

sis and dissolves in the solution to be titrated. It is unlikely that any appreciable amount will dissolve, however.

After the preliminary pyrolyses the dropping funnel was charged with 126 g. (0.477 mole) of sulfone diacetate X and dropped through the column at a rate of 1 drop per 2 seconds. Due to excessive charring on the column, the column was replaced with a clean one after one-half of the diacetate had been pyrolyzed.

The pyrolysate was washed with four 20-ml. portions of water. Each fraction was titrated for acetic acid; a total value of 53% was obtained which is considered low since the fourth washing still contained a considerable amount of acid. A closer approximation would be 60–65%. The washings were combined and filtered to give 3 g. (4.2%) of a brown solid which was shown to be starting material X. Three recrystallizations from ethanol–ether gave a white solid, m.p. 89.5–92.5° (repeated recrystallizations did not narrow this range); saponification equivalent 130 (calculated 132); ebullioscopic molecular weight 277 (calculated 264); infrared spectrum of the solid in  $\text{CHCl}_3$  is identical to the spectrum of the liquid reported as the sulfone diacetate X. This was the first solid sample of X obtained.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{10}\text{O}_6\text{S}$ : C, 45.42; H, 6.07; S, 12.12. Found: C, 45.78; H, 6.15; S, 12.50.

After the aqueous washings were filtered they were extracted seven times with 50-ml. portions of ether. The combined ether washings and neutralized organic layer from pyrolysis were dried. Two fractions were isolated by distillation.

**Fraction I.**—The first fraction was fractionated through a 12-in. Holtzmann column to give 1 g. of yellow liquid, b.p. 79° (0.1–0.3 mm.);  $n_D^{20}$  1.4761;  $\lambda_{\text{Diox}}^{227-232}$   $\mu$  (no max. obtained<sup>12</sup>);  $\nu(\text{cm}^{-1})$   $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  890, conj. 1605,  $\text{C}=\text{O}$  1740, 1237, 1039 (probable),  $\text{C}-\text{CH}_3$  1367. The above data were consistent with 2-methyl-3-acetoxymethyl-1,3-butadiene (XVI). An analytically pure sample was not obtained.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_2$ : C, 68.57; H, 8.57. Found: C, 71.73; H, 9.11.

(12) R. B. Woodward, *THIS JOURNAL*, **63**, 1123 (1941); **64**, 76 (1942).

**Fraction II.**—This material was twice fractionated through a 12-in. Holtzmann column to give an orange liquid, b.p. 132–135° (0.04 mm.);  $n_D^{21}$  1.500;  $\lambda_{\text{max}}^{\text{Diox}}$  211  $\mu$  ( $\log \epsilon$  3.005<sup>13</sup>);  $\nu(\text{cm}^{-1})$   $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  1655, 916,  $\text{C}=\text{O}$  1735, 1240, 1040 (probable),  $\text{SO}_2$  1313, 1130,  $\text{C}-\text{CH}_3$  1369. The data are consistent with 3-methylene-4-acetoxymethylthiophane sulfone (XIV). The yield after the first fractionation was 3 g. (3.1%).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_4\text{S}$ : C, 47.06; H, 5.88; S, 15.67. Found: C, 47.44; H, 6.01; S, 15.60.

**Pyrolysis of Tetraethyl Thiophane-3,3,4,4-tetracarboxylate (IV).**—The procedure and apparatus for pyrolysis were identical to that previously described. An average drop rate of 1 drop per 1.5 seconds was used, and the column was heated to  $565 \pm 5^\circ$  during pyrolysis.

Through the Fenske column was dropped 20 g. (0.053 mole) of tetraester IV. The column was badly charred after pyrolysis and the pyrolysate was a dark brown liquid. The only product isolated was a brown solid which was recrystallized from benzene–acetone to give 0.2 g. (2.2%) of a white crystalline solid which analyzed for the thioanhydride XVII, m.p. 159–160°;  $\nu(\text{cm}^{-1})$  1727, 1687, 817 and 688.

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{O}_2\text{S}_2$ : C, 41.38; H, 3.45; S, 36.80. Found: C, 41.52; H, 3.49; S, 36.98.

