

26. *Photo-reactions. Part VII. Reactions in Sunlight involving (a) Rupture of the Ethane Linkage, (b) Dehydrogenation effected by Quinone and Benzophenone Derivatives, (c) Addition Reactions between Ketones and Methanes.*

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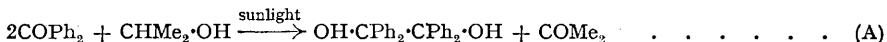
The photo-chemical formation of benzpinacols by the action of acetone on benzhydrols is described (D). Xanthopinacol (I) and fluorenopinacol (II) are photo-chemically transformed in the presence of acetone into xanthone and fluorenone respectively (rupture of the ethane C-C linkage) (B). Similar rupture occurs when the pinacols (VIII) to (XIV) are treated with *p*-benzoquinone in sunlight (C).

Quinone in sunlight dehydrogenates diphenylmethane, fluorene, xanthen, anthrone, and dinaphthapyran, derivatives of ethane being formed (E).

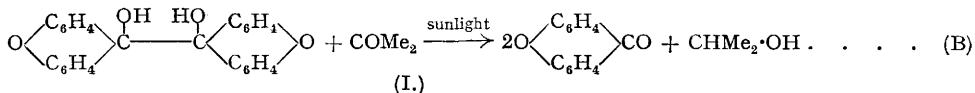
The photo-chemical dehydrogenation of diphenylmethane derivatives by diaryl ketones, with formation of derivatives of ethane, is described (F and G).

None of the reactions mentioned proceeds in the dark.

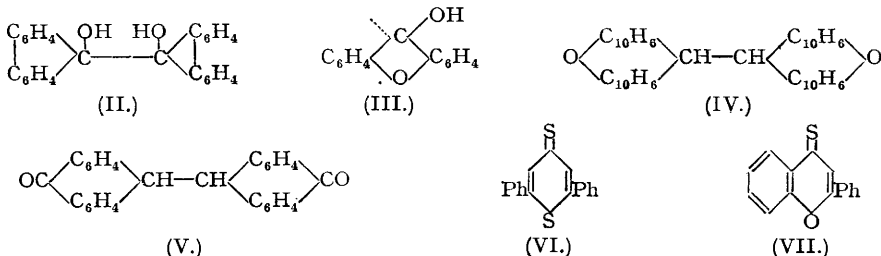
(1) *Photo-experiments with Pinacols*.—(i) Cohen's statement (*Rec. Trav. chim.* 1920, **39**, 243) that benzo-phenone in isopropyl alcohol is almost quantitatively reduced to benzpinacol in sunlight has been confirmed



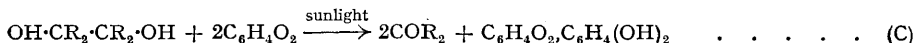
by Bachmann (*Org. Synth.*, **14**, 8). We have carried out corresponding reactions with *pp'*-dimethoxybenzo-phenone and *pp'*-dichlorobenzophenone, but have been unable to reduce xanthone by this method: the stability of fluorenone to isopropyl alcohol in sunlight has been demonstrated by Bachmann (*J. Amer. Chem. Soc.*, 1933, **55**, 394). In the cases of xanthopinacol (I) and fluorenopinacol (II), the reverse of reaction (A) takes place, xanthone and fluorenone respectively being formed together with isopropyl alcohol:



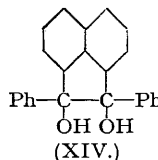
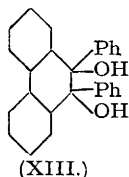
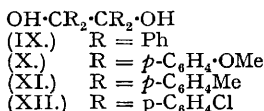
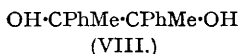
This is an example of the breaking of the C-C linkage during a photo-chemical process in sunlight. Reaction (B) (and the corresponding reaction with fluorenopinacol) does not proceed in the dark under similar conditions. There are several ways by which the mechanism of (B) may be explained; e.g., xanthopinacol (I) may split into free radicals (III), which are dehydrogenated by acetone:



