50. *Photo-reactions. Part IX. The Action of Aldehydes on Phenanthraquinoneimine in Sunlight.*

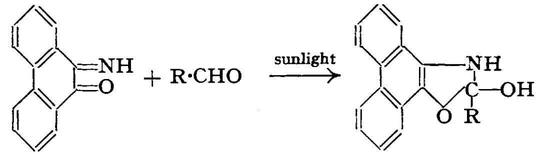
By Alexander Schönberg and William Ibrahim Awad.

In sunlight, aldehydes react with phenanthraquinoneimine with formation of 2-hydroxy-2 : 3-dihydrophenanthroxazole derivatives (see A). These decompose with loss of water on heating. There is a similarity between reaction (A) and the photo-reaction between phenanthraquinone and aldehydes which leads to substances of the general formula (III) (*e.g.*, R = Ph). The possibility of ring-chain tautomerism (II)$\rightleftarrows$(IV) is discussed.

Stein and Day (*J. Amer. Chem. Soc.*, 1942, **64**, 2567) found that phenanthraquinoneimine (I) and benzaldehyde do not react when refluxed in alcohol, but in presence of a catalyst, *e.g.*, piperidine or triethylamine, reaction occurs with elimination of water and formation of 2-phenylphenanthroxazole :

$$\text{(I)} + \text{Ph·CHO} \longrightarrow H_2O + C_{21}H_{13}ON$$

We have found that phenanthraquinoneimine does not react (or only to a very small extent) with benzaldehyde in benzene solution at room temperature in the dark, but in sunlight 2-hydroxy-2-phenyl-2 : 3-dihydrophenanthroxazole (II*b*) is formed. Similar reactions were carried out with acetaldehyde, *p*-anisaldehyde, *p*-chlorobenzaldehyde, piperonal, and 2-methoxy-1-naphthaldehyde. Reaction proceeds very rapidly with acetaldehyde, benzaldehyde, and *p*-anisaldehyde, but is considerably slower with 2-methoxy-1-naphthaldehyde, possibly owing to steric hindrance (ortho-effect).

(I.)


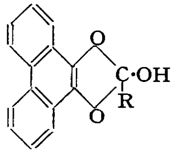
(II.) (Scheme A)

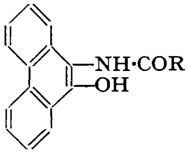
[II*a*, R = Me. II*b*, R = Ph. II*c*, R = C_6H_4·OMe (*p*). II*d*, R = *p*-C_6H_4Cl. II*e*, R = $C_6H_3{:}O_2CH_2$. II*f*, R = 2-OMe-1-$C_{10}H_6$]

Properties of the Photo-products.—The photo-products (II) are colourless or almost colourless crystalline substances of high m. p. They give colour reactions with concentrated sulphuric acid and are insoluble in cold aqueous sodium hydroxide. On oxidation with chromium trioxide phenanthraquinone is formed. They are also attacked when heated with precipitated selenium in a stream of air; from (II*b*), benzoic acid is thus formed. When heated, they decompose with loss of water and formation of the corresponding phenanthroxazole; (II*b*), *e.g.*, gives 2-phenylphenanthroxazole.

Constitution of the Photo-products. Possibility of Ring-chain Tautomerism.—The constitution of the photo-products is based on their insolubility in cold alkali and on their similarity with the products (III) formed when phenanthraquinone reacts with aldehydes in sunlight (Schönberg and Moubacher, J., 1939, 1430).

That the photo-products do not react vigorously with diazomethane is also in favour of the cyclic formula (II). There seems to be a strong 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). It is possible that in solution the substances show ring-chain tautomerism, (II)$\rightleftarrows$(IV).

(III.)




(IV.)

The substances (II*a*) and (II*b*) have been prepared by Pschorr (*Ber.*, 1902, **35**, 2733) and Auwers (*Annalen*, 1911, **378**, 216), respectively, who gave them formula (IV, R = Me or Ph).

Experimental.

General Remarks.—The photo-chemical reactions were carried out in a Monax glass tube, the air being displaced by dry carbon dioxide, and the tube sealed by fusion.* The benzene was thiophen-free and dried over sodium.

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* The experiments of Schönberg and Mustafa (J., 1944, 67) also were carried out in Monax glass tubes, a fact not stated in the original paper.

Photo-chemical Reaction between Aldehydes and Phenanthraquinoneimine (I).—*Acetaldehyde.* The imine (1 g.) and acetaldehyde (10 g.) in benzene were exposed to sunlight for 11 days (August), the benzene then evaporated in a vacuum, and the residue washed with a small amount of benzene. It separated from benzene in colourless crystals, m. p. about 217° (red-brown melt), of 2-hydroxy-2-methyl-2 : 3-dihydrophenanthroxazole (II*a*), difficultly soluble in cold alcohol; it was soluble in concentrated sulphuric acid and boiling aqueous sodium hydroxide, giving orange solutions. The photo-product did not depress the m. p. of the substance described as 9-acetylamino-10-hydroxyphenanthrene by Pschorr (*loc. cit.*) (Found : C, 76·1; H, 5·4; N, 5·4. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%).