**Acknowledgments.**—Microanalytical work was done by J. Nemeth, E. Fett, L. Chang and M. Benassi of the Microanalytical Laboratory of the University of Illinois; Clark Microanalytical Laboratory, Urbana, Illinois; and Micro-Tech Laboratory, Skokie, Illinois. Infrared spectra were run by J. Brader. Ultraviolet spectra were run by G. Meerman. Nuclear magnetic resonance spectrum and interpretation was done by A. Saika.

(13) H. P. Koch, *J. Chem. Soc.*, 387, 408 (1949).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

## Dimerization Reactions in Sunlight. IV.<sup>1</sup> Photodimerization of Thianaphthene-1,1-dioxide and its Substituted Derivatives and of 3-Benzylidene-6,7-benzophthalide

BY AHMED MUSTAFA AND SALAH MOHAMED ABDEL DAYEM ZAYED

RECEIVED JULY 23, 1956

Investigation of our previous finding that thianaphthene-1,1-dioxide and its 3-methyl derivative undergo photodimerization in sunlight now has been extended. 2-Methyl-, 2-bromo-, 5-methyl-, 6-methyl-, 7-methyl- and 7-chlorothianaphthene-1,1-dioxides similarly give high-melting crystalline dimers, which are considered to contain a central cyclobutane structure, as in IV or V. 3-Methoxy- and 5-methyl-3-acetoxithianaphthene-1,1-dioxides proved to be stable toward the action of sunlight under similar conditions. 3-Benzylidene-6,7-benzophthalide forms a photodimer analogous to those from arylidene phthalides. This dimer gave the monomer when heated.

(a) **Photodimerization of Thianaphthene-1,1-dioxide and its Substituted Derivatives.**—Recently it was shown<sup>1c</sup> that the 2,3-double bond in thianaphthene-1,1-dioxide (Ia) undergoes a photodimerization reaction, analogous to that of the similarly situated bond in indone derivatives, for example 2-methyl-3-phenylindone.<sup>2</sup> Thus when a benzene solution of Ia is exposed to sunlight for three days (July), it forms the difficultly soluble photodimer IVa or Va. While the work was in progress, Davies and James<sup>3</sup> reported similar re-

sults on exposure of Ia to sunlight for 20 days. The photodimer sublimes readily at 300° under reduced pressure, a fact which excludes the possibility that it could be regarded as a Diels–Alder dimerization adduct<sup>4</sup> II. Similar to that of Davies and James,<sup>3</sup> our photodimer is stable toward the action of potassium permanganate in boiling acetone and/or the action of lithium aluminum hydride in boiling benzene.

The rejection of the theoretically possible structures II and III,<sup>3</sup> analogy with the photodimers previously<sup>5</sup> reviewed and the formal analogy with

(1) For previous papers comp. (a) A. Mustafa, *Nature*, **166**, 108 (1950); (b) A. Mustafa and A. M. Islam, *J. Chem. Soc.*, 381 (1949); (c) A. Mustafa, *Nature*, **175**, 992 (1955).

(2) R. De Fazi, *Gazz. chim. ital.*, **54**, 58, 1000 (1924).

(3) W. Davies and F. C. James, *J. Chem. Soc.*, 314 (1955).

(4) F. G. Bordwell, W. H. McKellin and D. Babcock, *THIS JOURNAL*, **73**, 5566 (1951).

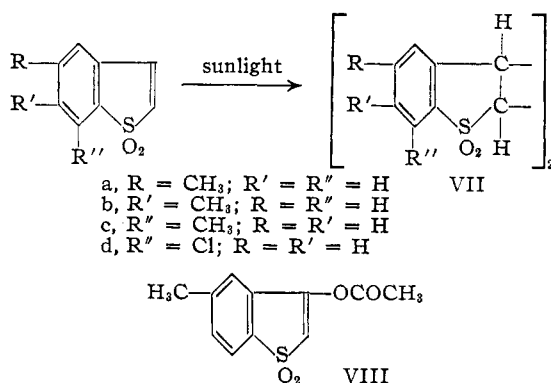
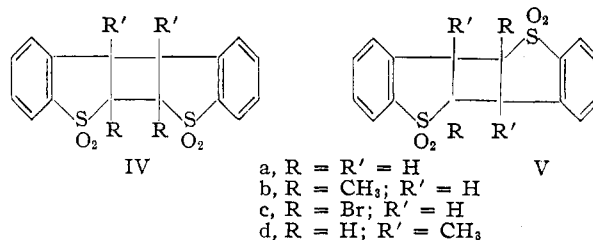
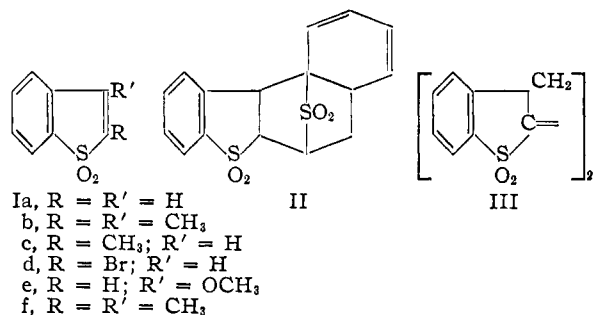
(5) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

