DIMERIZATION REACTIONS IN SUNLIGHT

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I. INTRODUCTION

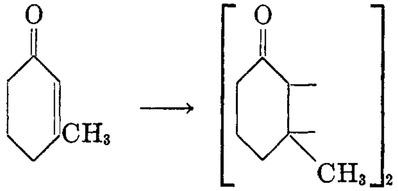
The chemistry of photodimers extends back to 1867, when the first synthetic photodimer was obtained by Fritzsche (25), who observed the formation of an insoluble substance when a benzene solution of anthracene was irradiated with sunlight. The recognition that this precipitate was dianthracene was due to early observers such as Fritzsche (25), Elbs (17), and Orndorff and Cameron (50).

This review will deal mainly with photodimerization reactions carried out in sunlight, leading to products of *known* constitution. The physicochemical aspects are outside the scope of this review.

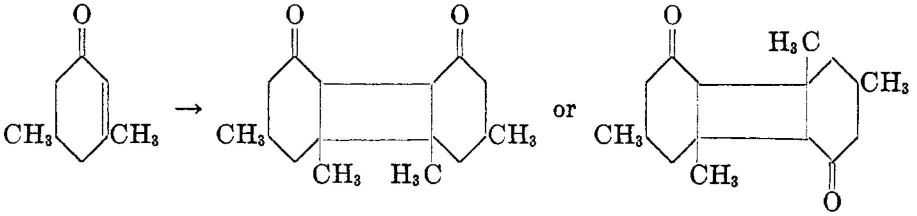
II. PHOTODIMERS WHICH ARE DERIVATIVES OF CYCLOBUTANE

A. PHOTODIMERS OBTAINED FROM HOMOCYCLIC SIX-MEMBERED RINGS OF NONAROMATIC CHARACTER

3-Methylcyclohexenone and 3,5-dimethylcyclohexenone undergo photodimerization when their solutions in dilute alcohol are exposed to sunlight, yielding I and IIa (or IIb), respectively (96).

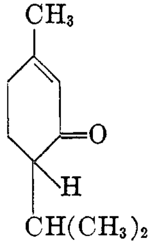


I

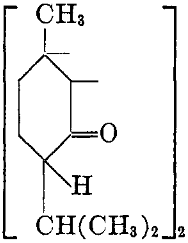


IIa IIb

Piperitone (III) in aqueous acetic acid or ethyl alcohol undergoes dimerization when exposed to sunlight. Evidently the photodimerization in this case has occurred through the double bond, probably with the formation of a four-membered ring (IV) (95).



III
Piperitone

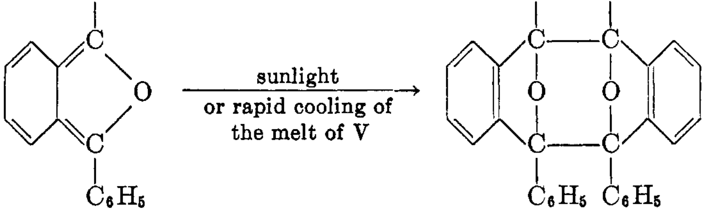


IV

B. PHOTODIMERS OBTAINED FROM AROMATIC COMPOUNDS

1. Photodimerization involving heterocyclic five-membered rings

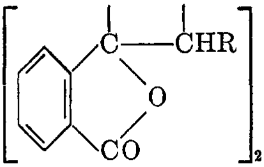
The yellow-orange 1,3-diphenylisobenzofuran (V) is readily transformed by the action of sunlight into a dimer (VI) (1, 26). Schönberg and Mustafa (65, 67) found that when V is heated at 270°C. in a sealed tube in an atmosphere of dry carbon dioxide, and the melt is chilled in ice water as quickly as possible, an excellent yield of the dimer (VI) is obtained.



V
1,3-Diphenyliso-
benzofuran

VI

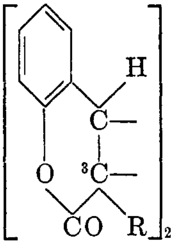
When a benzene solution of benzylidenephthalide is exposed to sunlight, a colorless photodimer (VIIa) (63) is obtained. Similarly, α-naphthylidene and β-naphthylidenephthalide form the corresponding photodimers VIIb and VIIc, respectively (47).



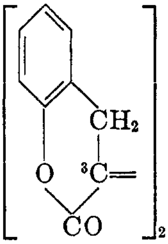
VIIa : R = C_6H_5
VIIb : R = α-$C_{10}H_7$
VIIc : R = β-$C_{10}H_7$

2. Photodimerization involving heterocyclic six-membered rings

Dimerization occurs when coumarin, in the solid state, dissolved in alcohol, or suspended in water, is exposed to sunlight. Formulas VIIIa and IX have been discussed for the resulting photoproduct (9, 10, 30, 32); formula IX is still widely used (55). Fisher (24) has given to the photodimer of umbelliferone methyl a formula analogous to IX, but its correctness was questioned by Wessely and Plaichinger (99).



VIIIa: R = H
VIIIb: R = C_6H_5



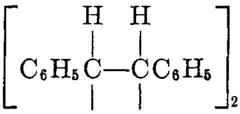
IX

Photodimerization of coumarin and its derivatives, with the formation of IX or its analogs, is possible only when the hydrogen in position 3 is unsubstituted. 3-Phenylcoumarin in sunlight is easily converted in excellent yield into a similar photodimer (VIIIb) (63); therefore the dimers must be cyclobutane derivatives

[redacted]

3. *Photodimerization of stilbene, acenaphthylene, and stilbazoles*

Stilbene: When a benzene solution of stilbene is exposed to sunlight, it acquires a pale yellow color and partially undergoes polymerization, forming a compound having the formula $(C_{14}H_{12})_2$ (XI) (9). The photochemical equilibrium stilbene $\rightleftharpoons$ distilbene in benzene solution lies very far towards the right, while in alcohol, ether, chloroform, trichloroethylene, or pyridine there is apparently no dimerization (72).

