REACTIONS OF NON-ENOLIZABLE KETONES IN SUNLIGHT

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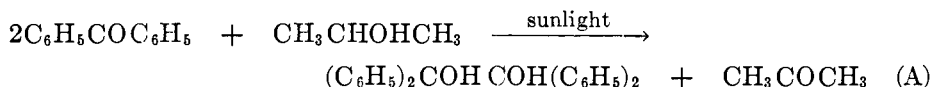
CONTENTS

I. INTRODUCTION

During the last decade, interest in the photochemical reactions of organic compounds has centered mainly on their mechanism; the number of new photochemical reactions of synthetic value discovered during this period is very limited, in particular with regard to those reactions carried out in sunlight.

But, during the same period, considerable progress has been made in the field of non-enolizable ketones in connection with photochemical reactions in sunlight; some of them are of special interest because they furnish an easy way to substances so far unavailable by dark reactions, a fact which justifies their review in this paper.

Photochemical syntheses utilizing sunlight are not in general, and especially on an industrial scale, suitable for use in Europe or in the northern part of America, where sunlight is unreliable and often unavailable; this is also the case in many other parts of the world. In tropical and many subtropical regions, however, conditions are different, so that the prospects for the *industrial* development of such syntheses can be considered promising.

II. PHOTOCHEMICAL FORMATION OF PINACOLS FROM DIARYL KETONES IN THE PRESENCE OF ALCOHOLS, AND RELATED REACTIONS

Ciamician and Silber (10) have shown that when an ethyl alcohol solution of benzophenone is exposed to sunlight, the alcohol is oxidized to aldehyde and the ketone reduced to benzopinacol; in the place of ethyl alcohol, isopropyl alcohol (12) has frequently been used.

$$2C_6H_5COC_6H_5 \ + \ CH_3CHOHCH_3 \ \xrightarrow{\ \text{sunlight}\ }$$
$$(C_6H_5)_2COH\,COH(C_6H_5)_2 \ + \ CH_3COCH_3 \quad (A)$$

A large number of benzophenone derivatives react in the presence of alcohols as above: e.g., p,p'-dimethoxybenzophenone (26, 43), p,p'-dichlorobenzophenone (43), and 4-phenylbenzophenone (3).

Banchetti (5) has investigated the action of hydrogen chloride gas on a mixture of benzophenone in isopropyl alcohol and benzene in sunlight.

A. Aromatic ketones which are resistant to alcohols in sunlight

Bachmann (3) has reported that fluorenone is stable to isopropyl alcohol in sunlight, and Schönberg and Mustafa (43) were unable to reduce xanthone to the corresponding pinacol. They found that in the case of xanthopinacol and fluorenopinacol, the reverse of reaction A takes place, xanthone and fluorenone, respectively, being formed, together with isopropyl alcohol.
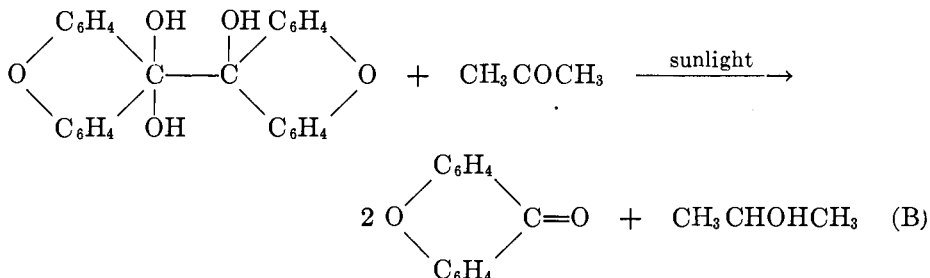
It is a true photoreaction, the pinacols being stable to acetone in the dark. Reaction B is an example of the breaking of the —C—C—linkage during a photochemical process in sunlight. There are several ways in which the mechanism of reaction B may be explained; e.g., xanthopinacol may split into free radicals (I) which are dehydrogenated by acetone.

It seems not impossible that the reaction between aromatic ketones and iso-propyl alcohol (*cf.* scheme A) as well as the reaction between aromatic pinacols and acetone (*cf.* scheme B) leads to an equilibrium which favors, in one case, the formation of pinacols, and in other cases, the formation of aromatic ketones.

B. Reactions of diaryl ketones with alcohol in sunlight in the presence of small amounts of sodium alcoholate

This reaction leads to the formation of benzohydrols, which are formed by the action of sodium alcoholate on benzopinacol, and proceeds, according to Bachmann (3), as follows:

$$2(C_6H_5)_2C=O \ + \ (CH_3)_2CHOH \ \xrightarrow{\text{sunlight}}$$

$$CH_3COCH_3 \ + \ \begin{matrix} (C_6H_5)_2COH \\ | \\ (C_6H_5)_2COH \end{matrix}$$

$$\begin{matrix} (C_6H_5)_2COH \\ \vdots \\ (C_6H_5)_2COH \end{matrix} \ + \ (CH_3)_2CHONa \ \longrightarrow$$

$$\begin{matrix} (C_6H_5)_2CONa \\ | \\ (C_6H_5)_2CONa \end{matrix} \ \rightleftharpoons \ 2(C_6H_5)_2CONa \atop \vdots$$

$$(\text{ketyl})$$

$$2(C_6H_5)_2\underset{|}{C}ONa \ + \ 2(CH_3)_2CHOH \ \longrightarrow \ 2(C_6H_5)_2\underset{|}{C}OH \ + \ 2(CH_3)_2CHONa$$

$$2(C_6H_5)_2\underset{|}{C}OH \ \longrightarrow \ (C_6H_5)_2C=O \ + \ (C_6H_5)_2CHOH \qquad (C)$$

4-Phenylbenzophenone was reduced nearly quantitatively to 4-phenylbenzo-hydrol. 4-Methylbenzophenone, 4,4'-dimethylbenzophenone, 4-methoxyben-zophenone, 4-chloro-4'-methoxybenzophenone, and 4-chlorobenzophenone react also in accordance with scheme C. In the case of benzophenone, the above reaction is suitable for the preparation of benzopinacol (4).

