# S 15. *Reactions with Phenanthraquinone, 9-Benzylideneanthrone, and 9-Methyleneanthrone in Sunlight.*

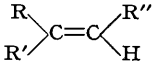
By Ahmed Mustafa and Ahmed Medhat Islam.

Photochemical addition of phenanthraquinone to various substances containing an olefinic linkage has been carried out. The olefinic compounds include 2 : 3-diphenylbenzfuran (III), in which the ethylenic linkage forms a part of a five-membered ring system, and olefins (II*a*—II*c*), in which one carbon atom of the ethylenic linkage is a member of a five- or a six-membered ring system. The photo-products obtained are represented by the formulæ (IV—VI).

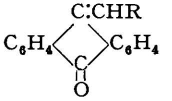
Photochemical polymerisation of 9-benzylideneanthrone (II*b*) yields the colourless dimer (VII).

The behaviour of benzene solution of 9-methyleneanthrone (II*a*) in sunlight in the presence of oxygen is described.

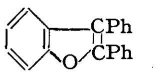
Recently, Schönberg and Mustafa (*Chem. Reviews*, 1947, **40**, 181; *J.*, 1944, 387; 1945, 551; 1947, 997; 1948, 2126) showed that phenanthraquinone reacted with certain unsaturated compounds to form derivatives of phenanthro-1 : 4-dioxen. We have now extended this reaction to 2-phenylbut-2-ene (I*a*), 2-phenyl-1 : 1-di-*p*-phenylylethylene (I*b*), 9-benzylideneanthrone (II*b*), 9-anisylideneanthrone (II*c*), and 2 : 3-diphenylbenzfuran (III), thus showing that the reaction proceeds, not only when the double bond is in an open-chain system or when one of the two carbon atoms is in a ring, but also when the double bond is wholly in a heterocyclic ring.



(I*a*, R = Ph, R′ = R″ = Me;
I*b*, R = R′ = *p*-$C_6H_4$Ph; R″ = Ph.)

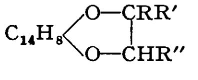


(II*a*, R = H;
II*b*, R = Ph;
II*c*, R = *p*-$C_6H_4$·OMe.)

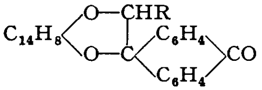


(III.)

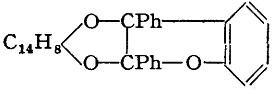
The *photo-products* obtained from (I*a* and I*b*), (II*b* and II*c*), and (III) have the structures (IV*a* and IV*b*), (V*a* and V*b*), and (VI), respectively. All these products are colourless. On pyrolysis, phenanthraquinone and the original ethylenic compound were obtained, except that (I*a*) was not obtained from (IV*a*), probably because of its thermolability.



(IV*a*, R = Ph, R′ = R″ = Me;
IV*b*, R = R′ = *p*-$C_6H_4$Ph, R″ = Ph.)



(V*a*, R = Ph;
V*b*, R = *p*-$C_6H_4$·OMe.)

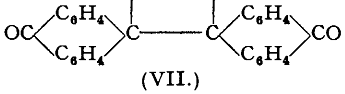


(VI.)

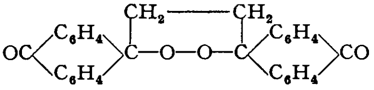
When the benzene solution of 9-benzylideneanthrone (II*b*) was exposed to sunlight, an almost colourless photo-dimer (VII) was formed. The constitution of (VII) is based on the facts that (i) it lacks colour, (ii) on being heated at 270°, it regenerates (II*b*), and (iii) it has the correct molecular weight. The cleavage is in agreement with the proposed four-membered ring system (compare the cleavage of the photo-dimer of α-naphthaquinone; Schönberg, Mustafa, and Barakat, *Nature*, 1947, **160**, 401; *J.*, 1948, 2126).

Further examples of the photo-dimerisation of 9-arylidene-anthrone and -xanthen derivatives are under investigation.

Exposure of a benzene solution of methyleneanthrone (II*a*) to sunlight in the presence of air yielded an almost colourless peroxide (VIII) (compare Schönberg and Mustafa, *J.*, 1945, 657; 1947, 997), but on long exposure, anthraquinone was obtained. That (VIII) was a peroxide was established by the fact that it liberated iodine from potassium iodide solution in acetic acid; it formed anthraquinone on pyrolysis.