2-methyl-3-phenylindone, make it likely that the single photodimer obtained from I contains a cyclobutane ring (IVa or Va).

We now have found that not only Ia and 3-methylbenzothianaphene-1,1-dioxide (Ib) dimerize readily in sunlight, but also 2-methyl- (Ic), 2-bromo- (Id), 5-methyl- (VIa), 6-methyl- (VIb), 7-methyl- (VIc), and 7-chlorothianaphthene-1,1-dioxides (VIId) give high melting crystalline photodimers IVb or Vb, IVc or Vc, VIIa, VIIb, VIIc, VIId, respectively. The stability of the photodimers to permanganate solution at room temperature indicates that they contain no exocyclic methylene group (*cf.* III).

2,3-Dimethylthianaphthen-1,1-dioxide (If) proved to be stable when its benzene solution was exposed to sunlight under similar experimental conditions. This may be compared with the stability of 2,3-dimethyl-1,4-naphthoquinone<sup>6</sup> toward the action of sunlight and the ready photodimerization of 3-methyl-1,4-naphthoquinone.

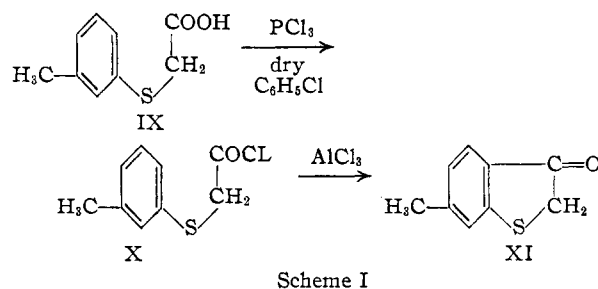
Other thianaphthen-1,1-dioxide derivatives which have been found to be stable toward the action of sunlight are 3-methoxythianaphthen-1,1-dioxide (Ie) and 5-methyl-3-acetoxythianaphthen-1,1-dioxide (VIII). The stability of Ie and VIII toward photodimerization may be attributed to their slight solubility in benzene.



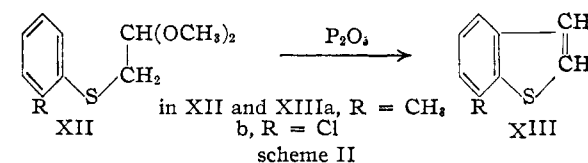
Similar to the finding of Davies and James,<sup>3</sup> we have also found that irradiation of phenyl vinyl sulfone having the SO<sub>2</sub>CH=CH— group outside a ring gives, besides the recovered material, some unidentified oil which is under further investigation.

The preparation of the thianaphthene-1,1-dioxide and its derivatives was carried out by known methods, with the following modifications.

Tarbell and Fukushima<sup>7</sup> have reviewed different methods of preparation of 6-methyl-3(2H)thianaphthenone (XI). The cyclization of *m*-thiocresoxyacetic acid (IX) *via* corresponding acid chloride X, by the action of anhydrous aluminum chloride gave a 14% yield of XI. We now have found that when phosphorus trichloride is allowed to react with a solution of *m*-thiocresoxyacetic acid in dry chlorobenzene medium at 100° for two hours followed by treatment with 1.1 moles of anhydrous aluminum chloride, XI is obtained in 69% yield. This procedure has been successfully used by Dalglish and Mann<sup>8</sup> for the preparation of the 5-methyl and 7-methyl isomers (*cf.* scheme I).



