

186. Photochemical Reactions in Sunlight. Part XII. Reactions with Phenanthraquinone, 9-Arylxanthenes, and Diphenyl Triketone.

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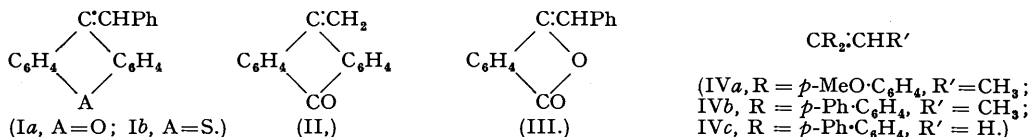
(a) The photochemical addition of phenanthraquinone or retenequinone to various substances containing an olefinic linkage has been carried out. The olefinic compounds include diphenylketen and a number of olefins, (I)—(III), in which one carbon atom of the ethylenic linkage is a member of a five- or six-membered ring system. The photo-products obtained are represented by the formulæ (V)—(VIII).

(b) Reaction scheme (A), which shows the photo-formation of peroxides from 9-arylxanthenes, was carried out in five cases. Some of the arylxanthenes are new and were prepared according to scheme (B). 9-Benzylxanthen was stable in sunlight in the presence of oxygen.

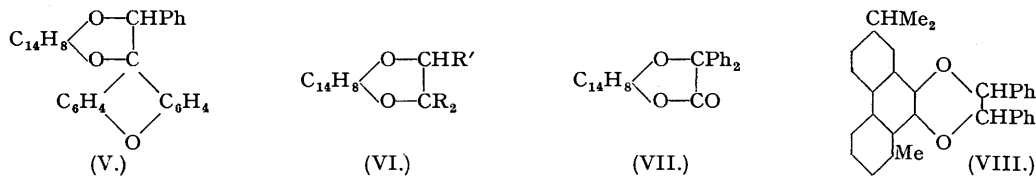
(c) The photo-reaction between phenanthraquinone and aromatic aldehydes was studied in three cases (see C); steric hindrance (ortho-effect) may explain the slow rate of the photo-reaction in the case of 2-methoxy-1-naphthaldehyde.

(d) Diphenyl triketone in sunlight forms benzil.

(a) RECENTLY (*J.*, 1944, 387; 1945, 551) we showed that phenanthraquinone reacted with certain unsaturated compounds to form derivatives of phenanthro-1:4-dioxen. We have now extended this reaction to 9-benzylidene-xanthen and -thioxanthen (I, *a* and *b*), methyleneanthrone (II), benzylidenephthalide (III), 1:1-di-*p*-anisylpropylene (IV*a*), 1:1-dixenylpropylene (IV*b*), *as*-dixenylethylene (IV*c*), and diphenylketen.



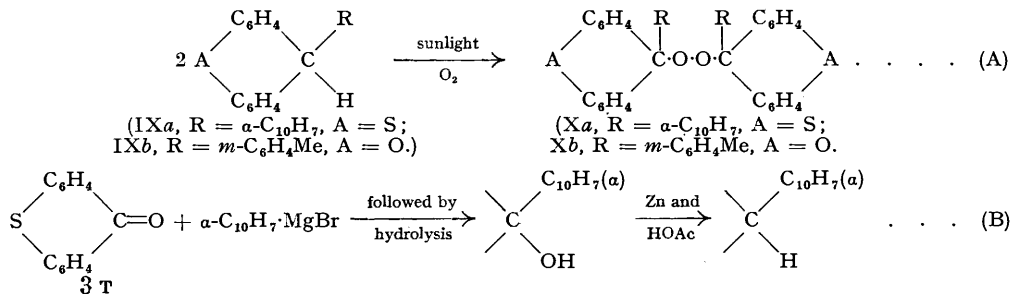
The photo-product obtained from (I*a*) has the structure (V), and those from (I*b*), (II), and (III) are analogous. Those from (IV, *a*, *b*, and *c*) are of type (VI), in which R and R' are as in the three formulæ. Diphenylketen gives the compound (VII). The condensation product from



retenequinone and stilbene is assigned the structure (VIII). All these products are colourless except (VIII), which is light yellow. On pyrolysis, the compounds were resolved into their generators except that diphenylketen was not obtained from (VII), probably because of its thermolability.