Benzaldehyde. The experiment was carried out, as described above, with 0·5 g. of the imine and 2 g. of freshly distilled benzaldehyde in benzene (30 c.c.). After 3 hours, the colourless or slightly yellow crystals were collected, washed with benzene, and recrystallised from benzene, giving an almost quantitative yield of colourless 2-hydroxy-2-phenyl-2 : 3-dihydrophenanthroxazole (II*b*), m. p. about 236° (decomp.; red-brown melt), insoluble in dilute and in concentrated hydrochloric acid, difficultly soluble in hot benzene, soluble in boiling alcohol, and soluble in hot aqueous sodium hydroxide, giving a reddish-brown solution. It did not depress the m. p. of the product described as 9-benzoylamino-10-hydroxyphenanthrene by Auwers (*loc. cit.*), but in its preparation we avoided (in contrast to Auwers) the crystallisation from acetic acid (which seems to affect the substances) and crystallised it only from benzene (Found : C, 80·7; H, 5·0. Calc. for $C_{21}H_{15}O_2N$: C, 80·5 : H, 4·8%).

p-*Anisaldehyde.* The imine (1 g.) and *p*-anisaldehyde(4 g.), dissolved in benzene (50 c.c.), were exposed for 1 day (August). The colourless crystals obtained were purified as described in the preceding experiment, giving 2-*hydroxy*-2-p-*anisyl*-2 : 3-*dihydrophenanthroxazole* (II*c*), m. p. about 231° (becoming reddish-brown on further heating), insoluble in dilute and in concentrated hydrochloric acid, soluble in boiling aqueous sodium hydroxide to a reddish-brown solution (Found : C, 76·4; H, 4·9. $C_{22}H_{17}O_3N$ requires C, 76·9; H, 5·0%).

p-*Chlorobenzaldehyde.* A solution of the imine (1 g.) and *p*-chlorobenzaldehyde (4 g.) in benzene (50 c.c.) was exposed to sunlight for 1 day (August). The crystals formed were recrystallised from benzene, giving colourless 2-*hydroxy*-2-p-*chlorophenyl*-2 : 3-*dihydrophenanthroxazole* (II*d*) in almost quantitative yield, m. p. about 221° to a red-brown melt, easily soluble in hot alcohol and hot benzene and soluble in concentrated sulphuric acid to an olive-green solution after some minutes (Found : C, 72·3; H, 3·9; N, 4·05; Cl, 10·5. $C_{21}H_{14}O_2NCl$ requires C, 72·5; H, 4·0; N, 4·0; Cl, 10·2%).

Piperonal. The imine (0·5 g.) and piperonal (1 g.) in benzene (50 c.c.) were exposed for 4 days (end of February); no crystals were formed. The benzene was driven off in a vacuum, and the residue washed with dilute sodium bicarbonate solution and crystallised from benzene. 2-*Hydroxy*-2-(3′ : 4′-*methylenedioxyphenyl*)-2 : 3-*dihydrophenanthroxazole* (II*e*) formed colourless crystals, m. p. 236° (decomp.) (Found : C, 73·4; H, 4·4; N, 4·25. $C_{22}H_{15}O_4N$ requires C, 74·0; H, 4·2; N, 3·9%).

2-*Methoxy*-1-*naphthaldehyde.* The imine (0·5 g.) and the aldehyde (1 g.), dissolved in benzene (30 c.c.), were exposed for a fortnight (September); no crystals were formed. The benzene was removed in a vacuum, and the residue washed with a small amount of benzene and crystallised from benzene. The almost colourless crystals (about 0·2 g.), m. p. 217°, of 2-*hydroxy*-2-(2′-*methoxy*-1′-*naphthyl*)-2 : 3-*dihydrophenanthroxazole* (II*f*) were difficultly soluble in cold alcohol. When it was treated with concentrated sulphuric acid at room temperature, an orange colour was obtained (Found : C, 79·2; H, 5·1; N, 3·3. $C_{26}H_{19}O_3N$ requires C, 79·4; H, 4·8; N, 3·6%).

Action of Heat on 2-*Hydroxy*-2-*phenyl*-2 . 3-*dihydrophenanthroxazole.*—The pyrolysis was carried out in a stream of dry carbon dioxide in a vessel fitted with a long side tube externally cooled; the vessel was immersed in a bath of ethyl cinnamate (b. p. 271°). An almost colourless deposit formed, together with drops of water (blue colour with anhydrous copper sulphate), on the walls of the side tube. The deposit, after crystallisation from benzene, showed no depression of m. p. when mixed with authentic 2-phenylphenanthroxazole prepared according to Stein and Day (*loc. cit.*) (Found : C, 85·2; H, 4·9; N, 4·8. Calc. for $C_{21}H_{13}ON$: C, 85·4; H, 4·4; N, 4·8%).

Action of Selenium and Air on 2-*Hydroxy*-2-*phenyl*-2 : 3-*dihydrophenanthroxazole.*—A mixture of the material (0·1 g.) and precipitated selenium (1 g.) (B.D.H.) was heated at about 300° (bath temp.) in a 50 c.c. distillation flask fitted with a capillary; the side tube was connected with an air condenser and air was sucked through the capillary. After 10 minutes' heating, suction was continued for 2 hours while the bath cooled. The colourless crystals deposited on the neck of the flask proved to be benzoic acid.

Action of Chromium Trioxide on 2-*Hydroxy*-2-p-*anisyl*-2 : 3-*dihydrophenanthroxazole.*—To the phenanthroxazole (3·2 g.), partly dissolved in glacial acetic acid (15 g.), a hot solution of chromium trioxide (8 g.) in glacial acetic acid (20 g.) was gradually added; the mixture boiled vigorously. It was poured into water (250 c.c.) after cooling, and the orange precipitate collected (pump) and extracted with hot concentrated sodium bisulphite solution. To the filtered solution, dilute sulphuric acid was added; the orange precipitate thus obtained, after crystallisation from alcohol, gave phenanthraquinone (0·8 g.).

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