7-Methylthianaphthene (XIIIa) and 7-chlorothianaphthene (XIIIb) have been prepared recently<sup>9</sup> by the cyclization of *o*-tolyl-2,2-dimethoxy ethyl sulfide (XIIa) and *o*-chlorophenyl 2,2-dimethoxyethyl sulfide (XIIb) with a mixture of phosphorus pentoxide and phosphoric acid in an optimum yield of 37% (compare scheme II).



We now have prepared XIIIa and XIIIb in about 50% yield by the reduction of 7-methyl- and 7-chloro-3(2H)thianaphthenones which are prepared by the cyclization of the acid chloride of *o*-tolyl and *o*-chlorophenyl thioglycolic acids, respectively, with aluminum chloride after the procedure described by Dalglish and Mann.<sup>8</sup>

The new 2-methyl- (Ic), 6-methyl- (VIb), 7-chlorothianaphthene-1,1-dioxides (VIId) and 5-methyl-3-acetoxythianaphthene-1,1-dioxide (VIII) have been prepared by the oxidation of their corresponding thianaphthene derivatives by 30% hydrogen peroxide in the presence of a mixture of glacial acetic acid and acetic anhydride.

(7) D. S. Tarbell and D. K. Fukushima, *THIS JOURNAL*, **68**, 1456 (1946).

(8) C. E. Dalglish and F. G. Mann, *J. Chem. Soc.*, 893 (1945).

(9) A. V. Sunthakar and B. D. Tilak, *Proc. Indian Acad. Sci.*, **32A**, 396 (1950).

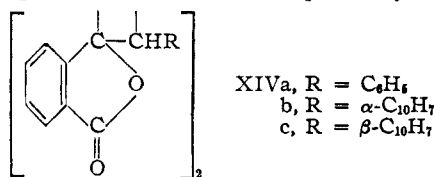
(6) A. Schöenberg, A. Mustafa and M. Z. Barakat, *J. Chem. Soc.*, 2196 (1948).

TABLE I  
PHOTODIMERS

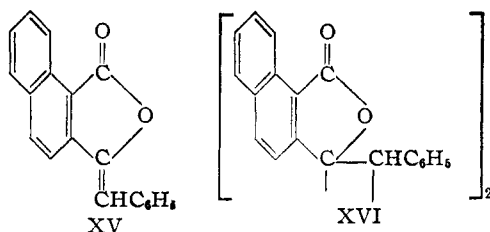
Monomer wt., g.	Benzene, ml.	Time of irradiation, days	Dimer yield,	M.p., °C.	Solvent for crystn.	Formula	Carbon, %		Hydrogen, %		Sulfur, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
Ia <sup>a</sup> (1)	30	3 (July)	IVa or Va, 78	333	A	C <sub>16</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>	57.83	57.67	3.61	3.60	19.27	19.10
Ib <sup>b</sup> (0.8)	25	5 (Jan.)	IVd or Vd, 82	312	B	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	60.00	59.73	4.44	4.31	17.77	17.70
Ic <sup>c</sup> (0.6)	20	4 (Feb.)	IVb or Vb, 79	314	C	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	60.00	59.82	4.44	4.40	17.77	17.40
Id <sup>d</sup> (0.7)	35	4 (Jan.)	IVc or Vc, 76	Above 360	D	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>2</sub> <sup>h</sup>	39.18	38.97	2.04	2.10	13.06	12.90
VIa <sup>e</sup> (0.8)	25	3 (Sept.)	VIIa, 87	300	C	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	60.00	59.78	4.44	4.32	17.77	17.46
VIIb (0.5)	20	4 (Jan.)	VIIb, 74	325	D	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	60.00	60.01	4.44	4.34	17.77	17.61
VIIc (0.7)	30	2 (Apr.)	VIIc, 77	296	C	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub>	60.00	59.91	4.44	4.28	17.77	17.61
VId (0.7)	30	1 (Apr.)	VIIId, <sup>f</sup> 92	Above 360	D	C <sub>18</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	47.88	47.66	2.49	2.41	15.96	15.60
XV <sup>d</sup> (1)	40	14 (Nov.)	XVI, 72	252 <sup>g</sup>	E	C <sub>18</sub> H <sub>24</sub> O <sub>4</sub>	81.08	81.10	4.50	4.38		

