when it completely dissolved giving a yellow solution. The solution was concentrated until crystals appeared, acidified with hydrochloric acid, allowed to cool and left for two hours. The formed crystals were filtered off and refluxed with 6 cc. of 20% potassium hydroxide solution for one hour, cooled and acidified. The crystals obtained (from ethyl acetate) proved to be identical with *trans*-6-hydroxy-7-methoxy-5-coumaranoyl-β-acrylic acid.

Demethylation of Xanthotoxin (Ib).—A solution of 4.3 g. of (Ib) in dry benzene was added to magnesium iodide dissolved in a mixture of dry ether and benzene (from 10.16 g. iodine and 0.97 g. magnesium). The solvents were evaporated in vacuum at 120° (bath temperature) until the residue was practically dry and then further heated at 160–170° (bath temperature) for two hours. The resulting solid residue was decomposed with dilute sulfuric acid and the filtered precipitate washed with water, suspended in dilute sodium bisulfite solution, again filtered, washed with water and finally crystallized from dioxan as colorless crystals m. p. 246° which proved to be xanthotoxol (Ia)[10] (mixed m. p. and yellow color with sulfuric acid). *Anal.* Calcd. for $C_{11}H_6O_4$: C, 65.3; H, 3.0. Found: C, 65.2; H, 3.0.

Methylation of Xanthotoxol (Ia).—A mixture of 0.2 g. of (Ia), 3 g. potassium carbonate, 50 cc. acetone and 2 cc. methyl iodide was refluxed for 24 hours. The acetone filtrate and washings (20 cc. × 5) were evaporated to dryness and the residue after washing with water, separated from alcohol as colorless crystals which proved to be xanthotoxin (Ib) (m. p. and mixed m. p. and yellow color with sulfuric acid). *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.7; H, 3.7. Found: C, 66.4; H, 3.5.

Preparation of Ethers of Xanthotoxol (8-Hydroxy-4',5',6,7-furocoumarin) (Ia).—The preparation of the following ethers was similar to that described above in methylation of xanthotoxol. The ethers (Ic-g.), if not otherwise stated, form colorless crystals and gave with sulfuric acid a yellow color.

Ethyl Ether (Ic).—Obtained from (Ia) and ethyl iodide. It was crystallized from a mixture of benzene and petroleum ether (60–90°); m. p. 108–109°; on warming with aqueous potassium hydroxide it dissolved giving a yellow colored solution. It is difficultly soluble in petroleum ether (60–90°), easily soluble in hot benzene and hot alcohol. *Anal.* Calcd. for $C_{14}H_{10}O_4$: C, 67.8; H, 4.3. Found: C, 67.8; H, 4.2.

***n*-Propyl Ether (Id).**—Obtained from (Ia) and *n*-propyl iodide. It was crystallized from petroleum ether (60–90°) after being distilled twice in vacuum, m. p. 84–85°. (Id) was easily soluble in alcohol, benzene and hot petroleum ether (60–90°). *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.8; H, 4.9. Found: C, 68.5; H, 5.0.

***n*-Butyl Ether (Ie).**—From (Ia) and *n*-butyl iodide. It was crystallized from petroleum ether (60–90°), m. p. 83°. *Anal.* Calcd. for $C_{15}H_{14}O_4$: C, 69.8; H, 5.4. Found: C, 69.9; H, 5.4.

8-ω-Carboethoxymethoxy-4',5',6,7-furocoumarin (If).—Obtained from (Ia) and ethyl bromoacetate. After evaporation of acetone, the oily residue was heated in a vacuum at 140° (bath temperature) to remove excess ester. After washing with water and pressing, the solid residue separated from ethyl alcohol or petroleum ether (60–90°) as light yellow crystals of (If) m. p. 115°. *Anal.* Calcd. for $C_{15}H_{12}O_6$: C, 62.5; H, 4.2. Found: C, 62.1; H, 4.2.

8-ω-Carboxymethoxy-4',5',6,7-furocoumarin (Ig).—0.3 g. of (If) was dissolved in 8 cc. of glacial acetic acid and then 8 cc. of water containing 0.5 cc. sulfuric acid (98%) was added and the mixture refluxed for one hour, diluted to 50 cc. with water and allowed to stand. The crystalline deposit was filtered off, washed with water and finally crystallized from alcohol, m. p. 210°. (Ig) dissolved in sodium bicarbonate solution with evolution of gas. *Anal.* Calcd. for $C_{13}H_8O_6$: C, 60.0; H, 3.1. Found: C, 60.3; H, 3.4.

