304. *Photochemical Reactions in Sunlight. Part XVI.* (a) *Photo-reduction of Phenylglyoxylic Acid.* (b) *Photo-reactions between Aldehydes and* o-*Quinones.* (c) *Reactions between* o-*Quinones and Ethylenes in the Dark and in the Light.*

By ALEXANDER SCHÖNBERG, NAZIH LATIF, RADWAN MOUBASHER, and ALY SINA.

s-Dihydroxydiphenylsuccinic acid was obtained by the photo-reduction of phenylglyoxylic acid.

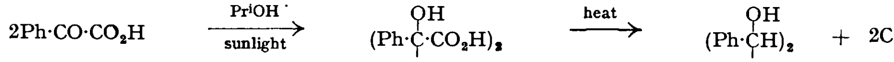
Tetrachloro- and tetrabromo-*o*-benzoquinone and 3 : 4-dichloro-β-naphthaquinone were allowed to react in light with aldehydes (see scheme A).

Tetrabromo-*o*-benzoquinone and 3 : 4-dichloro-β-naphthaquinone react with stilbene in the dark in hot benzene solutions and in cold solutions in sunlight (see scheme B). Tetrachloro-*o*-benzoquinone reacts in light in a similar way with styrene, 1-2′-naphthyl-2-phenylethylene, and 3-phenyl*iso*coumarin.

Phenanthraquinone reacts with xanthotoxin (VIII), khellinone (X*a*), and visnaginone (X*b*) in sunlight, giving the photo-adducts (IX), (XI*a*), and (XI*b*), respectively.

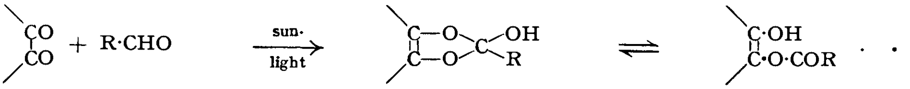
The action of light on 2-phenyl-α-naphthaquinone is discussed.

Photochemical Reduction of Phenylglyoxylic Acid.—Very little seems to be known about the *s*-diaryldihydroxysuccinic acids. *s*-Dihydroxydiphenylsuccinic acid was hitherto unknown; attempts to synthesise it having failed (Steinkopf und Wolfram, *Annalen*, 1923, **430**, 122; Burton, *Ber.*, 1883, **16**, 2232), but by photochemical reduction of phenylglyoxylic acid in the presence of *iso*propyl alcohol, *i.e.*, in the absence of acids, alkalis, salts, etc., we obtained this acid in good yield. When heated it decomposes to give *iso*hydrobenzoin.



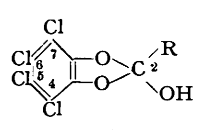
$$2\mathrm{Ph{\cdot}CO{\cdot}CO_2H} \xrightarrow[\text{sunlight}]{\mathrm{Pr^iOH}} (\mathrm{Ph{\cdot}\overset{OH}{C}{\cdot}CO_2H})_2 \xrightarrow{\text{heat}} (\mathrm{Ph{\cdot}\overset{OH}{C}H})_2 + 2\mathrm{CO_2}$$

Photo-action of Aldehydes on Derivatives of o-*Benzoquinone and* β-*Naphthaquinone.*—It has been shown (Schönberg and Moubasher, *J.*, 1939, 1430; Mustafa, *J.*, 1949, S 83) that the photo-addition products of phenanthraquinones with aldehydes are to be regarded as derivatives of methylene ethers of 9 : 10-dihydroxyphenanthrene, exhibiting ring-chain tautomerism as follows :

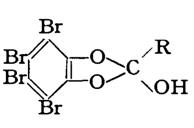


. . . (A)

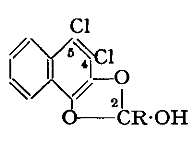
Similar products from *o*-benzoquinone and β-naphthaquinone have not yet been described. In view of the instability of these two quinones, we have used their halogenated derivatives and obtained the products (I*a*)—(III), analogous to the foregoing photo-products. In most cases the photo-products separated in good yield as almost pure crystals during irradiation. The ferric chloride reaction shown by the photo-addition products and the solubility in alkali (see Table I) are in agreement with the open-chain form (see scheme A).



(I*a*; R = Me.)
(I*b*; R = Ph.)
(I*c*; R = *p*-$\mathrm{Me{\cdot}C_6H_4}$.)
(I*d*; R = *p*-$\mathrm{MeO{\cdot}C_6H_4}$.)
(I*e*; R = CH:CHPh.)