(ii) Pinacol itself is stable to *p*-benzoquinone in sunlight, being recovered unchanged after 10 days' exposure, but the substances (VIII) to (XIV) react according to (C). Photo-oxidation takes place after several hours

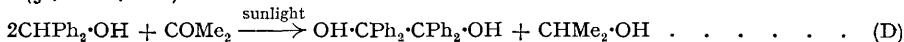


and quinhydrone separates. No reaction takes place in the dark under similar conditions [the photo-action of *p*-benzoquinone on (IX) and XIV) was examined by Schönberg and Mrs. Said].



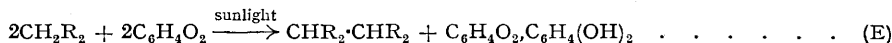
Triphenylcarbinol does not react with *p*-benzoquinone in benzene in sunlight.

(iii) Benzpinacol is produced photo-chemically, not only by method (A) but also by the action of acetone on benzhydrol in sunlight (J., 1943, 276):



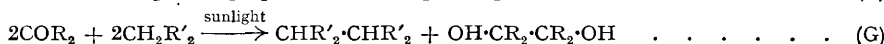
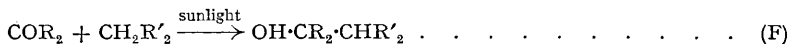
Similar reactions can be carried out with *pp'*-dimethoxybenzhydrol and *pp'*-dimethylbenzhydrol.

(2) *Photo-chemical Reactions with Diarylmethanes*.—(i) Reaction (E), where R is an aromatic residue,



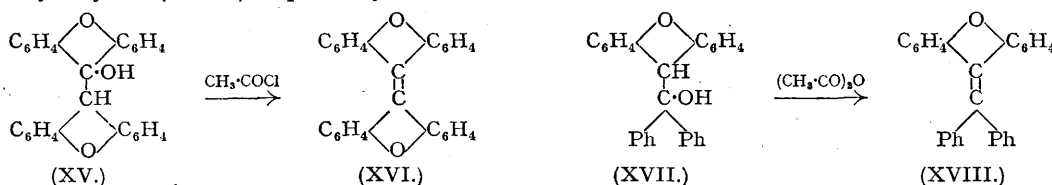
takes place with diphenylmethane, fluorene, xanthen, anthron, and dinaphthapyran (Wolff, *Ber.*, 1893, **26**, 84) in sunlight, but not in the dark: photo-oxidation is proved by the formation of quinhydrone. *s*-Tetraphenyl-ethane is not affected by *p*-benzoquinone in sunlight.

(ii) The photo-chemical reaction between ketones of the benzophenone type and diphenylmethanes either is additive (F) or gives the corresponding pinacols (G).



Reaction (F), previously carried out with diphenylmethane and benzophenone by Paternó and Chieffi (*Gazzetta*, 1909, **39**, II, 415), has now been effected with xanthen and xanthone and with xanthen and benzophenone. The speed of the reaction is remarkable, xanthen and xanthone, for example, requiring only a few hours' irradiation. As the ethane derivative (XV) separates in crystals of great purity, this reaction is of interest from the synthetical point of view. The two ethane derivatives obtained from the above pairs of

compounds are given formulæ (XV) and (XVII) respectively because they are colourless, show halochromy with concentrated sulphuric acid, and are dehydrated as shown below to dixanthylene (XVI) and *oo'*-oxido-tetraphenylethylene (XVIII) respectively.



Without investigating the fate of the ketones used in the experiments, we have found that, in sunlight, tetraphenylethane is produced from diphenylmethane and anthraquinone and also from diphenylmethane and xanthone, dianthrone (V) from anthrone and xanthone, and *bisdinaphthaxanthen* (IV) from dinaphthapyran and xanthone.