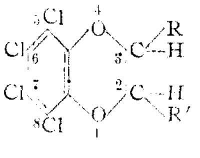
CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
ABBASSIA, CAIRO, EGYPT

RECEIVED FEBRUARY 7, 1950

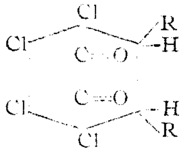
Action of Stilbene on Tetrachloro-*o*-benzoquinone

BY ALEXANDER SCHÖNBERG AND NAZIH LATIF

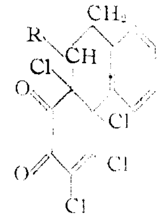
Our investigation of the photoaction of stilbene on *o*-quinones[1] has been continued with tetrachloro-*o*-benzoquinone. When stilbene and *p*-methylstilbene were used 2,3-diphenyl-5,6,7,8-tetrachlorobenzodioxene (Ia) and 2-phenyl-3-(*p*-tolyl)-5,6,7,8-tetrachlorobenzodioxene (Ib) were obtained respectively.



I



II



III

(a) R = R' = C_6H_5
(b) R = C_6H_5; R' = p-$CH_3C_6H_4$

Ia was obtained in a dark reaction using boiling benzene as a solvent whereas, so far, all reactions between *o*-quinones and ethylenes leading to dioxens were carried out as photoreactions. Ia on heating decomposes with the formation of stilbene. Ia and Ib are colorless substances. Ia does not form a quinoxaline derivative when treated with *o*-phenylene diamine; thus excluding formula II or III (R = phenyl or *p*-toly) of a diketone.

Experimental

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

Photoreactions of Tetrachloro-*o*-benzoquinone. (I) **With Stilbene.**—Tetrachloro-*o*-quinone (1 g.)[2] and stilbene (0.8 g.) in benzene (30 cc.) were exposed to sunlight for thirteen days (November). Most of the benzene was then driven off; after cooling a few drops of acetone were added when colorless crystals were obtained which were recrystallized from acetone. The addition product Ia formed colorless crystals m. p. about 172°. It gave no color reaction with concd. sulfuric acid.

Anal. Calcd. for $C_{20}H_{12}Cl_4O_2$: C, 56.3; H, 2.8. Found: C, 57.0; H, 2.9.

(II) With *p*-Methylstilbene.—Tetrachloro-*o*-quinone (0.6 g.) (ref. 1) and *p*-methylstilbene (0.5 g.)[3] in benzene (25 cc.) were exposed to sunlight for ten days (December). The benzene was filtered, evaporated and the residue extracted with hot petroleum (60–80°). The residue was dissolved in boiling absolute alcohol and left to cool. Pale yellow crystals separated which were recrystallized from benzene–methyl alcohol. Ib formed colorless crystals m. p. 132°.

Anal. Calcd. for $C_{21}H_{14}Cl_4O_2$: C, 57.2; H, 3.1; Cl, 32.2. Found: C, 57.4; H, 3.4; Cl, 31.7.

Reaction between Tetrachloro-*o*-quinone and Stilbene in the Dark.—Tetrachloro-*o*-quinone (1.2 g.) and stilbene (0.9 g.) in benzene were refluxed for fifteen hours in the dark. The benzene was filtered, evaporated and the residue left to cool. A few cc. of acetone were then added when almost colorless crystals were obtained. Ia was re-

---

(1) Compare Schönberg and Mustafa, *Chem. Rev.*, **40**, 181 (1947).
(2) Jackson and MacLaurin, *Am. Chem. J.*, **37**, 7 (1907).
(3) Meerwein, *et al.*, *J. prakt. Chem.*, **152**, 237 (1939).

crystallized from acetone in colorless crystals; mixed m.p. determination with the photoproduct gave no depression; yield 70% and more.

Thermal Decomposition.—Ia was heated in a boiling ethyl phthalate-bath under reduced pressure (oil pump vacuum) for fifteen minutes. The reaction vessel was left to cool in vacuum. The crystals collected on the upper parts were recrystallized from methyl alcohol and proved to be stilbene (m. p. and mixed m. p.).

o-Phenylenediamine and Ia.—Equimolecular amounts in acetic acid (90%) were refluxed for two hours and the mixture left to cool. The crystals separated were washed with methyl alcohol and proved to be Ia (mixed m. p.).

DEPARTMENT OF CHEMISTRY
UNIVERSITY FOUAD I
ABBASSIA, CAIRO, EGYPT

RECEIVED MARCH 6, 1950

Esters of Tetraphenylphthalic Acid

BY ERIC C. SCHREIBER[1] AND ERNEST I. BECKER

Only the methyl and ethyl esters of tetraphenylphthalic acid have been described. The methyl ester has been obtained by the action of diazomethane on the free acid,[2] by heating methyl acetylenedicarboxylate with tetracyclone (tetraphenylcyclopentadienone) at 160°,[2] and by heating methyl maleate with tetracyclone over a free flame.[3] The ethyl ester has not been prepared directly, but has been synthesized from ethyl acetylenedicarboxylate and tetracyclone.[2,3] Attempts to saponify these esters have failed.[2,3] In an effort to prepare a series of these esters in order to study their unique unreactivity, a new synthesis was applied,

Synerholm has recently reported that the reaction between tetracyclone and chloromaleic anhydride in bromobenzene gives 75 per cent. of tetraphenylphthalic anhydride.[4] This elegant procedure was duplicated here[5] and it suggested the application to the synthesis of the desired esters.

