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Photooxidation of Anthracene[*1]

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It was found that anthracene (I) was converted to 9,10-anthraquinone (III) and bianthrone (IV) by irradiation *via* anthracene peroxide (II). The reaction proceeded most effectively in carbon disulfide. Also IV was found to be oxidized to III by oxygen in singlet state.

Many reports on the photochemical oxidation of anthracene (I) and its derivatives have been found in literature. Among the photooxidation products of I, its dimer, anthraquinone (III), and anthracene peroxide (II)[1–8] have been reported. We have found that I afforded bianthrone (IV) beside III, the yield being 29% for IV and 21% for III. We have also found that the irradiation of II gave III and IV. This paper deals with the experiments on the formation of III and IV by the photoreaction of I or II, and the intermediacy of II, as well as the photochemical formation of III from IV.

Results and Disscution

When a solution of I in carbon disulfide was irradiated at room temperature with a 500 W high-pressure mercury lamp for 50 hr, five new spots appeared on thin-layer chromatography. These spots showed R_f values of 0.60 (A), 0.54 (B),

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1) C. Dufraisse and M. Gerard, *Bull. Soc. Chim. France*, **4**, 2052 (1937).

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4) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879 (1964).

5) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

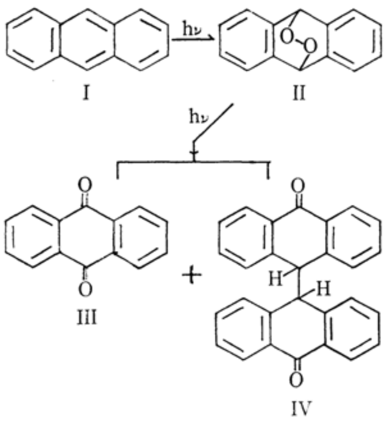
6) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

7) C. S. Foote, S. Wexler, W. Ando and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).

8) G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

0.43 (C), 0.33 (D), and 0.00 (E), respectively. The products A and B were isolated from the irradiation mixture by silica gel column chromatography. The product A was identified with authentic 9,10-anthraquinone (III) by IR and UV spectra, and mixture melting point. The product B, $C_{28}H_{18}O_2$, showed UV absorption maxima (ε) at 267(26700), 297(8700), and 315(5800) nm, and IR absorption bands at 1658, 1348, 1318 (one strong peak), and 690 cm^{-1}. The NMR spectrum of B showed signals in $CDCl_3$ at 4.74 (singelt), 6.80 (multiplet) and 7.90 (multiplet) at δ from TMS. The mass spectrum of B showed a parent peak at 386 *m/e* and base peak at 193 *m/e* (just half of the parent *m/e*). These physical data, elemental analysis and properties of IV described by Friend and co-worker[9] strongly suggested that B was 10,10′-bianthronyl(bianthrone) (IV).

In order to confirm the intermediacy of II in the photooxidation of I to III and IV, the authentic sample of II[7] saturated in carbon disulfide was irradiated. The reaction was followed at intervals by thin-layer chromatography. After 18 hr irradiation, III and IV were detected. The fact indicates that II is an intermediate in the photooxidation of I.



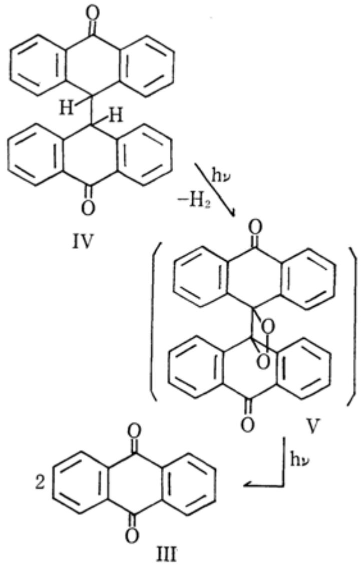
Scheme I

When an acetone solution of I was irradiated for an hour, only II was detected. The irradiation of the same solution for 50 hr gave only III. When a benzene solution of I was irradiated for an hour, II was detected. But if the irradiation period was prolonged for 50 hr, III with other products detected, but not IV.