(II*a*); R = *p*-$\mathrm{Me{\cdot}C_6H_4}$.)
(II*b*; R = *p*-$\mathrm{MeO{\cdot}C_6H_4}$.)



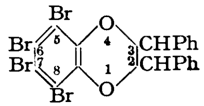
(III; R = *p*-$\mathrm{MeO{\cdot}C_6H_4}$.)

As it is established that methylene ethers of *o*-dihydroxy-compounds may be formed by photo-addition of aldehydes to phenanthraquinones [*e.g.*, chrysoquinone (Schönberg and Moubasher; Mustafa (*locc. cit.*); acenaphthenequinone (Sircar and Sen, *J. Indian Chem. Soc.*, 1931, **8**, 605)] as well as to derivatives of *o*-benzoquinone and β-naphthaquinone, reaction (A) can now be regarded as typical for *o*-quinones.

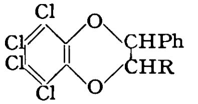
Dark and Photo-reactions between o-*Quinones and Ethylenes.*—Recently Schönberg and Latif (*J. Amer. Chem. Soc.*, 1950, **72**, 4828) stated that tetrachloro-*o*-benzoquinone differs from all other quinones and similar compounds previously investigated in that it reacts with ethylenes, not only in the light, but also in the dark :

. . . . (B)

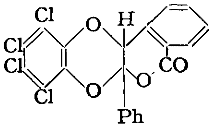
We have now found similar behaviour in the dark by tetrabromo-*o*-benzoquinone and 3 : 4-dichloro-β-naphthaquinone towards stilbene, leading to (IV) and (VII), respectively. Also, the reactions recorded in Table II were carried out in sunlight. They proceed according to scheme (B). In agreement with the proposed formulæ for the products are the fact that they are colourless, or almost so, and the results of their pyrolysis.



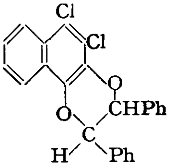
(IV.)



(V*a*; R = H.)
(V*b*; R = β-Naphthyl.)



(VI.)



(VII.)

Photo-action between Phenanthraquinone and Xanthotoxin and Related Compounds.—Xanthotoxin (VIII), a major constituent of the fruits of *Ammi majus* (Schönberg and Sina, *Nature*, 1948, **161**, 481; *J. Amer. Chem. Soc.*, 1950, **72**, 4862), contains two double bonds, one in the five-, and the other in the six-membered heterocyclic ring, both of which might react with phenanthraquinone. However, in our experiment only one molecule of phenanthraquinone was added, with the formation of (IX). This formula is based on analogy; coumarin does not

TABLE I.

(Reaction A).

(For systematic names, see Table III.)

o-Benzoquinone and wt. (g.).	Aldehyde, and wt. (g.).	C_6H_6, c.c.	Time of irradiation, days.	M. p. (and colour with $FeCl_3$[1]) of addition product.*	Formula.	Analysis of addition product. Found, %. C.	H.	Cl(Br).	Reqd., %. C.	H.	Cl(Br).
Tetrachloro- (0·4)	Acetaldehyde (0·3)	20	3 (March)	(I*a*),[2] 128—130°	$C_8H_4O_3Cl_4$	33·8	1·3	48·1	33·1	1·3	48·9
Tetrachloro- (1·0)	Benzaldehyde (0·5)	25	10 (Nov.)	(I*b*), 174°,[3] yellow	$C_{13}H_6O_3Cl_4$	44·5	2·0	—	44·3	1·7	—
Tetrachloro- (0·8)	*p*-Tolualdehyde (0·4)	30	10 (Dec.)	(I*c*), 201°	$C_{14}H_8O_3Cl_4$	46·3	2·3	39·0	45·9	2·1	38·7
Tetrachloro- (1·0)	Anisaldehyde (0·5)	25	5 (Dec.)	(I*d*), 208°,[4, 5] yellow	$C_{14}H_8O_4Cl_4$	43·9	2·3	37·4	43·9	2·0	37·1
Tetrachloro- (0·8)	Cinnamaldehyde (0·4)	40	7 (Dec.)	(I*e*),[5] 187°, yellow	$C_{15}H_8O_3Cl_4$	47·5	1·8	37·4	47·6	2·1	37·5
Tetrabromo- (0·8)	*p*-Tolualdehyde (0·4)	20	20 (Feb.)	(II*a*), 221°	$C_{14}H_8O_3Br_4$	30·9	1·4	(58·3)	30·8	1·4	(58·8)
Tetrabromo- (2)	Anisaldehyde (1·2)	30	4 (Jan.)	(II*b*), 246°	$C_{14}H_8O_4Br_4$	30·2	1·5	(57·0)	30·0	1·4	(57·1)
3 : 4-Dichloro-β-naphthaquinone (0·7)	Anisaldehyde (1·0)	25	2 (May)	(III), 207°[6]	$C_{18}H_{12}O_4Cl_2$	60·0	3·5	19·3	59·5	3·3	19·5

