173. *Photochemical Reactions in Sunlight. Part XI.* (a) *Formation of Triarylmethyl Peroxides by the Action of Oxygen on Triarylmethanes.* (b) *Dehydrogenation effected by Oxygen.* (c) *Dehydrogenation effected by* p-*Benzoquinone and Phenanthraquinone.*

By Alexander Schönberg and Ahmed Mustafa.

(*a*) The action of sunlight on certain diaryl- and triaryl-methanes, which are closely related to free radicals of long life, in the presence of oxygen was investigated. Methanes stable towards oxygen in sunlight are listed in Table I(*a*), those forming the corresponding peroxides in Table I(*b*), and those forming the corresponding ethanes in Table I(*c*). An explanation is advanced (see schemes A and B) for the results recorded in Table I(*b*). The photo-peroxides, of type (VI), liberate iodine from potassium iodide solution in acetic acid. 9-Phenyl- and 9-*p*-bromophenyl-xanthyl peroxides formed xanthone on pyrolysis. The ready formation of the peroxide from 9-phenylxanthen is remarkable, for the corresponding naphthalene derivative (II) is stable in sunlight in the presence of oxygen (steric hindrance ?).

(*b*) The action of oxygen in sunlight on some methanes which are not related to free radicals of long life, *e.g.*, thioxanthen, dinaphthapyran, and anthrone, produced the corresponding ethane (IX, X, and XI).

(*c*) *p*-Benzoquinone effects dehydrogenation in sunlight, thioxanthen being converted into *dithiodixanthyl* (IX) ; and phenanthraquinone is also able to effect the photo-dehydrogenation of thioxanthen and of diphenylmethane into dithiodixanthyl and *s*.-tetraphenylethane, respectively.

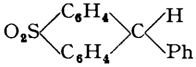
None of the reactions mentioned proceeds in the dark.

(a) *Action of Oxygen on Triarylmethanes and on* (IV) *and* (V) *in Sunlight.*—Triphenylmethyl bromide forms triphenylmethyl when its solutions are irradiated (Halford and Anderson, *Proc. Nat. Acad. Sci.*, 1933, **19**, 759), but if a solution in benzene is exposed to sunlight, in contact with air, it becomes deep yellow and deposits crystals of triphenylmethyl peroxide.

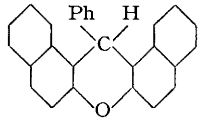
The object of the present investigation was to determine whether solutions of diaryl- and triaryl-methanes behave similarly, and in this section we deal with those methanes which are closely related to free radicals of long life. The methanes investigated are listed in Table I, and the free radicals of long life to which they are allied in Table II.

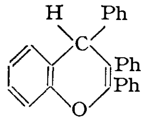
TABLE I.

(*a*) *Compounds stable towards oxygen in sunlight.* Triphenylmethane, 9-phenylfluorene, 2 : 2′-sulphonidotriphenylmethane (I), diphenylacetophenone, 9-phenyldinaphthapyran (II), and 2 : 3 : 4-triphenylbenzo-γ-pyran (III).

(I.) 

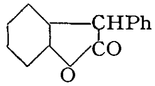
$O_2S{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}C{<}\genfrac{}{}{0pt}{}{H}{Ph}$

(II.) 

(III.) 

(*b*) *Triarylmethanes forming peroxides in sunlight in the presence of air.* 9-Phenylxanthen, 9-phenylthioxanthen, 9-*o*-tolylxanthen (the last two examples were examined in part with M. F. EL NEWEIHY), 9-p-*bromophenylxanthen*, and 9-phenylanthrone.

(*c*) *Diarylmethanes forming ethane compounds in sunlight in the presence of air.* Lactone of *o*-hydroxydiphenylacetic acid (IV) and 2-phenyl-3-keto-2 : 3-dihydrothionaphthen (V).

(IV.) 

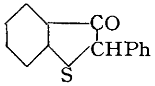
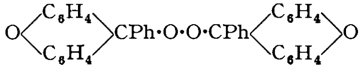
 (V.)