(VII.)



(VIII.)

## Experimental.

All reactions occurred in solution unless otherwise stated. The benzene was free from toluene (compare Schönberg and Mustafa, *J.*, 1947, 997) and thiophen and had been dried over sodium. The reaction mixtures were placed in a Schlenk tube (Schlenk and Thal, *Ber.*, 1913, **46**, 2655; Houben, " Die Methoden der Organischen Chemie", 2nd Edn., Vol. IV, 960) of Pyrex glass, the air displaced by dry carbon dioxide, and the tube sealed. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

*Photo-reactions with Phenanthraquinone.*—2-*Phenylbut*-2-*ene* (I*a*). Phenanthraquinone (1 g.) and (I*a*) (Klages, *Ber.*, 1902, **35**, 2633) (2·4 g.) in benzene (30 c.c.) were exposed to sunlight for 25 days (November–December), the phenanthraquinone gradually dissolving completely and the orange colour fading to pale yellow. The benzene was evaporated, and the oily residue was washed with light petroleum (b. p. 30—50°); the remaining oil gave crystals after standing for 48 hours. These were washed with cold ethyl alcohol and recrystallised from benzene–ethyl alcohol, forming colourless crystals, m. p. 134° (yellow melt) (Found : C, 84·5; H, 5·7. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). 2-*Phenyl*-2 : 3-*dimethylphenanthro*(9′ : 10′-5 : 6)*dioxen* (IV*a*) gave no colour with sulphuric acid at room temperature, but an olive-green colour at 100°; it was soluble in benzene and difficultly soluble in cold ethyl alcohol. When it was heated at 270° (bath temp.) in a stream of dry carbon dioxide (the height of the decomposition tube being about 25 cm.) during ½ hour, red-brown fumes were evolved, and an orange liquid collected on the walls of the tube. After 24 hours, this liquid solidified to orange crystals, proved to be phenanthraquinone (identified, after recrystallisation from alcohol, by m. p. and mixed m. p., and colour reaction with sulphuric acid).

2-*Phenyl*-1 : 1-*di*-p-*diphenylylethylene* (I*b*).—Phenanthraquinone (1 g.) and the ethylene (I*b*) (Pfeiffer and Schneider, *J. pr. Chem.*, 1931, **129**, 129) (1·6 g.) were exposed to sunlight for 18 days (January). The benzene was evaporated in a vacuum, and the oily residue solidified on being rubbed with cold light petroleum (b. p. 50—70°). The solid was washed with cold ether and crystallised from benzene–light petroleum (b. p. 50—70°), forming almost colourless crystals, m. p. 234° (orange melt) (Found : C, 89·3; H, 5·0. $C_{46}H_{32}O_2$ requires, C, 89·6; H, 5·2%). 3-*Phenyl*-2 : 2-*di*-p-*phenylylphenanthro*(9′ : 10′-5 : 6)-*dioxen* (IV*b*), when treated at room temperature with sulphuric acid, gave a violet colour changing to olive-green at 100°; it was soluble in hot benzene, but difficultly soluble in cold ethyl alcohol.

The thermal decomposition of the product was carried out for ½ hour at about 300° (bath temp.) as described above. An orange liquid collected on the walls of the tube and after 24 hours solidified to a mixture of orange and almost colourless crystals; extraction with hot light petroleum (b. p. 100—150°) left a residue of phenanthraquinone (identified by m. p. and mixed m. p.). The extract was concentrated, and the resulting crystals recrystallised from benzene, proved to be 2-phenyl-1 : 1-di-*p*-phenylylethylene (I*b*) (m. p. and mixed m. p.).