Reactions of type (G), previously observed with benzophenone and di-*p*-anisylmethane (Bergmann and Fujise, *Annalen*, 1930, 483, 67), have now been carried out with xanthone and acetophenone, 4 : 4'-dimethoxybenzophenone, or 4 : 4'-dichlorobenzophenone.

(3) *Photo-activity of Thio-ketones and the Corresponding Ketones*.—In contrast to the ready reduction of benzophenone and *pp'*-dimethoxybenzophenone by isopropyl alcohol in sunlight (A), *pp'*-dimethoxythiobenzophenone, 4 : 4'-bisdimethylaminothiobenzophenone, xanthione, thioxanthione, *N*-phenylthioacridone, 2 : 6-diphenyldithiopyrone (VI), and 4-thioflavone (VII) do not react under similar conditions after 7 days' exposure. Further, diphenylmethane reacts with *pp'*-dimethoxybenzophenone according to (G) (Bergmann and Fujise, *loc. cit.*), but not with *pp'*-dimethoxythiobenzophenone. These are cases in which thio-ketones show greater chemical resistance than the corresponding ketones; the opposite is usually the case.

#### EXPERIMENTAL.

*General Remarks*.—The benzene was thiophen-free and dried over sodium (Kahlbaum); the acetone (Hopkin and William's analytical reagent) was free from isopropyl alcohol.

The photo-chemical reactions were carried out, unless otherwise stated, in a glass tube, the air being displaced by dry carbon dioxide and the tube being sealed by fusion. In some cases, indicated below by the term "mercury sealing," a Pyrex glass tube was filled to the neck with solution, closed with a waxed cork, and inverted in mercury.

The expression "dark experiment negative" denotes that, in experiments carried out in the dark but otherwise under the same conditions as the photo-experiment, there was no reaction.

(1) *Photo-chemical Reactions in isopropyl Alcohol, Acetone, or Benzene*.—(i) In the four experiments tabulated below, the solution of the substance was exposed to sunlight for the time stated, the solvent then removed in a vacuum, and the product washed with absolute ethyl alcohol and crystallised from petroleum (b. p. 100—110°). Identity was established by a mixed m. p. determination with an authentic specimen. The yield in the first two experiments was quantitative or almost quantitative.

Substance.	Solvent.	Exposure (days).	Products.
<i>pp'</i> -Dimethoxybenzophenone (2 g.)	isoPropyl alcohol (25 c.c.)	15	4 : 4' : 4'' : 4'''-Tetramethoxybenzpinacol
* <i>pp'</i> -Dichlorobenzophenone (2 g.)	" (20 c.c.)	30	4 : 4' : 4'' : 4'''-Tetrachlorobenzpinacol
Xanthopinacol (5 g.)	Acetone (25 c.c.) †	31	Xanthone, isopropyl alcohol
Fluorenopinacol (5 g.)	" (25 c.c.) †	31	Fluorenone, isopropyl alcohol

\* Mercury sealing.

† Dark experiment negative.

The isopropyl alcohol formed in the last two photo-experiments was detected in the acetone by means of *p*-nitrobenzoyl chloride, isopropyl *p*-nitrobenzoate (0.227 g.) being obtained.

(ii) In the following experiments, the two reactants in benzene solution (15—25 c.c.) were exposed to sunlight for the time stated, the crystals of quinhydrone then removed, the benzene evaporated in a vacuum, and the residue (except in the first experiment) washed with light petroleum or cold alcohol and crystallised from the hot solvent. The products were identified by mixed m. p. determinations.