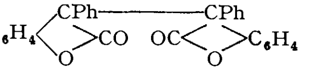
TABLE II.

Free radicals of long life. Triphenylmethyl, 9-phenylfluorenyl, 2 : 2′-sulphonidotriphenylmethyl (Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1947) (cf. I), 9-phenylxanthyl, 9-phenylthioxanthyl, 2 : 3 : 4-triphenylchromenyl (cf. III) (Löwenbein and Rosenbaum, *Annalen*, 1926, **448**, 223), benzoyldiphenylmethyl (Löwenbein and Schuster, *ibid.*, 1930, 481, 106), (VIII*a*) and (XII).

The methane derivatives listed in Table I(*a*) were not affected, those in Table I(*b*) formed the corresponding peroxides, *e.g.*, 9-phenylxanthen gave (VI), and those in Table I(*c*) gave the corresponding ethanes, *e.g.*, (IV) gave 2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (VII).

(VI.) 

$O{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}CPh\cdot O\cdot O\cdot CPh{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}O$

 (VII.)

The velocity of the formation of some of these peroxides, *e.g.*, 9-phenylxanthyl peroxide, is remarkable. This should be contrasted with the stability of the phenyldinaphthapyran (II) : it may be that this is one of the rare cases of steric hindrance observed in photochemical reactions.

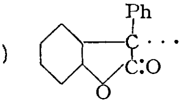
Mechanism of the Photo-reaction.—Several explanations of these photo-reactions are possible; the simplest is that, under the influence of sunlight, the methanes listed in Table I(*b*) dissociate according to the scheme $CHRR'R'' \longrightarrow CRR'R''\ldots. + H$ (A.). The free methyl radical thus produced reacts with atmospheric oxygen. This dark reaction is already known in the case of 9-phenylxanthen (Gomberg and Cone, *Annalen*, 1909, **370**, 158), 9-phenylthioxanthen (*idem, ibid.*, 1910, **376**, 204), and 9-phenylanthrone (Liebermann *et al.*, *Ber.*, 1904, **37**, 3340), in which the free radicals were prepared by the action of metals on the corresponding chlorides.

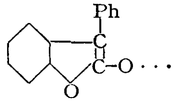
It is possible also that with the methanes listed in Table I(*c*), an analogous reaction takes place, *i.e.*, removal of one hydrogen atom, but the free radicals thus formed do not form peroxides, undergoing dimerisation instead. This behaviour may be due to the fact that the corresponding free radicals are to be regarded as resonance hybrids, *e.g.*, (VIII*a*) and (VIII*b*), and that the latter form contains univalent oxygen; such radicals are known to be not readily affected by atmospheric oxygen (Goldschmidt and Schmidt, *Ber.*, 1922, **55**, 3202). The stability of the free radicals (VIII*a*) and (XII) towards oxygen was noted by Löwenbein and Simonis (*Ber.*, 1924, **57**, 2047) and by Kalb and Bayer (*Ber.*, 1913, **46**, 3884), respectively.

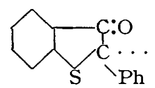
The formation of peroxides from triarylmethanes by oxygen *in the presence of sunlight*, and of ethanes from (IV) and (V) under the same conditions, may be explained without the formation of free radicals, as shown in (B) and (C).

$$2CHR_3 + 2O_2 \longrightarrow 2CR_3\cdot O\cdot OH \longrightarrow CR_3\cdot O\cdot O\cdot CR_3 + H_2O_2 \quad \text{(B.)}$$

$$2CHR_3 + O_2 \longrightarrow CR_3\cdot O\cdot OH + CHR_3 \longrightarrow CR_3\cdot CR_3 + H_2O_2 \quad \text{(C.)}$$

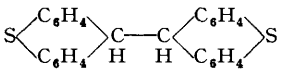
(VIII*a*.) 