C. Photochemical reduction of 1,2,3-triketones by isopropyl alcohol in the presence of sunlight

The red triketohydrindene (II) is the only substance of this type which has been investigated as far as we know. The reaction does not lead to pinacol formation, but to an ether: namely, the colorless hydrindantin (III) (39) which has previously been obtained in the dark by the action of hydrogen sulfide on ninhydrin (IV). It should be noted that the structure (III) for the reduction product is not beyond doubt and that the formula of the corresponding pinacol is not quite excluded.

$$2C_6H_4 \overset{\displaystyle CO}{\underset{\displaystyle CO}{\diamondsuit}} CO \longrightarrow C_6H_4 \overset{\displaystyle CO}{\underset{\displaystyle CO\ OH}{\diamondsuit}} C-O-C \overset{\displaystyle CO}{\underset{\displaystyle H\ CO}{\diamondsuit}} C_6H_4$$

$$\text{II} \qquad\qquad\qquad\qquad\qquad\qquad \text{III}$$

$$C_6H_4 \overset{\displaystyle CO}{\underset{\displaystyle CO}{\diamondsuit}} C \overset{\displaystyle OH}{\underset{\displaystyle OH}{\diamondsuit}}$$

$$\text{IV}$$

Ninhydrin

D. Further methods for the photochemical formation of pinacols

In a number of cases, pinacols have frequently been obtained from diaryl ketones, as by-products, when the ketones were treated with methane derivatives; e.g., when benzophenone is treated with phenylacetic acid (14).

It should also be mentioned that benzopinacol (42) and substituted benzo-pinacols (43)—e.g., 4,4′,4″,4‴-tetramethylbenzopinacol—may be obtained in excellent yield when the corresponding benzohydrols are exposed to sunlight in the presence of acetone, the reaction proceeding rapidly. Acetone may be replaced by ethyl methyl ketone (42).

$$2C_6H_5CHOHC_6H_5 \ + \ CH_3COCH_3 \xrightarrow{\ \text{sunlight}\ }$$
$$(C_6H_5)_2COHCOH(C_6H_5)_2 \ + \ CH_3CHOHCH_3$$
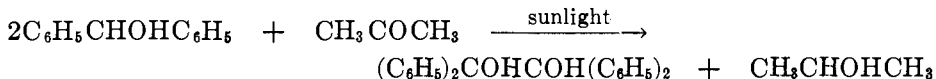
III. PHOTOCHEMICAL DEHYDROGENATION EFFECTED BY QUINONES RESULTING IN (*a*) FORMATION OF ALDEHYDES FROM ALCOHOLS, (*b*) FORMATION OF DIARYL KETONES FROM AROMATIC PINACOLS, AND (*c*) FORMATION OF ETHANES FROM THE CORRESPONDING METHANES

Until recently, only the action of *p*-quinones on primary and secondary alcohols had been investigated.
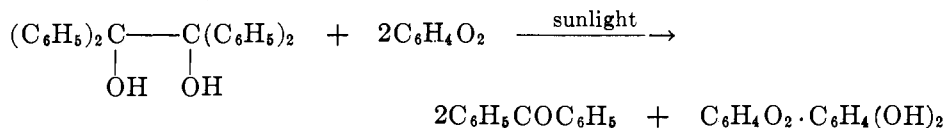
(*a*) *p*-Quinones have the tendency to add hydrogen, changing to hydroquinone; methyl alcohol is thus transformed into formaldehyde (18).

$$C_6H_4O_2 \ + \ CH_3OH \xrightarrow{\ \text{sunlight}\ } C_6H_4(OH)_2 \ + \ HCHO$$
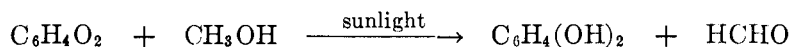
Ethyl alcohol is changed in sunlight into acetaldehyde, and isopropyl alcohol into acetone (9, 11). Dorcas and Forbes (15) selected the action of *p*-benzo-quinone on 50 per cent alcohol for actinometric studies. The quantum yield of the reaction has been investigated by Leighton and Forbes (22).

Thymoquinone reacts with ethyl alcohol, acetaldehyde and thymohydro-quinone (9, 11) being formed.
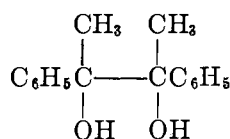
(*b*) Recently, photochemical dehydrogenation has been investigated in various fields (43). Whereas pinacol itself is stable to *p*-benzoquinone in sunlight, acetophenonepinacol (V), benzopinacol (VI), 9,10-dihydroxy-9,10-diphenyldi-hydrophenanthrene (X), and 1,8-diphenylacenaphtheneglycol (XI) are readily dehydrogenated by the action of *p*-benzoquinone in sunlight.
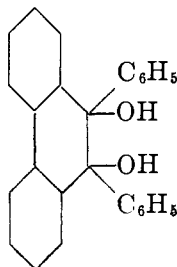
$$(C_6H_5)_2C{\underset{\overset{|}{OH}}{\text{——}}}C(C_6H_5)_2 \quad + \quad 2C_6H_4O_2 \xrightarrow{\text{sunlight}}$$

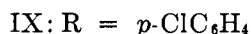$$2C_6H_5COC_6H_5 \quad + \quad C_6H_4O_2 \cdot C_6H_4(OH)_2$$
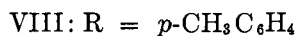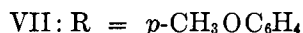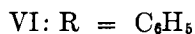
Several derivatives of benzopinacol have also been investigated, e.g., those in which the phenyl group is replaced by VII, VIII, or IX. In all these cases a rupture of a
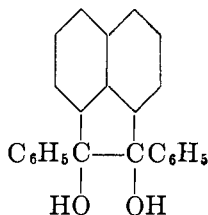
$$-{\underset{\overset{|}{OH}}{\overset{|}{C}}}{\text{——}}{\underset{\overset{|}{OH}}{\overset{|}{C}}}-$$
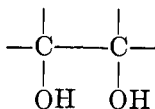
linkage is effected and quinhydrone is formed.

$$C_6H_5{\underset{\overset{|}{OH}}{\overset{\overset{|}{CH_3}}{C}}}{\text{——}}{\underset{\overset{|}{OH}}{\overset{\overset{|}{CH_3}}{C}}}C_6H_5$$

V

CR_2OHCR_2OH

VI: R $= C_6H_5$

VII: R $= p\text{-}CH_3OC_6H_4$

VIII: R $= p\text{-}CH_3C_6H_4$

IX: R $= p\text{-}ClC_6H_4$

X

XI

(c) The formation of tetraarylethanes from diarylmethanes by the action of a quinone in sunlight has been established by Schönberg and Mustafa (43) in the case of diphenylmethane, fluorene, xanthene, anthrone, and dinaphthopyran; e.g., xanthene leads to the formation of dixanthyl (XIIa).

