S 16. *Reactions in Sunlight of* (a) *Phenanthraquinone, Retenequinone, and Chrysenequinone with Ethylenes;* (b) *Retenequinone and Chrysenequinone with Aromatic Aldehydes; and* (c) o-*Formylbenzoic Acid with* iso*Propyl Alcohol.*

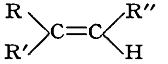
By AHMED MUSTAFA.

(*a*) Phenanthraquinone reacts in sunlight with the unsaturated compounds (I*a*—I*c*, II*c*, III, and IV) to give the photo-products (VII*a*—VII*c*, VIII, IX, and X, respectively); similarly, retenequinone reacts with (V) and (VI) forming (XI*a*) and (XI*b*), respectively, and the photo-product obtained from chrysenequinone and triphenylethylene has the structure (XII).

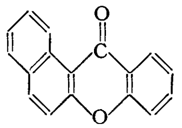
(*b*) The photo-reaction between retenequinone and anisaldehyde to give (XIII), and that between chrysenequinone and benzaldehyde or anisaldehyde, giving (XIV*a*) and (XIV*b*), is described.

(*c*) A solution of *o*-formylbenzoic acid in *iso*propyl alcohol, on exposure to sunlight, gave (XVI).

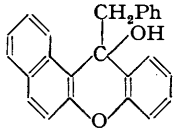
(*a*) IN continuation of previous work (Schönberg and Mustafa, *Chem. Reviews*, 1947, **40**, 181; *J.*, 1944, 387; 1945, 551; 1947, 997; 1948, 2126), the action of phenanthraquinone on 2-phenylpent-2-ene (I*a*), 1 : 1-diphenylbut-1-ene (I*b*), benzylidenedeoxybenzoin (I*c*), *benzylidene*-1 : 2-*benzoxanthen* (II*c*), *benzylidene*-2 : 3-7 : 8-*dibenzoxanthen* (III), and 1 : 3-diphenyl*iso*benzfuran (IV), of retenequinone on 9-benzylidenexanthen (V) and methyleneanthrone (VI), and of chrysenequinone on triphenylethylene was investigated. The two new compounds (II*c*) and (III) were prepared by the action of benzylmagnesium chloride on the corresponding xanthone derivative, followed by hydrolysis and dehydration of the resulting *carbinol* (*e.g.*, II*b*). So far, photo-addition reaction of this type has been carried out with phenanthraquinone, retenequinone, and benzil (Schönberg and Mustafa, *loc. cit.*), but it has now been extended to chrysenequinone.



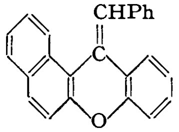
(I*a*, R = Ph, R′ = Me, R″ = Et;
I*b*, R = R′ = Ph, R″ = Et;
I*c*, R = R″ = Ph, R′ = COPh.)



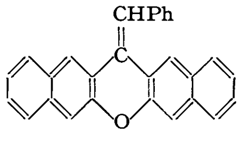
(II*a*.)



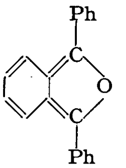
(II*b*.)



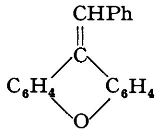
(II*c*.)



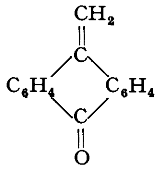
(III.)



(IV.)



(V.)

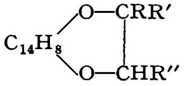


(VI.)

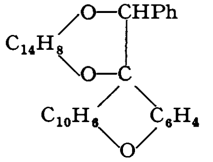
The products from (I*a*), (I*b*), and (I*c*) are, respectively, 2-*phenyl*-2-*methyl*-3-*ethyl*- (VII*a*), 2 : 2-*diphenyl*-3-*ethyl*- (VII*b*), and 3-*benzoyl*-2 : 3-*diphenyl-phenanthro*-9′ : 10′-5 : 6-*dioxen* (VII*c*); those from (II*c*), (III), and (IV) have the structures (VIII), (IX), and (X) respectively. The *photo-products* obtained from retenequinone and (V) and (VI) are assigned the structures (XI*a*) and (XI*b*), and that obtained from chrysenequinone and triphenylethylene is of the type (XII). These constitutions are based on the facts that the products are colourless or almost colourless, in contrast with the deep colour of the original quinones, and that heating decomposes the products into their generators.

