Photochemical Reaction of Phenanthraquinone and Benzene

By MORDECAI B. RUBIN* and ZIVA NEUWIRTH-WEISS

(*Department of Chemistry, Technion—Israel Institute of Technology, Haifa, Israel*)

PHOTOCYCLOADDITIONS of benzene with olefinic and acetylenic compounds have been known[1] for some time. Recently, there have been indications that benzene may also undergo reaction with a photoexcited carbonyl-group in various ketones and diketones,[2] including benzophenone,[3] biacetyl,[4] duroquinone,[5] and 1,1,4,4-tetramethyltetralin-2,3-dione.[6] Evidence is available from quantum yield, flash photolysis, and e.s.r. studies but the nature of the products has not been established. We now report the products of reaction of 9,10-phenanthraquinone (PQ) with benzene.

Irradiation at 4358 Å of a degassed,† $3{\cdot}5 \times 10^{-4}$M-solution of PQ in benzene resulted in disappearance[7] of the PQ absorption, with an initial quantum yield of 0·25. Continued irradiation led to a colourless solution with a u.v. spectrum characteristic of derivatives of 9,10-dihydroxyphenanthrene[8] (λ_{max} 256, 274sh, 297, 307, 327sh, 345, and 360 nm.). Isosbestic points were observed at 320, 355, and 370 nm.

Repetition of the reaction under nitrogen on a preparative scale‡ with a filter to eliminate radiation below 3800 Å, resulted in precipitation

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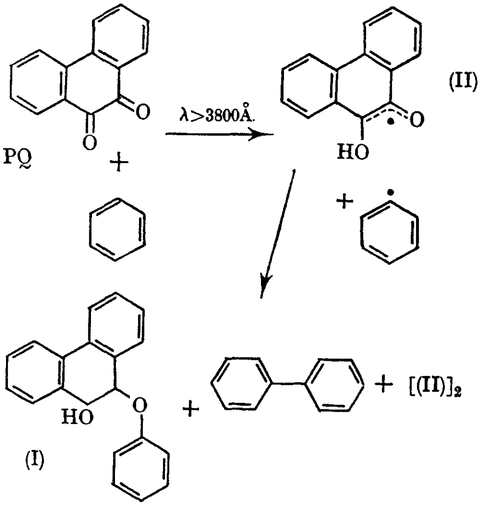
† The presence of oxygen resulted in appreciable retardation and led to unidentified products.

‡ A solution of 1 g. of PQ in 200 ml. of benzene was irradiated for six days with a 450 w Hanovia immersion lamp while bubbling purified nitrogen through the solution.

of phenanthraquinhydrone (10%). Chromatography of the filtrate on Florisil afforded biphenyl (19%,§ a crystalline product [(I); 13%], and PQ (30%), as well as 15% of uncharacterized, amorphous material. The compound (I), m.p. 140—141°, was a 1:1 adduct of PQ and benzene (M^+ 286). Its melting point was identical with that reported[9] for the monophenyl ether of 9,10-dihydroxyphenanthrene and its elemental analysis and spectroscopic properties (i.r. λ_{max} 2·95, 6·15, 6·25 μm.; u.v. cited above: n.m.r., complex multiplets at τ 1·2—1·8, 2·2—3) are in full agreement with this structure.



The formation of (II) might be rationalized by an addition–rearrangement sequence. However, the presence of biphenyl, (I), and the quinhydrone strongly suggest the intermediacy of phenyl and PQ semiquinone radicals (II). The simplest explanation for their formation is the assumption that excited PQ¶ abstracts a hydrogen atom from benzene to give the two radicals followed by product formation. The possibility of a mechanism involving energy transfer to benzene is most unlikely in view of the low triplet energy of PQ (E_T *ca.* 49 kcal.). Photoreactions involving *n*, π^* excitation of other carbonyl compounds in benzene may follow a similar course. Clearly, inclusion of benzene in the category of inert solvents in photochemical reactions can be unjustified.

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§ The actual yield of biphenyl is estimated to be about 25% since appreciable losses due to volatilization of biphenyl were observed in a control experiment.

¶ Benzene is completely transparent at the wavelengths used.

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[6] G. E. Greame, J. C. Paice, and C. C. R. Ramsay, *Austral. J. Chem.*, 1967, **20**, 1671.

[7] Decolourization of solutions of PQ in benzene upon exposure to light was first observed by R. A. Reith.

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