<sup>a</sup> F. G. Bordwell, B. B. Lampert and W. H. McKellin, *THIS JOURNAL*, **71**, 1704 (1949). <sup>b</sup> E. G. G. Werner, *Rec. trav. chim.*, **68**, 520 (1949). <sup>c</sup> D. S. Tarbell, D. K. Fukushima and H. Dam, *THIS JOURNAL*, **67**, 1643 (1945). <sup>d</sup> C. F. Koelsch, *ibid.*, **58**, 1328 (1936). <sup>e</sup> All photodimers melt with decomposition. <sup>f</sup> When refluxed with zinc dust and acetic acid for three hours, it gave a product which crystallized from acetic acid in colorless crystals, m.p. 328°, and which is under further investigation. <sup>g</sup> The dimer was obtained after evaporation of the reaction mixture. <sup>h</sup> Br: calcd. 32.65, found 32.21. <sup>i</sup> Cl: calcd. 17.71, found 17.40. <sup>j</sup> A, ethylene glycol; B, acetic acid; C, xylene; D, nitrobenzene; E, benzene.

(b) Photodimerization of 3-Benzylidene-6,7-benzophthalide.—Recently<sup>8,10</sup> it has been pointed out that arylidene phthalides, *e. g.*, benzylidene-,  $\alpha$ -naphthylidene- and  $\beta$ -naphthylidenephthalides undergo photodimerization when their benzene solutions are exposed to sunlight, yielding the colorless photodimers XIVa-c, respectively.



We now have found that 3-benzylidene-6,7-benzophthalide (XV) dimerizes when its benzene solution is exposed to sunlight to give the photodimer XVI; when heated, the product regenerates the monomer.



### Experimental

**6-Methyl-3(2H)-thianaphthenone (XI).**—A solution of 18 g. of *m*-thiocresoxyacetic acid<sup>7</sup> (IX) in 100 ml. of dry chlorobenzene was treated portionwise with 11.5 ml. of phosphorus trichloride. The vigorously stirred reaction mixture was heated (steam-bath) for 2 hours. It was then cooled, and 14.7 g. of anhydrous aluminum chloride was added gradually; when the reaction subsided the mixture was heated on a boiling water-bath for 1.5 hours. The cooled reaction mixture was poured into crushed ice and then subjected to steam distillation. After the chlorobenzene had passed over, the steam was replaced by superheated steam and XI was then collected by filtration of the cooled distillate; yield 11 g. of colorless crystals, m.p. 88–90°. Without further purification, it was found pure enough to proceed to the following step.

**6-Methylthianaphthene.**—Reduction of 5 g. of XI after the procedure described by Tarbell and Fukushima<sup>7</sup> gave 2 g. of 6-methylthianaphthene.

**7-Methyl- (XIIIa) and 7-Chlorothianaphthene (XIIIb).**—These were prepared by reduction of 5 g. of each of 7-methyl-

and of 7-chloro-3(2H)thianaphthenone, using the same procedure for the preparation of 6-methylthianaphthene, and were obtained in *ca.* 50% yield in each case.

**Preparation of 2-Methyl- (Ic), 6-Methyl- (VIIb), 7-Methyl- (VIc) and 7-Chlorothianaphthene-1,1-dioxides (VId).**—Two grams of each of the corresponding thianaphthene derivatives were treated with 15 ml. of glacial acetic acid, 5 ml. of acetic anhydride and 8 ml. of hydrogen peroxide (30%). The reaction mixture was heated (steam-bath) for one hour; after cooling it was poured into crushed ice and kept overnight. The colorless crystals that separated were filtered and crystallized. The yield was about 1.2 g. in each case.

Ic formed colorless crystals from water or dilute alcohol, m.p. 102°. It was readily soluble in cold benzene and gave no color with cold concentrated sulfuric acid. *Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>SO<sub>2</sub>: C, 60.00; H, 4.44; S, 17.77. Found: C, 59.69; H, 4.28; S, 17.60.

VIIb gave colorless crystals from water, m.p. 135°; it dissolved readily in ethyl alcohol, acetic acid and cold benzene, but was sparingly soluble in petroleum ether (b.p. 40–60°). *Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>SO<sub>2</sub>: C, 60.00; H, 4.44; S, 17.77. Found: C, 59.91; H, 4.34; S, 17.39.