$$+ \quad 2C_6H_4O_2 \xrightarrow{\text{sunlight}}$$

$$+ \quad C_6H_4O_2 \cdot C_6H_4(OH)_2$$

XIIa
Dixanthyl
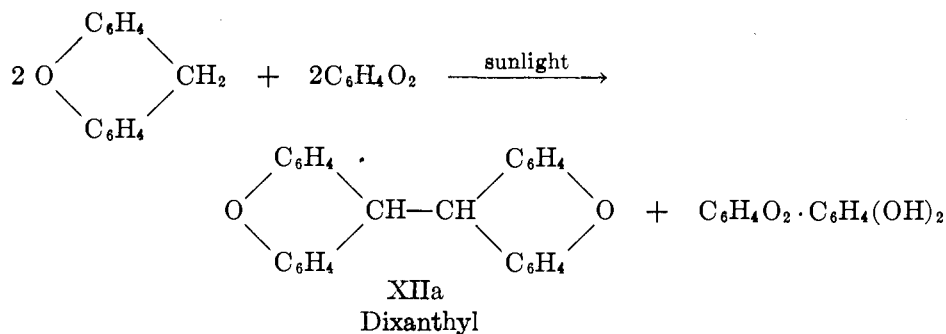
Further, dithiodixanthyl (XIIb) has been produced by the action of p-benzo-quinone on thioxanthene, and it was also found that in the presence of sunlight
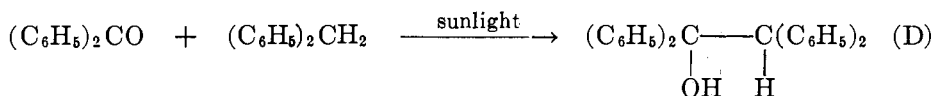
(a) s-tetraphenylethane is produced from diphenylmethane and anthraquinone and also from diphenylmethane and xanthone, (b) dianthrone (XIV) is formed from anthrone and xanthone, and (c) bisdinaphthoxanthene (XIII) is obtained from dinaphthopyran and xanthone.


XIIb
Dithiodixanthyl

XIIII
Bisdinapthoxanthene

XIV
Dianthrone
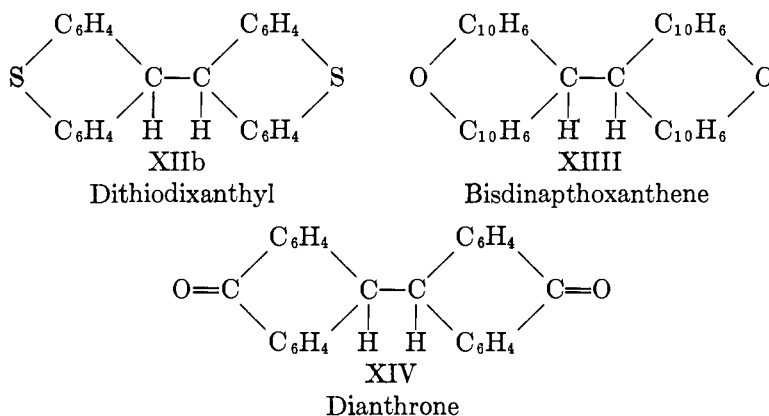
Phenanthrenequinone also is able to effect the photochemical dehydrogenation of thioxanthene to dithiodixanthyl (XIIb) (46).

IV. ADDITION REACTIONS BETWEEN KETONES AND METHANES; EXISTENCE OF A PHOTOCHEMICAL EQUILIBRIUM

Paternó and Chieffi (27, 28) have found that diphenylmethane reacts with benzophenone in sunlight with the formation of s-tetraphenylethyl alcohol; a similar reaction takes place between benzophenone and dianisylmethane (7).

$$(C_6H_5)_2CO \; + \; (C_6H_5)_2CH_2 \xrightarrow{\text{sunlight}} (C_6H_5)_2C\!-\!\!-\!\!C(C_6H_5)_2 \quad (D)$$
$$\underset{OH}{\quad}\;\underset{H}{\quad}$$

The reaction between xanthene and xanthone and between xanthene and benzophenone (43) proceeds similarly; the resulting products are XV and XVI. The speed of this reaction is remarkable. 9-Hydroxydixanthyl (XV) separates in crystals of great purity when solutions of xanthene and xanthone in benzene are illuminated by sunlight for a few hours.

XV
9-Hydroxydixanthyl

XVI
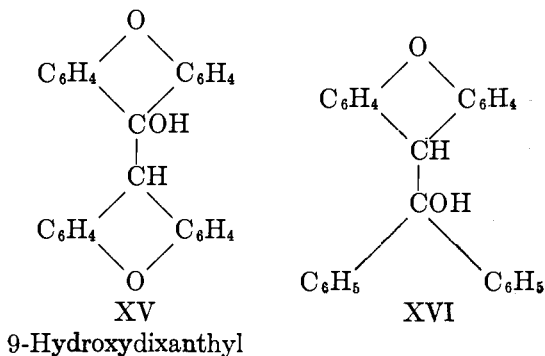
In all these cases, no indication was found that the photoreaction between diaryl ketones and diarylmethanes is reversible, but when the yellow thioxanthone was allowed to react with xanthene (45), both dissolved in benzene, the reaction product (XVII) was formed in small yields and attempts to increase the yield by prolonged illumination were unsuccessful. This failure was due to a photochemical equilibrium.

$$S \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} C{=}O \;+\; H_2C \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} O \;\rightleftharpoons$$

$$S \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} \begin{array}{c} C{-}C \\ | \quad | \\ OH \;\; H \end{array} \begin{array}{c} C_6H_4 \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ C_6H_4 \end{array} O \qquad (E)$$

XVII

9-Xanthylthioxanthydrol
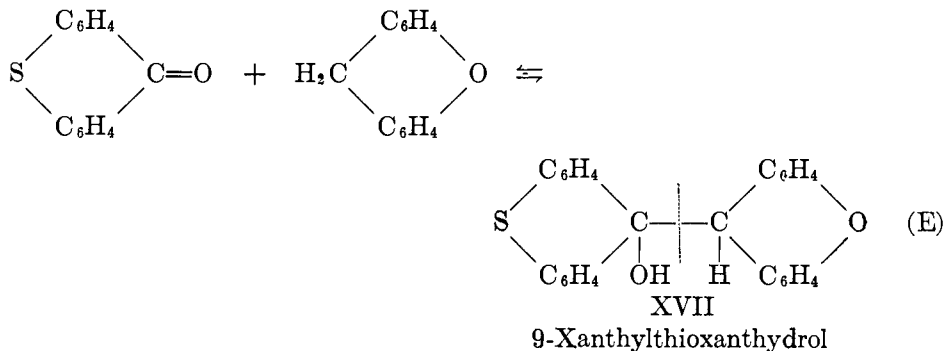
When 9-xanthylthioxanthydrol (XVII) was suspended in benzene and exposed to sunlight, it partly dissolved and xanthene and thioxanthone were isolated from the solution; moreover, XVII was stable in the dark.

