TABLE V

CONDITIONS[a] USED IN THE PYROLYSES OF BENZOXAZOLE-2-THIONE (3) AND RESULTS

Quantity, g	Temp, °C	3, % recovd	10, %	9, %	12, %	13, %	14, %	11, %	15, %	5, %	Total, %
1.854	850	59.9	1.3	0.2	2.0	0.9	1.0	8.6	0.9	0	74.8
1.620	900	33.9	1.3	1.3	4.1	3.6	4.1	24.1	4.4	0	76.8
1.603	950	14.2	1.5	2.0	5.1	6.2	7.4	27.3	11.1	0	74.8
1.603	1000	0	1.3	3.2	3.2	12.3	14.9	37.7	6.7	2.0	81.3
1.914[b]	1000	0	1.2	1.7	1.8	8.2	12.8	24.3	0	0	50.0
1.769[c]	1050	0	3.6	4.7	5.2	0	0	55.7	0	0	69.2

[a] A N_2 flow rate of 0.20–0.22 l./min was used and a system pressure of 1–4 Torr was maintained. [b] CH_3OH was used as a trapping agent following method B. [c] CH_3OH was used as a trapping agent following method A.

TABLE VI

CONDITIONS[a] USED FOR THE PYROLYSES OF 10 AND RESULTS

Quantity, g	Temp, °C	10, % recovd	11, %	12, %	Total, %
1.960	900	4.0	81.6	0	85.6
1.728	1000	2.8	55.0	1.6	59.4

[a] A N_2 flow rate of 0.25 l./min and a system pressure of 1–2 Torr were used.

TABLE VII

CONDITIONS[a] USED IN THE PYROLYSES OF 11 AND RESULTS

Quantity, g	Temp, °C	11, % recovd	5, %	12, %	Total, %
1.464	900	74.1	1.5	0	75.6
1.498	1000	58.5	3.6	6.1	68.2
1.807[b]	1000	88.8	2.1	0	90.9

[a] A N_2 flow rate of 0.22 l./min and a system pressure of 1–3 Torr were used. [b] CH_3OH was used as a trapping agent *via* method B.

were eluted with a mixture of solvents, *ca.* 300 ml, and then the volume was reduced to 20–30 ml under vacuum. Gas chromatographic analyses using the same columns and the same programming used in the pyrolyses of **3** were used.

Pyrolysis of 2-Cyanophenol (11).—The conditions used in the pyrolyses of 2-cyanophenol (**11**) and the results are given in Table VII. The glpc work-up was the same as that used in the study of the pyrolyses of **3**. In addition to **5** and **12**, gc/mass spectrum revealed a minor amount of a component with a molecular ion at *m/e* 91 which loses 27 mu, probably cyanocyclopentadiene (**7**). A minor amount of toluene was also detected by the LKB 9000.

Registry No.—**1**, 4464-58-8; **2**, 2080-59-3; **3**, 14955-23-8; **4**, 95-16-9; **6**, 51-17-2; **8**, 1885-29-6; **10**, 273-53-0; **11**, 611-20-1.

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Reaction of 1,1-Dichloro-2-phenylsulfonylcyclopropanes with Sodium Alkoxides[1]

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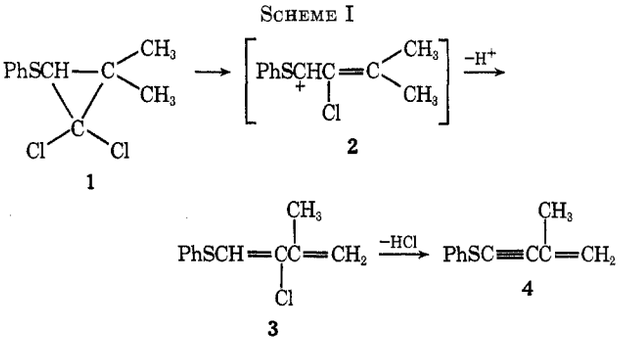
Reaction of 1,1-dichloro-2,2-dimethyl-3-phenylsulfonylcyclopropane (**5**) with sodium methoxide in methanol or sodium ethoxide in ethanol at room temperature gives excellent yields of the corresponding cyclopropyl ketals (**6a, 6b**); the corresponding thioketal (**7**) is formed with thiophenoxide. The cyclopropyl ketals are unstable in hot alcohols and are converted quantitatively into ortho esters (**8a, 8b**) or mixed ortho esters (**8c**). Reactions with two other analogous dihalocyclopropanes (**13**) are described; conversion to ortho esters proceeds generally and in high yield.