To the list of ethylenes which showed the scope of the photo-reaction (Schönberg and Mustafa, *loc. cit.*), therefore, we now add the 16 ethylenes mentioned above. Phenanthraquinone reacts with all the 17 substances, retenequinone with methyleneanthrone and 9-benzylidenexanthen, and chrysenequinone with triphenylethylene.

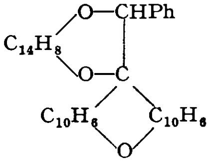
(*b*) Schönberg and Mustafa (*J.*, 1947, *loc. cit.*) described a number of photo-reactions between phenanthraquinone and aromatic aldehydes. A similar reaction has been carried out with retenequinone and anisaldehyde, and with chrysenequinone and benzaldehyde or anisaldehyde, affording the p-*methoxyphenylhydroxymethylene ether* of 9 : 10-dihydroxyretene (XIII), and the *phenylhydroxymethylene* and p-*methoxyphenylhydroxymethylene ethers* of 1 : 2-dihydroxychrysene (XIV*a* and *b*).



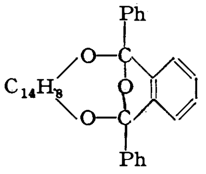
(VII*a*, R = Ph, R′ = Me, R″ = Et; VII*b*, R = R′ = Ph, R″ = Et; VII*c*, R = R″ = Ph, R′ = COPh.)



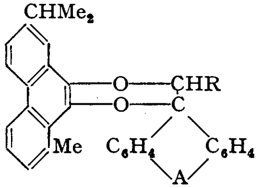
(VIII.)



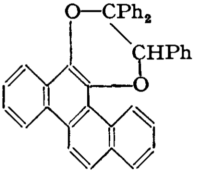
(IX.)



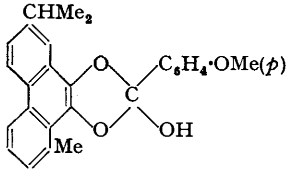
(X.)



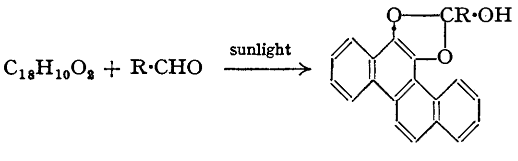
(XI*a*, R = Ph, A = O; XI*b*, R = H, A = CO.)



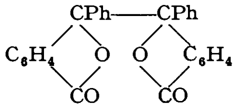
(XII.)



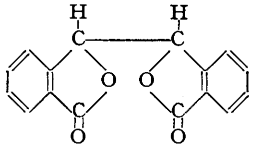
(XIII.)



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



(XV.)



(XVI.)

(*c*) Limaye (*J. Univ. Bombay*, 1932, **1**, Pt. 2, 52) found that when an alcoholic solution of *o*-benzoylbenzoic acid is exposed to direct sunlight in a sealed glass tube, the dilactone of 1 : 2-diphenyl-1 : 2-di-*o*-carboxyphenylethane-1 : 2-diol (XV) is obtained. It is now found that *o*-formylbenzoic acid in *iso*propyl alcohol similarly affords diphthalidyl (XVI).

EXPERIMENTAL.