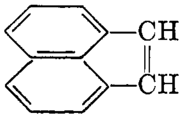


$$\left[C_6H_5\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{|}{C}}C_6H_5\right]_2$$

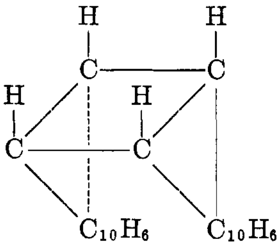
XI

2,4-Dinitrostilbene undergoes dimerization in sunlight to give a crystalline dimer, $(C_{14}H_{10}O_4N_2)_2$ (61). The action of light on 2-nitrostilbene yielded resinous substances, the nature of which has not yet been elucidated (61).

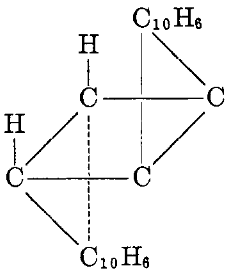
Acenaphthylene: Acenaphthylene (XII) has the advantage of being incapable of *cis–trans* interchanges. On exposure of the bright yellow compound (XII) in benzene solution to sunlight, it forms a colorless dimeric product (XIII) which is a mixture of two stereoisomeric forms (15, 16); these forms are *cis–trans* isomers and may be represented as XIIIa and XIIIb, respectively.



XII
Acenaphthylene



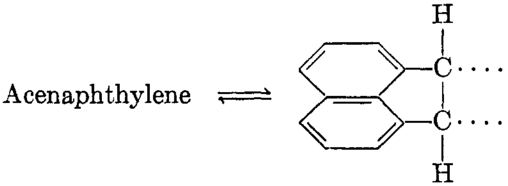
XIIIa



XIIIb

Both photodimers yield naphthalic anhydride on oxidation and are partly converted into XII in the molten state, but they form different picrates and bromo compounds. In view of the seven rings present, the name "heptacyclene" was proposed. As it is not known which of the isomers is the labile modification, it was suggested that the forms with the higher and the lower melting points be called α- and β-heptacyclene, respectively. α-Heptacyclene is the chief product when the benzene solution of acenaphthylene is irradiated with sunlight, but the β-form predominates when petroleum ether is used as a solvent.

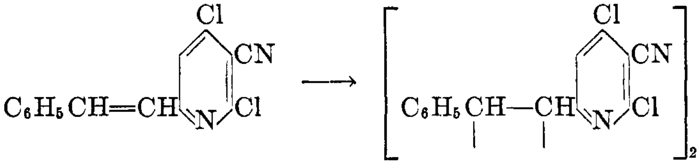
Recently, Bowen and Marsh (6) have shown that the mechanism of the photodimerization of acenaphthylene is probably not of a "collisional type," but depends on the existence of van der Waals complexes in the solution. The reviewer suggests that the photodimerization of acenaphthylene is analogous to that of anthracene and that it is very probable that there is a photoequilibrium between the normal form and the diradical form (XIV) (62).



XIV

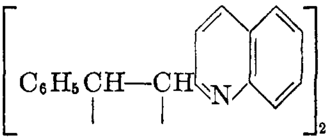
For the constitution of the dimer (XIII), reference is made to Dunitz and Weissman (14).

Stilbazoles: Koller (35) has shown that 2,4-dichloro-3-cyano-6-styrylpyridine (XV) changes in sunlight into a substance (XVI) of double the molecular weight. That the dimerization involves the formation of the cyclobutane ring is indicated by (*a*) the lack of color of the product and (*b*) its resistance towards the action of potassium permanganate in cold acetone. All attempts to effect similar photodimerization of stilbazole in sunlight, in the solid state, in benzene solution, or in hydrochloric acid solution were unsuccessful (28).



XV XVI

2-Styrylquinoline, when exposed to sunlight in the dry state or in benzene solution, forms a photodimer (XVII) (28).



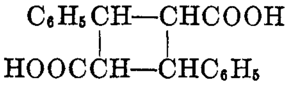
XVII

4. Photodimerization involving olefinic linkages not situated in a ring

(a) Cinnamic acid and its derivatives

Cinnamic acid exhibits an interesting photochemical reaction because, in addition to the features common to acids, the presence of a double bond in the side chain offers new possibilities of dimerization and stereoisomerization.

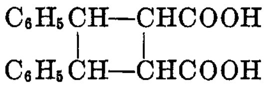
When solid cinnamic acid or its aqueous suspensions are exposed to sunlight, dimerization is accompanied by stereoisomerization (29, 73, 81, 84, 90). *α-trans*-Cinnamic acid yields mainly the dimer α-truxillic acid (XVIII) with a small amount of the β-truxinic acid (XIX), whereas the metastable β-form of cin-



$$\begin{array}{c} C_6H_5CH{-}CHCOOH \\ |\qquad| \\ HOOCCH{-}CHC_6H_5 \end{array}$$

XVIII

Truxillic acid



$$\begin{array}{c} C_6H_5CH{-}CHCOOH \\ |\qquad| \\ C_6H_5CH{-}CHCOOH \end{array}$$

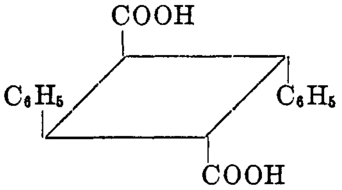
XIX

Truxinic acid

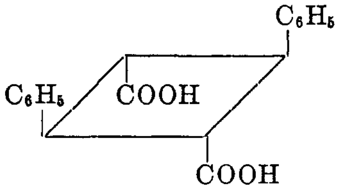
namic acid (*trans*), which is much more readily isomerized than the stable α-*trans*-cinnamic acid, yields much β-truxinic acid and a small amount of α-truxillic acid (81).

Allocinnamic acid (*cis*) dimerizes chiefly to β-truxinic acid, together with the stereoisomerization product, *trans*-cinnamic acid and its dimer (α-truxillic acid) (33). This photochemical change took place to the extent of 71 per cent after 196 hr. exposure to sunlight.

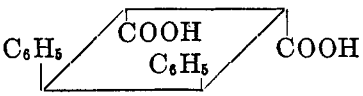
Irradiation of solutions of cinnamic acid, e.g., in benzene or methyl alcohol, produces generally stereoisomerization but no dimerization (9, 84).



