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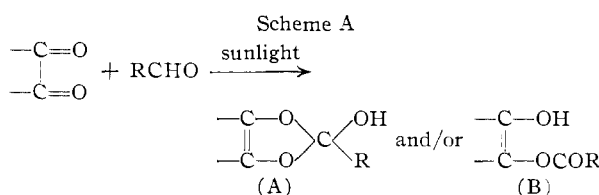
**Photochemical Addition and Photochemical Dehydrogenation Reactions in Sunlight**

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The photochemical addition reaction of aldehydes to *o*-quinones has been extended to 6-bromo-1,2-naphthoquinone, phenanthraquinone and 3-phenylbenzo[f]quinoxaline-5,6-quinone (V). The reaction proceeds according to scheme A, yielding the photo-products listed in Tables (I-III). Thioxanthene 5,5-dioxide undergoes a photochemical dehydrogenation reaction when its benzene solution is allowed to react in sunlight, and in the absence of oxygen with benzophenone, thioxanthene 5,5'-dioxide (VIII d), xanthone and/or anthraquinone, yielding, in all cases, 9,9'-bithioxanthene 5,5'-dioxide (XIc) and benzopinacol in the case of benzophenone. The formation of 9,9'-bixanthene (XIa) by the action of VIII d on xanthene and of *sym*-tetraphenylethane from diphenylmethane and VIII d now has been established.

It has been shown that the photo-addition of aldehydes to *o*-quinones is a general reaction which may be carried out with *o*-benzoquinone,<sup>1a</sup>  $\beta$ -naphthoquinone<sup>1a</sup> derivatives, phenanthraquinone,<sup>1b</sup> acenaphthenequinone,<sup>1c</sup> chrysene-5,6-dione<sup>1d</sup> and 1,2-benzophenazine-3,4-quinone.<sup>1e</sup> The reaction proceeds according to scheme A.



The photo-addition products are to be regarded as derivatives of methylene ethers of *o*-dihydroxy compounds (A), exhibiting ring-chain tautomerism (*cf.* scheme A), and they are in agreement with the open-chain form (B) in the case of tetrachloro-*o*-benzoquinone and aldehydes<sup>1a</sup> and in the case of phenanthraquinone and benzaldehyde.<sup>2</sup>

Similar products from 1,2-naphthoquinone have not yet been described. In view of the instability of this quinone, we have allowed the 6-bromo-1,2-naphthoquinones to react with aromatic aldehydes in sunlight in the absence of oxygen, and have found that addition takes place in molecular proportions. The colorless photo-products (*cf.* Table I) are obtained in good yield in most cases. It is believed that these 7-bromo-2-arylnaphtho(1,2-)1,3-dioxol-2-ol derivatives have the constitution (Ia-f) or the corresponding open form (*cf.* scheme A).

It is typical of compounds (Ia-f). It is colorless, contains an active hydrogen atom, is insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride. It yields on hydrolysis with concentrated hydrochloric acid, *p*-methoxybenzoic acid and 6-bromo-1,2-dihydroxynaphthalene. It reacts with an ethereal diazomethane solution to give a monomethyl derivative which, upon treatment with alcoholic potassium hydroxide followed by acidification, yields the 1(or 2)-methyl ether of 6-bromo-1,2-dihydroxynaphthalene.

Similarly, the addition of aromatic aldehydes and

phenanthraquinone in sunlight takes place in molecular proportions. The photo-products, 2-arylphenanthro(9,10)-1,3-dioxol-2-ol derivatives (IIa-d; *cf.* Table II) separate during exposure as pale-yellow crystals. IIa-c, when finely powdered, dissolve in cold dilute aqueous sodium hydroxide solution and/or in alcoholic sodium hydroxide solution and are regenerated on acidification. They do not give a color with ferric chloride.<sup>2</sup> II d is insoluble in cold aqueous alkali solution and does not give a ferric chloride test.