It is believed that the first step in the photodissociation of the carbinol (XVII) is the formation of two free radicals (see broken line in scheme E), which are stabilized by disproportionation. The fact that XVII is colorless, whereas thioxanthone is yellow, is in agreement with the constitution shown above. At 270°C. XVII decomposes into its generators, showing that the ethane linkage in the carbinol is weak.

With regard to the complicated reaction between benzophenone and benzohydrol methyl ether, which may be regarded as a derivative of diphenylmethane, the original literature should be consulted (7).

de Fazi (14) found that when benzophenone was treated with phenylacetic acid in sunlight, an addition product (XVIII) was obtained.

$$(C_6H_5)_2CO \;+\; C_6H_5CH_2COOH \xrightarrow{\;\text{sunlight}\;} (C_6H_5)_2C(OH)CH(C_6H_5)COOH$$
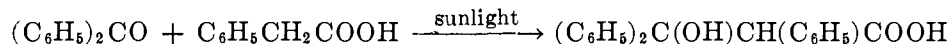
Benrath and Meyer (6) state that an addition reaction takes place when phenanthrenequinone is exposed to sunlight with o- or p-xylene (cf. XIX). An addition reaction also occurs when phenanthrenequinone is allowed to react with quinaldine.

$$\begin{array}{c} C_6H_4C{=}O \\ | \qquad | \\ C_6H_4C{=}O \end{array} \;+\; o\text{-}C_6H_4(CH_3)_2 \xrightarrow{\;\text{sunlight}\;} \begin{array}{c} C_6H_4COCH_2C_6H_4CH_3 \\ | \qquad \| \\ C_6H_4COH \end{array}$$

XIX
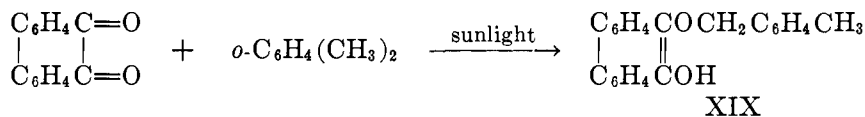
V. PHOTOPOLYMERIZATION REACTIONS OF α,β-UNSATURATED KETONES AND p-QUINONES

A large number of these reactions have been described, the majority of them leading to compounds of doubtful constitution.

Chalcone (benzylideneacetophenone), on irradiation in sunlight, forms two dimers: the dimer A, melting at 124°C. (truxinic ketone type), and the dimer B (truxillic ketone type) are believed to be formed (52, 53).

3-Phenyl-2-methylindone gives rise to two different dimeric compounds, believed to be of the following structures (XX and XXI) (13):

XX   XXI
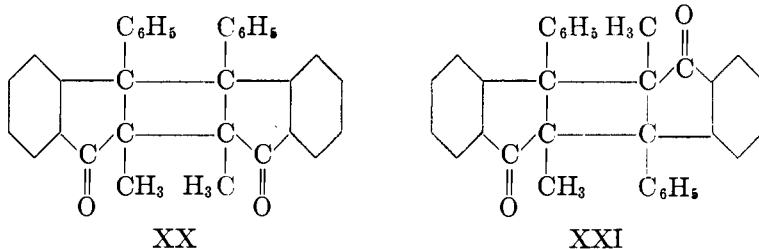
Thymoquinone in ether forms a polymerization product, which on heating dissociates with the formation of thymoquinone (23). 2-Methyl-α-naphtho-quinone forms a colorless dimeric product, believed to be a cyclobutane deriva-tive (24).

VI. PHOTOCHEMICAL ADDITION OF ALDEHYDES TO (a) p-BENZOQUINONE, (b) PHENANTHRENEQUINONE, (c) PHENANTHRENEQUINONIMINE

(a) *p-Benzoquinone:* Klinger and Kolvenbach (20) have shown that p-benzo-quinone reacts with acetaldehyde, yielding $CH_3COC_6H_3(OH)_2$; with isovaleral-dehyde, isovalerohydroquinone is obtained (21). Benzaldehyde gives p-dihy-droxybenzophenone, $C_6H_5COC_6H_3(OH)_2$ (20, 21).

Angeletti and Baledini (2) allowed toluquinone and benzaldehyde to react in benzene in sunlight and obtained, *inter alia*, benzoic acid and toluhydroquinone. The photoreaction between cinnamaldehyde and toluquinone has also been investigated (1).

(b) *Phenanthrenequinone:* According to Klinger (19) benzaldehyde reacts with phenanthrenequinone, yielding XXII; acetaldehyde, isovaleraldehyde, anisaldehyde, and cinnamaldehyde react similarly. According to Schönberg and Moubasher (38), the reaction products should be formulated according to XXIII. They are not soluble in an alkaline medium; furthermore, it was found that the photoproducts of phenanthrenequinone and p-chlorobenzaldehyde, when treated with diazomethane, yielded a product which must have the constitution XXIV, since on hydrolysis 9,10-dihydroxyphenanthrene and methyl p-chloro-benzoate were obtained. Further addition products have been prepared (47), e.g., with 2,4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde, and cuminaldehyde. Some of the ortho-substituted benzaldehydes—e.g., 2-methoxy-1-naphthaldehyde—were found to react very slowly with phenanthrenequinone when compared with benzaldehyde; this may be due to steric hindrance (ortho effect).
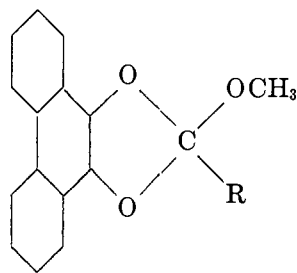
The pyrolysis of the photoproducts obtained by the action of phenanthrene-quinone and aldehydes has been investigated. The photoreaction product
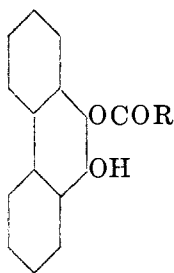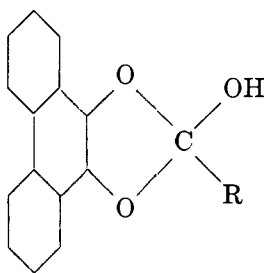
XXII   XXIII   XXIV
(R = C_6H_5)   (R = C_6H_5)   (R = p-ClC$_6$H$_4$)

(XXIII) yields benzaldehyde and phenanthrenequinone and a small amount of benzoic acid and fluorenone. For an explanation for the formation of these substances, the original literature should be consulted.

