

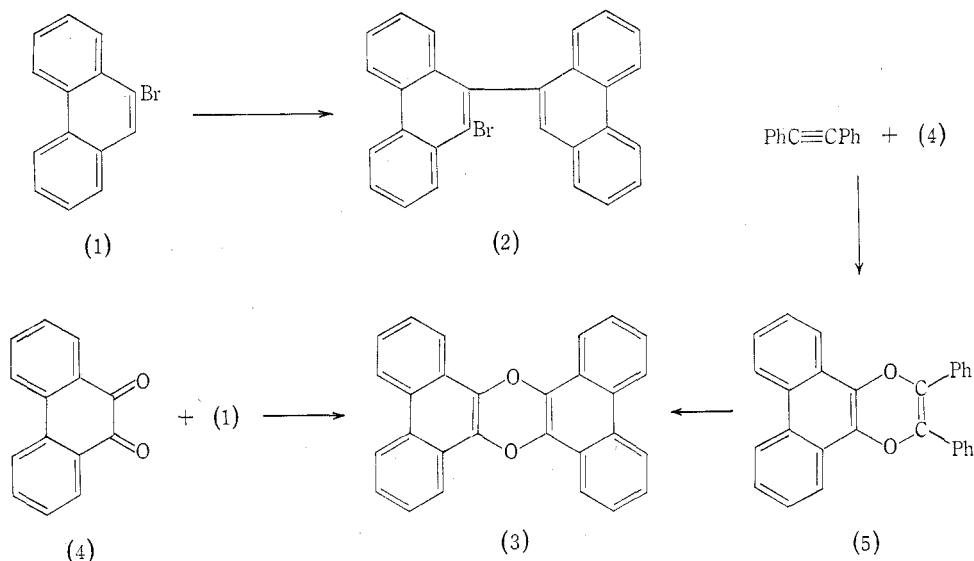
SOME PHOTOCHEMICAL REACTIONS OF 9-BROMOPHENANTHRENE

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[Manuscript received June 16, 1970]

The report by Farid and Hess¹ on the photochemistry of 9-bromophenanthrene (1) prompts us to record some related observations.

Irradiation of (1) in degassed hexane gave a hexane-soluble photoproduct which was purified by chromatography on silica gel. The compound, C₂₈H₁₇Br, which was more polar than (1), had spectral properties (infrared, ultraviolet, and n.m.r., see Experimental) consistent with those of a simple phenanthrene derivative. Since the photoproduct also gave 9,9'-biphenanthryl² on debromination, it has been assigned structure (2).



The formation of (2) represents an unusual coupling of two molecules of an aromatic monohalide with retention of one of the halogen atoms. While photochemical reactions of aromatic bromides and iodides are well known,³ they usually involve attack of the generated free radical upon aromatic or olefinic solvents, or an intramolecular attack of the free radical upon another suitably located ring. We are not aware of a close precedent for the conversion of (1) into (2).

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¹ Farid, S., and Hess, D., *Chem. Ber.*, 1969, **102**, 3747.

² Bachmann, W. E., *J. Am. chem. Soc.*, 1934, **56**, 1363.

³ Sharma, R. K., and Kharasch, N., *Angew. Chem. int. Edn*, 1968, **7**, 36.

Some years ago, we observed the formation (in very low yield) of an exceedingly insoluble compound, $C_{28}H_{16}O_2$, m.p. $>340^\circ$, when a solution of (1) in non-degassed benzene was exposed to sunshine. Its spectral properties (in particular, its n.m.r. spectrum which is quite similar to that of (4)⁴), and the formation of a transient blue-green colour with H_2SO_4 - HNO_3 , suggested that it was the dibenzo-*p*-dioxin derivative⁵ (3). Confirmation of the correctness of this assignment was obtained in two ways. Firstly, the compound was formed in low yield (12%) when a mixture of 9-bromophenanthrene (1) and phenanthrene-9,10-quinone (4) was irradiated in benzene; this reaction has now been independently described by Farid and Hess.¹ Secondly, compound (3) was formed in very low yield (4%) after an equimolecular mixture of (4) and tolan (diphenylacetylene) in benzene had been irradiated. In this reaction, compound (3) is undoubtedly formed via (5)⁶ which subsequently forms the phenanthrene system by the reaction investigated in detail by Mallory.⁷

The reaction of compound (3) with H_2SO_4 - HNO_3 is noteworthy since the blue-green colour fades within seconds at room temperature to give a clear, straw-coloured solution. These changes indicate the almost instantaneous disappearance of (3), which is itself not noticeably soluble in H_2SO_4 alone. Dilution of the mixture with water gave two products: the major one proved to be 2,5-dinitrophenanthrene-9,10-quinone, while the minor one has been tentatively identified as 2,7-dinitrophenanthrene-9,10-quinone by thin-layer chromatography. Both these products are formed⁸ when phenanthrene-9,10-quinone (4) is nitrated.