1,2-Benzophenazine-3,4-quinone (III) gives violet photo-addition products in sunlight with benzaldehyde and *p*-methoxybenzaldehyde<sup>1e</sup> (IVa and IVb, respectively). The orange-red 3-phenylbenzo(f)quinoxaline-5,6-quinone (V) adds to aromatic aldehydes in molecular proportions. The photo-products, 2-aryl-3-phenylbenzo[f]quinoxaline-(5,6)-1,3-dioxol-2-ol derivatives (VIa-f; *cf.* Table III), are yellow as expected (*cf.* the yellow color of 5,6-diacetoxy-3-phenylbenzo[f]quinoxaline (VIIb) which is prepared by the action of acetic anhydride on 5,6-dihydroxy-3-phenylbenzo[f]quinoxaline (VIIa), obtained by reduction of V with phenylhydrazine). The photo-products are insoluble in cold aqueous alkali solution and give no color with ferric chloride. In contrast to the marked thermochromic properties of the solution of IVa-b in ethyl benzoate,<sup>1e</sup> solutions of VIa and VIc in the same solvent show no such properties.

Whereas, photochemical addition reaction takes place between xanthone (VIIIa) and xanthene and between xanthene<sup>3</sup> and 2-chloroxanthone<sup>4</sup> (VIIIb) to yield IXa-b, respectively, VIIIa and VIIIb effect a photochemical dehydrogenation reaction,<sup>5</sup> forming 9,9'-bixanthene (XIa) when their benzene solutions are allowed to react with xanthene in sunlight and in the absence of oxygen. Similarly, 10-thioxanthene (VIIIc) undergoes a photochemical addition reaction with xanthene<sup>3</sup> and a photochemical dehydrogenation reaction with thioxanthene<sup>6</sup> in sunlight, yielding IXc and XIb, respectively.

We now have found that a similar photochemical dehydrogenation reaction occurs when a benzene

(1) (a) A. Schönberg, N. Latif, R. Moubasher and A. Sina, *J. Chem. Soc.*, 1364 (1951); (b) A. Schönberg and R. Moubasher, *ibid.*, 1430 (1939); A. Mustafa, *ibid.*, 997 (1947) and A. Mustafa, *Nature*, **166**, 108 (1950); (c) A. Sircal and S. Sen, *J. Indian Chem. Soc.*, 997 (1947); (d) A. Mustafa, *J. Chem. Soc.*, 1034 (1951); (e) A. Schönberg, A. Mustafa and S. M. A. D. Zayed, *THIS JOURNAL*, **75**, 4302 (1953).

(2) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); H. Klinger, *Ann.*, **249**, 137 (1888).

(3) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, **67**, (1944) *Chem. Revs.*, **40**, 181 (1947).

(4) A. Mustafa, W. Asker and M. E. E. Sobhy, *THIS JOURNAL*, **77**, 5121 (1955).

(5) *Cf.* the photochemical dehydrogenation of diphenylmethane and anthrone by xanthone to give *sym*-tetraphenylethane and 10,10'-bianthrone, respectively (ref. 3).

(6) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

TABLE I  
PHOTO-ADDITION PRODUCTS FROM 6-BROMO-1,2-NAPHTHOQUINONE

Addition <sup>d, e</sup> product <i>o</i> -Quinone <sup>a</sup> (yield, %) wt., g.	Aldehyde and wt. (g.)	Benzene, ml.	Time of irradia- tion, days	M.p., <sup>f</sup> °C.	Color with H <sub>2</sub> SO <sub>4</sub>	Formula	Carbon, %		Hydrogen, %		Halogen, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
Ia (72)	0.5 Benzaldehyde (1.0)	20	1 <sup>b</sup>	172	Olive-green	C <sub>17</sub> H <sub>11</sub> BrO <sub>3</sub>	59.47	59.34	3.21	3.20	23.32	23.13
Ib (68)	0.5 <i>m</i> -Tolualdehyde (0.8)	25	1 <sup>c</sup>	148	Violet	C <sub>18</sub> H <sub>13</sub> BrO <sub>3</sub>	60.50	60.32	3.64	3.52	22.41	22.36
Ic (76)	1.0 <i>p</i> -Tolualdehyde (1.4)	20	1 <sup>b</sup>	178	Violet	C <sub>18</sub> H <sub>13</sub> BrO <sub>3</sub>	60.50	60.41	3.64	3.45	22.41	22.24
Id (65)	0.8 <i>o</i> -Methoxybenz- aldehyde (1.0)	30	7 <sup>c</sup>	125-126	Olive- green	C <sub>18</sub> H <sub>13</sub> BrO <sub>4</sub>	57.91	57.86	3.49	3.41	21.44	21.52
Ie (82)	1.0 <i>p</i> -Methoxybenz- aldehyde (1.2)	30	7 <sup>b</sup>	190	Violet	C <sub>18</sub> H <sub>13</sub> BrO <sub>4</sub> <sup>g</sup>	57.91	57.62	3.49	3.52	21.44	21.34
If (64)	0.7 <i>o</i> -Chlorobenz- aldehyde (1.1)	25	7 <sup>c</sup>	156	Pale blue	C <sub>17</sub> H <sub>10</sub> BrClO <sub>3</sub>	54.06	54.00	2.65	2.53	30.62	30.54