(c) *Phenanthrenequinonimine:* The yellow phenanthrenequinonimine (33) reacts with benzaldehyde in sunlight with the formation of the colorless 2-hydroxy-2-phenyl-2,3-dihydrophenanthroxazole (XXV), a substance which on heating yields 2-phenylphenanthroxazole; this result is in agreement with the proposed formula of the photoproduct (XXV). Similar photoreactions were carried out with acetaldehyde, p-anisaldehyde, p-chlorobenzaldehyde, piperonal, and 2-methoxy-1-naphthaldehyde. The reaction proceeds very rapidly with acetaldehyde, benzaldehyde, and p-anisaldehyde.
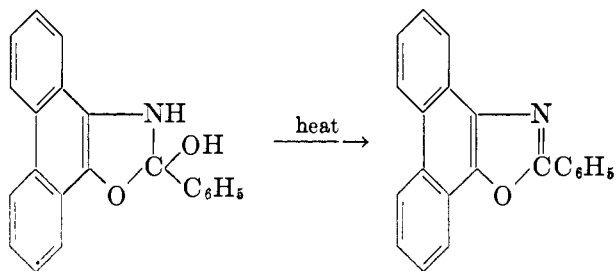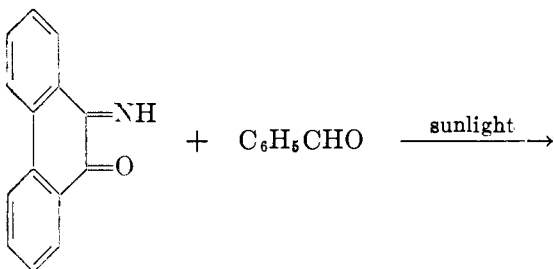
XXV

Retenequinonimine (XXVI) reacts with acetaldehyde, benzaldehyde, and p-anisaldehyde according to the following scheme (34). The constitution of retenequinonimine has not yet been completely elucidated, as it is not known whether the methyl or the isopropyl group is closer to the carbonyl group.

$$ \text{XXVI} + \text{RCHO} \xrightarrow{\text{sunlight}} $$
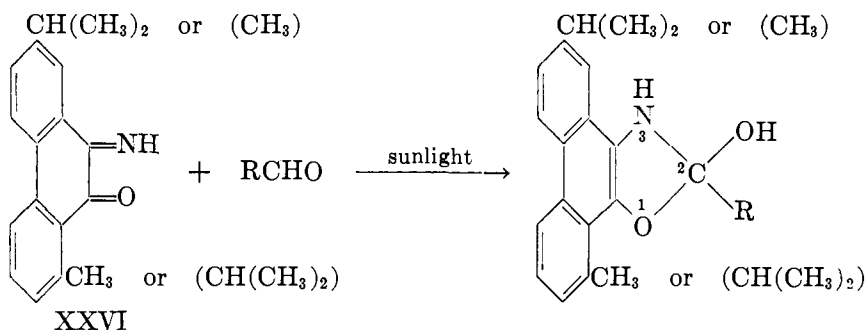
VII. THE ACTION OF SUNLIGHT ON DIPHENYL TRIKETONE

Lately, two methods have been described for converting diphenyl triketone into benzil by dark processes: namely, (a) the action of aluminum chloride and (b) the action of selenium (precipitated) in the presence of oxygen (40).

It has now been found (47) that when the triketone in benzene solution is exposed to sunlight it is converted into benzil. No reaction takes place in the dark.

$$ C_6H_5COCOCOC_6H_5 \xrightarrow{\text{sunlight}} C_6H_5COCOC_6H_5 $$
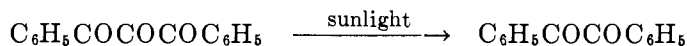
VIII. PHOTOREACTIONS BETWEEN OLEFINS AND 1,2-DIKETONES AND o-QUINONES

Schönberg and Mustafa (44, 45, 47) found that when benzil, phenanthrenequinone, or retenequinone (35) in benzene solution was exposed with olefins in sunlight, addition reactions took place, leading to the formation of 1,4-dioxins.

$$ C_6H_5CH{=}CHC_6H_5 \; + \xrightarrow[\text{heat}]{\text{sunlight}} \quad \text{(F)} $$
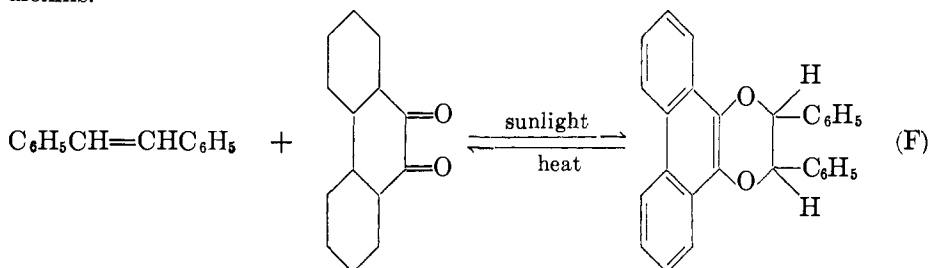
The velocity of the reaction is remarkable in some cases, e.g., in the case illustrated in scheme F. In general, the velocity with which benzil reacts is much less when compared with phenanthrenequinone. Among the 1,2-diketones which so far have been investigated successfully were only benzil, phenanthrenequinone, and retenequinone. On the other hand a great variety of ethylenes (methyleneanthrone (XLI) and diphenylketone (XLII) among others) were found to be reactive.[1] Further details may be taken from table 1.

[1] Other ethylenes which were added in sunlight to 1,2-diketones or o-quinones are: styrene (XXXII), α,α-diphenylethylene (XXXI), p,p'-dimethoxystilbene (XXXIII), triphenylethylene (XXXIV), α,α-diphenyl-Δα-propylene (XXXV), α,α-di(p-diphenylyl)-β-methylethylene (XXXVI), α-stilbazole (XXXVII), β-chlorostilbene (XXXVIII), 9-benzylidenexanthene (XXXIX), 9-benzylidenethioxanthene (XL), and benzylidenephthalide (XLIII).