We have previously shown that 2,2-dichlorocyclopropyl phenyl sulfides of type **1** are unstable in hot alcohols, and in the presence of the strong base potassium *tert*-butoxide[3] give enynes (**4**) as illustrated for **1** in Scheme I. The accelerating effect of the sulfur atom is considered to be a driving force for this exocyclic ring opening reaction, since sulfur can stabilize the positive charge developed in the transition state (or intermediate **2**).

Replacement of the phenylmercapto group in **1** by the phenylsulfonyl group (as in **5**) would destabilize an intermediate ion corresponding to **2**, and, as expected, dihalo-2-phenylsulfonylcyclopropanes have been found to be comparatively thermally stable. These sulfones do, however, react readily with alkoxides

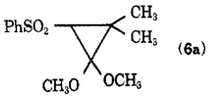
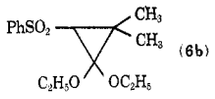
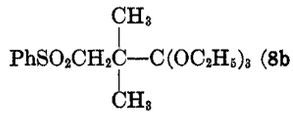
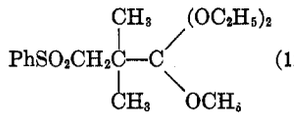
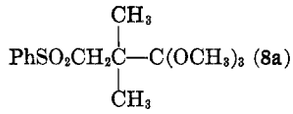
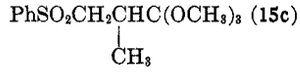
SCHEME I



(1) Supported in part by National Science Foundation Grant GP-11918.
(2) Paul M. Gross Chemical Laboratory, Duke University, Durham, N. C.
(3) W. E. Parham, S. Kajigaeshi, and S. H. Groen, *Bull. Chem. Soc. Jap.*, **45**, 509 (1972).

TABLE I

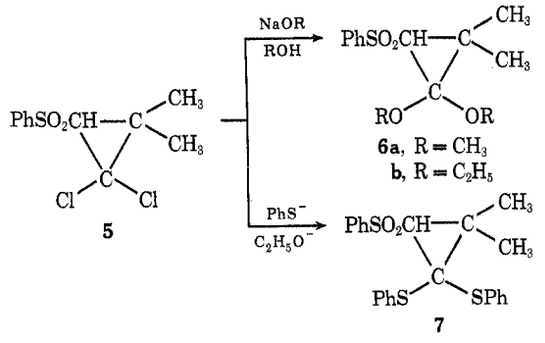
FORMATION OF 1,1-DIALKOXY-3-PHENYLSULFONYLCYCLOPROPANES AND ALKYL β-PHENYLSULFONYL ORTHOPROPIONATES[a]

No.	Sulfone	Sodium alkoxide (ROH)	Δ, °C (hr)	Product	Mp [bp (mm)], °C	Yield, % (isolated, pure)	Anal. Found (calcd) C, %	H, %	S, %	Formula
1	5	$NaOCH_3$ (CH_3OH)	32 (15) 65 (4)	 (6a)	70.5–72 [95–97 (0.04)]	93	57.57 (57.76)	6.73 (6.71)		$C_{13}H_{18}O_4S$
2	5	$NaOC_2H_5$ (C_2H_5OH)	32 (24)	 (6b)	86–87	92	60.63 (60.37)	7.62 (7.43)	10.45 (10.75)	$C_{15}H_{22}O_4S$
3	5	$NaOC_2H_5$ (C_2H_5OH)	78 (23)	6b 8b	86–87 50.5–52	~45 ~45				
4	6b	C_2H_5OH	78 (72)	 (8b)	50.5–52	71	59.42 (59.27)	8.05 (8.19)	9.07 (9.31)	$C_{17}H_{28}O_5S$
5	6b	CH_3OH	65 (72)	 (12)	49–50.5	71	58.22 (58.16)	8.01 (7.93)		$C_{16}H_{26}O_5S$
6	6a	CH_3OH	65 (72)	 (8a)	52–55	65	55.42 (55.61)	7.20 (7.33)	10.71 (10.60)	$C_{14}H_{22}O_5S$
7	13a	$NaOCH_3$ (CH_3OH)	65 (2)	$PhSO_2CH_2CH_2C(OCH_3)_3$ (15a)	Oil	90				$C_{12}H_{18}O_5S$
8	13a	$NaOC_2H_5$ (C_2H_5OH)	78 (4) 32 (6)	$PhSO_2CH_2CH_2C(OC_2H_5)_3$ (15b)	49.5–51.0	85 65	56.93 (56.94)	7.75 (7.65)		$C_{15}H_{24}O_5S$
9	13b	$NaOCH_3$ (CH_3OH)	65 (4)	 (15c)	48–49.5	86	53.36 (54.16)	6.77 (6.99)		$C_{13}H_{20}O_5S$

[a] The 1,1-dialkoxy-2-phenylsulfonylcyclopropanes and alkyl β-phenylsulfonylorthopropionates are converted to alkyl π-phenylsulfonylpropionates (**9**, **16**) by moisture in air.