* All eight products were colourless (or very nearly so). All were ultimately crystallised from benzene, except II*a* (from xylene).

[1] The reaction was carried out by adding to a cold alcoholic solution of the substance an aqueous solution of ferric chloride. [2] The benzene was evaporated to very small bulk; addition of light petroleum (b. p. 30—50°) then precipitated an oil. The liquid was decanted and to the residue a few c.c. of benzene were added; when left to concentrate slowly, the liquid deposited crystals, which were washed with benzene. [3] Yield, 70%. [4] Yield, almost quantitative. [5] The product dissolved when treated with 6% alkali. [6] Deposited crystals first washed with light petroleum (b. p. 40—60°).

TABLE II

(Reaction B).

(For names of products, see Table III.)

Quinone, and wt. (g.).*	Ethylene deriv., and wt. (g.).	C_6H_6, c.c.	Time of irradiation, days.	Product and m.p.[3]		Analysis of addition product.					
						Found, %.			Reqd., %.		
					Formula.	C.	H.	Cl(Br).	C.	H.	Cl(Br).
A (1·2)	Stilbene (0·5)	30	20 (Jan.)	(IV), 215° (decomp.)	$C_{20}H_{12}O_2Br_4$	40·0	1·7	(53·7)	39·7	1·9	52·9
A (1·2)	Stilbene (0·5)	30	Dark expt.[1]	,, ,,	—	—	—	—	—	—	—
B (0·8)	Styrene (0·4)	30	12 (Dec.)	(V*a*), 79°	$C_{14}H_8O_2Cl_4$	47·9	1·8	—	47·9	2·2	—
B (0·4)	1-2′-Naphthyl-2-phenylethylene (0·3)	20	10 (Dec.)	(V*b*), 180°	$C_{24}H_{14}O_2Cl_4$	61·0	3·3	28·9	60·5	2·9	29·8
B (0·3)	3-Phenyl*iso*coumarin (0·2)	20	15 (Jan.)	(VI), 159°	$C_{21}H_{10}O_4Cl_4$	53·8	2·1	30·1	53·7	2·1	30·3
C (0·9)	Silbene (0·7)	25	21 (May–June)	(VII), 165°	$C_{24}H_{16}O_2Cl_2$	70·6	3·9	—	70·7	3·9	—
C (0·8)	Stilbene (0·6)	30	Dark expt.[2]	,, ,,	—	—	—	—	—	—	—
D (0·42)	Xanthotoxin (VIII) (0·43)	30	3 (Feb.)	(IX), 230° (decomp.)	$C_{26}H_{16}O_6$	73·3	3·9	—	73·6	3·8	—
D (0·8)	Khellinone (X*a*) (0·95)	40	3 (May)	(XI*a*), 231° (decomp.; red-brown melt) [4]	$C_{26}H_{20}O_7$	70·4	4·5	—	70·3	4·5	—
D (0·8)	Visnaginone (X*b*)	40	3 (May)	(XI*b*), 200—220° (decomp.) [4, 5]	$C_{25}H_{18}O_6$	72·5	4·7	—	72·5	4·4	—
D (0·42)	Coumarin (0·29)	25	14 (March)	Nil	—	—	—	—	—	—	—

* A = Tetrabromo-*o*-benzoquinone. B = Tetrachloro-*o*-benzoquinone. C = 3 : 4-Dichloro-β-naphthaquinone. D = Phenanthraquinone.

[1] 10 Hours' refluxing. [2] 14 Hours' refluxing. [3] For methods of working up products, see later footnotes correspondingly numbered. All the products were colourless or nearly so, except that (IX) was pale yellow. The products of the two " dark " experiments were identical (mixed m. p.) with those from the corresponding irradiation experiments. [4] $FeCl_3$ reaction : red-brown. The reaction was carried out as noted under Table I (footnote 1). [5] The crystals gradually became reddish.