<sup>a</sup> K. Fries and K. Schimmelschmidt, *Ann.*, **484**, 271 (1930). <sup>b</sup> August. <sup>c</sup> February. <sup>d</sup> The photo-addition products are colorless or almost colorless. <sup>e</sup> For working up the reaction products see the text. <sup>f</sup> All melting points are uncorrected. <sup>g</sup> Active hydrogen, calcd.: 0.27; found: 0.24.

TABLE II  
PHOTO-ADDITION PRODUCTS FROM PHENANTHRAQUINONE

Addition <sup>d</sup> product (yield, %)	<i>o</i> -Quinone wt., g.	Aldehyde and wt. (g.)	Benzene, ml.	M.p., <sup>e</sup> °C.	Color with H <sub>2</sub> SO <sub>4</sub>	Time of irradia- tion, days	Formula	Carbon, %		Hydrogen, %	
								Calcd.	Found	Calcd.	Found
IIa (72)	1.0	<i>o</i> -Phthalaldehyde <sup>a</sup> (0.7)	30	206	Red-brown	6 <sup>f</sup>	C <sub>22</sub> H <sub>14</sub> O <sub>4</sub>	77.19	76.94	4.09	3.96
IIb (65)	1.0	Isophthalaldehyde <sup>b</sup> (0.7)	25	195	Brown changing to green	4 <sup>g</sup>	C <sub>22</sub> H <sub>14</sub> O <sub>4</sub>	77.19	76.87	4.09	4.00
IIc (78)	1.0	Terephthalaldehyde <sup>a</sup> (0.88)	30	227	Dark green	4 <sup>g</sup>	C <sub>22</sub> H <sub>14</sub> O <sub>4</sub> <sup>i</sup>	77.19	77.07	4.09	3.83
IId (73)	0.8	3-Pyrenealdehyde <sup>c</sup> (0.88)	40	225	Olive-green	8 <sup>h</sup>	C <sub>31</sub> H <sub>18</sub> O <sub>3</sub> <sup>j</sup>	84.93	84.72	4.11	3.94