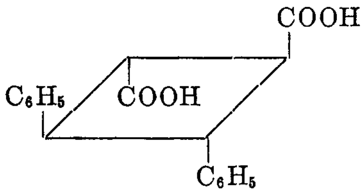
α-Truxillic acid



ε-Truxillic acid



β-Truxinic acid

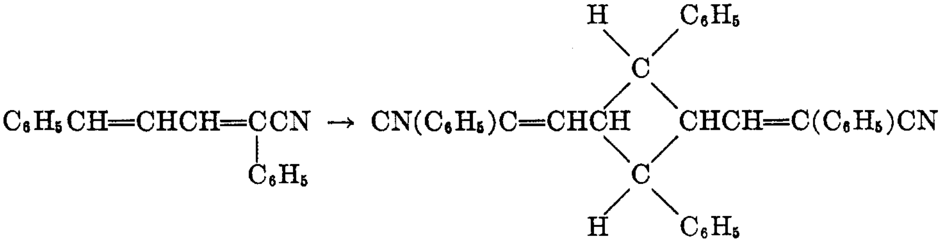


δ-Truxinic acid

The photodimerizations of cinnamic acid and its derivatives described in this review have been carried out under the influence of sunlight, unless otherwise stated (*cf.* table 1). Short ultraviolet rays hinder this type of reaction and effect depolymerization of truxinic acid and truxillic acid, yielding the corresponding monomer from which the dimer is originally obtained.

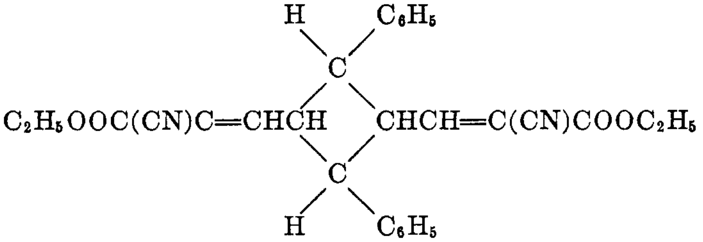
(b) Compounds containing the cinnamylidene group

Acids containing the cinnamylidene residue and their nitriles have been extensively investigated. Solutions of α-phenylcinnamylideneacetonitrile (XXI) in benzene or chloroform, in either the presence or the absence of iodine in sunlight, form two dimers, one melting at 197°C. and the other at 215°C. (71, 80). The former is 1,3-diphenylcyclobutane-2,4-diatroponitrile (XXII). The isomerism of the two dimers may be of the *cis–trans* type, depending on a difference of location of the phenyl and cyano groups at one or both of the double bonds of the side chain, since on treatment with potassium permanganate both yield α-truxillic acid.



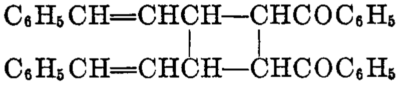
XXI XXII

According to Lohaus (42), exposure of a solution of the stable ethyl cinnamylidenecyanoacetate in ethyl alcohol to sunlight in the presence of a little sulfuric acid yields a cyclobutane derivative (XXIII), previously described by Reimer (54). In the absence of sulfuric acid, however, the original compound polymerizes to an open-chain dimer.



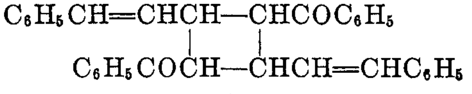
XXIII

Cinnamylideneacetophenone dimerizes in the solid state under the action of sunlight in the presence or absence of iodine, giving XXIVa or XXIVb (79, 83).



$$\begin{array}{l} C_6H_5CH{=}CHCH{-}CHCOC_6H_5 \\ \qquad\qquad\quad\;\; | \quad\;\;\; | \\ C_6H_5CH{=}CHCH{-}CHCOC_6H_5 \end{array}$$

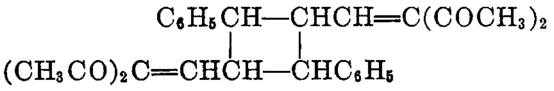
XXIVa



$$\begin{array}{l} C_6H_5CH{=}CHCH{-}CHCOC_6H_5 \\ \qquad\qquad\quad\;\; | \quad\;\;\; | \\ \quad C_6H_5COCH{-}CHCH{=}CHC_6H_5 \end{array}$$

XXIVb

Cinnamylideneacetylacetone is readily transformed into a colorless dimer (XXV) (60) by the action of sunlight; the correctness of the formula (XXV) proposed for the dimer has been questioned by Stobbe (79).



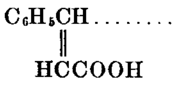
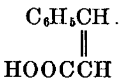
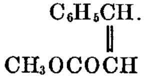
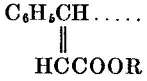
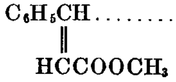
$$\begin{array}{r} C_6H_5CH{-}CHCH{=}C(COCH_3)_2 \\ |\quad\;\;\; |\qquad\qquad\qquad\quad \\ (CH_3CO)_2C{=}CHCH{-}CHC_6H_5\qquad\quad \end{array}$$

XXV

Similarly, cinnamylideneacetic acid gives a photodimer, believed to be XXVIa or XXVIb (57, 79). Cinnamylidenemalonic acid, when exposed to sunlight in