Working-up of Products.—In the following, D denotes the deposit formed during illumination, and R the residue obtained from the irradiated mixture after filtration and evaporation of solvent.

(IV). R was treated with a few c.c. of acetone; the crystals which separated were recrystallised from the same solvent.

(IV) (Dark expt.). As above, but R was crystallised from glacial acetic acid.

(V*a*). R was extracted with hot light petroleum (b. p. 60—80°). The extract was filtered and evaporated, and the oily residue cooled in ice; crystallisation occurred on scratching, and treatment with methyl alcohol afforded a pale yellow solid. This was dissolved in the minimum amount of hot benzene and left overnight. After the addition of a few c.c. of absolute alcohol, crystals separated.

(V*b*). R was treated with cold, absolute alcohol; the pale yellowish-brown solid which separated was dissolved in a very little hot benzene, the solution filtered, and methyl alcohol added till turbidity occurred. On slow cooling, a pale yellow solid separated and was recrystallised from acetone–absolute alcohol.

(VI). R was crystallised from acetone–methyl alcohol.

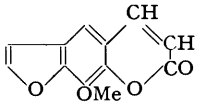
(VII). R was extracted with absolute alcohol, and then dissolved in a very little hot benzene. Light petroleum (b. p. 30—50°) was added dropwise till turbidity occurred, followed by a few c.c. of ether. Slow evaporation at room temperature afforded crystals, which were recrystallised from acetone with cooling to 0°.

(IX). The crystalline D was washed repeatedly with alcohol; it was difficultly soluble in hot alcohol, benzene, and light petroleum (b. p. 60—90°) and soluble in hot nitrobenzene.

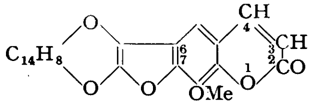
(XI*a*). D was difficultly soluble in hot alcohol and light petroleum (b. p. 60—90°), and soluble in hot benzene, from which it was recrystallised.

(XI*b*). D was recrystallised from hot benzene; it was difficultly soluble in alcohol.

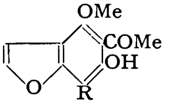
react photochemically with phenanthraquinone, whereas the benzofuran derivatives, khellinone (X*a*), visnaginone (X*b*), and 2 : 3-diphenylbenzofuran (Mustafa and Islam, *J.*, 1949, S 81), do so. For the photo-products obtained from phenanthraquinone and (X*a*) and (X*b*), we suggest formulæ (XI*a*) and (XI*b*), respectively; (IX), (XI*a*), and (XI*b*) when heated give their generators. The photo-behaviour of xanthotoxin is interesting in connection with its use in the light therapy of leukodermia (Fahmy and Abu-Shady, *J. Pharm. Pharmacol.*, 1947, **20**, 281; 1948, **21**, 499; El-Mofty, *J. Roy. Egypt. Med. Assoc.*, 1948, **31**, 1108).



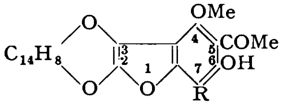
(VIII.)



(IX.)

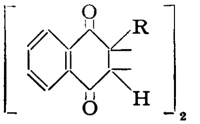


(X*a*; R = OMe.)
(X*b*; R = H.)



(XI*a*; R = OMe.)
(XI*b*; R = H.)

Action of Light on 2-*phenyl*-1 : 4-*naphthaquinone*.—When benzene solutions of this quinone are exposed to sunlight, a polymer is obtained in almost colourless crystals, which when heated regenerate the monomeric quinone (Breuer and Zincke, *Ber.*, 1878, **11**, 1403; Rügheimer and Hankel, *Ber.*, 1896, **29**, 2176). α-Naphthaquinone gives a similar photo-dimer for which the structure (XII*a*) has been advanced (Schönberg *et al.*, *J.*, 1948, 2126), so we assign the analogous structure (XII*b*) to the phenyl derivative. Neither quinone undergoes polymerisation readily in the solid state.



(XII*a*; R = H.)
(XII*b*; R = Ph.)

TABLE III.

Formal names of products given in Tables I *and* II.