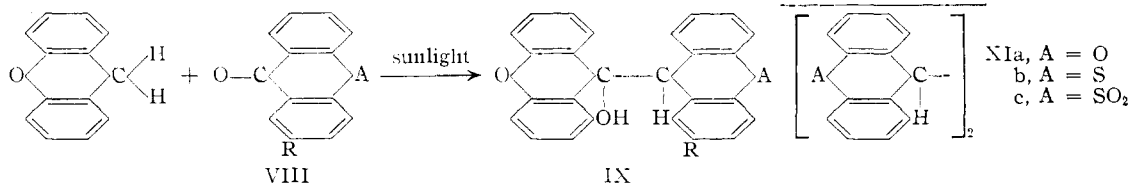
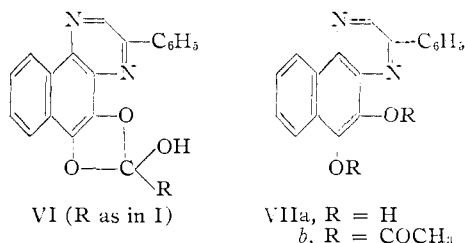
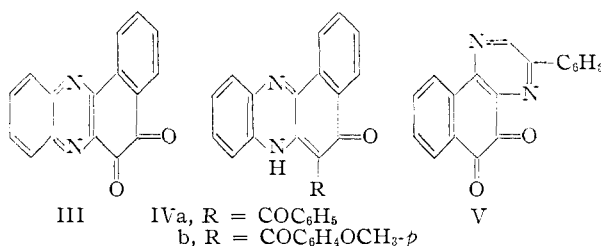
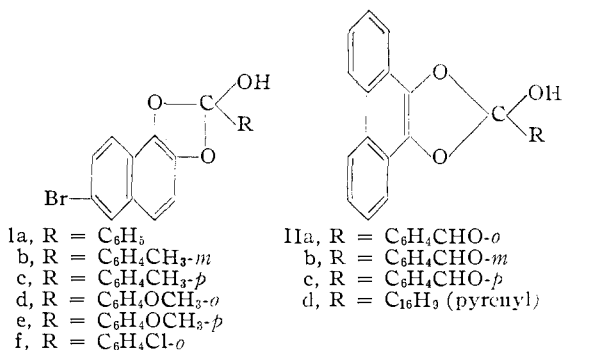
<sup>a</sup> J. Thiele and E. Winter, *Ann.*, **311**, 358 (1900). <sup>b</sup> J. H. Hunter and A. H. Nathan, *This Journal*, **69**, 2064 (1947). <sup>c</sup> H. Vollmann, H. Becker, M. Correll and H. Streck, *Ann.*, **531**, 35 (1937). <sup>d</sup> Solution of the photo-products reduces Tollens reagent. For working up the reaction products see the text. <sup>e</sup> All melting points are uncorrected. <sup>f</sup> October. <sup>g</sup> December. <sup>h</sup> May. <sup>i</sup> Mol. wt., calcd.: 342. Found: 322. <sup>j</sup> Active hydrogen, calcd.: 0.23; found: 0.21.

TABLE III  
PHOTO-ADDITION PRODUCTS FROM 3-PHENYLBENZO(f)QUINOXALINE-5,5-QUINONE (V)

Addition product (yield, %)	<i>o</i> -Quinone V wt., g.	Aldehyde and wt. (g.)	Benzene, ml.	Time of irradia- tion, days	M.p., <sup>e</sup> °C.	Solvent for cryst. <sup>f</sup>	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
VIa (75)	0.5	Benzaldehyde (0.4)	30	7 <sup>a</sup>	214	A	C <sub>25</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	76.53	76.34	4.08	4.01	7.14	6.98
VIb (68)	0.7	<i>m</i> -Tolualdehyde (0.6)	25	10 <sup>a</sup>	184	B	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	76.84	76.72	4.43	4.29	6.89	6.74
VIc (78)	0.7	<i>p</i> -Tolualdehyde (0.6)	40	5 <sup>b</sup>	206	B	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	76.84	76.59	4.43	4.42	6.89	6.67
VIc (46)	0.5	<i>o</i> -Methoxybenzaldehyde (0.47)	30	5 <sup>b</sup>	186	B	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	73.93	73.68	4.26	4.14	6.63	6.48
VIe (71)	0.5	<i>p</i> -Methoxybenzaldehyde (0.5)	40	10 <sup>b</sup>	226	C	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> <sup>d</sup>	79.93	73.65	4.26	4.30	6.63	6.51
VIc (53)	0.8	<i>o</i> -Chlorobenzaldehyde (0.74)	30	10 <sup>b</sup>	210	B	C <sub>25</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>3</sub> <sup>e</sup>	70.34	70.16	3.51	3.38	6.56	6.54

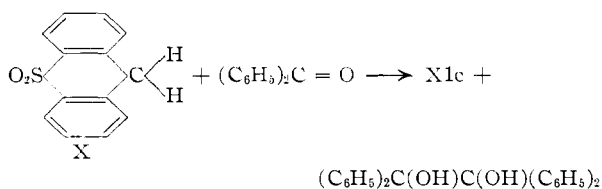
<sup>a</sup> March. <sup>b</sup> April. <sup>c</sup> Melting points are uncorrected. <sup>d</sup> Active hydrogen, calcd.: 0.24. Found, 0.231. <sup>e</sup> Calcd.: Cl, 8.3. Found, Cl, 8.1. <sup>f</sup> A, Benzene; B, a mixture of benzene and light petrolcum; C, xylene.

solution of thioxanthene 5,5-dioxide (X) is allowed to react with benzophenone in sunlight, yielding the corresponding ethane compound, namely 9,9'-bithi-



axanthene 5,5-dioxide (XIc) together with benzopinacol, the reduction product of the ketone (*cf.* scheme B).