External circumstances preclude continuation of this work.

Experimental

Melting points are uncorrected; infrared spectra were run in KBr disks.

Irradiation of 9-Bromophenanthrene

9-Bromophenanthrene (1.5 g) was irradiated (high-pressure Hg lamp, Pyrex vessel) in degassed hexane (150 ml) for 48 hr. The reaction mixture was filtered and chromatographed over SiO_2 . Hexane removed unchanged starting material, and hexane containing 2% benzene eluted 10-bromo-9,9'-biphenanthryl, recrystallized from hexane as pale-yellow crystals, m.p. 251 – 253° (360 mg, 12%); infrared spectrum: 3000, 1550, 1410, 1208, 1040, and 915 cm^{-1} ; λ_{max} (cyclohexane) 350.5, 343, 335, 327sh, 301, 289, 268sh, 258, and 228 nm ($\log \epsilon$ 2.7, 2.8, 2.9, 3.1, 4.3, 4.3, 4.7, 4.9, and 4.9); the n.m.r. showed only complex aromatic absorption (Found: C, 77.7; H, 3.8; Br, 18.8; m/e 432, 434. $C_{28}H_{17}Br$ requires C, 77.6; H, 4.0; Br, 18.4%; mol. wt., 433.3).

Debromination of 10-Bromo-9,9'-biphenanthryl (2)

A mixture of (2) (50 mg), 10% Pd/C (20 mg), 90% hydrazine hydrate (0.5 ml), water (0.5 ml), and ethanol (10 ml) was refluxed for 3 hr. After filtration the solution was evaporated to yield 9,9'-biphenanthryl, m.p. 184 – 186° (lit.² 184 – 185°) (from methanol-chloroform). The

⁴ Batterham, T. J., Tsai, L., and Ziffer, H., *Aust. J. Chem.*, 1964, **17**, 1963.

⁵ Kondo, H., and Tomita, M., *Arch. Pharm., Berl.*, 1936, **274**, 73; Tomita, M., and Tani, C., *J. Pharm. Soc. Japan*, 1942, **62**, 94.

⁶ Schönberg, A., and Mustafa, A., *J. chem. Soc.*, 1945, 551.

⁷ Wood, C. S., and Mallory, F. B., *J. org. Chem.*, 1964, **29**, 3373, and literature quoted therein.

⁸ Kato, S., Maezawa, M., Hirano, S., and Ishigaki, S., *Yuki Gasei Kagaku Kyōkai Shi*, 1957, **15**, 29 (*Chem. Abstr.*, 1957, **51**, 10462g).

product was identical (m.p. and mixed m.p., infrared spectrum) with a sample of 9,9'-biphenanthryl prepared by the method of Bachmann.²

9,10,9',10'-Diphenanthro-p-dioxin (3)

A solution of phenanthrene-9,10-quinone (0.5 g) and 9-bromophenanthrene (0.62 g) in non-degassed benzene (100 ml) was irradiated for 96 hr. The product (0.11 g, 12%) was filtered off, washed with benzene and methanol, and recrystallized from nitrobenzene to give colourless crystals, m.p. $>340^{\circ}$; infrared spectrum: 1630, 1610, 1462, 1365, 1350, 1080, 1047, 763, and 725 cm^{-1} ; δ ($\text{C}_6\text{D}_5\text{NO}_2$) $m\ 7.6$, $m\ 8.6$, $m\ 8.9$ (Found: C, 87.6; H, 4.4; $m/e\ 384$. $\text{C}_{28}\text{H}_{16}\text{O}_2$ requires C, 87.5; H, 4.2%; mol. wt., 384). A similar experiment using tolan (0.449 g) instead of 9-bromophenanthrene gave (3) (36 mg, 4%).

Nitration of the Dioxin (3)

Nitric acid (1 ml) was added dropwise to a slurry of (3) (300 mg) in sulphuric acid (5 ml). The initial blue-green color was quickly discharged, leaving a light yellow solution. The reaction mixture was poured onto ice (150 g), extracted into benzene, and the solvent evaporated. Chromatography of the yellow residue (preparative t.l.c., SiO_2 , CHCl_3) gave two major products: one ($R_F\ 0.7$) was 2,5-dinitrophenanthrene-9,10-quinone, yellow crystals, m.p. $224\text{--}228^{\circ}$ (lit.⁸ 228°) (from ethyl acetate-hexane). The compound was compared (mixed m.p. and i.r.) with a sample prepared by the direct nitration of phenanthrene-9,10-quinone. Although the second product ($R_F\ 0.5$) could not be isolated in a crystalline form, it had the same chromatographic characteristics as 2,7-dinitrophenanthrene-9,10-quinone, also formed by direct nitration of the parent quinone.