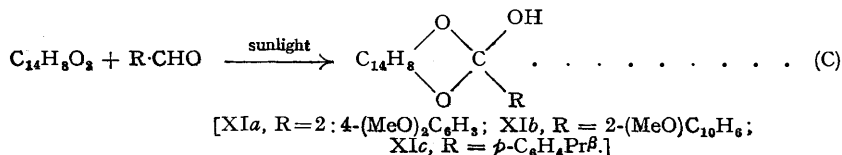
The photo-products from (III) and diphenylketen were insoluble in aqueous sodium hydroxide, but were readily attacked when heated with aqueous-alcoholic sodium hydroxide, a behaviour according with the lactone structure assigned to them; the resulting solutions were orange-coloured.

(b) To the list of triarylmethanes forming peroxides in air and sunlight by route (A) (Schönberg and Mustafa, *J.*, 1945, 657), we now add 9- α -naphthylthioxanthen, 9-*m*-tolylxanthen, and 9-*p*-tolyl-, 9-*p*-anisyl-, and 9- α -naphthyl-xanthen. The first two are new and were prepared as shown in (B) for the naphthyl compound:



9-Benzylxanthen in benzene was unchanged when exposed to sunlight in presence of oxygen. It seems that an aryl group in position 9 in xanthyl is necessary for the formation of peroxides in sunlight by the action of oxygen.

(c) Schönberg and Moubasher (*J.*, 1939, 1430) described a number of photo-reactions between phenanthraquinone and aromatic aldehydes according to (C). We have carried out similar reactions with 2 : 4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde, and cuminaldehyde; the first two reactions are much slower than that between benzaldehyde and phenanthraquinone in sunlight : this may be due to steric hindrance (ortho-effect).



(d) Lately, two methods have been described for conversion of diphenyl triketone into benzil by processes in the dark, namely, by the action (i) of aluminium chloride and (ii) of selenium (precipitated) in the presence of oxygen (Schönberg and Azzam, *J.*, 1939, 1430; Schönberg and Moubasher, in the press). It has now been found that the conversion is also effected when a benzene solution of the triketone is exposed to sunlight, but no reaction takes place in the dark in the absence of catalysts.

EXPERIMENTAL.

All substances were in solution unless otherwise stated. The benzene used was free from toluene* and thiophen and had been dried over sodium. The reaction mixtures were placed in a Schlenk tube (Schlenk and Thal, *Ber.*, 1913, 46, 2655; comp. Houben, "Die Methoden der Organischen Chemie", 2nd Edition, Vol. 4, p. 960) of Pyrex glass, and the air was then displaced by dry carbon dioxide and the tube sealed by fusion.

The photo-formation of peroxides was carried out as above, but in the presence of dry air.

Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

(a, i) *Photo-reactions with Phenanthraquinone.—9-Benzylidenexanthen.* Phenanthraquinone (1 g.) and 9-benzylidenexanthen (Ia) (Decker, *Ber.*, 1905, 38, 2493) (1.3 g.) in benzene (50 c.c.) were exposed to sunlight for 4 months (February—June), the phenanthraquinone gradually dissolving completely. The benzene was evaporated off in a vacuum, and the residual dark solid washed with cold acetone and crystallised from benzene—light petroleum (b. p. 30—50°), forming almost colourless crystals, m. p. 241° (red brown melt) (Found : C, 84.8; H, 4.9. C₃₄H₂₂O₃ requires C, 85.3; H, 4.6%). The product (V), when treated with sulphuric acid, gave an olive-green colour; it was soluble in hot benzene and ligroin (b. p. 100—150°).

Thermal decomposition. The foregoing product was heated for ½ hour at about 270° (bath temp.) in a stream of dry carbon dioxide (the height of the decomposition tube being about 25 cm.); red-brown fumes were evolved, and an orange liquid collected on the walls of the tube. After 24 hours, this solidified to a mixture of orange and almost colourless crystals; extraction with hot light petroleum (b. p. 50—60°) left a residue of phenanthraquinone (identified, after recrystallisation from alcohol, by m. p., mixed m. p., and colour reaction with sulphuric acid). The extract was concentrated, and the resulting crystals, recrystallised from ethyl alcohol, proved to be 9-benzylidenexanthen (Ia).

9-Benzylidenethioxanthen. Phenanthraquinone (1 g.) and 9-benzylidenethioxanthen (Ib) (Decker, *loc. cit.*) (1.4 g.) in 30 c.c. of benzene were exposed to sunlight for 3 months (August—November), the phenanthraquinone dissolving as before and the orange colour of the solution fading to pale yellow. The crystals that separated were filtered off, washed several times with hot absolute ethyl alcohol, and recrystallised from benzene, forming colourless crystals, m. p. 245° (orange melt) (Found : C, 82.6; H, 4.6; S, 5.9. C₃₄H₂₂O₂S requires C, 82.6; H, 4.4; S, 6.5%). The product (as V) gave a brown colour with sulphuric acid at room temperature; it was difficultly soluble in cold ethyl alcohol, but soluble in hot benzene; when heated as described above, it yielded its generators, which were separated as above.