#### Scheme B



Similar photochemical dehydrogenation of X to XIc can be effected by allowing a benzene solution of X to react with 10-thioxanthene 5,5-dioxide (VIII d), xanthone (VIII a) and/or anthraquinone. The fate of the ketone or the quinone has not yet been established.

The formation of 9,9'-bixanthene (XIa) by the action of VIII d on xanthene, and of *sym*-tetraphenylethane from diphenylmethane and VIII d now has been demonstrated.

## Experimental

**General Remarks.**—The photochemical reactions were carried out in sealed Pyrex glass Schlenk tubes,<sup>7</sup> under dry carbon dioxide. The benzene was thiophene-free (Kahlbaum) and dried over sodium. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

**Isolation of the Photo-products.**—The photo-products are listed in Tables (I-III). In the following, D denotes the deposit formed during illumination, and R the residue obtained from the irradiated mixture after filtration and evaporation of the solvent.

Ia: R was washed several times with cold light petroleum<sup>7a</sup> (*ca.* 60 ml.), and the solid, so obtained, was washed with cold benzene (5 ml.) and crystallized from benzene.

Ib: R was washed with cold light petroleum (*ca.* 40 ml.) and the solid obtained was crystallized from a mixture of benzene and light petroleum; it was easily soluble in hot alcohol, but difficultly soluble in petroleum ether.

Ic: R was washed with light petroleum (b.p. below 40°) and the solid, so obtained, was crystallized from hot alcohol; it was soluble in benzene, but sparingly soluble in cold alcohol and light petroleum.

Id: D was recrystallized from hot alcohol, it was soluble in benzene, but difficultly soluble in cold alcohol.

Ie: D was recrystallized from a mixture of benzene and light petroleum; it was soluble in hot benzene, but sparingly soluble in light petroleum.

If: D was recrystallized from benzene; it was difficultly soluble in cold alcohol and cold benzene.

IIa: R was washed with light petroleum (*ca.* 40 ml.) and then with hot ethyl alcohol (*ca.* 10 ml.) and the solid so obtained was crystallized from a mixture of benzene and light petroleum.

IIb: D was recrystallized from xylene; it was sparingly soluble in cold benzene and alcohol, but soluble in hot benzene and xylene.

IIc: D was recrystallized from xylene; it was soluble in hot absolute ethyl alcohol, but sparingly soluble in cold light petroleum.

IId: D was recrystallized from xylene; it was insoluble in aqueous sodium hydroxide solution and did not give color with ferric chloride. It was difficultly soluble in cold benzene and alcohol, but soluble in hot xylene. The

photo-products (VIa-f), listed in Table III, separated during irradiation in crystalline form. They gave a violet color with concentrated sulfuric acid, were insoluble in cold aqueous sodium hydroxide, did not give color with ferric chloride and were difficultly soluble in cold alcohol and petroleum ether, but soluble in hot xylene.

**Action of Hydrochloric Acid on Ie.**—A solution of 0.2 g. of Ie in a mixture of 10 ml. of glacial acetic acid and 5 ml. of hydrochloric acid (d. 1.18) was refluxed for 40 minutes. The reaction mixture was cooled and the crystals so obtained were collected and proved to be unchanged Ie (m.p. and mixed m.p.) in an almost quantitative yield.

The above experiment was repeated, using 0.25 g. of Ie, 10 ml. of glacial acetic acid and 10 ml. of hydrochloric acid and the reaction mixture was refluxed for five hours.<sup>8</sup> It was filtered while hot and allowed to cool. The reaction mixture upon concentration gave colorless crystals (*ca.* 0.1 g.) identified as *p*-methoxybenzoic acid (m.p. and mixed m.p.).

The mother liquor was extracted several times with ether (*ca.* 80 ml.) and the ethereal layer was washed with cold,

(7) W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913).

(7a) Light petroleum is the fraction boiling at 40-60° and petroleum ether 60-80°; the boiling range of other fractions is specified.