In the case of the irradiation in ethanol solution, neither II, IIII nor IV was detected. Consequently, the photochemical reaction in an alcohol solution seems to be different from those in the other three solutions.

When a dioxane solution of IV was kept under a scattered light for 10 days, IV was quantitatively converted to III. If the solution was protected from any light with or without bubbling with oxygen, no reaction was observed.

Corey and Taylor[5] reported that I is converted to II with singlet excited O_2 produced by the method of Foner and Hudson.[10] Our experiment shows that IV is converted to III, and this conversion seems to be promoted by visible light. In fact, when IV in a dioxane solution was irradiated with 125 W high-pressure mercury lamp, III was not detected. Therefore, the formation of III from IV might be based on the photooxidation of IV with singlet excited O_2 corresponding to the excitation energy, $^1\Delta_g$ 0.977 eV (12700 Å) and $^1\Sigma_g$ 1.63 eV (7630 Å).[5] The excited oxygen might add to C_{10} and $C_{10'}$ position of IV with elimination of hydrogen to make V as intermediate, and the cleavage of O–O bond and C–C bond of V will take place between C_{10} and $C_{10'}$ position to give III.



Scheme II

Charier and Crippa[11] reported that I in acetic acid containing hydrogen peroxide, as oxidant, was converted to IV accompanying other products by sun-light irradiation for 60 hr. Our result shows that I is oxidized to III and IV without oxidant in fairly good yield, 29%. The qualitative studies of the solvent effect showed that carbon disulfide promoted most effectively the formation of IV. This suggests that the CS radical produced

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[9] K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.*, **28**, 2435 (1963).

[10] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 601 (1956); *ibid.*, **23**, 1974 (1955).

[11] G. Charier and G. B. Crippa, *Gazz. Chim. Ital.*, **57**, 741 (1927).

effectively by irradiation on CS$_2$ with Hg-vapor lamp,[12] plays an important role for cleavage of the O-O bond of II. Without CS radical II converts solely to III, as in the case of acetone and benzene solutions. This interpretation may be supported by the fact that no formation of III or IV in alcohol solution was detected.

Experimental

As a light source, a Daika 500 W high-pressure mercury lamp was used for the irradiation experiment in carbon disulfide, benzene or ethanol, and a Toshiba 110 V 200 W lamp for the preparation of anthracene peroxide. All solvents were freshly distilled before use. Anthracene was recrystallized twice from benzene.

Anthracene Peroxide (II). The method by Foote *et al.*[7] was modified. A solution of anthracene (0.54 g, 0.003 mol) and methylene blue (50 mg) in 250 m*l* of chloroform was placed in hydrogenation apparatus filled with O$_2$ gas and irradiated with stirring for 3 hr. The solution temperature was kept below 15°C during the irradiation. The consumed O$_2$ volume was 43 m*l* (0.00244 mol). The solution was passed through the column of silica gel (Kieselgel, Merck) to remove methylene blue. The colorless solution was obtained and evaporated to dryness under reduced pressure. The residue was chromatographed over silica gel with benzene to give 0.17 g of II, mp 146—147°C, R_f 0.34 (silicagel-benzene), IR (KBr disk) 1460, 1170, 950, 770 and 720 cm^{-1}, UV $\lambda_{\max}$ (Dioxane) (log ε) 270 (2.9) and 278 (2.8) nm.[7,13]

Irradiation of (II) in Carbon Disulfide. A saturated solution of II in carbon disulfide (about 10^{-2} mol/l) was sealed in a Pyrex tube and irradiated with a high-pressure mercury lamp for 18 hr. The reaction mixture was chromatographed on silica gel. When benzene (50 m*l*) was passed through the column, 9,10-anthraquinone (III) was eluted. Then the mixture of benzene and ethyl acetate (7:3) was passed through, bianthrone (IV) was eluted. III and IV were respectively identified with an authentic sample by mp, IR, UV, and R_f.