All substances were in solution unless otherwise stated. The benzene was free from toluene (cf. Schönberg and Mustafa, 1947, *loc. cit.*) and thiophen-free and had been dried over sodium. The reaction mixtures were placed in a Schlenk tube (Schlenk and Thal, *Ber.*, 1913, **46**, 2655; see Houben, " Die Methoden der Organischen Chemie ", 2nd Edition, Vol. IV, p. 960) of Pyrex glass, and the air was then 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.—(a) 2-*Phenylpent*-2-*ene* (I*a*). Phenanthraquinone (1 g.) and the ethylene (I*a*) (Klages, *Ber.*, 1902, **35**, 2633) (prepared by Ahmed Mohamed Gad) (2·1 g.) in 25 c.c. of benzene were exposed to sunlight for 20 days (November—December), the phenanthraquinone gradually dissolving and the orange colour fading to pale yellow. The benzene was evaporated off in a vacuum and the residual dark oil was extracted several times with light-petroleum (b. p. 30—50°); the extract on slow evaporation gave colourless crystals, which, recrystallised from benzene–ethyl alcohol, had m. p. 142° (yellow melt) (Found : C, 84·6; H, 6·0. $C_{25}H_{22}O_2$ requires C, 84·8; H, 6·2%). 2-*Phenyl*-2-*methyl*-3-*ethylphenanthro*-9′ : 10′-5 : 6-*dioxen* (VII*a*) gave no colour with sulphuric acid at room temperature, but an olive-green colour at 100°; it was soluble in benzene, but difficultly soluble in ethyl alcohol.

This product 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 solidified to orange crystals, proved to be phenanthraquinone (identified after recrystallisation from ethyl alcohol, m. p. and mixed m. p., and colour reaction with sulphuric acid).

(b) 1 : 1-*Diphenylbut*-1-*ene* (I*b*). Phenanthraquinone (1 g.) and (I*b*) (Sabatier and Murat, *Compt. rend.*, 1913, **156**, 1434) (1·7 g.) in 30 c.c. of benzene were exposed to sunlight for 21 days (November), the phenanthraquinone dissolving and the colour changing as before. Working up and recrystallisation as in (a) afforded almost colourless crystals, m. p. 164—165° (yellow melt, changing to orange at 180°) (Found : C, 86·3; H, 5·5. $C_{30}H_{24}O_2$ requires C, 86·5; H, 5·7%). 2 : 2-*Diphenyl*-3-*ethylphenanthro*-9′ : 10′-5 : 6-*dioxen* (VII*b*) gave an olive-green colour with sulphuric acid at 100°; it was soluble in hot benzene, but difficultly soluble in light petroleum (b. p. 70—80°) and cold ethyl alcohol. The thermal decomposition was carried out as described above, and phenanthraquinone obtained.

(c) *Benzylidenedeoxybenzoin* (I*c*). Phenanthraquinone (1 g.) and (I*c*) (Knoevenagel and Weissgerber, *Ber.*, 1893, **26**, 442) (1·1 g.) were exposed to sunlight for 8 months (April—November), the solution becoming brownish-yellow. The crystals that separated were filtered off, washed with hot ethyl alcohol, then with cold ether and finally with light petroleum (b. p. 70—80°) and recrystallised from benzene–light petroleum (b. p. 30—50°), forming almost colourless crystals, m. p. 233° (brown-red melt) (Found : C, 85·3; H, 4·7. $C_{35}H_{24}O_3$ requires C, 85·4; H, 4·9%). 3-*Benzoyl*-2 : 3-*diphenylphenanthro*-9′ : 10′-5 : 6-*dioxen* (VII*c*) gave a brown colour with sulphuric acid. When heated as described above, it yielded its generators, which were separated by means of hot light petroleum (b. p. 70—80°) in which (I*c*) is soluble; (VII*c*) was soluble in hot benzene, but difficultly soluble in ether and ethyl alcohol.