VId crystallized readily from dilute acetic acid in colorless crystals, m.p. 227°. It was readily soluble in benzene, sparingly soluble in cold ethyl alcohol. *Anal.* Calcd. for C<sub>9</sub>H<sub>5</sub>SO<sub>2</sub>Cl: C, 47.88; H, 2.49; S, 15.96; Cl, 17.71. Found: C, 47.66; H, 2.41; S, 15.60; Cl, 17.40.

VIc was prepared after the above-mentioned procedure as colorless crystals from water or dilute acetic acid, m.p. 79–80°. It was readily soluble in cold benzene and gave no color with concentrated sulfuric acid. *Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>SO<sub>2</sub>: C, 60.00; H, 4.44; S, 17.77. Found: C, 59.76; H, 4.28; S, 17.61.

**5-Methyl-3-acetoxythianaphthene-1,1-dioxide (VIII).**—5-Methyl-3-acetoxythianaphthene was prepared after the procedure described by v. Auwers and Thies<sup>12</sup> for the preparation of 3-acetoxythianaphthene.

The thianaphthene derivative, without further purification, was oxidized to the sulfone after the procedure described above. VIII formed colorless crystals from benzene, m.p. 200°. It was soluble in hot benzene, hot xylene, but sparingly soluble in ethyl alcohol and light petroleum; it gave yellow color with sulfuric acid. *Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>S: C, 55.46; H, 4.20. Found: C, 55.14; H, 4.17.

**Photodimerization Experiments. General Remarks.**—The photochemical experiments were carried out in Pyrex glass Schlenk tubes,<sup>13</sup> and the air then was displaced by dry carbon dioxide and the tube sealed by fusion.

The benzene was thiophene free (Kahlbaum) and dried over sodium. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

The properties of the colorless photodimers that separated out from the reaction mixtures during irradiation are given in Table I.

(11) A. V. Sunthakar and B. D. Tilak (ref. 9) gave m.p. 77° for VIc.

(12) K. v. Auwers and W. Thies, *Ber.*, **53**, 2291 (1920).

(13) W. Schlenk and A. Thal, *ibid.*, **46**, 2840 (1913).

(10) Cf. A. Schönberg and co-workers, *J. Chem. Soc.*, 374 (1950).

**Thermal Decomposition of XVI.**—The photodimer was heated under vacuum at 300° (bath) in a Pyrex test-tube for one hour. The oily drops of XV (m.p. and mixed m.p.) which accumulated in the upper part of the reaction vessel solidified after being allowed to cool in a vacuum.

**Behavior of If, Ie and Ig toward the Action of Sunlight.**—A solution of 1 g. of 2,3-dimethylthianaphthene-1,1-dioxide (If) in 30 ml. of dry benzene was exposed to sunlight for 15 days (November). When the reaction mixture was evaporated, it was recovered in an almost quantitative yield.

Similar results were obtained when a suspension of Ie and

of VIII in 40 ml. of dry benzene each was exposed to sunlight for 15 days (November).

The exposure of a solution of 1 g. of phenyl vinyl sulfone in 30 ml. of benzene for 7 days (January) gave, after evaporation, an oily residue which upon washing with petroleum ether (60 ml., b.p. 60–80°) gave a colorless solid, identified as unchanged material. The petroleum ether washings gave upon evaporation an oily substance which is under further investigation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## Bromination Studies with 5-Hydroxybenzothiophene

By M. MARTIN-SMITH<sup>1</sup> AND MARSHALL GATES

RECEIVED JUNE 11, 1956

An investigation of the products formed by the action of successive molar quantities of bromine on 5-hydroxybenzothiophene in acetic acid was undertaken. Once both the 4- and 6-positions have undergone substitution, the nature of the product of further bromination depends on the presence or absence of sodium acetate in the reaction mixture.