Methyleneanthrone. Phenanthraquinone (1 g.) and methyleneanthrone (II) (Clar, *Ber.*, 1936, 69, 1687) (1 g.) in 25 c.c. of benzene were exposed to sunlight for 40 days (February—April); the phenanthraquinone dissolved, and the resulting crystals were filtered off and washed with cold benzene, followed by hot ethyl alcohol; they recrystallised from chlorobenzene, forming almost colourless crystals, m. p. 165° (decomp.; green melt), and gave a bluish-green colour with sulphuric acid. The product (as V) (Found : C, 84.1; H, 4.3. C₂₉H₁₈O₃ requires C, 84.1; H, 4.4%) is difficultly soluble in hot ethyl alcohol, but soluble in benzene; when heated as described above, it yielded its generators, separated as before.

Benzylidenephthalide. Phenanthraquinone (1 g.) and benzylidenephthalide (III) (*Org. Synth.*, Coll. Vol. 2, p. 61) (1.1 g.) in benzene (25 c.c.) were exposed to sunlight for 20 days (May); the quinone dissolved, and the resulting crystals were filtered off and washed with light petroleum (b. p. 50—60°). The product crystallised from xylene in colourless crystals, m. p. 310° (red-brown melt) (Found : C, 80.3; H, 4.1. C₂₉H₁₈O₄ requires C, 80.9; H, 4.2%). It gave no colour with sulphuric acid at room

* Toluene in sunlight acts as a reducing agent; e.g., phenanthraquinone is transformed into 9 : 10-dihydroxyphenanthrene (Benrath and Meyer, *J. pr. Chem.*, 1914, 89, 258).

temperature, but a violet colour at 100°; it was difficultly soluble in cold ethyl alcohol and benzene, but soluble in hot xylene. Its behaviour with alkalis is described on p. 997.

Thermal decomposition was carried out for $\frac{1}{2}$ hour at about 330° (bath temp.) as described above. The resulting mixture was separated as before.

1: 1-*Di-p-xenylpropylene*.—Phenanthraquinone (1 g.) and the olefin (IVb) (Pfeiffer and Schneider, *J. pr. Chem.*, 1931, **129**, 129) were exposed to sunlight for 50 days (March—April). The benzene was evaporated off in a vacuum, and the residual dark oil extracted with hot ligroin (b. p. 100—150°). The extract, on slow evaporation in a vacuum, gave crystals, which recrystallised from ethyl alcohol in colourless crystals, m. p. 143° (orange melt) (Found: C, 88.9; H, 5.8. $C_{41}H_{30}O_2$ requires C, 88.8; H, 5.5%). 2: 2-*Dixenyl-3-methylphenanthro-9':10'-1:4-dioxen* (as VI) when treated with sulphuric acid gave an olive-green colour after a few minutes at room temperature; it was soluble in benzene and hot ethyl alcohol.

The thermal decomposition was carried out as described above for $\frac{1}{2}$ hour at about 270° (bath temp.); the mixture was separated as before.

Diphenylketen. Phenanthraquinone (1 g.) and diphenylketen (Staudinger, *Ber.*, 1911, **44**, 1622) (2 g.) in 30 c.c. of benzene were exposed to sunlight for 3 months (March—May), the phenanthraquinone dissolving as before and the solution becoming brown. The crystals that separated were filtered off, washed with cold benzene, and recrystallised from hot benzene, forming almost colourless crystals, m. p. 227—230° (decomp.; orange melt) (Found: C, 83.5; H, 4.5. $C_{28}H_{18}O_3$ requires C, 83.6; H, 4.5%). The compound (VII) gave no immediate colour with sulphuric acid, but a dirty-green colour developed after some time; it was difficultly soluble in ligroin (b. p. 90—100°) and ethyl alcohol, but soluble in hot benzene; for its behaviour with alkali, see p. 997.