(d) *Benzylidene*-1 : 2-*benzoxanthen* (II*c*). To a Grignard solution of benzylmagnesium chloride [prepared from magnesium (0·8 g.), benzyl chloride (5·5 g.), and ether (50 c.c.)], dry benzene (30 c.c.) was added, and the mixture treated gradually with powdered 1 : 2-benzoxanthone (II*a*) (Graebe and Feer, *Ber.*, 1886, **19**, 2612; Kostanecki, *Ber.*, 1892, **25**, 1643) (5 g.). The mixture was refluxed for 2 hours, set aside overnight, poured into ice-cold dilute hydrochloric acid, extracted with ether, and the extract dried and evaporated. The residue, on being washed with light petroleum (b. p. 30—50°), formed a solid mass which was crystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 155° (Found : C, 85·0; H, 5·1. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·3%). *Benzyl*-1 : 2-*benzoxanthhydrol* (II*b*) is easily soluble in benzene but difficultly soluble in light petroleum (b. p. 50—70°) and gives an orange-red colour with sulphuric acid. The carbinol (II*b*) (1 g.) was refluxed with glacial acetic acid (15 c.c.) for 2 hours, then poured into ice-water. The solid that separated was filtered off, washed with water, and crystallised from benzene–light petroleum (b. p. 50—70°), forming almost colourless crystals, m. p. 140° (Found : C, 89·8; H, 4·9. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%). *Benzylidene*-1 : 2-*benzoxanthen* (II*c*) gave a yellow colour with bluish-green fluorescence with sulphuric acid, and was readily soluble in hot benzene, but difficultly soluble in light petroleum (b. p. 60—70°) and cold ethyl alcohol.

Phenanthraquinone (1 g.) and (II*c*) (1·4 g.) in benzene (50 c.c.) were exposed to sunlight for 2 months (January—March), the phenanthraquinone gradually dissolving completely. The resulting crystals were filtered off, and crystallised from benzene–alcohol, forming colourless crystals, m. p. 250° (orange melt) (Found : C, 86·2; H, 4·4. $C_{38}H_{24}O_3$ requires C, 86·4; H, 4·5%). The *product* (VIII) gave an olive-green colour with sulphuric acid at room temperature; it was difficultly soluble in ethyl alcohol, and soluble in hot benzene. When heated for ½ hour at about 330° (bath temp.) as described above, it yielded its generators, which were separated as before.

From the original mother-liquor, further amounts of the photo-product (VIII) were obtained by evaporation, and purification of the resulting oil.

(e) *Benzylidene*-2 : 3-7 : 8-*dibenzoxanthen* (III). The xanthone (Strohbach, *Ber.*, 1901, **34**, 4144) (5 g.) was treated with an ethereal solution of benzylmagnesium chloride (prepared as above) in the presence of dry benzene (40 c.c.) and refluxed for 2 hours. The mixture was left overnight, decomposed with ice-cold dilute hydrochloric acid, extracted with ether, dried (Na_2SO_4), and evaporated. The oily residue solidified when washed with cold ethyl alcohol and crystallised from benzene–light petroleum (b. p. 30—50°) in colourless crystals, m. p. 220° (Found : C, 86·6; H, 4·9. $C_{28}H_{20}O_2$ requires C, 86·8; H, 5·1%). *Benzyl*-2 : 3-7 : 8-*dibenzoxanthhydrol* (gave a violet-red colour with sulphuric acid, and was soluble in hot benzene and xylene, but difficultly soluble in ethyl alcohol. This carbinol (1 g.) was dehydrated as described for (II*b*) and recrystallised from benzene–light petroleum (b. p. 50—70) forming almost colourless crystals, m. p. 178° (Found : C, 90·6; H, 4·7. $C_{28}H_{18}O$ requires C, 90·8; H, 4·9%). *Benzylidene*-2 : 3-7 : 8-*dibenzoxanthen* (III) gave a brown-red colour with sulphuric acid, and was easily soluble in benzene but difficultly soluble in ethyl alcohol.