Recently<sup>2,3</sup> it was shown that the product resulting from the action of two moles of bromine on 5-hydroxybenzothiophene in acetic acid in the presence of sodium acetate was not the 3,4-dibromo compound as postulated by earlier workers,<sup>4</sup> and this substance was reassigned the structure 4,6-dibromo-5-hydroxybenzothiophene.<sup>3</sup> Final proof that this assignment is correct has now been obtained by the decarboxylation of 4,6-dibromo-5-methoxybenzothiophene-2-carboxylic acid to 4,6-dibromo-5-methoxybenzothiophene, which was identical with the product resulting from the action of diazomethane on the dibromo compound, which consequently must be 4,6-dibromo-5-hydroxybenzothiophene (Chart I).

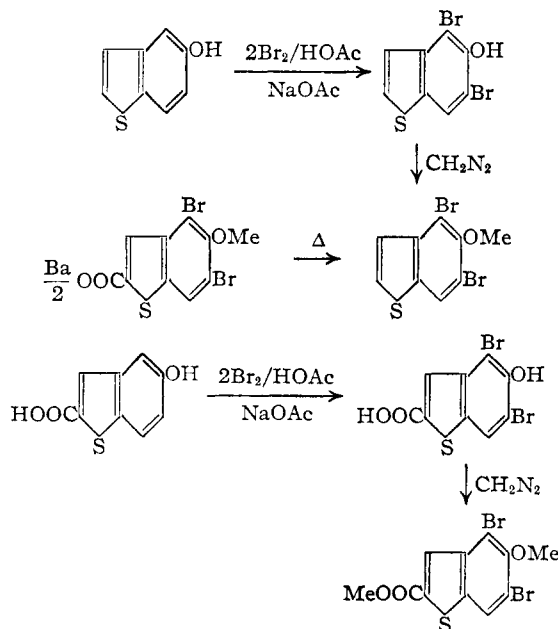


CHART I

Further treatment of 4,6-dibromo-5-hydroxybenzothiophene with one mole of bromine in acetic acid led to either of two products, depending on whether or not sodium acetate was present. In the absence of acetate ion the uptake of bromine was slow, yielding a compound which proved to be 5-hydroxy-3,4,6-tribromobenzothiophene, as it was identical with a specimen prepared by the action of bromine on 3,4-dibromo-5-hydroxybenzothiophene<sup>2,3</sup> in acetic acid in the presence of sodium acetate. On the other hand, the uptake of bromine was instantaneous in the presence of acetate ion to yield 4,5-dihydro-5-keto-4,4,6-tribromobenzothiophene<sup>5</sup> (Chart II). This compound was readily reconverted to 4,6-dibromo-5-hydroxybenzothiophene

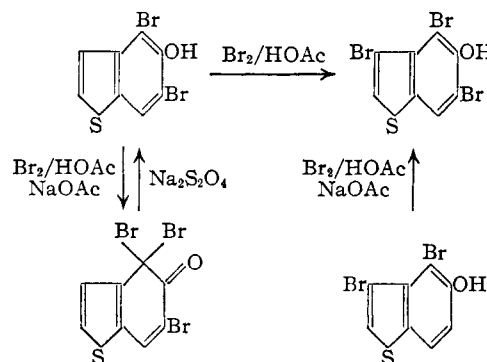


CHART II

by the action of sodium hydrosulfite in aqueous ethanol. On treatment with hydrobromic acid in acetic acid it gave a mixture of 4,6-dibromo-5-hydroxybenzothiophene and 5-hydroxy-3,4,6-tribromobenzothiophene.

Similarly, 5-hydroxy-3,4,6-tribromobenzothiophene on further treatment with one mole of bromine in acetic acid gave 5-hydroxy-2,3,4,6-tetrabromobenzothiophene in the absence of acetate ion with slow uptake of bromine. In the presence of acetate ion the product was 4,5-dihydro-5-keto-3,4,4,6-tetrabromobenzothiophene (Chart III).

(5) The infrared spectrum of this compound showed a strong carbonyl absorption at 6.03  $\mu$  and no absorption in the 3- $\mu$  region in accordance with the assigned structure.

(1) Fulbright Exchange Student 1951–1954; Beaunit Mills Fellow 1953–1954.

(2) F. G. Bordwell and H. Stange, *This Journal*, **77**, 5939 (1955).

(3) M. Martin-Smith and M. Gates, *ibid.*, **78**, 5351 (1956).

(4) K. Fries, H. Heering, K. Hemmecke and G. Siebert, *Ann.*, **527**, 83 (1936).