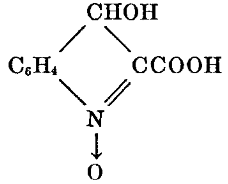
TABLE 1

A. Photoreactions of cinnamic acid, its esters, and amides

MONOMER		PHOTODIMER	REFERENCES
 $\begin{array}{c} C_6H_5CH \\ \Vert \\ HCCOOH \end{array}$	*trans*-Cinnamic acid (solid)	α-Truxillic acid (up to 85%) ε-Truxillic acid β-Truxinic acid (indirect)	(5, 9, 36, 56, 70, 73, 81, 84, 86, 87, 89)
	trans-Cinnamic acid (solution)	–	
 $\begin{array}{c} C_6H_5CH \\ \Vert \\ HOOCCH \end{array}$	*cis*-Cinnamic acid (solid)	β-Truxinic acid (up to 68%) α-Truxillic acid (indirect)	(5, 9, 36, 56, 70, 73, 81, 84, 86, 87)
	cis-Cinnamic acid (solution)	–	
 $\begin{array}{c} C_6H_5CH \\ \Vert \\ CH_3OCOCH \end{array}$	*cis*-Cinnamic methyl ester (solid)	α-Truxillic dimethyl ester and β-truxinic dimethyl ester	(76)
 $\begin{array}{c} C_6H_5CH \\ \Vert \\ HCCOOR \end{array}$	*trans*-Cinnamic methyl ester (solid)	α-Truxillic dimethyl ester	(31, 40, 75)
	trans-Cinnamic ethyl ester (liquid)	Trimeric cinnamic ethyl ester	(38, 39, 40, 75)
 $\begin{array}{c} C_6H_5CH \\ \Vert \\ HCCOOCH_3 \end{array}$	*trans*-Cinnamic ester (solid, in presence of salts) after de Jong	α- and ε-Truxillic esters, β- and δ-truxinic esters	(31)
	trans-Cinnamic ester (solid, in presence of salts) after Stobbe	α- Truxillic and β-truxinic esters	(76)
	trans-Cinnamic ester (solution)	–	
$C_6H_5CH{=}CHCONH_2$	*trans*-Cinnamamide	α-Truxillic acid diamide (up to 75%)	(75)
$C_6H_5CH{=}CHCONHC_6H_5$	*trans*-Cinnamanilide	–	(75)

B. Cinnamic acid derivatives substituted in the ring

Cinnamic acid derivatives substituted in the ring (see below) were exposed to sunlight in the solid state; no stereoisomerization products were isolated, with the exception of solid *o*-nitrocinnamic acid, which isomerizes to hydroisatogenic acid (XX) (94)



XX

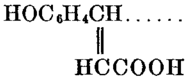
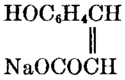
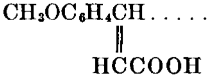
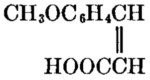
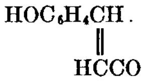
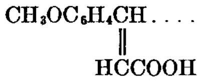
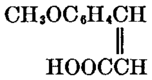
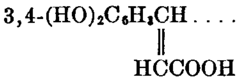
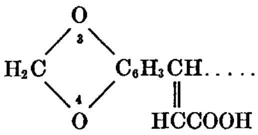
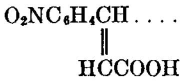
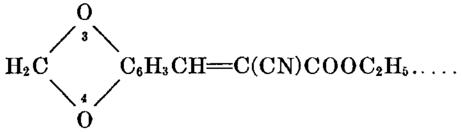
MONOMER		PHOTODIMER	REFERENCES
 $\begin{array}{l}HOC_6H_4CH\\ \quad\;\, \|\\ \quad HCCOOH\end{array}$	*o*-Coumaric acid	Di-*o*-hydroxy-α-truxillic acid (di-*o*-coumaric acid)	(5, 74, 93)
	o-Coumaric acid (sodium salt)	Di-*o*-coumaric acid (sodium salt)	(5, 74, 93)
 $\begin{array}{l}HOC_6H_4CH\\ \quad\;\, \|\\ NaOCOCH\end{array}$	Coumarinic acid (sodium salt)	Di-*o*-coumaric acid (sodium salt)	(5, 74, 93)
 $\begin{array}{l}CH_3OC_6H_4CH\\ \qquad\;\, \|\\ \quad\; HCCOOH\end{array}$	Methyl-*o*-coumaric acid	Di-*o*-methoxy-α-truxillic acid (di-*o*-methylcoumaric acid)	(76)
	Ethyl-*o*-coumaric acid	Diethyl-*o*-coumaric acid	(76)
	Propyl-*o*-coumaric acid	Dipropyl-*o*-coumaric acid	(76)
	Acetyl-*o*-coumaric acid	Diacetyl-*o*-coumaric acid	(76)
 $\begin{array}{l}CH_3OC_6H_4CH\\ \qquad\;\, \|\\ \; HOOCCH\end{array}$	Methylcoumarinic acid	Dimethyl-*o*-coumaric acid	(76)

TABLE 1—*Concluded*

MONOMER		PHOTODIMER	REFERENCES
 $\begin{array}{l}HOC_6H_4CH\\ \quad\ \|\\ \quad HCCOOH\end{array}$	*p*-Coumaric acid	Di-*p*-coumaric acid (trace)	(76)
 $\begin{array}{l}CH_3OC_6H_4CH\\ \qquad\ \|\\ \quad HCCOOH\end{array}$	Methyl-*p*-coumaric acid	–	(76)
 $\begin{array}{l}CH_3OC_6H_4CH\\ \qquad\ \|\\ \quad HOOCCH\end{array}$	Methyl-*p*-coumarinic acid	–	(76)
 $\begin{array}{l}3,4\text{-}(HO)_2C_6H_3CH\\ \qquad\quad\ \|\\ \qquad\ HCCOOH\end{array}$	*trans*-Caffeic acid	No dimer is isolated	(76)
	Piperonylacrylic acid	–	(76)
 $\begin{array}{l}O_2NC_6H_4CH\\ \quad\ \|\\ \ HCCOOH\end{array}$	*trans*-*o*-Nitrocinnamic acid *trans*-*m*-Nitrocinnamic acid *trans*-*p*-Nitrocinnamic acid	No dimer is isolated – –	(94) (76) (76)