Phenanthraquinone (1 g.) and (III) (1·5 g.) in benzene (50 c.c.) were exposed to sunlight for 2 months (April, May), the phenanthraquinone gradually dissolving completely. The crystals that separated were filtered off, washed with ethyl alcohol, and crystallised from xylene, forming almost colourless crystals, m. p. 260° (orange melt) (Found : C, 87·0; H, 4·4. $C_{42}H_{26}O_3$ requires C, 87·2; H, 4·5%). The *product* (as IX) gave an olive-green colour with sulphuric acid at room temperature; it was difficultly soluble in ethyl alcohol, but soluble in hot benzene. On thermal decomposition for ½ hour at about 330° (bath temp.) as described above, it decomposed into its generators, which were separated by means of hot ethyl alcohol, in which (III) is insoluble.

(f) 1 : 3-*Diphenyl*iso*benzfuran* (IV). Phenanthraquinone (1 g.) and (IV) (Guyot and Catel, *Bull. Soc. chim.*, 1906, **35**, 1127) (1·4 g.) were exposed to sunlight for 17 days (January), the usual changes occurring. The benzene was evaporated, and the oily residue was extracted several times with light petroleum (b. p. 30—50°); the extract, on concentration, gave almost colourless crystals which were recrystallised from xylene, m. p. 220° (orange melt; decomp.) (Found : C, 85·2; H, 4·5. $C_{34}H_{22}O_3$ requires C, 85·4; H, 4·6%). The *product* (as X) gave an olive-green colour with sulphuric acid at room temperature; it was soluble in hot benzene or hot xylene, but difficultly soluble in ethyl alcohol. When heated as described above, it yielded its generators, which were separated by means of hot light petroleum (b. p. 50—60°), in which (IV) is soluble.

Photo-reactions with Retenequinone.—9-Benzylidenexanthen (V). Retenequinone (1 g.) and (V) (Decker, *Ber.*, 1905, **38**, 2493) (1·3 g.) in benzene (50 c.c.) were exposed to sunlight for 2 months (May—July), the retenequinone gradually dissolving completely. The benzene was evaporated off in a vacuum, and the residual dark oil was washed with hot light petroleum (b. p. 30—50°), followed by hot ethyl alcohol. Both washings on evaporation gave colourless crystals; recrystallised from benzene, m. p. 170—171° (red-brown melt) (Found : C, 85·5; H, 5·3. $C_{38}H_{30}O_3$ requires C, 85·4; H, 5·6%). The *product* (as XI*a*), when treated with sulphuric acid, gave an olive-green colour; it was soluble in hot benzene and ligroïn (b. p. 100—150°). At 270° (bath temp.), it decomposed into retenequinone (identified, after crystallisation from chloroform–ethyl alcohol, by mixed m. p. and colour reaction with sulphuric acid) and 9-benzylidenexanthen (V) (recrystallised from ethyl alcohol and identified by m. p. and mixed m. p.).

Methyleneanthrone (VI). Retenequinone (1 g.) and methyleneanthrone (VI) (Clar, *Ber.*, 1936, **69**, 1687) (1 g.) in 25 c.c. of benzene were exposed to sunlight for 13 days (May); the retenequinone dissolved, and the resulting crystals were filtered off and washed with cold benzene; they were recrystallised from chloroform–light petroleum (b. p. 30—50°), forming almost colourless crystals, m. p. 190° (red melt) (Found : C, 84·1; H, 5·4. $C_{33}H_{26}O_3$ requires C, 84·3; H, 5·5%). The *product* (as XI*b*) gave a reddish-brown colour with sulphuric acid; it was difficultly soluble in hot ethyl alcohol, but soluble in hot benzene. When heated as described above, it yielded its generators, separated by hot light petroleum (b. p. 80—90°) in which (VI) is soluble.