Reactants.	Exposure (days).	Product.
Acetophenonepinacol (2 g.)	40	Acetophenone *
<i>p</i> -Benzoquinone (1.2 g.)		
Benzpinacol (0.5 g.)	14	Benzophenone
<i>p</i> -Benzoquinone (0.3 g.)		
4 : 4' : 4'' : 4'''-Tetramethoxybenzpinacol (1 g.)	31	4 : 4'-Dimethoxybenzophenone †
<i>p</i> -Benzoquinone (0.5 g.)		
4 : 4' : 4'' : 4'''-Tetramethylbenzpinacol (2 g.)	10	4 : 4'-Dimethylbenzophenone †
<i>p</i> -Benzoquinone (1.2 g.)		
4 : 4' : 4'' : 4'''-Tetrachlorobenzpinacol	20	4 : 4'-Dichlorobenzophenone †
<i>p</i> -Benzoquinone (0.4 g.)		
9 : 10-Dihydroxy-9 : 10-diphenyldihydrophenanthrene (4 g.)	14	2 : 2'-Dibenzoyldiphenyl †
<i>p</i> -Benzoquinone (2.4 g.)		
1 : 8-Diphenylacenaphthene glycol (1.17 g.)	7	1 : 8-Dibenzoylnaphthalene
<i>p</i> -Benzoquinone (1.1 g.)		
Xanthopinacol (1 g.)	24	Xanthone †
<i>p</i> -Benzoquinone (0.8 g.)		

\* Isolated from the residue by steam-distillation and identified by conversion into the semicarbazone (acetophenonepinacol is not converted into acetophenone by the action of steam).

† Yield quantitative or almost quantitative.

(iii) 4 : 4' : 4'' : 4'''-Tetramethoxybenzpinacol. A solution of *pp'*-dimethoxybenzhydrol (4 g.) in acetone (20 c.c.) was exposed to sunlight for one month, becoming yellow. The acetone was removed in a vacuum (distillate A), leaving a pale yellow, oily residue which solidified on treatment with light petroleum. The solid was washed with hot petroleum (b. p. 100—110°), from which, on cooling, a small amount of unchanged hydrol was obtained. The residue, crystallised from absolute alcohol, gave 4 : 4' : 4'' : 4'''-tetramethoxybenzpinacol, which was identified by comparison with an authentic specimen. The presence of *isopropyl* alcohol in distillate A was shown by its conversion into *isopropyl p*-nitrobenzoate by refluxing with *p*-nitrobenzoyl chloride.

*pp'*-Dimethylbenzhydrol. The benzhydrol (2 g.) was treated as in the previous experiment (but with mercury sealing) for 58 days. The yellow oily residue obtained on evaporation of the acetone in a vacuum was washed with cold absolute alcohol and crystallised from petroleum (b. p. 100—110°), giving 4 : 4' : 4'' : 4'''-tetramethylbenzpinacol, m. p. 176°, not depressed by an authentic specimen.

(2) Photo-chemical Reactions with Diarylmethanes. (i) (a) Diphenylmethane (4 g.) and *p*-benzoquinone (1.2 g.) in benzene (20 c.c.) were exposed to sunlight for 1 month. Quinhydrone, which began to separate after a few hours' exposure, was then removed, the benzene driven off in a vacuum, and the coloured oily residue subjected to steam-distillation to remove diphenylmethane and *p*-benzoquinone and extracted with ether. The extract was dried (anhydrous sodium sulphate), the ether removed in a vacuum, and the residue treated with light petroleum. The semi-solid mass obtained separated from petroleum (b. p. 100—110°) in fine colourless crystals (0.7 g.), m. p. 210°, not depressed by authentic *s*-tetraphenylethane.

(b) After fluorene (2 g.) and *p*-benzoquinone (0.64 g.) in benzene (15 c.c.) had been exposed for 3 months, the mixture was treated as described in (a). The residue was freed from fluorene (about 0.1 g.) by steam-distillation, washed with alcohol, and crystallised from benzene-alcohol, giving difluorenyl, m. p. 243°, not depressed by an authentic specimen.

(c) Xanthen (1 g.) and *p*-benzoquinone (0.3 g.) in benzene (15 c.c.) were exposed for 4 days, quinhydrone beginning to separate after 2 hours. The brown oily residue obtained after the usual treatment was solidified by the addition of a few drops of cold absolute alcohol, washed with cold alcohol (*p*-benzoquinone being easily soluble), and crystallised twice from petroleum (b. p. 100—110°) and finally from glacial acetic acid, giving fine colourless needles, m. p. 209°, not depressed by authentic dixanthyl.