TABLE 1

List of photo-addition products obtained from 1,2-diketones and ethylenes

The ethylenes and photoproducts obtained are designated by the same Roman numeral, but the letter "a" is added in the case of the photoproduct; e.g., XXVIIIa is the photo-addition product of XXVIII and benzil
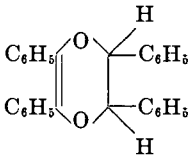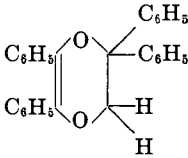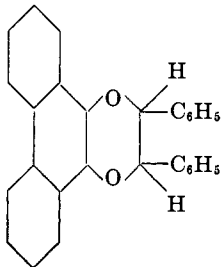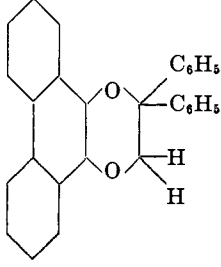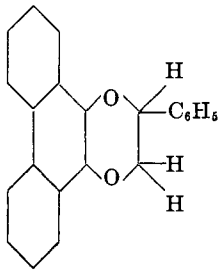
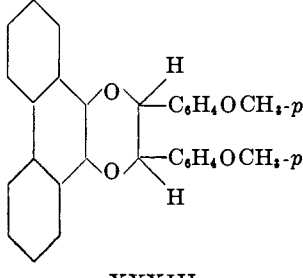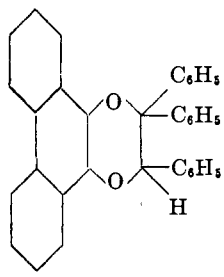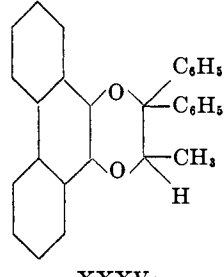| OLEFIN	FORMULAS OF PHOTOADDITION PRODUCTS WITH BENZIL, PHENANTHRENEQUINONE, OR RETENEQUINONE
Reactions with benzil	
$C_6H_5CH=CHC_6H_5$ (XXVIII)	
$(C_6H_5)_2C=CH_2$ (XXIX)	XXVIIIa
	XXIXa
Reactions with phenanthrenequinone	
$C_6H_5CH=CHC_6H_5$ (XXX)	
$(C_6H_5)_2C=CH_2$ (XXXI)	XXXa
	XXXIa

TABLE 1—*Continued*

OLEFIN	FORMULAS OF PHOTOADDITION PRODUCTS WITH BENZIL, PHENANTHRENEQUINONE, OR RETENEQUINONE
Reactions with phenanthrenequinone—*Continued*	

$C_6H_5CH\!=\!CH_2$ (XXXII)

$p\text{-}CH_3OC_6H_4CH\!=\!CHC_6H_4OCH_3\text{-}p$ (XXXIII)

XXXIIa

XXXIIIa

$\begin{array}{c}C_6H_5 \quad\quad C_6H_5 \\ \diagdown\quad\quad\diagup \\ C\!=\!C \\ \diagup\quad\quad\diagdown \\ C_6H_5 \quad\quad H\end{array}$ (XXXIV)

$\begin{array}{c}C_6H_5 \quad\quad CH_3 \\ \diagdown\quad\quad\diagup \\ C\!=\!C \\ \diagup\quad\quad\diagdown \\ C_6H_5 \quad\quad H\end{array}$ (XXXV)

XXXIVa

XXXVa

TABLE 1—*Continued*
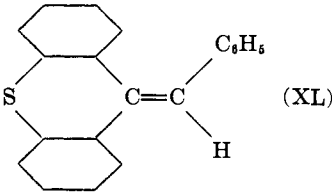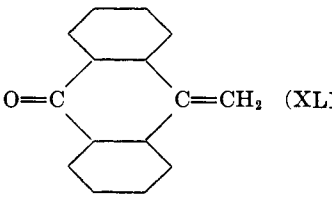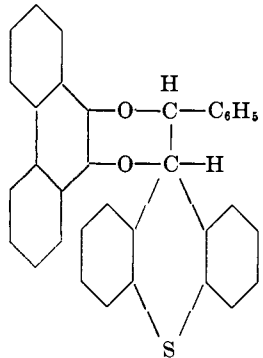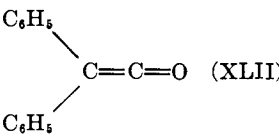
OLEFIN	FORMULAS OF PHOTOADDITION PRODUCTS WITH BENZIL, PHENANTHRENEQUINONE, OR RETENEQUINONE

Reactions with phenanthrenequinone—*Continued*

(XXXVI)
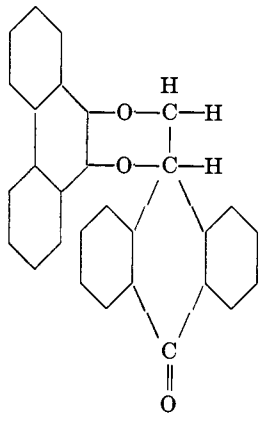
XXXVIa

(XXXVII)

XXXVIIa

C_6H_5CH=$CClC_6H_5$ (XXXVIII)

XXXVIIIa*

(XXXIX)

XXXIXa

TABLE 1—*Continued*

OLEFIN	FORMULAS OF PHOTOADDITION PRODUCTS WITH BENZIL, PHENANTHRENEQUINONE, OR RETENEQUINONE
Reactions with phenanthrenequinone—*Continued*	

C₆H₅

S   C=C   (XL)

H

XLa

O=C   C=CH₂   (XLI)

XLIa

C₆H₅

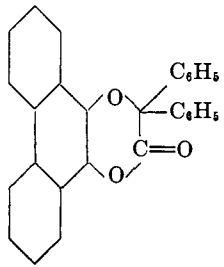C=C=O   (XLII)

C₆H₅
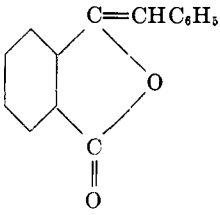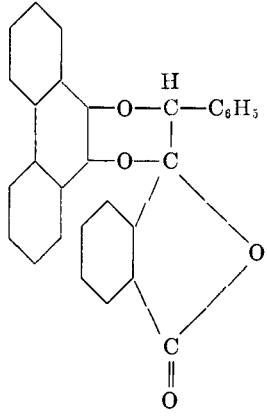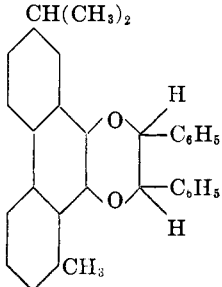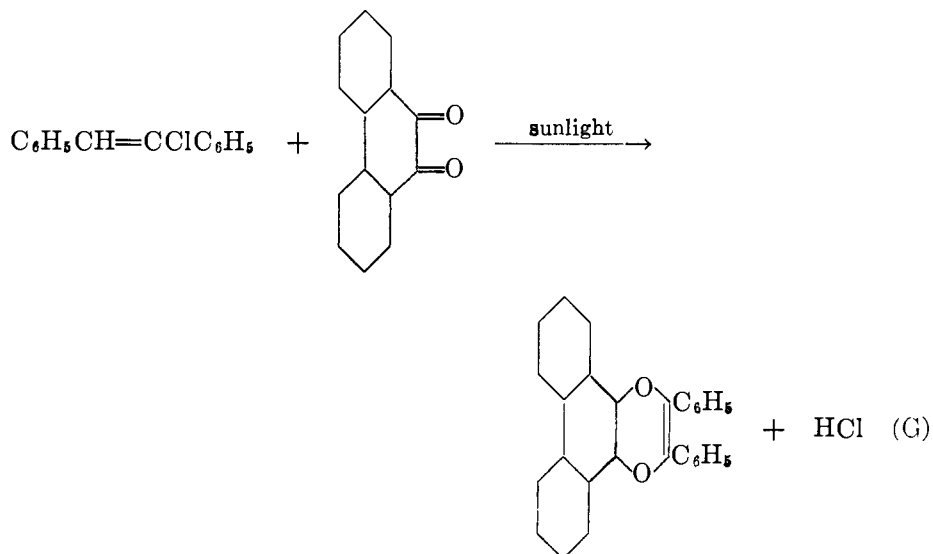
XLIIa