C. Cinnamic acid derivatives substituted in the side chain

MONOMER		PHOTODIMERS	REFERENCES
$C_6H_5CH=C(CH_3)COOH$	α-Methylcinnamic acid*	–	(91)
$C_6H_5CH=C(C_2H_5)COOH$	α-Ethylcinnamic acid	–	(88)
$C_6H_5CH=C(C_6H_5)COOH$	α-Phenylcinnamic acid*	–	(91)
$C_6H_5C(CH_3)=CHCOOH$	β-Methylcinnamic acid	Di-β-methylcinnamic acid	(88)
$C_6H_5C(C_6H_5)=CHCOOH$	β-Phenylcinnamic acid	–	(88)
$C_6H_5CH=C(COOH)_2$	Benzylidenemalonic acid	–	(76)
$C_6H_5CH=C(CN)COOH$	Benzylidenecyanoacetic acid	–	(76)
$C_6H_5CH=C(CN)COOC_2H_5$	Benzylidenecyanoacetic ethyl ester	–	(76)
$C_6H_5CH=C(COCH_3)COOC_2H_5$	Benzylideneacetoacetic ethyl ester	–	(76)
$C_6H_5CH=C(COC_6H_5)COOC_2H_5$	Benzylidenebenzoylacetic ethyl ester	–	(76)
$CH_3OC_6H_4CH=C(CN)COOC_2H_5$	o-Methoxybenzylidenecyanoacetic ethyl ester	Di-o-methoxydicyanotruxillic ethyl ester	(76)
$CH_3OC_6H_4CH=C(CN)COOC_2H_5$	p-Methoxybenzylidenecyanoacetic ethyl ester	–	(76)
$CH_3OC_6H_4CH=C(COCH_3)COOC_2H_5$	p-Methoxybenzylideneacetoacetic ester	Di-p-methoxybenzylideneacetoacetic ester	(76)
	Piperonylidenecyanoacetic ethyl ester	–	(76)

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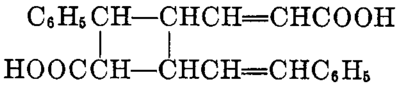
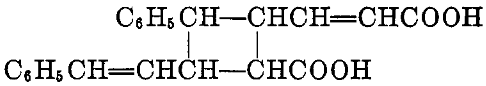
* The source of light was a quartz mercury lamp.



$$\begin{array}{l} C_6H_5CH{-}CHCH{=}CHCOOH \\ HOOCCH{-}CHCH{=}CHC_6H_5 \end{array}$$

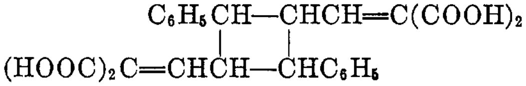
XXVIa



$$\begin{array}{l} C_6H_5CH{-}CHCH{=}CHCOOH \\ C_6H_5CH{=}CHCH{-}CHCOOH \end{array}$$

XXVIb

the solid state or suspended in hydrochloric acid, yields a photodimer (XXVII) (34, 56).

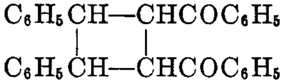


$$\begin{array}{l} C_6H_5CH{-}CHCH{=}C(COOH)_2 \\ (HOOC)_2C{=}CHCH{-}CHC_6H_5 \end{array}$$

XXVII

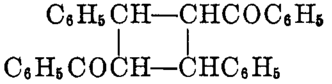
(c) Chalcones and their derivatives

The condensation product of benzaldehyde and acetophenone, benzylideneacetophenone, is known as chalcone. On exposure to sunlight, unless otherwise stated, it forms two dimers (76, 78): dimer A (truxinic ketone type) and dimer B (truxillic ketone type). Irradiation of chalcone in solution with sunlight gives dimer A only, the yields being about 35 per cent in the solvents acetic acid, chloroform, or ethanol, less being formed in benzene. (For the photodimerization of chalcones substituted in the ring see table 2A.)



$$\begin{array}{l} C_6H_5CH{-}CHCOC_6H_5 \\ C_6H_5CH{-}CHCOC_6H_5 \end{array}$$

Dimer A (truxinic ketone type)

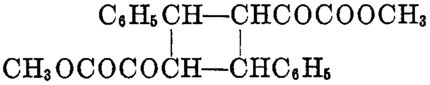


$$\begin{array}{l} C_6H_5CH{-}CHCOC_6H_5 \\ C_6H_5COCH{-}CHC_6H_5 \end{array}$$

Dimer B (truxillic ketone type)

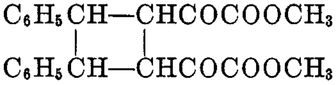
(d) Benzylidenepyruvic acid

Methyl benzylidenepyruvate, in the dry form, on exposure to sunlight gives a small amount of a dimeric product (XXVIII) (54) (truxillic acid series) melting at 154°C. In benzene solution it gives a dimer melting at 117°C. (truxinic acid series) (XXIX). The formation of the latter was explained by assuming, as in the case of cinnamic acid, that in solution stereoisomerization first occurred and then dimerization.



$$\begin{array}{l} C_6H_5CH{-}CHCOCOOCH_3 \\ CH_3OCOCOCH{-}CHC_6H_5 \end{array}$$

XXVIII



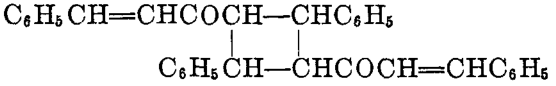
$$\begin{array}{l} C_6H_5CH{-}CHCOCOOCH_3 \\ C_6H_5CH{-}CHCOCOOCH_3 \end{array}$$

XXIX

When a benzene solution of β-bromobenzylidenepyruvic acid is exposed to sunlight, it yields a crystalline dimer, whereas in the solid state it gives an isomeric dimer of that obtained on exposure of its benzene solution (53a).

(e) Dibenzylideneacetone

Dibenzylideneacetone is readily transformed into 90 per cent of the colorless bisdibenzylideneacetone (XXX) (52) when its acetic acid solution is exposed to sunlight in the presence of uranyl salts. The addition compounds of dibenzylideneacetone with uranyl chloride or stannic chloride in benzene in sunlight favor the formation of XXX (77). XXX is readily transformed into the monomer



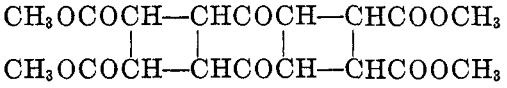
$$\begin{array}{l} C_6H_5CH{=}CHCOCH{-}CHC_6H_5 \\ \qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad C_6H_5CH{-}CHCOCH{=}CHC_6H_5 \end{array}$$

XXX

when heated above its melting point or by the action of the light of a quartz mercury lamp.

Di-*p*-methoxybenzylideneacetone is similarly dimerized, but its addition compounds with uranyl or stannic chlorides do not appear to yield a dimer when exposed to sunlight.