Three hitherto undescribed esters of chloromaleic acid—the *n*-propyl, *n*-butyl[6] and *n*-amyl—were prepared in from 58–66% yield by reaction of the chosen alcohol with chloromaleic anhydride in the presence of *p*-toluenesulfonic acid (Table I). An excess of each of these esters was refluxed with tetracyclone at atmospheric pressure. In each case carbon monoxide and hydrogen chloride were eliminated and colorless, crystalline esters of tetraphenylphthalic acid were obtained in from 67–76% yield[7] (Table II).

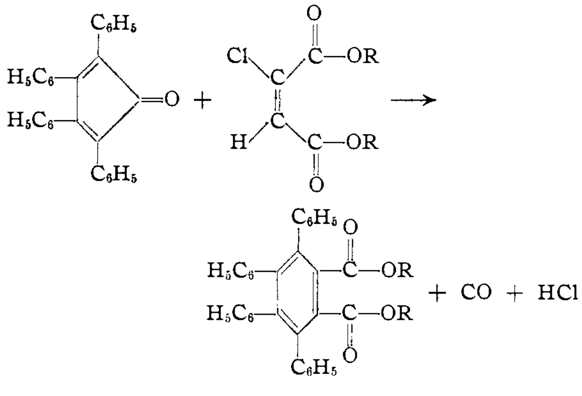
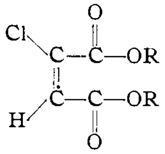


TABLE I

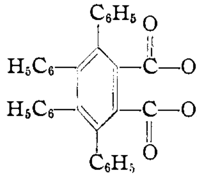
ESTERS OF CHLOROMALEIC ACID



R is		n-C_3H_7	n-C_4H_9	n-C_5H_{11}
Yield, %		66	60	58
B. p.	°C.	89–90	150	47
	Mm.	1	11	0.6
d^{25}_4		1.108	1.072	1.028
n^{20}_D		1.4571	1.4566	1.4559
Formula		$C_{10}H_{15}ClO_4$	$C_{12}H_{19}ClO_4$	$C_{14}H_{23}ClO_4$
Carbon, %	Calcd.	51.18	54.85	57.82
	Found	51.23	54.63	57.47
Hydrogen, %	Calcd.	6.44	7.29	7.97
	Found	6.48	7.02	7.80
Chlorine, %	Calcd.	15.11	13.50	12.20
	Found	15.14	13.27	12.01

TABLE II

ESTERS OF TETRAPHENYLPHTHALIC ACID



R is		n-C_3H_7	n-C_4H_9	n-C_5H_{11}
Yield, %		76	70	67
M. p., °C.		196.5–197.5	193–194	190–191.5
Formula		$C_{38}H_{34}O_4$	$C_{40}H_{38}O_4$	$C_{42}H_{42}O_4$
Carbon, %	Calcd.	82.28	82.49	82.59
	Found	82.21	82.25	82.22
Hydrogen, %	Calcd.	6.18	6.57	6.93
	Found	5.93	6.17	6.73

It is interesting to report that recrystallization of the *n*-propyl ester from ethanol gave the ethyl ester. This was established by melting point, mixed melting point with known ethyl tetraphenylphthalate and analysis for carbon and hydrogen. This facile *trans*-esterification is unusual in view of the failure of the methyl or ethyl ester of tetraphenylphthalic acid to hydrolyze and also of the failure to synthesize either of these esters from the acid and the alcohol.[2,3]

---

[1] Taken from a thesis submitted for the Bachelor of Science degree, Polytechnic Institute of Brooklyn, June, 1951.

[2] W. Dilthey, I. Thewalt and O. Trösken, *Ber.*, **67**, 1959 (1934).

[3] C. F. H. Allen and L. J. Sheps, *Can. J. Research*, **11**, 171 (1934).

[4] M. E. Synerholm, THIS JOURNAL, **67**, 1229 (1945).

[5] John A. Romano, thesis submitted for the Bachelor of Science degree, Polytechnic Institute of Brooklyn, June, 1949.

[6] *n*-Butyl chloromaleate has been mentioned by C. H. Fisher and W. C. Mast (*Ind. Eng. Chem.*, **40**, 107 (1948)), but its preparation and properties were not given.

[7] Preliminary experiments with methyl chloromaleate and ethyl chloromaleate had given the already known methyl and ethyl esters of tetraphenylphthalate (see ref. 5).