending on the multiplicity of the precursor for the usual radicals having similar g-values via S-T_o-mixing ($\Delta g = 0$, hfc $\neq$ 0)].[3] Figure 1 shows the observed CIDEP for the photolysis of benzene solution of **1a** and acridine at [acridine] = 2.8×10^{-2} M, [**1a**] = 2.8×10^{-1} M (upper spectrum A) and at [acridine] = [**1a**] = 2.8×10^{-2} M (lower spectrum B). Both spectra (A and B) clearly show doublet-triplet signals assignable to 2,6-di-*tert*-butylphenoxy radical. The signals of acridanyl radical have been reported to have a broad pattern[4] and would appear among the signals of 2,6-di-*tert*-butylphenoxy radical as a little concave or convex baseline. The observed polarization in Figure 1A is interpreted by E pattern (TM) which is distorted by E/A pattern (RPM). The phase-pattern clearly indicates the hydrogen abstraction from the triplet state of acridine. The contribution of RPM is larger at lower concentration of the phenol (Figure 1B). Thus, the radical pair mechanism initiated by the hydrogen abstraction by the triplet state of acridine is established by the CIDEP experiment.

Although the reactive excited state of acridine is clearly shown to be the triplet state, it is not clear whether the reactive acridine is of hydrogen bonding state or not. Inspection of electronic spectral change of acridine by addition of **1a** showed the absence of the characteristic change due to the change of free acridine to hydrogen bonding acridine, although the change has been observed in acridine-unsubstituted phenol combination by Mataga and Tsuno.[5] In our previous study of decarboxylation of carboxylic acids, the reactive hydrogen bonding state was established by the fact that addition of a small amount of *tert*-butanol, which would break the hydrogen bond of carboxylic acid-acridine, dramatically decreases the yield of decarboxylated products. However, in the case of acridine and **1a**, addition of *tert*-butanol gave no effect as recognized in Table 1 (the second

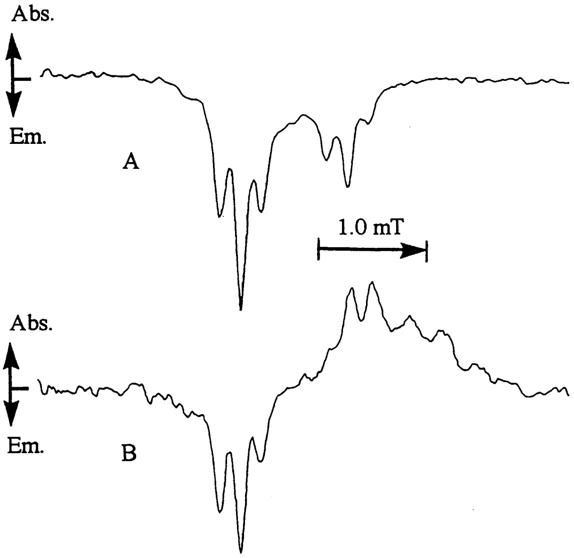
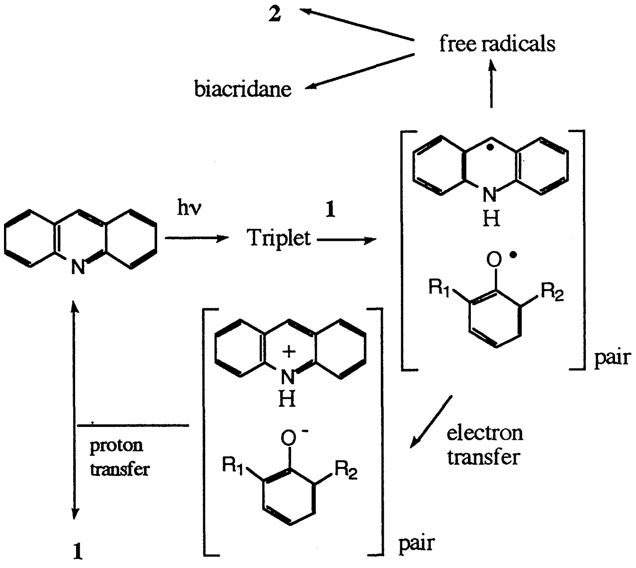


Figure 1. CIDEP observed in the photoreaction of acridine with **1a** in benzene. A: [acridine] = 2.8×10^{-2} M, [**1a**] = 2.8×10^{-1} M; B: at [acridine] = [**1a**] = 2.8×10^{-2} M.



Scheme 1.

run). For these reasons, the reactive excited state of hydrogen abstraction in the present reactions is most reasonably assigned to the triplet state of free acridine.

From these results, we propose the overall reaction mechanism in Scheme 1. Scheme 1 includes a conceivable deactivation path of the initially formed radical pair. The path involves an electron transfer[6] and successive proton transfer regenerating the starting materials. Although this path is not experimentally proved, the intervention of these processes can rationalize the following two results as follows: 1) the ortho-substituent effect can be explained since the bulky substituent may decrease the rate of electron transfer process and gives a net probability to produce the free radicals, and 2) the expected cross coupling product between the acridanyl and phenoxy radicals was not obtained because the formation of such product requires (via either direct formation or after reencounter of the free radicals) the formation of singlet radical pair that is to be deactivated by the proposed cascade or to be separated to free radicals after intersystem crossing; in other words, the recombination of singlet radical pair in this case would be much slower than the electron transfer process.

References and Notes

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1 K. Okada, K. Okubo, and M. Oda, *Tetrahedron Lett.*, **30**, 6733 (1989), b) K. Okada, K. Okubo, and M. Oda, *J. Photochem. Photobiol. A: Chem.*, **57**, 265 (1991).

2 Although there is no experimental evidence, the participation (in part) of photochemical electron transfer mechanism in acetonitrile may give the same radical pair after the proton transfer; the electron transfer process is a little endothermic (0.4 kcal/mol by Rehm-Weller equation) for the S_1 state of acridine and may occur at room temperature.

3 H. Murai and H. Hayashi in "Radiation Curring in Polymer Science and Technology," ed by J. P. Fouassier and J. F. Pabek, Elsevier, New York (1993), Vol. 2, Chap. 2, pp 63-154.

4 S. Yamauchi and N. Hirota., *J. Phys. Chem.*, **44**, 4631 (1984).

5 N. Mataga and S. Tsuno, *Bull. Chem. Soc. Jpn.*, **30**, 711 (1957).

6 The electron transfer process is obviously exothermic (ca. 43 kcal/mol); the oxidation potential of sodium salt of 2,6-di-*tert*-butylphenol was measured to be +1.42 V (peak potential) *vs* S. C. E. in acetonitrile (electrolyte: tetraethylammonium perchlorate) and the reduction potential of acridinium salt (-0.43 V *vs* S. C. E.) was taken from the literature; S. Fukuzumi, S. Koumitsu, K. Hironaka, and T. Tanaka, *J. Am. Chem. Soc.*, **109**, 305 (1987).