Similarly, methyl γ-ketopentadienedicarboxylate is readily transformed into a dimer (XXXI) by the action of sunlight (77, 92). XXXI is not oxidized by potassium permanganate and does not add bromine.

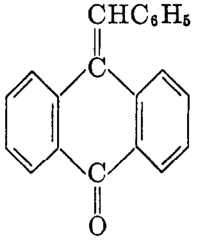


$$\begin{array}{l} CH_3OCOCH{-}CHCOCH{-}CHCOOCH_3 \\ \qquad\qquad | \qquad\quad | \qquad\qquad | \qquad\quad | \\ CH_3OCOCH{-}CHCOCH{-}CHCOOCH_3 \end{array}$$

XXXI

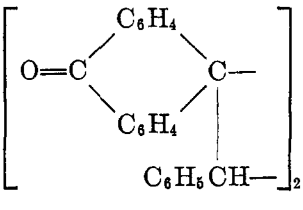
(f) 9-Benzylideneanthrone

When a benzene solution of 9-benzylideneanthrone (XXXII) is exposed to sunlight, an almost colorless photodimer (XXXIII) is obtained (48). The constitution of XXXIII is based on the following facts: (*1*) it lacks color, (*2*) on being heated at 270°C. it regenerates XXXII, and (*3*) it has the correct molecular weight.



XXXII

9-Benzylideneanthrone



XXXIII

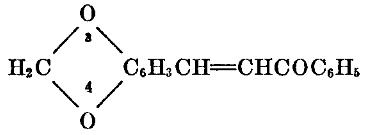
5. Photodimerization involving indone derivatives

In benzene solution 2-methyl-3-phenylindone when exposed to sunlight gives rise to two dimethyldiphenyltruxones, believed to have the structures XXXIVa and XXXIVb, respectively (22), which react with concentrated sulfuric acid to form 2-methyl-3-phenylindone.

TABLE 2

A. Chalcones substituted in the ring

MONOMER		TIME OF EXPOSURE	PHOTODIMER	REFERENCES
		days		
$C_6H_5CH{=\!=}CHCOC_6H_5$	Chalcone (pulverized solid)	65	Dichalcones A and B	(78)
	Chalcone (solution in acetic acid, chloroform, alcohol, or benzene)	132	Dichalcone A	(78)
	Chalcone (alcoholic solution containing chlorophyll)		Dichalcones A and B (1%)	(78)
$C_6H_5CH{=\!=}CHCOC_6H_4CH_3$	*p*′-Methylchalcone (pulverized solid)	85	Di-*p*′-methylchalcones C and D (stereoisomers of B)	(76)
	p′-Methylchalcone (solution in ethyl alcohol)	16	Dimers A and B	(76)
$CH_3C_6H_4CH{=\!=}CHCOC_6H_5$	*p*-Methylchalcone (pulverized solid)	111	Di-*p*-methylchalcone	(76)
	p-Methylchalcone (solution in chloroform)	44	Resin	(76)
$CH_3OC_6H_4CH{=\!=}CHCOC_6H_4CH_3$	*p*-Methoxy-*p*′-methylchalcone (pulverized solid)	85	Brown resin	(76)
	p-Methoxy-*p*′-methylchalcone (solution in alcohol)	81	Di-*p*-methoxy-*p*′-methylchalcone (?) (2.5%)	(76)
$CH_3OC_6H_4CH{=\!=}CHCOC_6H_4OCH_3$	*p*,*p*′-Dimethoxychalcone (solid)	145 hr.*	Brown resin	(76)

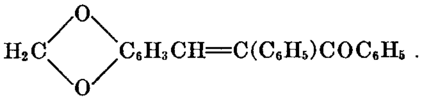
	p,*p*′-Dimethoxychalcone (solution in alcohol)	230 hr.*	Brown resin	(76)
$CH_3OC_6H_4CH{=}CHCOC_6H_5$	*o*-Methoxychalcone (solid)	Not reported	Resin	(78)
	o-Methoxychalcone (benzene solution containing iodine)	35	Brown resin	(78, 85)
	p-Methoxychalcone (solid)	Not reported	Di-*p*-methoxychalcone A	(78)
	p-Methoxychalcone (solution in chloroform)	150	Resin	(78)
	3,4-Methylenedioxychalcone (solid)	95	Resin	(85)
	3,4-Methylenedioxychalcone (solution in chloroform)	95	Brown resin	(85)
$O_2NC_6H_4CH{=}CHCOC_6H_5$	*o*-Nitrochalcone (solid)	Not reported	Di-*o*-nitrochalcone	(76)
	m-Nitrochalcone (solid)	Not reported	Di-*m*-nitrochalcone	(76)
	p-Nitrochalcone (solid)	Not reported	Di-*p*-nitrochalcone	(76)

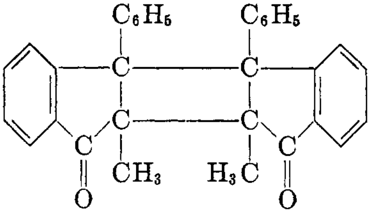
* The source of light was a quartz mercury lamp.

TABLE 2—*Concluded*

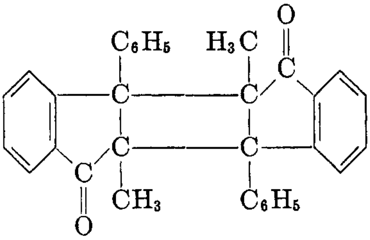
B. Chalcones with an α-substituted ethylene group: ArCH═CRCOAr′

Chalcones with an α-substituted ethylene group, ArCH═CRCOAr′, readily isomerize in sunlight when R is a methyl or phenyl group, but not when it is an acetyl or —$COOC_2H_5$ group (see below). In neither case did photodimerization occur; the only β-substituted chalcone examined (dypnone, β-methylchalcone) was unaffected by ultraviolet light when exposed alone or in solution.