Thermal decomposition (15 mins. at bath temp. ca. 300°) afforded drops of an orange oil which solidified after 24 hours and were identified as phenanthraquinone.

as-*Dixenylethylene*. Phenanthraquinone (1 g.) and the ethylene (IVc) (1.6 g.) (Pfeiffer and Schneider, *loc. cit.*) were exposed to sunlight for 3 months (March—June). The separated solid was collected, washed with cold ether and then with hot acetone, and recrystallised from benzene in colourless crystals, m. p. 234° (Found: C, 89.5; H, 5.3. $C_{40}H_{28}O_3$ requires C, 88.9; H, 5.2%). 2: 2-*Dixenylphenanthro-9':10'-1:4-dioxen* (as VI), when treated with sulphuric acid, gave a red-brown colour at room temperature; it was soluble in hot benzene and difficultly soluble in ligroin (b. p. 90—100°).

For separation of the products of thermal decomposition (15 minutes at bath temp. ca. 290°), hot ligroin (b. p. 90—100°), in which (IVc) is soluble, was used.

1: 1-*Di-p-anisylpropylene*. Phenanthraquinone (1 g.) and the olefin (IVa) (Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 145) (1.1 g.) were exposed to sunlight for 3 months (March—June). The benzene was evaporated off in a vacuum and the brownish oily residue was extracted several times with ligroin (b. p. 70—80°). The extract, on slow evaporation, gave an almost colourless solid residue which recrystallised from benzene-light petroleum (b. p. 50—60°) in colourless crystals, m. p. 181° (orange-brown melt) (Found: C, 80.2; H, 5.6. $C_{31}H_{26}O_4$ requires C, 80.5; H, 5.6%). 2: 2-*Di-p-anisyl-3-methylphenanthro-9':10'-1:4-dioxen* (as VI) when treated with sulphuric acid at room temperature gave a dark brown colour changing after a few minutes into olive-green; it was soluble in hot benzene, difficultly soluble in cold ethyl alcohol.

The products of thermal decomposition (bath temp. ca. 270°) were separated as in the preceding case.

(a, ii) *Photo-reaction between Retenequinone and Stilbene*.—Retenequinone (1 g.) and stilbene (0.7 g.) in 25 c.c. of benzene were exposed to sunlight for 21 days (March), the quinone then having dissolved. The benzene was evaporated off in a vacuum, and the solid residue was washed with cold light petroleum (b. p. 80—100°), and crystallised from ethyl alcohol, forming very light yellow crystals, m. p. 224—226° (decomp.; red melt) (Found: C, 86.8; H, 6.5. $C_{33}H_{28}O_3$ requires C, 86.5; H, 6.3%). 5: 6-*Diphenyl-(1-methyl-7-isopropylphenanthro)-9':10'-1:4-dioxen* (VIII) gave no colour with sulphuric acid at room temperature, but a red colour at 100° and was soluble in hot benzene. At ca. 270° (bath temp.) it decomposed into retenequinone (identified, after recrystallisation from chloroform and ethyl alcohol, by mixed m. p. and colour reaction with sulphuric acid) and stilbene (recrystallised from ethyl alcohol and identified by m. p. and mixed m. p.). (This experiment was carried out with M. Z. Barakat.)

(b) *Action of Oxygen on Triarylmethanes in Sunlight*.—(1) 9-*a-Naphthylxanthen*. Reduction of 9-*a-naphthylxanthryl* (Gomberg and Schoepfle, *J. Amer. Chem. Soc.*, 1917, **39**, 1668) was carried out as described by Ullmann and Engi (*Ber.*, 1904, **37**, 2371) for the phenyl compound, *i.e.*, by means of zinc dust and acetic acid with platinum chloride as a catalyst. 9-*a-Naphthylxanthen* recrystallised from benzene-light petroleum (b. p. 30—50°), m. p. 184° (Found: C, 89.5; H, 5.1. Calc. for $C_{23}H_{16}O$: C, 89.6; H, 5.2%).* Kovache (*Ann. Chim.*, 1918, **10**, 184) gives m. p. 184°. It was soluble in benzene and gave no colour with sulphuric acid.

9-*a-Naphthylxanthen* was insolated for 5 days (February). The colourless crystals that separated were recrystallised from xylene; m. p. 228° (decomp.; dark melt) (Found: C, 85.3; H, 4.7. Calc. for $C_{40}H_{30}O_2$: C, 85.4; H, 4.7%). For the peroxide, Gomberg and Schoepfle (*loc. cit.*) gave m. p. 228—230°. The peroxide was practically insoluble in light petroleum (b. p. 30—50°) or in cold benzene, but soluble in hot benzene or xylene, and gave a deep red solution with sulphuric acid.