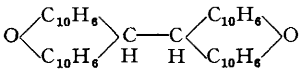
(VIII*b*.) 

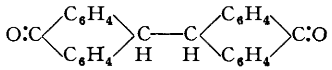
(XII.) 

Constitution and Reactions of Peroxides in Table I(*b*).—The peroxides obtained from these compounds were already known, except that from 9-*o*-anisylxanthen. That this was a peroxide was established by the fact that it liberated iodine from potassium iodide solution in acetic acid. 9-Phenyl- and 9-*p*-bromophenyl-xanthyl peroxides (as VI) formed xanthone on pyrolysis.

(b) *Action of Oxygen in Sunlight on Thioxanthen, Dinaphthapyran, and Anthrone.*—These methane derivatives, which are not related to free radicals of long life, were exposed to sunlight and air and found to form the corresponding ethanes, *viz.*, *dithiodixanthyl* (IX), bisdinaphthaxanthenyl (X), and dianthronyl (XI), according to scheme C.


(IX.)


(X.)


(XI.)

(c) *Action of* p-*Benzoquinone and Phenanthraquinone on Methanes in Sunlight.*—Schönberg and Mustafa (*J.*, 1944, 67) found that at room temperature and in sunlight, *p*-benzoquinone converted diphenylmethane into *s.*-tetraphenylethane, being itself reduced to quinhydrone. Similarly, dithiodixanthyl (IX) has now been produced by the action of *p*-benzoquinone on thioxanthen. Phenanthraquinone is also able to effect photochemical dehydrogenation of diphenylmethane to *s.*-tetraphenylethane and of thioxanthen to dithiodixanthyl.

In sunlight, dithiodixanthyl (IX) is produced from thioxanthen and xanthone, and dianthronyl (XI) from anthrone and benzophenone.

EXPERIMENTAL.

All insolations, unless otherwise stated, were carried out upon 1 g. of the substance in 10—20 c.c. of benzene with free access of air. Control experiments in the dark, but otherwise under identical conditions, showed no reaction. The benzene was thiophen-free and dried over sodium. The photochemical reactions were carried out, unless otherwise stated, in a Pyrex-glass tube, the air being displaced by dry carbon dioxide and the tube sealed by fusion. The photoreactions in the presence of oxygen were carried out in an open Pyrex-glass tube.

(a) *Action of Oxygen on Triarylmethanes in Sunlight* [cf. Table I (*b*)].—(1) 9-*Phenylxanthen.* 9-Phenylxanthen (Ullmann and Engi, *Ber.*, 1904, **37**, 2371) was insolated for 15 days (November) in air. (After one day, colourless crystals had separated, and the solution had become yellow.) The crystals, recrystallised from benzene, had m. p. 230° (decomp. from about 210° according to rate of heating). For 9-phenylxanthyl peroxide Gomberg and Cone (*loc. cit.*) give m. p. 219°. It is insoluble in ether and light petroleum (Found : C, 82·9; H, 4·7. Calc. for $C_{38}H_{26}O_4$: C, 83·4; H, 4·8%). Further concentration of the original benzene mother-liquor gave more peroxide (total yield, *ca.* 80%).

(2) 9-*Phenylthioxanthen.*—A solution of 9-phenylthioxanthhydrol (1 g.) (Ullmann and Engi, *Ber.*, 1904, **37**, 2937) in boiling absolute ethyl alcohol (30 c.c.) was added gradually to metallic sodium (6 g.), the mixture heated under reflux for 2 hours, and then poured into ice-cold water. The 9-phenylthioxanthen was separated, and crystallised from alcohol as colourless crystals, m. p. 96°. It was freely soluble in benzene and acetone, and soluble in hot alcohol; it gave no coloration with concentrated sulphuric acid at room temperature, but dissolved to give an orange colour with green fluorescence when heated on the water-bath (Found : C, 83·0; H, 5·3; S, 11·9. Calc. for $C_{19}H_{14}S$: C, 83·2; H, 5·1; S, 11·7%).

