48. *The Photochemical Addition of Benzaldehyde to Quinones.*

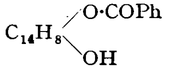
By R. F. Moore and William A. Waters.

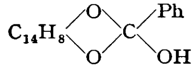
Chemical and spectroscopic evidence indicates that the photochemical addition product of benzaldehyde and phenanthraquinone has the formula (I) originally proposed by Klinger (*Annalen*, 1888, **249**, 143) and not the cyclic structure (II) suggested by Schönberg and Moubasher (*J.*, 1939, 1430). An analogue of (I) has been prepared from benzaldehyde and chloranil. A chain mechanism for the photochemical addition is proposed.

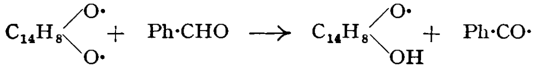
In connection with recent studies of the addition of free radicals to the oxygen atoms of quinones (Bickel and Waters, *J.*, 1950, 1764; Moore and Waters, *J.*, 1952, 2432) we have reinvestigated the photochemical addition of benzaldehyde to phenanthraquinone, first reported by Klinger (*loc. cit.*) and later studied by Schönberg and Moubasher (*loc. cit.*), Mustapha (*J.*, 1949, S 83), and Schönberg, Latif, Moubasher, and Sina (*J.*, 1951, 1354). Klinger, who exposed his mixture to sunlight in Germany for a few days, obtained a colourless crystalline product, m. p. 177—178°, to which, from the results of ultimate analysis and alkaline hydrolysis to benzoic acid, he assigned the constitution 9-benzoyloxy-10-hydroxyphenanthrene (I). Schönberg and Moubasher, who obtained a product of the same m. p. after exposing their mixture for several days to sunlight in Cairo, put forward the alternative cyclic formula (II) since (*a*) the product does not give a ferric chloride reaction and (*b*) from a similar reaction, using *p*-chlorobenzaldehyde, they obtained an analogous product which after methylation with diazomethane was hydrolysed by alkali to give methyl *p*-chlorobenzoate. In 1951 Schönberg and his colleagues suggested that the two forms might exhibit ring–chain tautomerism in solution.

We have now found that an identical substance can be prepared in nearly theoretical yield by shaking for 3 days, under nitrogen, a solution of phenanthraquinone in benzaldehyde in a thin-walled glass bulb exposed to the radiation from a 300-watt Hanovia ultra-violet lamp. All these reported yields are so high that a photochemical chain reaction of very long chain-length must be involved.

By the kindness of Professor A. Schönberg we have been able to compare our product with his. The two specimens have identical m. p.s and mixed m. p., and their infra-red spectra are completely identical between 5000 and 660 cm.$^{-1}$. The infra-red spectrum accords with formula (I), since it shows a pronounced absorption maximum at 5·82 μ corresponding to the stretching frequency of a C═O group in a benzoate ester. Other spectral features expected for structure (I) are exhibited. Since the infra-red spectra were measured by using pastes of the solid materials in a liquid-paraffin base there is little chance of conversion from (I) into (II).


$C_{14}H_8{<}\substack{O\cdot COPh\\ OH}$
(I)

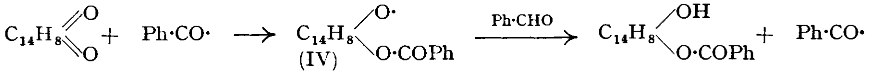

(II)


$C_{14}H_8{<}\substack{O\cdot\\ O\cdot} + Ph\cdot CHO \longrightarrow C_{14}H_8{<}\substack{O\cdot\\ OH} + Ph\cdot CO\cdot$
(III)

We have also methylated our product with diazomethane exactly as described by Schönberg and Moubasher and obtained a crystalline methyl ether, m. p. 134° (they give 80°), which on hydrolysis yielded benzoic acid and 9-hydroxy-10-methoxyphenanthrene. The latter on acetylation gave a stable acetoxy-derivative identical with that prepared by methylating 9-acetoxy-10-hydroxyphenanthrene.

Our photochemical addition product (I), when finely dispersed by precipitation with water from alcoholic solution, promptly dissolved in cold aqueous sodium hydroxide. It did not give a ferric chloride colour, but this is not a diagnostic test for a completely *ortho-* and *para*-blocked phenol. A similar sequence of reactions has been carried out with the photochemical addition product of anisaldehyde and phenanthraquinone (Klinger, *Annalen*, 1911, **382**, 218). Moreover, we have found that chloranil and benzaldehyde combine photochemically in a very similar way to give the monobenzoate of tetrachloroquinol : no ring closure is possible here.

We suggest, from the relation of this to our earlier work (*loc. cit.*), that the process has the following radical-chain mechanism : (i) Photochemical activation of the quinone to a di-radical (III). (ii) Hydrogen abstraction by (III) from benzaldehyde (chain-starting). (iii) A long chain reaction in which benzoyl radicals add on to unactivated phenanthraquinone molecules, giving aryloxy-radicals (IV) which can dehydrogenate fresh benzaldehyde molecules :


$C_{14}H_8{<}\substack{O\\ O} + Ph\cdot CO\cdot \longrightarrow C_{14}H_8{<}\substack{O\cdot\\ O\cdot COPh} \xrightarrow{Ph\cdot CHO} C_{14}H_8{<}\substack{OH\\ O\cdot COPh} + Ph\cdot CO\cdot$
(IV)

With unsymmetrical quinones, or quinoneimines, this chain would take a unidirectional course, the radical (IV) of greater stability being formed (compare Schönberg and Awad, *J.*, 1945, 197).