TABLE 1—*Concluded*

OLEFIN	FORMULAS OF PHOTOADDITION PRODUCTS WITH BENZIL, PHENANTHRENEQUINONE, OR RETENEQUINONE
Reactions with phenanthrenequinone—*Concluded*	
(XLIII) $C=CHC_6H_5$	XLIIIa
Reactions with retenequinone	
$C_6H_5CH=CHC_6H_5$ (XLIV)	XLIVa

* Compare scheme G.

In the case of β-chlorostilbene and phenanthrenequinone, on prolonged exposure 2,3-diphenylphenanthro[9,10]-1,4-dioxin (XXXVIIIa) was obtained, hydrogen chloride gas being evolved (*cf.* scheme G on p. 196).

Most of the photoproducts obtained are colorless or light yellow, a fact which is in agreement with their proposed constitution. On heating, the photoaddition products decompose, yielding benzil, phenanthrenequinone, or retenequinone, respectively, and the olefinic product which has been used in their synthesis.

The value of the reactions mentioned in this section lies in the fact that by them a large number of substances have been synthesized which seem to be inaccessible by any other method so far known.

$$C_6H_5CH{=}CClC_6H_5 \quad + \quad \text{[diketone structure]} \quad \xrightarrow{\text{sunlight}}$$

$$\text{[product structure]} \quad + \quad HCl \quad (G)$$

IX. PHOTOFORMATION OF HIGHLY CONDENSED AROMATIC RING SYSTEMS FROM AROMATIC KETONES BY ELIMINATION OF HYDROGEN ATOMS IN AROMATIC LINKAGES

Examples of these remarkable reactions, which lead to the formation of naphthadianthrone (XLVI) in acetic acid solution, have been observed in the case of XLV by Meyer and coworkers (25); neutral solvents, e.g., xylene or chlorobenzene, may also be used. The same product is also obtained by the irradiation of helianthrone (XLVIa) in acetic acid. Perkin and Yoda (29) have investigated similar cases and have prepared dimethoxynaphthadianthrone. Recently it was shown by Schönberg, Ismail, and Asker (37) that 10-(9'-xanthylene)anthrone (XLVIII) in benzene solution is transformed into oxapenenone (XLVII) in the presence of sunlight.

XLV $\xrightarrow{\text{sunlight}}$ XLVI $\xleftarrow{\text{sunlight}}$ XLVIa

XLVII   XLVIII
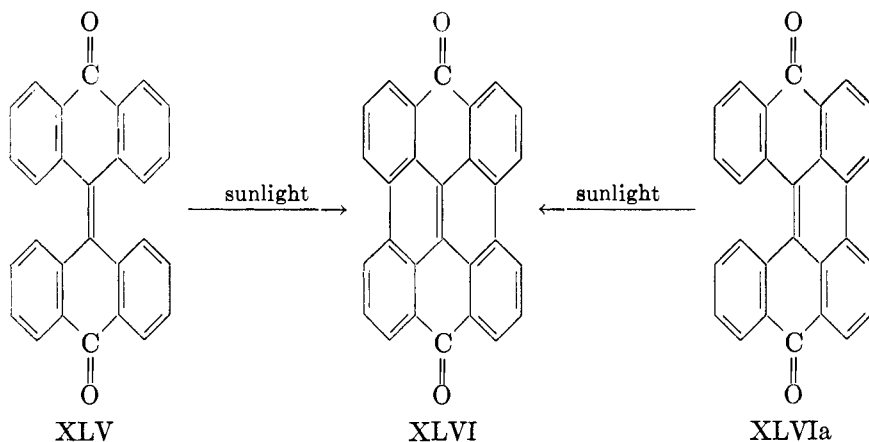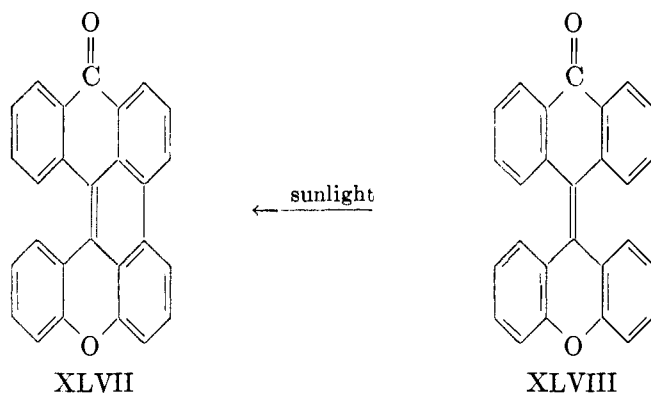
X. FORMATION OF HETEROCYCLIC KETONES IN SUNLIGHT

The formation of cyclic ketonic compounds in which the carbon atom of the ketonic group is a member of a five-membered ring system has been observed by Pfeiffer (30). The following reaction was carried out in pyridine and led to the formation of 6-nitro-2-phenylisatogen (XLIX); as an intermediate product 2,4-dinitrotolan is believed to exist. Pfeiffer and Kramer (31) have obtained 6-nitro-2-phenylisatogen (XLIX) from 2,4-dinitrotolan in sunlight.