9-Phenylthioxanthen was insolated for about 10 days (Jan.–Feb.); the solution became orange-red after 2 days. The colourless crystals that separated were recrystallised from benzene–light petroleum (b. p. 50—70°); m. p. 188° (red melt) (Found : C, 78·9; H, 4·6; S, 11·1. Calc. for $C_{38}H_{26}O_2S_2$; C, 78·8; H, 4·6; S, 11·1%). Gomberg and Cone (*loc. cit.*) give m. p. 188° for 9-phenylthioxanthyl peroxide. It dissolved in sulphuric acid with a red colour.

(3) 9-o-*Tolylxanthen.* The reduction of 9-*o*-tolylxanthhydrol (Decker and v. Fellenberg, *Annalen*, 1907, **356**, 311) was carried out as described in the preceding case. The colourless 9-*o*-tolylxanthen, crystallised from alcohol, had m. p. 135°. Decker (*loc. cit.*) gives m. p. 119°. It gave no coloration with sulphuric acid (Found : C, 87·7; H, 5·9. Calc. for $C_{20}H_{16}O$: C, 88·2; H, 5·9%).

9-*o*-Tolylxanthen was insolated for 15 days (June–July). Colourless crystals began to separate after 3 days; finally, these were recrystallised from benzene–light petroleum and had m. p. 229° (deep red melt). This 9-*o*-tolylxanthyl peroxide dissolved with difficulty in xylene, and gave a yellow colour with sulphuric acid (Found : C, 83·5; H, 5·5. Calc. for $C_{40}H_{30}O_4$: C, 83·6; H, 5·2%).

Experiments (2) and (3) were carried out by M. F. El Neweihy.

(4) 9-p-*Bromophenylxanthen.* Reduction of 9-*p*-bromophenylxanthhydrol (Gomberg and Cone, *Annalen*, 1909, **370**, 142) was carried out as described by Ullmann and Engi (*loc. cit.*) for 9-phenylxanthen by means of zinc dust and acetic acid with platinum chloride as a catalyst. 9-p-*Bromophenylxanthen* recrystallised from absolute ethyl alcohol in colourless crystals, m. p. 120°. It was soluble in benzene and gave no colour with sulphuric acid (Found : C, 68·1; H, 4·0; Br, 23·1. $C_{19}H_{13}OBr$ requires C, 67·8; H, 3·8; Br, 23·7%).

9-*p*-Bromophenylxanthen was insolated for 5 days (May). The colourless crystals that separated were recrystallised from xylene; m. p. 211° (red brown melt) (Gomberg and Cone, *loc. cit.*, give m. p. 210—211°). 9-*p*-Bromophenylxanthyl peroxide is insoluble in hot ether, difficultly soluble in hot benzene, and gives a brilliant yellow solution with sulphuric acid (Found : C, 64·6; H, 3·4; Br, 22·5. Calc. for $C_{38}H_{24}O_4Br_2$: C, 65·1; H, 3·4; Br, 22·7%).

(5) 9-*Phenylanthrone.* 9-Phenylanthrone (Schlenk and Bergmann, *Annalen*, 1928, **463**, 162) was insolated for about 3 months (January–March). The solution became yellow and pale yellow crystals separated; these recrystallised from benzene in almost colourless crystals, m. p. 203° depending on the rate of heating (red brown melt; decomp.) (Found: C, 83·5; H, 4·8. Calc. for $C_{40}H_{26}O_4$: C, 84·2; H, 4·5%). Liebermann *et al.* (*loc. cit.*) give m. p. 219° for 9-phenylanthrone peroxide. More peroxide was recovered from the original mother-liquor. It gives a violet coloration with sulphuric acid.

Diaryl- and Triaryl-methanes Stable towards Oxygen in Sunlight [cf. Table I(*a*)].—The substances shown in the table were irradiated under the usual conditions (see above) for the time stated, the benzene evaporated in a vacuum, and the residue crystallised. The unchanged compounds (m. p. and mixed m. p.) were recovered quantitatively or nearly so.