MONOMER		REFERENCES TO DIMER
$C_6H_5CH{=}C(CH_3)COC_6H_4OCH_3$	α-Methyl-*p*′-methoxychalcone (solid)	(76)
	α-Methyl-*p*′-methoxychalcone (solution)	(76)
$C_6H_5CH{=}C(C_6H_5)COC_6H_5$	α-Phenylchalcone (solid)	(82)
	α-Phenylchalcone (solution)	(82)
	α-Phenyl-3,4-methylenedioxychalcone (solid)	(85)
$O_2NC_6H_4CH{=}C(C_6H_5)COC_6H_5$	α-Phenyl-*o*-nitrochalcone (solid)	(85)
	α-Phenyl-*m*-nitrochalcone (solid)	(85)
$C_6H_5CH{=}C(COCH_3)COC_6H_5$	α-Acetylchalcone	(76)
$C_6H_5CH{=}C(COOC_2H_5)COC_6H_5$	α-Carboxychalcone ethyl ester (ethyl benzylidenebenzoylacetate)	(76)
$CH_3OC_6H_4CH{=}C(COOC_2H_5)COC_6H_5$	Ethyl *p*-methoxybenzylidenebenzoylacetate	(76)

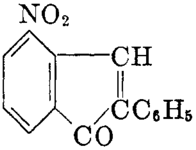


XXXIVa

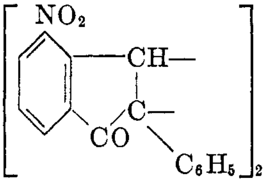


XXXIVb

Bakunin (3, 4) has studied the photochemical behavior of nitrophenylindones. 4-Nitro-2-phenylindone (XXXV), in the solid state in sunlight, yields only a dimeric product (XXXVI), which regenerates XXXV on distillation, whereas solutions of XXXV in ether, benzene, or chloroform give mixtures of dimers. 6-Nitro-2-phenylindone remains unchanged in sunlight in the solid state, but its solution in benzene gives a mixture of dimers.



XXXV
4-Nitro-2-phenylindone

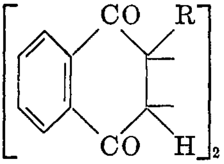


XXXVI

6. Photodimerization involving quinones

Quinones were found to dimerize in sunlight. Thymoquinone in ether, when exposed to sunlight, forms a dimeric product, which on heating decomposes into its generators (37).

When the benzene solution of the yellow α-naphthoquinone is exposed to sunlight, the colorless photodimer (XXXVIIa) is formed (67); it decomposes when heated at 270°C. with regeneration of α-naphthoquinone. XXXVIIa is not phenolic, for it is insoluble in alkali and does not react with diazomethane. The assignment of a dimeric structure is based on the fact that 2-methyl-1,4-naphthoquinone gives, in sunlight, a photodimer (45).



XXXVIIa: R = H
XXXVIIb: R = C_6H_5

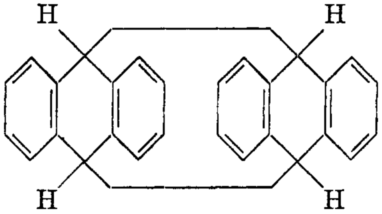
Similarly, when a benzene solution of 2-phenyl-1,4-naphthoquinone is exposed to sunlight, a colorless dimer (XXXVIIb) is obtained, which when heated regenerates the monomeric quinone (7, 59). Its structure has been assigned analogously to that of the α-naphthoquinone dimer (XXXVIIa) (64).

2,3-Dimethyl-1,4-naphthoquinone was found to be stable when exposed to sunlight in benzene solution or in the solid state (67).

III. PHOTODIMERS WHICH ARE NOT CYCLOBUTANE DERIVATIVES

A. PHOTODIMERS OBTAINED FROM ANTHRACENE AND ITS DERIVATIVES

In 1867 Fritzsche (25) found that anthracene was capable of forming a photodimer (XXXVIII) when its solutions were irradiated with sunlight. XXXVIII was recognized as dianthracene by Fritzsche (25), Elbs (17), and Orndorff and Cameron (50).



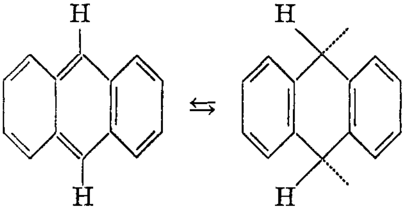
XXXVIII
Dianthracene

The formation of dianthracene is a true photochemical process; anthracene was found to be stable (43) in the dark.

Choice of solvents for the formation of dianthracene: Although the photodimerization of anthracene has been carried out in the solid state (44), it generally occurs in solution, e.g., in toluene, xylene, absolute ethyl alcohol, acetic acid, ethyl benzoate (41), or nitrobenzene (49). Dufraisse and Gèrard (13) have shown that chloroform and carbon disulfide inhibit the photodimerization of anthracene, whereas ether promotes it.

The transformation of anthracene to dianthracene is a reversible reaction. In the darkness dianthracene in boiling phenetole or anisole is completely changed to anthracene.

The mechanism of the photodimerization of anthracene has been explained recently by Schönberg (62), who assumed that there is a photoequilibrium between the normal form and the diradical form (XXXIX).



XXXIX

Many anthracene derivatives, when irradiated with sunlight, form photodimers, behaving similarly to anthracene (*cf.* table 3). In this connection, it should be mentioned that 9-phenylanthracene, 9,10-diethylanthracene, and 9,10-diphenylanthracene do not dimerize in sunlight (100). The nonoccurrence of the photodimeric products of the previously mentioned anthracene derivatives is probably due to their thermolability (62).

Attention should be drawn to the fact that the ready transformation of anthracene to dianthracene by the action of light and the ready depolymerization of the latter to anthracene have been employed for the removal of anthracene from such materials as phenanthrene and fluorene, which it contaminates (8).