EXPERIMENTAL

Irradiation of Phenanthraquinone with Benzaldehyde.—The quinone (5 g.) and dry benzaldehyde (15 g.), sealed under nitrogen in a thin-walled bulb of soda-glass, were shaken for 75 hours in the radiation from a 300-w. Hanovia ultra-violet lamp. The quinone dissolved, giving a dark orange solution from which a white solid separated. After removal of excess of benzaldehyde under reduced pressure, this residue (6·5 g.) was washed with, and crystallised from benzene, forming colourless woolly needles, m. p. 185° (some decomp.) (Found : C, 80·1 ; H, 4·7. Calc. for $C_{21}H_{14}O_3$: C, 80·3; H, 4·4%), which had the properties described above. The infra-red spectrum of a dispersion of the solid in paraffin paste exhibited the following characteristic bands: 2·99 μ, H–O stretching; 5·82 μ, C═O stretching in benzoate ester; 7·8—8·0 μ, –O–CO– stretching ; 13·32 μ, bending frequencies of C_6H_4 in phenanthrene rings ;

13·85 and 14·16 μ, bending frequencies of C_6H_5. A sample of the solid, thought to have structure (II), sent to us by Prof. A. Schönberg had an identical m. p. and mixed m. p. and a completely coincident infra-red spectrum.

Benzoylation of our material gave 9 : 10-dibenzoyloxyphenanthrene, m. p. 218° unchanged in admixture with an authentic specimen.

Methylation of our Photochemical Product (cf. Schönberg and Moubasher, *loc. cit.*).—To ethereal diazomethane (from 4·5 g. of methylnitrosourea) at 0°, 3 g. of the substance were added gradually, and the solution was stored at 0° for 24 hours. The product (2·8 g.) formed colourless prisms (from ethanol), m. p. 134° (Found : C, 80·3; H, 5·2. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%), evidently of 9-*benzoyloxy*-10-*methoxyphenanthrene*, having an infra-red spectrum with strong absorption bands at: 5·74 μ, due to C=O stretching; grouped bands at 7·9—8·15 μ, due to C–O–C stretching; 13·30 μ, due to C_6H_4; 13·79 and 14·15 μ, due to C_6H_5.

The methyl ether (1 g.) was refluxed for 15 minutes with potassium hydroxide (3 g.) in water–ethanol (10 ml., 20 ml.). The dried chloroform extract of the acidified solution on evaporation gave an oil which was obtained as colourless needles (from light petroleum), m. p. 95—102°, after some difficulty (Goldschmidt and Schmidt, *Ber.*, 1922, **55**, 320, give m. p. 103° for 9-hydroxy-10-methoxyphenanthrene). These were acetylated by warming them for 2½ hours with acetic anhydride. The product (Found : C, 76·5, H, 5·4. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·2%) formed prisms (from ethanol), m. p. 113° unchanged after admixture with a specimen of 9-*acetoxy*-10-*methoxyphenanthrene*, prepared by methylating the hydroxy-phenanthrene (*idem, ibid.*, give m. p. 170°, decomp.)

Irradiation of Phenanthraquinone and Anisaldehyde (cf. Klinger, 1911, *loc. cit.*).—Phenanthraquinone (3 g.) and anisaldehyde (9 g.) in benzene (20 ml.) were irradiated, as described above, for 70 hours. The white solid formed woolly needles (4·8 g., 100%), m. p. 231° (decomp.), from acetic acid (Found : C, 77·0; H, 4·9. Calc. for $C_{22}H_{16}O_4$: C, 76·8; H, 4·6%). This 9-anisoyloxy-10-hydroxyphenanthrene gives no colour with ferric chloride, and can be dissolved in cold sodium hydroxide only if finely divided by precipitation with water from alcohol or acetone solution. For methylation the solid (3 g.), which was very sparingly soluble in ether, was dissolved in dry dioxan–ether and added to ethereal diazomethane at 0°. The 9-*anisoyloxy*-10-*methoxyphenanthrene* (2 g.) crystallised from ethanol in needles, m. p. 158° (Found : C, 76·7; H, 5·2. $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·0%). Attempted hydrolysis of this substance by shaking it with 20% sodium hydroxide at 40° for ½ hour failed (cf. Schönberg and Moubasher, *loc. cit.*). Hydrolysis by alcoholic alkali, followed by acetylation, yielded *p*-anisic acid, m. p. 184°, and 9-acetoxy-10-methoxyphenanthrene, m. p. and mixed m. p. 113°.

Irradiation of Chloranil and Benzaldehyde.—Chloranil (2 g.) in benzaldehyde (10 ml.) was irradiated by a 500-w. Hanovia ultra-violet lamp for 96 hours, the excess of benzaldehyde removed under reduced pressure, and the residual gum rubbed with acetic acid until it solidified. Crystallisation from this solvent gave the *monobenzoate* of tetrachloroquinol as colourless prisms (1 g.), m. p. 180° (Found : C, 44·8; H, 1·9; Cl, 40·7. $C_{13}H_6O_3Cl_4$ requires C, 44·4; H, 1·7; Cl, 40·3%), which gave no ferric chloride colour but dissolved in cold dilute sodium hydroxide solution. Benzoylation with benzoyl chloride in boiling pyridine solution gave the dibenzoate, colourless prisms (from glacial acetic acid), m. p. 238° not depressed on admixture with a specimen prepared from tetrachloroquinol.

We thank Professor A. Schönberg for allowing us to carry out the direct comparison of our respective products, and also Dr. F. B. Strauss for help in the measurement and interpretation of the infra-red spectra. The micro-analyses were made by Drs. Weiler and Strauss.

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