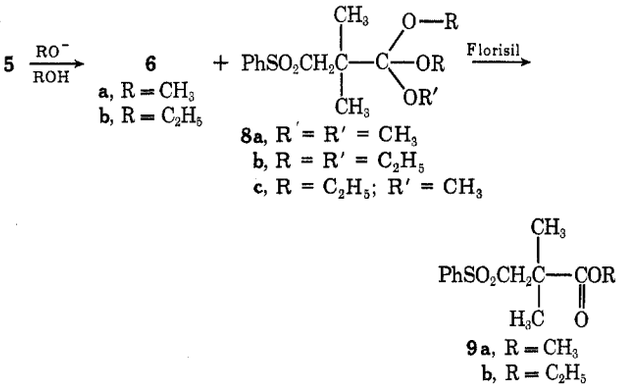
to give cyclopropyl ketals and/or ortho esters, a study which constitutes the subject of this report.

When **5** was treated with sodium methoxide in methanol either at room temperature (15 hr) or at the reflux temperature (4 hr), or with sodium ethoxide in ethanol at room temperature, the corresponding cyclopropyl ketals (**6a** and **6b**, respectively) were formed in



high yield (86–93%). These reactions are believed to occur by two successive processes, each of which involves elimination of hydrogen chloride to give the corresponding cyclopropene which subsequently adds alcohol to give product, a sequence of reactions for which there is ample precedent.[4] Treatment of **5** with thiophenol in ethanol containing more than 2 equiv of ethoxide gave the corresponding thioketal **7**, which was isolated in 100% yield. The thioketal **7** was quite stable and was recovered unchanged after prolonged treatment with hot aqueous sodium hydroxide, hot dilute hydrochloric acid, hot ethanol (17 days), and sodium ethoxide in boiling ethanol (67 hr).

When the reaction of **5** with ethoxide was carried out in boiling ethanol (23 hr), the product was a mixture of ketal **6b** and the ortho ester **8b** (~45% yield



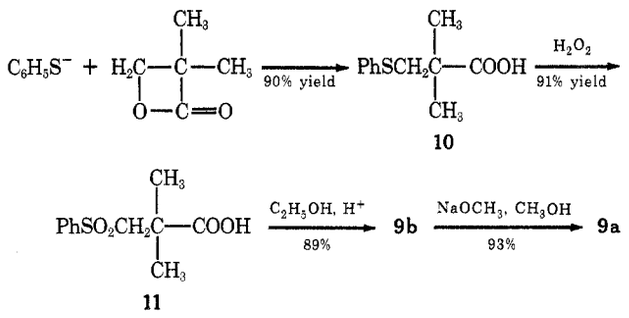
of each) which was resolved by recrystallization. This result suggested that the ketals **6** were unstable in hot alcohol, and this was shown to be the case. Prolonged treatment of **6b** with hot ethanol gave **8b**, and reaction of **6b** with hot methanol gave the mixed ortho ester **8c**. Similarly, reaction of **6a** with hot methanol gave **8a**. These conversions required reaction times of 48–72 hr and gave essentially quantitative yields of ortho esters (see Table I). While the exact mechanism

(4) (a) T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5425 (1967); (b) K. B. Baucom and G. B. Butler, *J. Org. Chem.*, **37**, 1730 (1972).

for the conversion of **6** to **8** is not known, the products are those expected by cleavage of a carbon–carbon bond in the cyclopropane ring in a manner consistent with the ability of the phenylsulfonyl group to stabilize a developing negative charge and the oxygen atoms of the ketal carbon atom to stabilize a developing positive charge (as represented in Scheme III). Conversion of **6** to **8** does not require acid catalysis, since **8** was formed from **6** in hot alcohol containing excess alkoxide.