(d) Anthrone (1 g.) and *p*-benzoquinone (0.5 g.) in benzene (20 c.c.) were exposed for 15 days. The quinhydrone and the photo-product were collected and digested with cold acetone, which dissolved the former. The dianthrone (V), crystallised from petroleum (b. p. 100—150°), had m. p. 256° (Found : C, 87.2; H, 5.1. Calc. for C<sub>28</sub>H<sub>18</sub>O<sub>2</sub> : C, 87.1; H, 4.7%).

(e) Dinaphthapyran (1 g.) (Wolff, *loc. cit.*) and *p*-benzoquinone (0.4 g.) in benzene (20 c.c.) were exposed for 1 month and the deposit of quinhydrone and the photo-product was collected and washed with acetone. The bisdinaphthaxanthen (IV) separated from petroleum (b. p. 100—110°) in colourless needles, m. p. above 300° (Found : C, 89.0; H, 4.7. Calc. for C<sub>42</sub>H<sub>26</sub>O<sub>2</sub> : C, 89.6; H, 4.6%) (compare Fosse, *Bull. Soc. chim.*, 1902, 27, 496).

(ii) Xanthen and xanthone. Equimolecular amounts of xanthen (1 g.) and xanthone in benzene (15 c.c.) were exposed (mercury-sealing) for 1 day; the solution acquired a green fluorescence, and the photo-product (XV) separated in colourless needles. These were collected, washed with benzene, and recrystallised from petroleum (b. p. 100—110°). The yield of 9-hydroxydixanthyl (XV), m. p. 194° (decomp.), was about 80%. It dissolved with difficulty in concentrated sulphuric acid, giving a yellow solution (Found : C, 82.1; H, 4.9; active H, 0.52. C<sub>26</sub>H<sub>18</sub>O<sub>3</sub> requires C, 82.5; H, 4.8%; 2 H, 0.53).

9-Hydroxydixanthyl was refluxed with acetyl chloride for 5 hours, the acetyl chloride distilled in a vacuum, and the residue recrystallised from xylene; m. p. above 300°, not depressed by authentic dixanthylene (XVI) (Schönberg, Schütz, and Nickel, *Ber.*, 1928, 61, 1384). It gave a green melt and both specimens formed orange-coloured solutions in thionyl chloride.

Xanthen and benzophenone. A solution of xanthen (1 g.) and benzophenone in equimolecular amount in benzene (25 c.c.), after being exposed for 10 days, acquired a green fluorescence; the benzene was then driven off in a vacuum. The yellow crystalline residue was freely soluble in benzene, acetone, and carbon tetrachloride and with difficulty in light petroleum (b. p. 80—90°). 9-Xanthyldiphenylcarbinol (XVII) readily crystallised from glacial acetic acid in colourless needles, m. p. 160°, and gave with concentrated sulphuric acid a yellow coloration changing to orange (Found : C, 85.5; H, 5.5. C<sub>26</sub>H<sub>20</sub>O<sub>2</sub> requires C, 85.7; H, 5.5%).

The carbinol (XVII) was refluxed with excess of acetic anhydride for 4 hours, and the solution concentrated in a vacuum and left over-night in the refrigerator. The yellow crystals obtained, m. p. 197°, became colourless when treated with animal charcoal and did not depress the m. p. of authentic *oo'*-oxidotetraphenylethylene (XVIII) (Schönberg and Nickel, *Ber.*, 1931, 64, 2323). It gave an orange colour with concentrated sulphuric acid.

