306. *Photo-reactions. Part IV.* Photo-reaction between Phenanthraquinone and Aromatic Aldehydes. A New Passage from Phenanthraquinone to Fluorenone.*

By Alexander Schönberg and Radwan Moubacher.

Phenanthraquinone readily adds *p*-chlorobenzaldehyde in the presence of light with formation of the cyclic *ether* (II*a*), the nature of which is established by the fact that the product of its methylation with diazomethane (IV*a*) yields methyl *p*-chlorobenzoate and 9 : 10-dihydroxyphenanthrene on alkaline hydrolysis under mild conditions. The photo-addition compounds of phenanthraquinone and other aromatic aldehydes are formulated similarly. (II) furnishes fluorenone and benzoic acid on pyrolysis at 200°. α-Stilbenediol diacetate decomposes at 165° with formation of benzil.

In direct sunlight, phenanthraquinone reacts with benzaldehyde in a sealed tube with formation of colourless crystals which Klinger (*Annalen*, 1888, **249**, 137) believed to be the *O*-monobenzoyl derivative of 9 : 10-dihydroxyphenanthrene (I). This formula accounts

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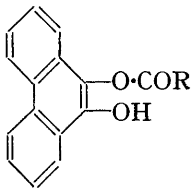
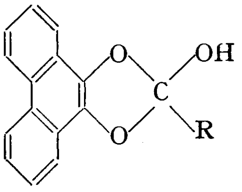
* Compare *Ber.*, 1933, **66**, 567; *Annalen*, 1935, **518**, 299; *Trans. Faraday Soc.*, 1936, **32**, 514.

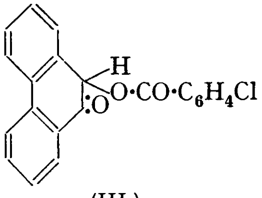
for the lack of colour of the compound and the formation of benzoic acid and 9 : 10-dihydroxyphenanthrene on hydrolysis, but cannot be reconciled with the insolubility of the substance in alkali and its inertness towards diphenyldiazomethane, which, so far as is known, reacts with all phenols (Staudinger and co-workers, *Ber.*, 1916, **49**, 1936). Our investigation shows that the photo-addition compound must be regarded as the cyclic *ether* (II). There seems to be a great tendency for 9 : 10-derivatives of phenanthrene to form rings; *e.g.*, phenanthrene-9 : 10-dicarboxylic acid is unstable and readily changes into the anhydride (Jeanes and Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2612).



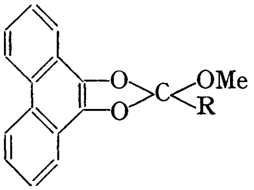
(I, R = C_6H_5.)
(I*a*, R = *p*-C_6H_4Cl.)



(II, R = C_6H_5.)
(II*a*, R = *p*-C_6H_4Cl.)



(III.)

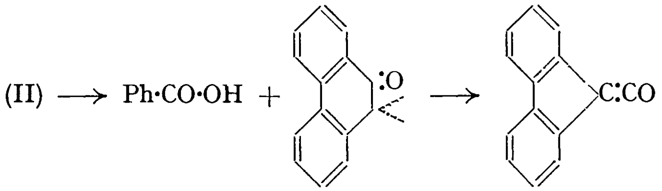


(IV, R = C_6H_5.)
(IV*a*, R = *p*-C_6H_4Cl.)

The photo-addition compounds of phenanthraquinone and benzaldehyde, *p*-chlorobenzaldehyde, and anisaldehyde are formed under the same conditions, manifest analogous chemical behaviour, and therefore must be regarded as having analogous constitutions.

The photo-addition compound of phenanthraquinone and *p*-chlorobenzaldehyde yields 9 : 10-dihydroxyphenanthrene on hydrolysis and therefore might have formula (I*a*), (II*a*), or (III). The structure (II*a*) is established by the fact that the product of methylation with diazomethane must have formula (IV*a*), since on hydrolysis it gives 9 : 10-dihydroxyphenanthrene and methyl *p*-chlorobenzoate (this ester is an easily identifiable, crystalline substance and it is for this reason that we selected the photo-addition compound of phenanthraquinone and *p*-chlorobenzaldehyde for investigation).

Thermal Decomposition of the Photo-addition Compound (II).—When the compound (II) was heated for one hour at 200° in a vacuum, benzaldehyde and phenanthraquinone were produced in relatively small quantities and benzoic acid and flourenone in better yields. The pyrolysis evidently proceeded in two different ways : (*a*) the reverse of the process of formation, and (*b*) the main reaction, illustrated by the following scheme, which shows the formation of diphenyleneketen. A somewhat similar scheme was advanced by Schröter (*Ber.*, 1909, **42**, 2336) to explain the formation of diphenylketen from azibenzil. The fact that the substance isolated was fluorenone may be due to the action of oxygen during recrystallisation, for diphenyleneketen is rapidly converted in air into fluorenone (Staudinger, *Ber.*, 1906, **39**, 3065).



Certain diol derivatives seem to be very sensitive to heat; *e.g.*, benzil is readily formed from α-stilbenediol diacetate.

EXPERIMENTAL.

Photo-chemical Reaction of Benzaldehyde and Phenanthraquinone.—Phenanthraquinone (5 g.) was shaken with benzaldehyde (10 g.) in a sealed quartz tube in sunlight for 4 days. The white precipitate formed was washed with small amounts of benzene and crystallised from this solvent, from which the *phenylhydroxymethylene* ether of 9 : 10-dihydroxyphenanthrene (II) separated in colourless needles (6·5 g.), m. p. 177—178° to a dark brown liquid (Found : C, 80·8; H, 4·7. $C_{21}H_{14}O_3$ requires C, 80·4; H, 4·4%). It was soluble in alcohol and acetic acid and immediately decolorised bromine in chloroform.