Compound.	Exposure (days).	Month of exposure.	Compound.	Exposure (days).	Month of exposure.
Triphenylmethane	36	April–May	2 : 3 : 4-Triphenylbenzo-γ-pyran (III) [2]	70	Sept.–Nov.
9-Phenylfluorene	120	Dec.–Mar.	Diphenylacetophenone [3]	40	July–Aug.
2 : 2′-Sulphonido-triphenylmethane (I) [1]	150	April–Sept.	9-Phenyldinaphthapyran (II) [4]	180	Jan.–June

[1] Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1947. [2] Löwenbein and Rosenbaum, *loc. cit.* [3] **Koelsch,** *J. Amer. Chem. Soc.*, 1932, **54**, 2051. [4] Claisen, *Annalen*, 1887, **237**, 266.

Thermal Decomposition of the Photo-peroxides.—9-*Phenylxanthyl peroxide.* While dry carbon dioxide was passing through the apparatus (Schönberg and Mustafa, *J.*, 1944, 305), the peroxide (2 g.) was heated (bath temp. about 270°) for 2 hours in a tube (A) as described in this vol., p. 553. A colourless crystalline sublimate was formed on the walls of the tube; this was recrystallised from absolute ethyl alcohol and proved to be xanthone (m. p. and mixed m. p.; blue fluorescence with sulphuric acid). 9-p-*Bromophenylxanthyl peroxide.* This peroxide (2 g.), similarly heated, also afforded xanthone.

Ethane Formation from the Corresponding Methane in Sunlight in the Presence of Air [Table I(*c*)].—*Lactone of* o-*hydroxydiphenylacetic acid* (IV). The lactone (Bistrzycki and Flatau, *Ber.*, 1895, **28**, 989) was insolated for 75 days (April–June). The colourless crystals that separated, recrystallised from benzene–light petroleum, had m. p. 178° (violet-red melt). The photo-product dissolved with difficulty in light petroleum (b. p. 80—90°) and glacial acetic acid, and gave a violet coloration with sulphuric acid; it was proved by mixed m. p. to be 2 : 2′-diketo-3 : 3′-diphenyl-3 : 3′-dicoumaranyl (Löwenbein and Simonis, *loc. cit.*) (Found : C, 80·1; H, 4·6. Calc. for $C_{20}H_{18}O_4$: C, 80·4; H, 4·3%).

2-*Phenyl*-3-*keto*-2 : 3-*dihydrothionaphthen* (V). The thionaphthen (Kalb and Bayer, *loc. cit.*) was irradiated for 2 days (July); the pale yellow crystals that separated were recrystallised from benzene; m. p. 236° (decomp.; green melt). The product dissolved with difficulty in cold benzene and hot glacial acetic acid, and gave a green colour with sulphuric acid; it was identified as 2 : 2′-diphenylthioindigo-white (Kalb and Bayer, *loc. cit.*) by mixed m. p. (Found : C, 74·7; H, 4·2; S, 13·9. Calc. for $C_{28}H_{18}O_2S_2$: C, 74·6; H, 4·0; S, 14·2%).

(b) *Action of Oxygen in Sunlight on* (i) *Thioxanthen*, (ii) *Dinaphthapyran, and* (iii) *Anthrone.*—(i) Thioxanthen (Graebe and Schultes, *Annalen*, 1891, **263**, 12), irradiated for one day (July), afforded a mass of colourless crystals; these were filtered off, washed with benzene, and crystallised from xylene, forming colourless needles, m. p. 325°, of *dithiodixanthyl* (IX). It was difficultly soluble in acetone and alcohol, slightly soluble in light petroleum (b. p. 100—150°), and soluble in hot xylene, and gave an orange colour with sulphuric acid (Found : C, 78·9; H, 4·5. $C_{26}H_{18}S_2$ requires C, 79·3; H, 4·6%). When this experiment was repeated in a sealed tube (carbon dioxide atmosphere), no crystals separated, and the initial thioxanthen was recovered almost quantitatively.