Irradiation of Anthracene (I) in Carbon Disulfide. The saturated solution of I (about 4 g) in 150 m*l* of carbon disulfide was irradiated with the high-pressure mercury lamp for an hour. The thin-layer chromatography of an aliquot from the reaction mixture showed a new spot at R_f 0.39 (benzene), corresponding to that of II. After irradiation for 50 hr, five new spots appeared on the thin-layer chromatogram (benzene-ethyl acetate 7 : 3), while the spot of II could not be found. The reaction mixture was evaporated to dryness, *in vacuo*, and 3.5 g of the mixture was obtained. The mixture (0.3 g) was dissolved in benzene and chromatographed on 20 g of silica gel. The first elution by benzene (120 m*l*) gave 0.063 g (21%) of product A (R_f, 0.62, benzene-ethyl acetate 7:3). The second elution by benzene-ethyl acetate (9:3) gave 0.079 g (29%) of product B (R_f 0.54, benzene-ethyl acetate 7 : 3). Other products, C (R_f 0.43), D (R_f 0.33) and E (R_f 0.00), were also obtained.

The product A showed IR absorption at 1675 (>C=O), 1596 (>C=C<, aromatic), 1355, 1320, 1306, 1285 ($^{=}$>C=O), and 690 (adjacent four protons of aromatic nuclei) cm^{-1}, UV absorption maxima at 252, 263, 272 and 325 nm in ethanol, and mp 272—282°C. These data were in accord with those of authentic 9,10-anthraquinone (III).[14]

The product B, recrystallized from benzene, light yellow needles, darkened at about 190°C and melted at 250—252°C (decomposition).

Found: C, 86.52; H, 4.66%. Calcd for C$_{28}$H$_{18}$O$_2$: C, 87.02; H, 4.69%. UV: $\lambda_{\max}^{\mathrm{EtOH}}$ (ε) at 267 (26700), 297 (8700) and 315 (5800) nm, IR: $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} at 1658 (>C=O), 1600 (>C=C<, aromatic), 1348, 1312 ($^{=}$>C=O), and 690 (adjacent four protons of aromatic nuclei). NMR: $\delta^{\mathrm{CDCl_3}}$, four kinds of signal at 4.74 (s, 2H, 10,10′-protons), 6.80 (m, 4H, 4,4′,5,5′-protons), 7.34 (m, 8H, 2,2′,3,3′,6,6′,7,7′-protons), and 7.90 (m, 4H, 1,1′,8,8′-protons). The mass spectrum gave parent peak at 386 *m*/*e* and base peak at 193 *m*/*e* (just half of the parent *m*/*e*).

Irradiation of I in Acetone. I (0.2 g) dissolved in acetone (14 m*l*), was irradiated at room temperature. In an hour, only the spot of R_f 0.34 (benzene) was detected, and after 50 hr, this spot completely disappeared and the spot of R_f 0.62 (benzene-ethyl acetate 7 : 3) appeared, indicating that II changed into III.

Irradiation of I in Benzene. I (0.2 g) dissolved in benzene (20 m*l*) was irradiated. In an hour, the spot of R_f 0.34 (benzene) was detected, and after 50 hr, five spots appeared, including a small spot of R_f 0.62 (benzene-ethyl acetate 7:3), corresponding to that of III.

Irradiation of I in Ethanol. As I was sparingly soluble in ethanol, the mixture of I and ethanol (60 m*l*) was stirred at boiling point. After the solution was placed for 24 hr at ordinary temperature, the excess of I was filtered and the filtrate was irradiated for 3 hr. II, III or IV was not detected, while the fluorescent of I disappeared.

Irradiation of Bianthrone (IV) in Dioxane. IV (1.3 mg) was dissolved in dioxane (200 m*l*) and the solution was allowed to stand. After 10 days, the UV spectrum showed that IV changed into III and the spot of R_f 0.62 (benzene-ethyl acetate 7:3) was detected. When intercepted from any light with or without oxygen, the reaction from IV to III did not take place.

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[12] W. Doran and A. E. Gillan, *J. Soc. Chem. Ind.*, **47**, 259$^{\mathrm{T}}$ (1928), for example.

[13] I. Gillet, *Bull. Soc. Chim. France*, **1950**, 1135.

[14] H. Hartmann, *Z. Naturforsch.*, **7a**, 360 (1952).