Action of Nitric Acid.—The above compound (1 g.) was heated with nitric acid (25 c.c.; *d* 1·30) for ¼ hour at 90°. The red product was washed with water and crystallised from benzene, from which phenanthraquinone separated in orange crystals (0·18 g.), m. p. and mixed m. p. 208° (Found : C, 80·6; H, 3·9. Calc. : C, 80·7; H, 3·8%).

Action of Diazomethane.—To an ethereal solution of diazomethane (prepared from nitrosomethylurethane, 1 g.) at 0° was added gradually 1 g. of the substance (II). Evaporation of the solvent after 24 hours left a substance which, crystallised from benzene, gave the *phenylmethoxymethylene* ether of 9 : 10-dihydroxyphenanthrene (IV) in white needles (0·85 g.), m. p. 80° (Found : C, 80·5; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%), soluble in benzene.

Action of Alkali on the Methoxy-ether (IV).—The compound (1 g.) was shaken with 20% aqueous sodium hydroxide (20 c.c.) at 40° for ½ hour, and air then bubbled through the cooled filtered liquid for 2 hours. The orange crystals obtained were recrystallised from benzene, giving phenanthraquinone, m. p. and mixed m. p. 208°.

Photo-chemical Reaction of p-*Chlorobenzaldehyde and Phenanthraquinone.*—Phenanthraquinone (2 g.) and *p*-chlorobenzaldehyde (1·5 g.) in dry benzene (100 c.c.) were shaken in a sealed quartz tube in sunlight for 2 days. The white precipitate obtained was washed and crystallised from benzene, from which the p-*chlorophenylhydroxymethylene* ether of 9 : 10-dihydroxyphenanthrene (II*a*) separated in colourless needles (3 g.), m. p. about 222° (decomp.) to a red-brown liquid (Found : C, 72·9; H, 4·2; Cl, 9·8. $C_{21}H_{13}O_3Cl$ requires C, 72·3; H, 3·8; Cl, 10·1%), soluble in alcohol, acetic acid, and benzene.

Action of Diazomethane.—1 G. of the substance (II*a*) was gradually added to an ethereal solution of diazomethane (von Pechmann, *Ber.*, 1895, **28**, 855) and then left at 0° for 24 hours. The solid obtained on evaporation of the solvent was crystallised from benzene, from which the p-*chlorophenylmethoxymethylene* ether of 9 : 10-dihydroxyphenanthrene (IV*a*) separated in colourless needles (0·95 g.), m. p. 170° (Found : C, 72·9; H, 4·4; Cl, 9·7. $C_{22}H_{15}O_3Cl$ requires C, 72·9; H, 4·4; Cl, 9·8%).

Hydrolysis of the p-*Chlorophenylmethoxymethylene Ether* (IV*a*).—The ether (1 g.) was heated with 20% sodium hydroxide solution (30 c.c.) at 40° for ½ hour. The solid product was collected when cold, washed with sodium bicarbonate solution and with cold water, dried, and dissolved in benzene. Evaporation of the filtered solution gave a residue, which was crystallised from benzene : the first crystals were rejected and methyl *p*-chlorobenzoate was then isolated; it had m. p. 48°, not depressed by an authentic sample prepared by the action of diazomethane on *p*-chlorobenzoic acid. The original alkaline filtrate gave phenanthraquinone, m. p. 208°, after 2 hours' aeration at 25°.

Thermal Decomposition of the Phenylhydroxymethylene Ether (II).—The ether (2 g.) was heated in a long-necked flask in an air-bath at 200° for 1 hour in such a way that only the lower part of the flask was in the bath. A vacuum was maintained during the process and throughout the subsequent cooling to room temperature. Four products were obtained : (1) A brown-red substance on the bottom of the flask, after several crystallisations from benzene, gave yellow crystals of fluorenone, m. p. and mixed m. p. 82° (Found : C, 86·7; H, 4·7. Calc. for $C_{13}H_8O$: C, 86·7; H, 4·4%). (2) A small quantity of substance which crystallised on the walls in orange needles was identified as phenanthraquinone, m. p. 208° (Found : C, 80·6; H, 4·0. Calc. for $C_{14}H_8O_2$: C, 80·7; H, 3·9%). (3) A substance which volatilised during the heating and solidified on the higher cold part of the apparatus in brilliant colourless crystals was recrystallised from alcohol, giving benzoic acid, m. p. and mixed m. p. 120° (Found : C, 68·7; H, 4·9. Calc. for $C_7H_6O_2$: C, 68·8; H, 4·9%). (4) The odour of benzaldehyde was perceptible in the flask.

α-*Stilbendiol Diacetate.*—This was prepared by Thiele's method (*Annalen*, 1899, **306**, 142), modified as follows : A solution of benzil (50 g.) in acetic anhydride (300 c.c.) was stirred at 70° while a mixture of concentrated sulphuric acid (50 c.c.) and glacial acetic acid (100 c.c.), followed by zinc dust (60 g.), was gradually added. The whole was left for ½ hour and ether then extracted α-stilbenediol diacetate. This was crystallised from benzene and (1 g.) then heated at 165° under the conditions described in the preceding paragraph. The oily residue obtained yielded, after 12 hours at room temperature, needles (0·45 g.), m. p. 93° after recrystallisation from benzene, not depressed by authentic benzil (Found : C, 80·0; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·7%).

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