(2) 9-*a-Naphthylthioxanthen*. To a Grignard solution of *a-naphthylmagnesium bromide* (magnesium, 1.2 g.; *a*-bromonaphthalene, 10.4 g.; dry ether, 50 c.c.), dry benzene (30 c.c.) was added, and the mixture treated gradually with powdered thioxanthen (Davis and Smiles, *J.*, 1910, **97**, 1296) (6 g.). The solution became yellow and a yellow precipitate formed; the mixture was refluxed for one hour, set aside overnight, poured into ice-cold dilute hydrochloric acid, extracted with ether, the extract dried, and the ether-benzene mixture evaporated. The residue, washed with cold ethyl alcohol and recrystallised from hot ethyl alcohol, had m. p. 191—192° (Found: C, 81.1; H, 4.3; S, 8.8. $C_{23}H_{16}OS$ requires C, 81.2; H, 4.7; S, 9.4%). 9-*a-Naphthylthioxanthryl* was soluble in cold benzene, ether, and hot ethyl alcohol, and gave a red colour with sulphuric acid. It was reduced as in the preceding case, and the colourless 9-*a-naphthylthioxanthen* crystallised from benzene with one molecule of solvent of crystallisation, m. p. 77° (Found: C, 86.7; H, 5.5; S, 7.9. $C_{23}H_{16}S_2C_6H_6$ requires C, 86.5;

H, 5.4; S, 7.9%). It was freely soluble in benzene, but difficultly soluble in ethyl alcohol; it gave no colour with sulphuric acid.

This xanthen was insolated for 4 days (February). The colourless crystals that separated, recrystallised from benzene-light petroleum (b. p. 30–50°), had m. p. 176° (efferv.). 9-*a*-Naphthylthioxanthyl peroxide (Found: C, 81.1; H, 4.4; S, 8.8. $C_{48}H_{30}O_2S_2$ requires C, 81.4; H, 4.5; S, 9.4%) is slightly soluble in hot benzene and soluble in hot xylene and gives a violet colour with sulphuric acid.

(3) 9-*m*-Tolylxanthen. 9-*m*-Tolylxanthhydrol, prepared substantially as for 9-*a*-naphthylthioxanthhydrol but from *m*-tolylmagnesium bromide (magnesium, 1.2 g.; *m*-bromotoluene, 9 g.; dry ether, 30 c.c.; dry benzene, 30 c.c.) and xanthone (5 g.), separated from benzene in colourless crystals, m. p. 149° (Found: C, 82.8; H, 5.6. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.5%). It was soluble in hot benzene and difficultly soluble in light petroleum (b. p. 30–50°) and gave a red colour with sulphuric acid.

Reduction of 9-*m*-tolylxanthhydrol was carried out as for the naphthyl analogue. The colourless 9-*m*-tolylxanthen, crystallised from ethyl alcohol, had m. p. 98° (Found: C, 88.1; H, 5.5. $C_{20}H_{14}O$ requires C, 88.2; H, 5.9%). It was difficultly soluble in cold ethyl alcohol, but soluble in hot ethyl alcohol or hot benzene; it gave no colour with sulphuric acid.

9-*m*-Tolylxanthen was insolated for 38 days (February–March), during which the benzene solution became yellow. The colourless crystals, obtained by evaporation of the benzene, followed by washing with absolute ethyl alcohol, were recrystallised from benzene-ethyl alcohol and had m. p. 205°. The peroxide (Found: C, 83.2; H, 5.4. $C_{40}H_{30}O_4$ requires C, 83.6; H, 5.2%) was soluble in cold benzene, but insoluble in hot ethyl alcohol; it gave a yellow colour with sulphuric acid.

(4) 9-*p*-Tolylxanthen. Reduction of 9-*p*-tolylxanthhydrol (Gomberg and Cone, *Annalen*, 1909, 370, 164) was carried out as above. The colourless 9-*p*-tolylxanthen, crystallised from ethyl alcohol, had m. p. 116° (Found: C, 87.7; H, 5.9. Calc. for $C_{20}H_{16}O$: C, 88.2; H, 5.9%) (Kovache, *loc. cit.*, gives m. p. 116°). It gave no colour with sulphuric acid.

9-*p*-Tolylxanthen was insolated for 2 days (April). Colourless crystals, which began to separate after a few hours, were finally recrystallised from benzene; m. p. 217–218° (decomp.) (Found: C, 83.3; H, 5.6. Calc. for $C_{40}H_{30}O_4$: C, 83.6; H, 5.3%). Gomberg and Cone (*loc. cit.*, p. 166) give m. p. 212° (not sharp) for the peroxide. It dissolved with difficulty in light petroleum (b. p. 30–50°) and gave a brownish-red colour with sulphuric acid.