Number.	Name.
I*a*	4 : 5 : 6 : 7-Tetrachloro-2-hydroxy-2-methylbenzodioxole.
I*b*	4 : 5 : 6 : 7-Tetrachloro-2-hydroxy-2-phenylbenzodioxole.
I*c*	4 : 5 : 6 : 7-Tetrachloro-2-hydroxy-2-*p*-tolylbenzodioxole.
I*d*	4 : 5 : 6 : 7-Tetrachloro-2-hydroxy-2-*p*-methoxyphenylbenzodioxole.
I*e*	4 : 5 : 6 : 7-Tetrachloro-2-hydroxy-2-styrylbenzodioxole.
II*a*	4 : 5 : 6 : 7-Tetrabromo-2-hydroxy-2-*p*-tolylbenzodioxole.
II*b*	4 : 5 : 6 : 7-Tetrabromo-2-hydroxy-2-*p*-methoxyphenylbenzodioxole.
III	4 : 5-Dichloro-2-hydroxy-2-*p*-methoxyphenyl-α-naphthodioxole.
IV	5 : 6 : 7 : 8-Tetrabromo-2 : 3-diphenylbenzodioxen.
V*a*	5 : 6 : 7 : 8-Tetrachloro-2-phenylbenzodioxen.
V*b*	5 : 6 : 7 : 8-Tetrachloro-3-2′-naphthyl-2-phenylbenzodioxen.
VI	5 : 6 : 7 : 8-Tetrachloro-2-phenyl*iso*coumarino(3′ : 4′-2 : 3)benzodioxen.
VII	3′ : 4′-Dichloro-5 : 6-diphenylnaphtho(1′ : 2′-2 : 3)dioxen.
IX	4′ : 5′-Phenanthrylenedioxyfurano(3′ : 2′-6 : 7)*iso*coumarin.
XI*a*	5-Acetyl-4 : 7-dimethoxy-2 : 3-phenanthrylenedioxybenzofuran.
XI*b*	5-Acetyl-4-methoxy-2 : 3-phenanthrylenedioxybenzofuran.

EXPERIMENTAL.

Pure benzene dried over sodium was used. The photochemical reactions were carried out in Pyrex-glass tubes sealed under carbon dioxide.

Action of iso*Propyl Alcohol on Phenylglyoxylic Acid*.—Phenylglyoxylic acid (2 g.) and *iso*propyl alcohol (20 g.) were left in sunlight for 4 weeks (May–June). The acid dissolved gradually to give a colourless solution. The illuminated solution was concentrated in a vacuum; the s-*dihydroxydiphenylsuccinic acid* was recrystallised first from benzene–light petroleum (b. p. 60—80°) and then from ligroin, forming colourless needles (1·2 g.), m. p. 155°, soluble in cold sodium hydroxide solution; the alcoholic solution reacted with aqueous sodium hydrogen carbonate solution with evolution of gas (Found : C, 63·2; H, 4·3; active H, 1·1. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6; active H, 1·2%).

Pyrolysis of photo-product. The photo-product was heated at 160° (bath-temp.) for 15 minutes under reduced pressure; an oily residue was obtained which solidified after 24 hours; the colourless crystals proved to be *iso*hydrobenzoin (m. p. and mixed m. p.).

Thermal Decomposition.—(*a*) *Of* (VII). This product was heated in a boiling ethyl phthalate bath under reduced pressure (oil-pump) for 15 minutes. The reaction vessel was left to cool in a vacuum, and the crystals collecting on the upper parts were recrystallised from methyl alcohol and proved to be stilbene (m. p. and mixed m. p.).

(b) *Of* (IX). The heating was carried out for 15 minutes, in an ethyl cinnamate bath; a mixture of brown and light-coloured crystals was formed on the walls of the tube. This was treated with 10% sodium hydroxide solution and filtered: filtrate (*f*), precipitate (*p*); (*p*) was purified by dissolving it in concentrated sulphuric acid and pouring the solution into water; the precipitate formed was washed with water and recrystallised from alcohol as orange crystals of phenanthraquinone (m. p. and mixed m. p.); (*f*) was acidified with hydrochloric acid, and the precipitate formed was washed with water and then separated from methyl alcohol as colourless crystals of xanthotoxin (m. p. and mixed m. p.; yellow colour with concentrated sulphuric acid).

(c) *Of* (XI*a*) *and* (XI*b*). Thermal decomposition and isolation of the products (phenanthraquinone and khellinone or visnaginone, respectively) were carried out as described under (b).

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