Anthraquinone and diphenylmethane. Equimolecular amounts of anthraquinone and diphenylmethane (1 g.) in benzene (25 c.c.) (the anthraquinone was in suspension) were exposed for 5 months, the benzene removed in a vacuum, and the dark residue washed with light petroleum. The residual solid separated from benzene (charcoal) in colourless crystals, m. p. 209°, not depressed by authentic *s*-tetraphenylethane.

Xanthone and diphenylmethane. Diphenylmethane and xanthone (1 g.) in equimolecular amount, in benzene (20 c.c.), were exposed for 3 months (Monax glass). The large colourless crystals (0.2 g.) obtained were recrystallised from petroleum (b. p. 100—110°) and proved to be *s*-tetraphenylethane. More of it was obtained from the benzene solution.

Xanthone and dinaphthapyran. Dinaphthapyran (1 g.) and xanthone (0.7 g.) in benzene (20 c.c.) were exposed for 10 days. The colourless crystals that separated were recrystallised from petroleum (b. p. 100—150°) and then had m. p. above 300°. Bisdinaphthaxanthen (IV) was stable towards boiling acetic anhydride (Found : C, 89.7; H, 5.3. C<sub>42</sub>H<sub>26</sub>O<sub>2</sub> requires C, 89.6; H, 4.6%). It gave an intense yellow colour and green fluorescence when treated with concentrated sulphuric acid. When heated with sulphur (2 parts) (bath temp. 260°) for 1 minute, it gave a brown melt, which was extracted with benzene. A crystal of mercuric chloride placed in the extract acquired a deep red deposit on its surface. This reaction is probably due to the formation of the thioketone  $O \left\langle \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} \right\rangle CS$ , which will react with mercuric chloride in a manner similar to that of xanthone, which forms an orange deposit (Schönberg, *Ber.*, 1925, 58, 1794).

Xanthone and anthrone. An equimolecular mixture of anthrone (1 g.) and xanthone in benzene (25 c.c.) was exposed for 1 month. The large crystals that separated were washed with benzene and recrystallised from petroleum (b. p. 100—110°); m. p. and mixed m. p. with authentic dianthrone (V) about 255° (Found : C, 86.5; H, 5.0. Calc. for C<sub>28</sub>H<sub>18</sub>O<sub>2</sub> : C, 87.1; H, 4.7%).

Acetophenone and Xanthen. Equimolecular amounts of xanthen (1 g.) and acetophenone were dissolved in benzene (20 c.c.) and exposed for 10 days; the solution acquired a green fluorescence after 1 day's exposure. The oily residue obtained after removal of the benzene in a vacuum formed a semi-solid mass on cooling. It was washed with light petroleum and crystallised from petroleum (b. p. 100—110°), giving colourless needles of dixanthyl (Found : C, 86.1;

H, 5.0. Calc. for  $C_{26}H_{18}O_2$ : C, 86.2; H, 5.0%). The motor-liquor on concentration gave a solid, which after crystallisation from light petroleum did not depress the m. p. of authentic acetophenonepinacol.

*pp'*-Dimethoxybenzophenone and Xanthen. These two substances also gave dixanthyl, the procedure being that described above.

The experiment was repeated and the yellow oil left on evaporation of the benzene in a vacuum was solidified by treating it with cold absolute alcohol, followed by repeated washing with hot absolute alcohol. On concentration, colourless crystals of 4:4':4'':4'''-tetramethoxybenzpinacol separated. It and also an authentic specimen gave a blue-green coloration in concentrated sulphuric acid (Found: C, 73.4; H, 6.2. Calc. for  $C_{30}H_{20}O_6$ : C, 74.1; H, 6.2%).

*pp'*-Dichlorobenzophenone and Xanthen. Here again dixanthyl was produced after 23 days' exposure. The oily residue was washed with cold absolute alcohol and crystallised from petroleum (b. p. 100–110°). The alcoholic washing on concentration gave 4:4':4'':4'''-tetrachlorobenzpinacol (Found: C, 61.6; H, 4.2. Calc. for  $C_{26}H_{18}O_2Cl_4$ : C, 61.8; H, 3.6%).

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