9-*Benzylideneanthrone* (II*b*). Phenanthraquinone (1 g.) and (II*b*) (Cook, *J.*, 1926, 2160) (1·4 g.) in benzene (30 c.c.) were exposed to sunlight for 3 months (March–June), the phenanthraquinone dissolving as before and the orange colour of the solution fading to pale yellow. The benzene was evaporated off in a vacuum, and the residual dark oil was washed with light petroleum (b. p. 30—50°) and cold ethyl alcohol. The solidified mass was filtered off and crystallised from benzene, forming colourless crystals, m. p. 248° (red melt) (Found : C, 85·5; H, 4·4. $C_{35}H_{22}O_3$ requires C, 85·7; H, 4·5%). The *product* (as V*a*) gave a deep red colour with sulphuric acid at room temperature; it was difficultly soluble in ethyl alcohol, but soluble in hot benzene; when heated as described above, it yielded its generators, which were separated by means of hot light petroleum (b. p. 50—60°), in which 9-benzylideneanthrone is soluble.

9-*Anisylideneanthrone* (II*c*). Phenanthraquinone (1 g.) and (II*c*) (Padova, *Compt. rend. Accad. Sci.*, 1905, **141**, 857) (1·3 g.) in benzene (50 c.c.) were exposed to sunlight for two months (April–June), the phenanthraquinone gradually dissolving completely. The crystals that separated were filtered off, and recrystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 264° (brown melt) (Found : C, 82·8; H, 4·6. $C_{36}H_{24}O_4$ requires C, 83·1; H, 4·6%). The *product* (as V*b*) gave a reddish-brown colour with sulphuric acid at room temperature; it was difficultly soluble in cold ether or ethyl alcohol, but soluble in hot benzene and toluene; when heated as described above, it yielded its generators, separated as before. From the mother-liquor, more of the photo-product (V*b*) was obtained.

2 : 3-*Diphenylbenzfuran* (III). Phenanthraquinone (1 g.) and (III) (Arventi, *Bull. Soc. chim.*, 1936, **3**, 598) (1·4 g.) in benzene (30 c.c.), exposed for 20 days (January), behaved as above. The benzene was evaporated off in a vacuum, and the residual oil extracted several times with hot light petroleum (b. p. 30—50°); on concentration, the extract gave almost colourless crystals; recrystallised from benzene–methyl alcohol, these had m. p. 152° (brown melt) (Found : C, 85·1; H, 4·5. $C_{34}H_{22}O_3$ requires C, 85·4; H, 4·6%). The *product* (VI) gave no colour with sulphuric acid at room temperature, but a brown colour at 100°; when heated as described above, it yielded its generators, which were separated by means of hot light petroleum (b. p. 70—80°) in which (III) is soluble.

*Action of Sunlight on* 9-*Benzylideneanthrone* (II*b*).—A solution of (II*b*) (Cook, *loc. cit.*) (1 g.) in benzene (30 c.c.) was exposed to sunlight for 7 days (June). The crystals that separated were filtered off, washed with light petroleum (b. p. 30—50°), and crystallised from benzene, forming almost colourless crystals, m. p. 225—226° (yellow melt) (Found : C, 89·1; H, 4·7; *M* (micro-Rast), 548. $C_{42}H_{28}O_2$ requires C, 89·4; H, 4·9%; *M*, 564). The *product* (VII) gave a deep-red colour with sulphuric acid, and was soluble in hot benzene or xylene, and difficultly soluble in ethyl alcohol. When heated at 270° (bath temp.), it afforded (II*b*) (m. p. and mixed m. p.).

*Action of Oxygen on Methyleneanthrone* (II*a*) *in Sunlight.*—Methyleneanthrone (Clar, *Ber.*, 1936, **69**, 1687) (1 g.) in benzene (25 c.c.) was exposed to sunlight for ten days (September) in presence of air. The almost colourless crystals that separated were recrystallised from benzene–light petroleum (b. p. 30—50°); m. p. 200° (decomp.; dark melt) (Found : C, 80·8; H, 4·4. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5%). The *product* (VIII) gave a yellow-brown colour with sulphuric acid; it was soluble in hot toluene, but difficultly soluble in ethyl alcohol. Thermal decomposition for ½ hour at 300° (bath temp.) afforded anthraquinone (m. p. and mixed m. p.) as a pale yellow sublimate.

When the exposure to sunlight was extended to 20 days, the pale yellow crystals that separated, recrystallised from xylene, had m. p. 277° and were anthraquinone (m. p. and mixed m. p.) (Found : C, 80·7; H, 3·6. Calc. for $C_{14}H_8O_2$ : C, 80·8; H, 3·8%).

Fouad I University, Faculty of Science,
Abbassia-Cairo, Egypt.

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