(8) *Cf.* the greater stability of 4-cyano-1,2-(diphenylmethylene-dioxy)-naphthalene to acid hydrolysis (A. Schönberg, A. Mustafa W. I. Awad and G. E. M. Moussa, *This Journal*, **76**, 2273 (1954)).

dilute aqueous sodium carbonate solution, then with water, dried and evaporated. The oily residue was crystallized from water as colorless crystals (*ca.* 0.1 g.), and identified as 6-bromo-1,2-dihydroxynaphthalene (m.p. and mixed m.p. of its diacetate).<sup>9</sup> It gave a green color with aqueous sodium hydroxide and a violet color with aqueous ferric chloride solution.

**Action of Ethereal Diazomethane Solution on Ie.**—To a suspension of 0.5 g. of Ie in 50 ml. of dry ether was added an ethereal solution of diazomethane (prepared from 5 g. of nitrosomethylurea) and the reaction mixture was kept at 0° overnight and then treated with a fresh amount of diazomethane. During the reaction, the solid Ie went into solution and the reaction product separated out. It was collected and recrystallized from a mixture of benzene and light petroleum as colorless crystals, m.p. 151°. The monomethyl derivative of Ie gave a green color changing to violet when treated with concentrated sulfuric acid at 70°; it was insoluble in aqueous sodium hydroxide and did not give color with ferric chloride. The yield was 87%.

*Anal.* Calcd. for C<sub>15</sub>H<sub>15</sub>BrO<sub>4</sub>: C, 58.91; H, 3.88; Br, 20.67. Found: C, 58.58; H, 3.81; Br, 20.56.

**Hydrolysis of the Diazomethane Product.**—A mixture of 0.5 g. of the above product and 20 ml. of alcoholic potassium hydroxide solution (15%) was refluxed for 15 minutes. The reaction mixture was acidified with cold dilute hydrochloric acid, and extracted with ether. The ethereal layer was extracted with aqueous sodium carbonate solution, washed with water, dried and evaporated. The solid residue was crystallized from hot water as colorless crystals (*ca.* 0.12 g.), m.p. 104°. The monomethyl ether of 6-bromo-1,2-dihydroxynaphthalene dissolved in cold aqueous sodium hydroxide with a violet coloration and gave a green color changing to violet when treated with sulfuric acid.

*Anal.* Calcd. for C<sub>11</sub>H<sub>7</sub>BrO<sub>2</sub>: C, 52.17; H, 3.55; Br, 31.62; act. H, 0.39; -OCH<sub>3</sub>, 12.25. Found: C, 51.89; H, 3.51; Br, 31.33; act. H, 0.37; -OCH<sub>3</sub>, 11.96.

The carbonate extract, on acidification with cold dilute hydrochloric acid, gave colorless crystals (*ca.* 0.14 g.) which were identified as *p*-methoxybenzoic acid (m.p. and mixed m.p.).

**Preparation of 5,6-Diacetoxy-3-phenylbenzo[f]quinoxaline (VIIb).**—5,6-3-Phenylbenzo[f]quinoxaline-5,6-quinone (V) was prepared after Crippa<sup>10</sup> and obtained as orange-red crystals from glacial acetic acid, m.p. 250°. It gave a deep-red color with concentrated sulfuric acid.

*Anal.* Calcd. for C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.52; H, 3.49; N, 9.78. Found: C, 75.34; H, 3.32; N, 9.73.

One gram of V was readily reduced by phenylhydrazine to VIIa after the procedure described by Badger, Pearce and Pettit.<sup>11</sup> VIIa formed yellow crystals from ethyl alcohol, m.p. 217°. It dissolved readily in aqueous sodium hydroxide with a green color and gave a violet color with sulfuric acid. The yield was almost quantitative.

*Anal.* Calcd. for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: N, 9.72. Found: N, 9.65.

When 0.7 g. of VIIa was boiled with acetic anhydride<sup>11</sup> for a few minutes, then cooled, VIIb was obtained as yellow crystals (*ca.* 0.56 g.), m.p. 210°. VIIb crystallizes readily from acetic anhydride and was insoluble in aqueous sodium hydroxide.

(9) L. F. Fieser and J. L. Hartwell, *THIS JOURNAL*, **57**, 1484 (1935).