Photo-reaction between 1 : 2-*Chrysenequinone and Triphenylethylene.*—The quinone (1 g.) and the ethylene (2·4 g.) in benzene (25 c.c.) were exposed to sunlight for 20 days (December), the quinone gradually dissolving, and the colour of the solution fading to pale yellow. The crystals that separated were filtered off, washed several times with hot ethyl alcohol, and recrystallised from benzene, forming almost colourless crystals, m. p. 248° (yellow melt; changing to red at 270°) (Found : C, 88·4; H, 4·9. $C_{38}H_{26}O_2$ requires C, 88·7; H, 5·1%). 2 : 2 : 3-*Triphenylchryseno*-(1′ : 2′-5 : 6)-*dioxen* (XII) gave no colour with sulphuric acid at room temperature, but a violet-blue colour at 100°. When heated as described above at 300° (bath temp.), it yielded chrysenequinone (identified after crystallisation from xylene by m. p. and mixed m. p. and colour reaction with sulphuric acid) and triphenylethylene (m. p. and mixed m. p.), which were separated by means of light petroleum (b. p. 50—60°), in which the latter is soluble. The original benzene mother-liquor on evaporation formed an oil from which more (XII) was obtained.

Photochemical Reaction between Retenequinone and Anisaldehyde.—The quinone (1 g.) and aldehyde (0·7 g.) in benzene (30 c.c.) were exposed to sunlight for 13 days (May). The colourless crystals that separated were washed with small amounts of cold benzene and crystallised from benzene–light petroleum (b. p. 30—50°), forming almost colourless crystals, m. p. 170° (Found : C, 77·9; H, 6·0. $C_{26}H_{24}O_4$ requires C, 78·0; H, 6·0%). The p-*methoxyphenylhydroxymethylene ether* of 9 : 10-dihydroxyretene (XIII) was difficultly soluble in cold benzene or ethyl alcohol, but soluble in hot benzene and xylene; it gave an olive-green colour with sulphuric acid.

Photochemical Reaction between Chrysenequinone and Aromatic Aldehydes.—(i) *Benzaldehyde.* The quinone (1 g.) and aldehyde (0·9 g.) in benzene (20 c.c.) were exposed to sunlight for 3 months (July—September), the quinone gradually dissolving. The benzene was concentrated and cooled; the crystalline deposit obtained was filtered off, washed with ethyl alcohol, and crystallised from benzene–ethyl alcohol, forming almost colourless crystals, m. p. 210—211° (red-brown melt) (Found : C, 83·2; H, 4·1. $C_{25}H_{16}O_3$ requires C, 83·3; H, 4·2%). The *phenylhydroxymethylene ether* of 1 : 2-dihydroxychrysene (XIV*a*) was soluble in benzene, but difficultly soluble in ethyl alcohol; it gave a blue-violet colour when treated with sulphuric acid, at 100°.

(ii) *Anisaldehyde.* The quinone (1 g.) and aldehyde (0·7 g.) in benzene (30 c.c.) were exposed to sunlight for one month (July, August). The colourless crystals that separated were filtered off, washed several times with cold acetone, and recrystallised from benzene, forming almost colourless crystals, m. p. 224° (red melt) (Found : C, 78·9; H, 4·5. $C_{26}H_{18}O_4$ requires C, 79·1; H, 4·6%). The p-*methoxyphenylmethylene ether* of 1 : 2-dihydroxychrysene (XIV*b*) was difficultly soluble in acetone, but soluble in hot benzene; it gave a violet-blue colour with sulphuric acid at 100°.

Photochemical Action of iso*Propyl Alcohol on* o-*Formylbenzoic Acid in Sunlight.*—A solution of the acid (*Org. Synth.*, 1936, **16**, 68) (1 g.) in *iso*propyl alcohol (10 c.c.) was exposed to sunlight for 44 days (October, November). The crystals that separated were filtered off, washed with light petroleum (b. p. 30—50°), and crystallised from benzene, forming colourless crystals, m. p. 257° [Found : C, 72·2; H, 3·6; *M* (micro-Rast), 256. Calc. for $C_{16}H_{10}O_4$: C, 72·2; H, 3·8%; *M*, 266], identified as diphthalidyl (XVI) (m. p. and mixed m. p.) (Graebe and Juillard, *Annalen*, 1887, **242**, 222, gave m. p. 257°).

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

[*Received, June 16th,* 1948.]