The Alkylation of 1-Hydroxyanthraquinone with Visible-light Irradiation

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Synopsis. The 2-position of 1-hydroxyanthraquinone was alkylated by the use of tertiary amine or methanol with visible-light irradiation (λ>400 nm).

Recently various new reactions of anthraquinones with visible-light irradiation have been reported and have attracte much attention.[1] We ourselves have now found a photochemical alkylation of 1-hydroxy-9, 10-anthraquinone (**1**) by the use of tertiary amine or methanol with visible-light irradiation.

When **1** in aerated methanol was irradiated with the light of λ>400 nm in the presence of triethylamine, 1-hydroxy-2-methyl-9,10-anthraquinone (**2**) was obtained in a 54% yield (Table 1). The photoproduct, **2**, was identified by means of elemental analysis, IR, ^{1}H NMR, UV, and visible-absorption spectra in comparison with those of an authentic sample.[2] In acetonitrile or 2-propanol, however, a 2-ethyl-substituted product (**3**) and its dimer (**4**) were obtained in the photoreaction with triethylamine. All the spectral data suggested that the structure of the dimer was **4**. A similar alkylation was also observed when trioctylamine was used as the tertiary amine (Table 1). Without a tertiary amine, the photoalkylation was not observed at all in any solvent. The alkyl group of the tertiary amine was transferred into the quinone nucleus except for the reaction in methanol, which gave the methylated product regardless of the amine used.

No alkylation occurred in the cases of 1-methoxyanthraquinone (**6**) and 1-acetylaminoanthraquinone (**7**) each of which has an absorption maximum (**6**: λ_{max}=380 nm; **7**: λ_{max}=398 nm in ethanol) similar to that of **1** (λ_{max}=403 nm in ethanol). 1-Hydroxyanthraquinones have been revealed to have tautomerism and acid-base equilibria in their excited states,[3] and their photochemical behavior has been expected to be different from that of the other derivatives, which are unable to be converted to the 1,10-quinonoid form. The alkylation may be connected with the tautomer of **1**, 9-hydroxy-1,10-anthraquinone. Although we have no substantial evidence for the reaction mechanism, the alkylation seems to be closely related to the reactions between the tertiary amine and the benzene derivertives[4] which are induced by an electron transfer from the amine to the excited aromatics, followed by proton transfer. In methanol, the methoxide ion presumably behaves as an electron donor, for no reaction occurs in the absence of the tertiary amine, which can cause a dissociation of the methanol.

Experimental

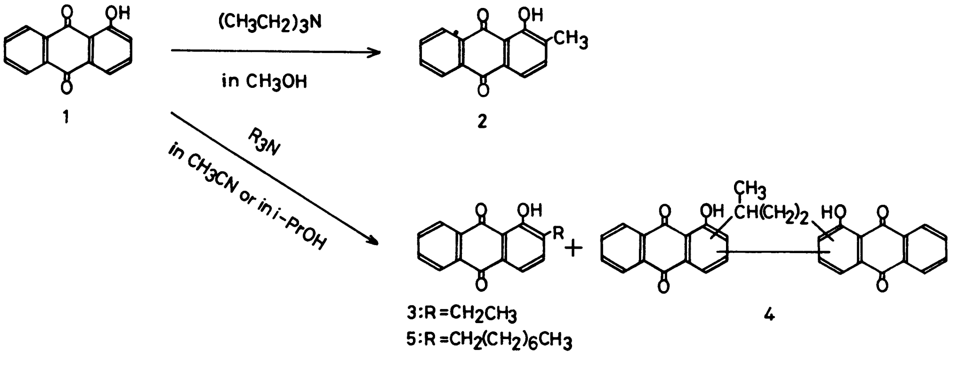
Light irradiation was carried out by means of a 500 W high-pressure mercury lamp (Eikosha) through a solution filter (saturated aqueous solution of $NaNO_2$ (5 mm path length)), until the **1** in aerated methanol, acetonitrile, or 2-propanol disappeared completely. The initial concentration were 5.0×10^{-4} (in methanol), 3.0×10^{-3} (in acetonitrile), and 1.0×10^{-3} mol dm^{-3} (in 2-propanol). After the solvent and amine had been evaporated from the irradiated solutions, the products were separated by silica-gel column chromatography, using benzene as the eluent, and then recrystallized from benzene.

1-Hydroxy-2-methylanthraquinone (2): Mp 183.2—183.7 °C. Found: C, 75.46; H, 3.97%; M$^+$, 238. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 3.97%; M$^+$, 238. IR(KBr) 2931, 2857, 1670, and 1637 cm^{-1}. ^{1}H NMR($CDCl_3$) δ=2.41 (3H, s, CH_3), 7.40 (1H, d, J=8 Hz), 7.5—7.9 (3H, m), 8.0—8.4 (2H, m), 12.93

TABLE 1. PHOTOCHEMICAL ALKYLATION OF **1**[a)]

[R_3N]/mol dm^{-3}		Solvent	Yield/%			
			2	**3**	**4**	**5**
$R=C_2H_5$	0.14	CH_3OH	54	—	—	—
$R=C_2H_5$	0	CH_3OH	0	—	—	—
$R=C_2H_5$	0.30	CH_3CN	—	43	19	—
$R=C_2H_5$	0.20	*i*-PrOH	—	43	4	—
$R=CH_2(CH_2)_6CH_3$	0.076	*i*-PrOH	—	—	—	67

a) Conversion was 100% in each run.



(1H, s, OH).

1-Hydroxy-2-ethylanthraquinone (3): Mp 167.9—168.8 °C. Found: C, 76.25; H, 4.60%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79%. IR(KBr) 2960, 2920, 2878, 1672, and 1634 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, J=8 Hz, CH_3), 2.77 (2H, q, J=8 Hz, CH_2), 7.49 (1H, d, J=8 Hz), 7.6—7.9 (3H, m), 8.0—8.5 (2H, m), 12.83 (1H, s, OH).

Dimer(4): Mp 221.9—223.2 °C. Found: C, 76.50; H, 4.07%; M^+, 500. Calcd for $C_{32}H_{20}O_6$: C, 76.79; H, 4.03%: M^+,500. IR(KBr) 2964, 2926, 1667, and 1629 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.41 (3H, d, J=7 Hz, CH_3), 1.8—2.5 (2H, m, $CHC\underline{H}_2CH_2$), 2.85 (2H, t, J=7 Hz, $CHCH_2C\underline{H}_2$), 3.1—3.9 (1H, m, CH), 7.5—8.0 (6H, m), 8.1—8.4 (4H, m), 13.03 (1H, s, OH), 13.18 (1H, s, OH).

1-Hydroxy-2-octylanthraquinone (5): Mp 113.8—114.9 °C. Found: C, 78.34; H, 7.03%. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%. IR(KBr) 2933, 2852, 1668, and 1629 cm^{-1}. ^1HNMR ($CDCl_3$) δ=0.87 (3H, t, J=4 Hz, CH_3), 1.0—2.0 (12H, m, $CH_2(C\underline{H}_2)_6CH_3$), 2.69 (2H, t, J=8 Hz, $C\underline{H}_2(CH_2)_6CH_3$), 7.40 (1H, d, J=8 Hz), 7.5—7.9 (3H, m), 8.0—8.4 (2H, m), 13.06 (1H, s, OH).

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2) An authentic sample of 1-hydroxy-2-methylanthraquinone was synthesized by the hydrolysis of diazotized 1-amino-2-methylanthraquinone, which had been obtained from 2-methylanthraquinone by nitration and subsequent reduction.

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