(10) G. B. Crippa, *Gazz. chim. ital.*, **59**, 330 (1929), gave m.p. 210° for the quinone.

(11) G. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 3204 (1951).

*Anal.* Calcd. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 70.96; H, 4.30; N, 7.52. Found: C, 70.81; H, 4.29; N, 7.34.

**Photochemical Dehydrogenation.** (a) **Thioxanthene 5,5-Dioxide (X) and Benzophenone.**—A solution of 1 g. of X<sup>12</sup> and 0.9 g. of benzophenone in 30 ml. of benzene, was exposed to sunlight for 20 days (May). The photo-product separated out during exposure as almost colorless crystals which were collected, washed with cold benzene (*ca.* 10 ml.) and recrystallized from xylene. The yield of 9,9'-bithioxanthene 5,5-dioxide (XIc) was *ca.* 82%; it did not melt up to 360° (turning brown at 300°).

*Anal.* Calcd. for C<sub>26</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>: C, 68.12; H, 3.93; S, 13.97. Found: C, 67.92; H, 4.10; S, 14.01.

It dissolved with difficulty in most organic solvents, but was soluble in hot xylene and nitrobenzene and gave an orange solution, acquiring deep green fluorescence when treated with concentrated sulfuric acid at 100°.

The benzene mother liquor was evaporated slowly at room temperature, and the yellow oily residue was triturated with 5 ml. of cold methyl alcohol turning into a solid mass. It was crystallized from hot absolute ethyl alcohol as colorless crystals, m.p. 187°; identified as benzopinacol (m.p. and mixed m.p.); yield 76%.

(b) **X and 10-Thioxanthene 5,5-Dioxide (VIIIId).**—The above experiment was repeated, using a mixture of 1 g. of X and 1.1 g. of VIIIId<sup>13</sup> dissolved in 25 ml. of benzene. The reaction mixture was exposed for 15 days (May); the solution acquired a yellow color after one day exposure. The crystalline photo-product that separated out during exposure was collected, washed with hot absolute ethyl alcohol (*ca.* 15 ml.) and recrystallized from xylene as almost colorless crystals which were identified as XIc. The yield was almost quantitative.

*Anal.* Calcd. for C<sub>26</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>: C, 68.12; H, 3.93; S, 13.97. Found: C, 67.76; H, 4.12; S, 13.77.

(c) **X and Xanthone (VIIIa).**—Similarly, XIc was obtained in almost quantitative yield when a solution of 1 g. of X and 0.9 g. of VIIIa in 25 ml. of benzene was exposed to sunlight for 20 days (May).

(d) **X and Anthraquinone.**—Exposure of a benzene solution of 1 g. of X and 0.9 g. of anthraquinone in 40 ml. of benzene to sunlight for 8 days (September) gave XIc in 78% yield.

(e) **VIIIId and Xanthene.**—A mixture of 1 g. of VIIIId and 0.8 g. of xanthene was dissolved in 25 ml. of benzene. The reaction mixture was exposed to sunlight for 30 days (June); the solution acquired yellow color after 5 days exposure. The crystals that separated during exposure were collected, washed with light petroleum (*ca.* 25 ml.) and crystallized from benzene as colorless crystals (*ca.* 0.41 g.), m.p. 201°; identified as 9,9'-bixanthene (m.p. and mixed m.p.).

(f) **VIIIId and Diphenylmethane.**—The above experiment was repeated, using a mixture of 1.4 g. of VIIIId and 1 g. of diphenylmethane dissolved in 35 ml. of benzene. The reaction mixture was exposed to sunlight for 20 days (July). The oily residue obtained after removal of benzene in a vacuum formed a semi-solid mass on cooling. It was washed with cold ethyl alcohol and crystallized from a mixture of benzene and light petroleum as colorless crystals (m.p. *ca.* 0.32 g.), m.p. 214°, identified as *sym*-tetraphenylethane (m.p. and mixed m.p.).

GIZA, CAIRO (EGYPT)

(12) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 361 (1952); H. Kloosterziel, M. H. Deinema and H. J. Backer, *ibid.*, **71**, 1231 (1952).

(13) M. Gomberg and E. C. Britton, *THIS JOURNAL*, **43**, 1296 (1921).