XLIX
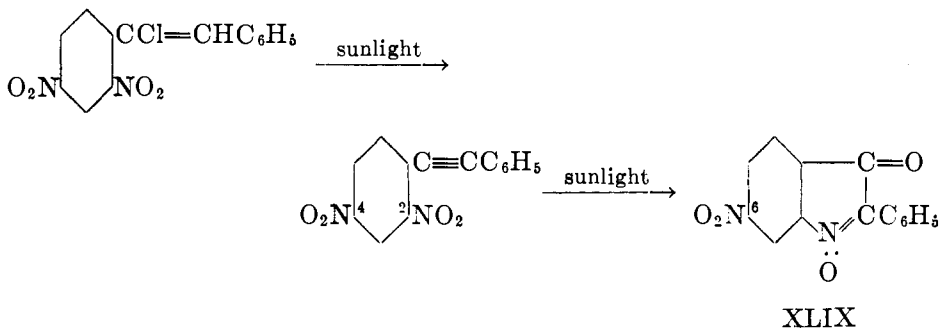
XI. EXPERIMENTS WITH NON-ENOLIZABLE THIOKETONES IN SUNLIGHT

A. Action of oxygen (41)

Thiobenzophenone is extremely sensitive to oxygen under laboratory conditions, being converted into benzophenone, elementary sulfur, sulfur dioxide, and the trisulfide (L) (49, 51). This change takes place even in the dark. On the other hand, 4,4'-dimethoxythiobenzophenone, 4,4'-bisdimethylaminothiobenzophenone, xanthione (LI), and thioxanthione (LII) in benzene solution are distinguished by their stability towards oxygen in the dark, but are converted into the corresponding ketones in sunlight in the presence of oxygen, sulfur and sulfur dioxide being formed. N-Phenylthioacridone (LIII), 4-thioflavone (LIV), and 2,6-diphenyldithiopyrone (LV) are stable or almost completely stable in the dark and in sunlight.

L

LIV

LV
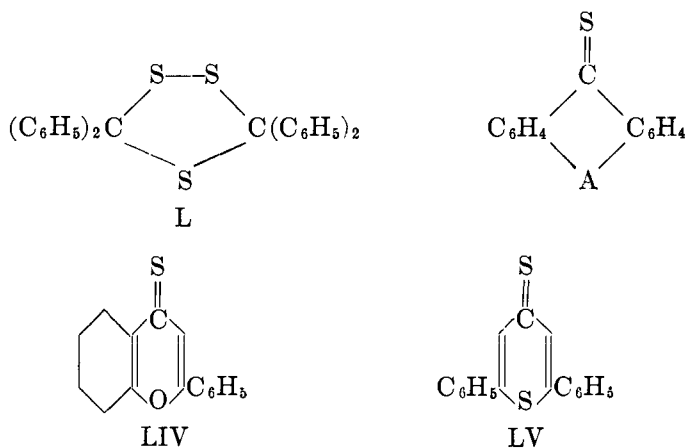
LI: A = O
LII: A = S
LIII: A = NC$_6$H$_5$

In order to explain the fact that the last three substances are resistant to oxygen in sunlight, it may be pointed out that they are not thioketones proper, but have the structure of zwitter ions (*cf.* LVI and LVII in the case of 4-thioflavone and *N*-phenylthioacridone, respectively) or that the zwitter-ion structure makes a great contribution to their resonance structures.

LVI

LVII
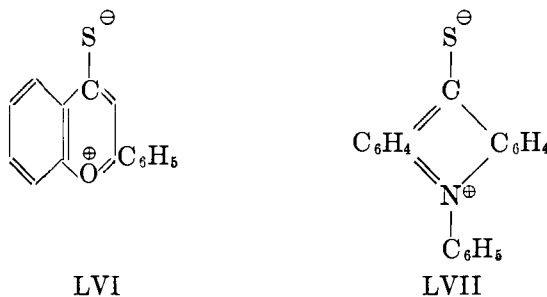
B. Stability of non-enolizable thioketones towards isopropyl alcohol in the presence of sunlight

In contrast to the ready reduction of benzophenone and p,p'-dimethoxybenzophenone (*cf.* scheme A, page 182), p,p'-dimethoxythiobenzophenone, 4,4'-bis-dimethylaminothiobenzophenone, xanthione (LI), thioxanthione (LII), *N*-phenylthioacridone (LIII), 2,6-diphenyldithiopyrone (LV), and 4-thioflavone (LIV) were found not to react with isopropyl alcohol after 7 days' exposure (43).

The photostability of thioketones under conditions under which the corresponding ketones react is remarkable, as in the dark thioketones frequently are more active than the corresponding ketones. Thus thiobenzophenone (but not benzophenone) reacts with copper powder (17, 48), diazomethane (8, 36), and phenyl azide (50) in the dark.

It seems possible that the photoactivation of thioketones is different from the photoactivation of ketones; it seems conceivable that, e.g., the photoactivation of benzophenone leads to molecules in which the distribution of electrons is nearly like those in LVIII; on the other hand, the distribution of electrons in the photoactivated thiobenzophenone may be in the direction of LIX.

$$
\begin{array}{cc}
\mathrm{C_6H_5} & \mathrm{C_6H_5} \\
\diagdown & \diagdown \\
\underset{\oplus\quad\ominus}{\mathrm{C-O}} & \underset{\substack{x\quad x \\ \downarrow\quad\downarrow}}{\mathrm{C-S}} \\
\diagup & \diagup \\
\mathrm{C_6H_5} & \mathrm{C_6H_5} \\
\mathrm{LVIII} & \mathrm{LIX}
\end{array}
$$

XII. EXPERIMENTAL NOTES

The authors have found that the most convenient method of carrying out photoreactions in sunlight is to dissolve the components in benzene and to use a Schlenk tube as a reaction vessel (figure 1). This tube is sealed while a stream
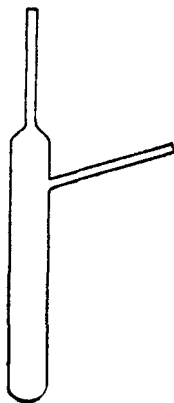

FIG. 1. Schlenk tube used for photoreactions

of dry carbon dioxide is allowed to pass through it. A similar method has been used by Schlenk for the preparation of ketyls in a nitrogen atmosphere (32).

Special care should be taken that the benzene used is not only thiophene-free, but also free of toluene, which can act as a strong reducing agent, e.g., phenanthrenequinone is transformed to 9,10-dihydroxyphenanthrene by the action of toluene in sunlight (6).

A number of earlier investigators have not stated whether their photoexperiments were carried out in the presence or absence of oxygen. It is necessary to avoid the presence of oxygen in view of the surprising reactivity of oxygen to organic compounds in sunlight (compare the transformation of 2-methylanthraquinone to the corresponding anthraquinonecarboxylic acid in the presence of air (16)).

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