(5) 9-*p*-Methoxyphenylxanthen. Reduction of 9-*p*-methoxyphenylxanthhydrol (Gomberg and West, *J. Amer. Chem. Soc.*, 1912, 34, 1528) was carried out as for the naphthyl analogue. The colourless xanthen, crystallised from ligroin (b. p. 70–80°), had m. p. 117° (Found: C, 82.9; H, 5.5. Calc. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.5%) (Kovache, *loc. cit.*, gives m. p. 115°). It gave no colour with sulphuric acid.

9-*p*-Methoxyphenylxanthen was insolated for 30 days (February–March). The colourless crystals that separated were recrystallised from xylene, m. p. 205° (decomp.; dark brown melt) (Found: C, 79.1; H, 5.2. Calc. for $C_{40}H_{30}O_6$: C, 79.2; H, 4.9%). Gomberg and West (*loc. cit.*) give m. p. 214° (decomp.) for *p*-methoxyphenylxanthyl peroxide. It was soluble in boiling benzene and toluene, slightly soluble in cold benzene, and insoluble in light petroleum (b. p. 30–50°), and gave a red-brown colour with sulphuric acid.

(6) 9-Benzylxanthen. 9-Benzylxanthen (Decker, *loc. cit.*) (2 g.) was insolated for four months (April–August) in the presence of air. On slow evaporation of the benzene solution, it was recovered practically unchanged.

(c) Photochemical Reaction between Phenanthraquinone and Aromatic Aldehydes.—(i) 2:4-Dimethoxybenzaldehyde. Phenanthraquinone (1 g.) and the aldehyde (0.8 g.) in benzene (30 c.c.) were exposed to sunlight for 10 days (August). The colourless crystals that separated were washed with small amounts of cold benzene and crystallised from benzene, from which the 2:4-dimethoxyphenylhydroxymethylene ether of 9:10-dihydroxyphenanthrene (XIa) separated in colourless needles, m. p. 223° (red brown melt) (Found: C, 73.4; H, 4.8. $C_{23}H_{18}O_5$ requires C, 73.8; H, 4.8%). It was soluble in hot chloroform and benzene and difficultly soluble in hot ethyl alcohol; it gave a green colour with sulphuric acid.

(ii) Cuminaldehyde. Phenanthraquinone (1 g.) and cuminaldehyde (0.7 g.) in benzene (30 c.c.) were exposed to sunlight for 6 days (September). The resulting colourless crystals, recrystallised from ligroin (b. p. 80–90°), had m. p. 168–170° (decomp.; red melt). The benzene solution on concentration, gave a further amount of the cuminyldihydroxymethylene ether of 9:10-dihydroxyphenanthrene (XIc) (Found: C, 80.1; H, 5.3. $C_{24}H_{20}O_5$ requires C, 80.9; H, 5.6%). It was difficultly soluble in cold ethyl alcohol, but soluble in hot benzene; it gave an olive-green colour with sulphuric acid.

(iii) 2-Methoxy-1-naphthaldehyde. Phenanthraquinone (1 g.) and 2-methoxy-1-naphthaldehyde (0.9 g.) in benzene (30 c.c.) were exposed for 10 days (September). The benzene was evaporated in a vacuum, and the residue washed with hot ethyl alcohol and crystallised from ligroin (100–150°), forming colourless crystals, m. p. 190° (orange melt) (Found: C, 79.1; H, 4.6. $C_{26}H_{18}O_4$ requires C, 79.1; H, 4.6%). The 2-methoxy-1-naphthylhydroxymethylene ether of 9:10-dihydroxyphenanthrene (XIb) was soluble in benzene and difficultly soluble in hot ethyl alcohol; it gave a green colour with sulphuric acid.

(d) Action of Sunlight on Diphenyl Triketone.—Diphenyl triketone (2 g.) (*Org. Synth.*, Coll. Vol. 2, p. 244) in benzene (20 c.c.) was exposed to sunlight for 21 days (May). The benzene solution on evaporation in a vacuum, gave a yellow residue. The latter, on crystallisation from ligroin (b. p. 70–80°) gave yellow crystals, m. p. 95°, proved to be benzil (m. p. and mixed m. p.); yield ca. 70%. The dark experiment was negative.