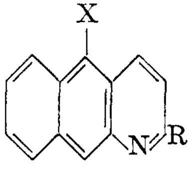
TABLE 3

Anthracene derivatives and their dimerization products

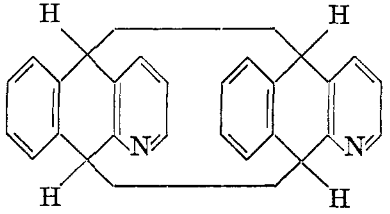
MONOMER	DIMER	MELTING POINT	REFERENCES
		°C.	
1-Methylanthracene	Di(1-methylanthracene)	246	(23)
2-Methylanthracene	Di(2-methylanthracene)	228	(51)
1-Chloroanthracene	Di(1-chloroanthracene)	235	(23)
1-Chloro-4-methylanthracene	Di(1-chloro-4-methylanthracene)	231	(23)
9-Bromoanthracene	Di(9-bromoanthracene)	274	(23, 46)
9-Bromo-1-chloroanthracene	Di(9-bromo-1-chloroanthracene)	220	(23)
9-Anthracenecarboxylic acid	Di(9-anthracenecarboxylic acid)	209–218	(98)
9-Methylanthracene	Di(9-methylanthracene)	250	(100)
9-Ethylanthracene	Di(9-ethylanthracene)	275	(100)

B. PHOTODIMERS OBTAINED FROM NITROGEN ANALOGS OF ANTHRACENE

We owe to Etienne the discovery of the photodimers of azaanthracene and its derivatives. When 1-azaanthracene (XLa) is irradiated with sunlight in alcohol, benzene, ether, or acetone, it gives a dimer (XLI). The same is true of 1-azaanthracene hydrochloride and 1-azaanthracene methiodide, which form dimers which decompose readily to monomers below their melting points (20). 9-Chloro- (XLb), 2-phenyl- (XLc), and 2-phenyl-9-chloro-1-azaanthracenes (XLd) form photodimers, respectively (19), but 9,10-diphenyl-1-azaanthracene does not appear to form a photodimer (18).



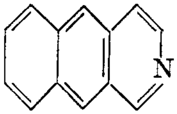
XLa: R = H, X = H
XLb: R = H, X = Cl
XLc: R = C_6H_5, X = H
XLd: R = C_6H_5, X = Cl



XLI

When 2,4-diphenyl-1-azaanthracene is irradiated with sunlight in benzene for 24 hr., it gives a colorless dimer $C_{50}H_{34}N_2$, which is depolymerized quantitatively to its monomer on melting (28a).

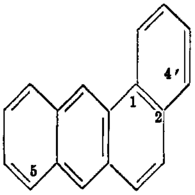
2-Azaanthracene (XLII), on exposure of its benzene solution to sunlight in the absence of air, is readily transformed to a photodimer (21).



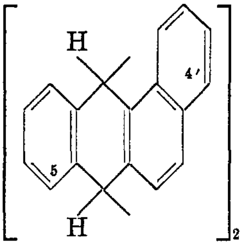
XLII
2-Azaanthracene

C. PHOTODIMERS OBTAINED FROM CARCINOGENIC HYDROCARBONS

Very little is known about the photodimerization of carcinogenic hydrocarbons. Schönberg and Mustafa (65, 67) have found that the weakly carcinogenic 1,2-benzanthracene (XLIII) (69) forms a difficulty soluble colorless photodimer, analogous to dianthracene (XXXVIII), under the influence of sunlight. The former dimer was obtained as a crystalline powder which is probably a mixture of isomers; whereas isomers are not possible for dianthracene, they are possible for di-1,2-benzanthracene (XLIV) and for substituted anthracenes; e.g., di-2-methylanthracene (97) can be either a symmetrical or an asymmetrical compound.



XLIII



XLIV

5-Methyl-1,2-benzanthracene, 20-methylcholanthrene, and 4-methyl-1,2-benzanthracene (11) similarly form polymers, which, by analogy with dianthracene, are believed to be dimeric and to have a constitution similar to that of dianthracene. These photoproducts are colorless and regenerate the monomers under the influence of heat, thus behaving like dianthracene (66).

The possibility of photodimerization should not be overlooked when substances are tested for carcinogenic activity, where the material is applied externally. When 1,2-benzanthracene is tested, the animal should be kept in the dark to avoid photodimerization of the material under investigation. Schönberg and Mustafa (67) have added that the above photoreactions are brought about by rays of comparatively long wave length, which are not absorbed by glass and which may be expected not to be absorbed by body fluids. Within the body, these rays may be produced by reactions accompanied by chemiluminescence;

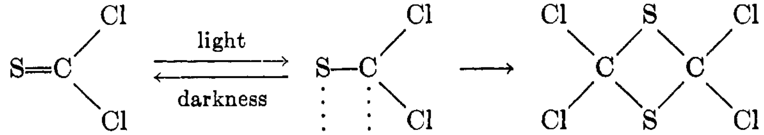
the importance of chemiluminescence for the cancer problem has been stressed by Anderson (2).

It is a remarkable fact that not only many carcinogenic hydrocarbons, but also a number of highly active carcinogenic compounds containing nitrogen, are derivatives of substances which undergo chemical reactions when their solutions are exposed to sunlight. Carcinogenic substances of this type are, *inter alia*, 4-dimethylazobenzene (butter yellow) and 2,3′-azotoluene, derivatives of azobenzene of which it is known that in solution the *cis* and *trans* forms are interconvertible (67). The carcinogenic derivatives of 4-aminostilbene (27) are derivatives of stilbene, which forms a dimer when its benzene solution is exposed to sunlight (9).

D. PHOTODIMERIZATION OF THIOPHOSGENE

Thiophosgene (XLV), when exposed to sunlight, forms a colorless photodimer (53) believed to be 2,2,4,4-tetrachloro-1,3-dithiacyclobutane (XLVI) rather than $ClCS_2CCl_3$ (12, 68); its condensation product with aniline is 4,4-dichloro-1,3-dithiacyclobutane-2-one anil (XLVII). XLVI is depolymerized in petroleum ether by the light of a quartz lamp.

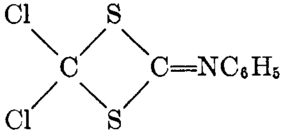
The photodimerization of thiophosgene is analogous to that of anthracene, and Schönberg (62) assumed that in the irradiated solution of thiophosgene a photochemical equilibrium exists (XLV $\rightleftarrows$ XLVa). The photodimers of thiophosgene and anthracene depolymerize on heating.



XLV
Thiophosgene

XLVa

XLVI



XLVII

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