(ii) Dinaphthapyran (Wolff, *Ber.*, 1893, **26**, 84) was insolated for one day (November). The crystals of bisdinaphthoxanthenyl (X) which separated were collected, washed with benzene, and recrystallised from light petroleum (b. p. 100—110°), forming colourless needles, m. p. above 300°. Fosse (*Compt. rend.*, 1902, **135**, 521; 1903, **136**, 379) gave m. p. above 300° (Found : C, 89·9; H, 4·9. Calc. for $C_{42}H_{26}O_2$: C, 89·6; H, 4·6%).

(iii) Anthrone (*Org. Synth.*, Coll. Vol. I, p. 52) (3 g.) was dissolved in benzene (25 c.c.) and exposed to sunlight and air for one week (March); pale yellow crystals of dianthrone (XI) separated and were filtered off and washed with benzene; recrystallised from light petroleum (b. p. 100—150°), they had m. p. *ca.* 260° (Found: C, 87·2; H, 5·1. Calc. for $C_{28}H_{18}O_2$: C, 87·1; H, 5·2%).

(c) *Action of* p-*Benzoquinone and of Phenanthraquinone on Methanes in Sunlight.*—p-*Benzoquinone and thioxanthen.* Thioxanthen (Graebe and Schultes, *loc. cit.*) (1 g.) and *p*-benzoquinone (0·8 g.) were dissolved in benzene (30 c.c.) and exposed to sunlight for 2 days (July). The deposit was filtered off and found to contain quinhydrone, as well as dithiodixanthyl (IX); the former was removed by dissolving it in acetone, and the latter then crystallised from xylene in colourless needles, m. p. 325° (Found : C, 79·4; H, 4·5%).

Phenanthraquinone and thioxanthen. Thioxanthen (1 g.) and phenanthraquinone (1·1 g.), dissolved in benzene (50 c.c.), were exposed for 30 days (Jan.–Feb.) to direct sunlight. The crystals that separated were collected, washed several times with hot benzene, followed by hot absolute ethyl alcohol, and recrystallised from hot xylene, forming colourless crystals, m. p. 323°, of dithiodixanthyl (IX) (mixed m. p.) (Found : C, 79·5; H, 4·7; S, 16·0%). This product was formed even after only one day's exposure.

Phenanthraquinone and diphenylmethane. Diphenylmethane (1 g.) and phenanthraquinone (1·24 g.; 1 mol.) were dissolved in benzene (20 c.c.) and exposed to sunlight for 50 days (Aug.–Sept.), the solution becoming dark brown. The benzene was driven off in a vacuum, the dark residue repeatedly extracted with hot light petroleum (b. p. 30—50°), and finally with light petroleum (b. p. 90—100°). The extract on evaporation at room temperature gave crystals, and recrystallisation from light petroleum (b. p. 90—100°) afforded colourless crystals of *s*.-tetraphenylethane (m. p. and mixed m. p.).

Photochemical Action of Xanthone on Thioxanthen.—An equimolecular mixture of thioxanthen (1 g.) and xanthone was dissolved in benzene (15 c.c.) and irradiated for 6 hours (July); the mass of pale crystals of dithiodixanthyl (IX) was filtered off, washed with benzene several times, and crystallised from xylene; m. p. 325° (yield *ca.* 80%) (Found : C, 79·3; H, 4·8%).

Photochemical Action of Benzophenone on Anthrone.—An equimolecular mixture of benzophenone (1 g.) and anthrone in benzene (25 c.c.) was exposed to sunlight for 23 days (April–May). The solution became yellow and large crystals of dianthrone (XI) separated; these were filtered off, washed with benzene, and crystallised from light petroleum (b. p. 100—110°); m. p. about 255° (Found : C, 86·4; H, 4·9. Calc. for $C_{28}H_{18}O_2$: C, 87·1; H, 4·7%).

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