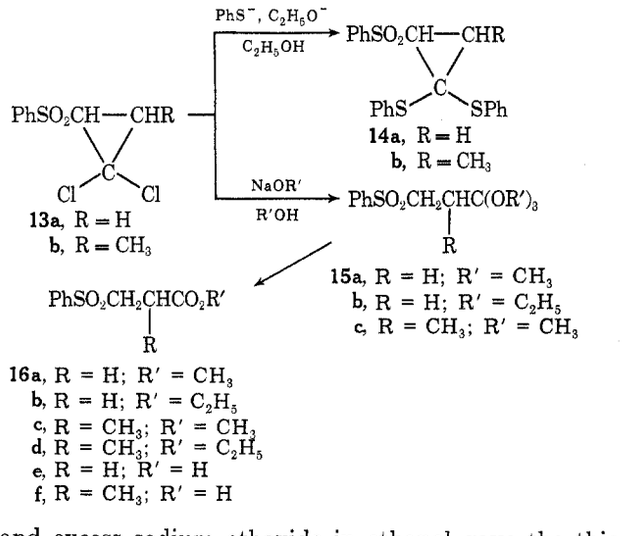
Both **6** and **8** were quite sensitive to acid or moisture in the air, and reaction of either with Florisil in benzene gave the esters **9** in essentially quantitative yield. Similar treatment of **8c** gave a mixture of **9a** and **9b** in the approximate ratio of 1:2. The esters **9** were readily hydrolyzed by alkali (or acid) to the corresponding acid **11**, and the structures of **9** and **11** were established by their independent synthesis as shown in Scheme II.

SCHEME II



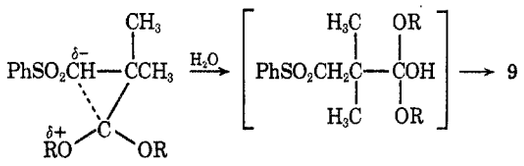
The ketals **6** react with water to give esters **9** and with hot aqueous sodium hydroxide to give the salt of **11** (100% yield). While these reactions could involve the intermediate cyclopropanone, followed by a Favorskii rearrangement, we believe that they involve ring opening by water to give **12** (Scheme III) in a manner analogous to that described above for methanol and ethanol.

Formation of ortho esters from 1,1-dichlorocyclopropanes appears to be general from cyclopropanes of type **13**. Reaction of **13a** and **13b** with thiophenol



and excess sodium ethoxide in ethanol gave the thioketals **14a** and **14b**, which were isolated in 88 and 74% yield, respectively. Reaction of **13a** and **13b** with

SCHEME III



sodium methoxide in boiling methanol (4 hr) gave only the ortho esters **15a** and **15c** (see Table I). Similarly, **13a** gave only the ortho ester **15b** when treated with sodium ethoxide in ethanol at room temperature. It is apparent that geminal alkyl substitution on carbon (as in **6**) increases the stability of the cyclopropyl ketal, and it is assumed that the basis of this stabilization of the cyclopropane by dialkyl substitution is steric in origin.[5]

The ortho esters **15a–c** were converted in high yields to esters **16a–c**[6] by action of acid, which were in turn hydrolyzed to the corresponding acids **16e**[7] and **16f**[8] by alkaline hydrolysis or by acid-catalyzed hydrolysis and ester interchange.

Experimental Section

1,1-Dichloro-2,2-dimethyl-3-phenylsulfonylcyclopropane (5) was obtained by oxidation of 2,2-dichloro-3,3-dimethylcyclopropyl phenyl sulfide[3] in acetic acid with hydrogen peroxide (80°, 3.5 hr): mp 102–103° (from ethanol); nmr (CCl_4) δ 1.46, 1.68 (two s, 6, CH_3), 2.58 (s, 1, CH), 7.40–8.00 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{12}Cl_2O_2S$: C, 47.32; H, 4.33; S, 11.48. Found: C, 47.33; H, 4.41; S, 11.36.

1,1-Dichloro-2-phenylsulfonylcyclopropane (13a) and 1,1-dichloro-2-methyl-3-phenylsulfonylcyclopropane (13b) were prepared as previously described.[9]

Reactions of 5 and 13 with Alkoxide in Alcohol.—A typical experimental procedure is as follows. Sodium metal (0.7 g, 0.03 g-atom) was dissolved in anhydrous ethyl alcohol (55 ml) in a dry nitrogen atmosphere. A solution of **13a** (2.5 g, 0.01 mol) in anhydrous ethanol (30 ml) was added slowly, and the resulting mixture was heated at the reflux temperature for 4 hr. The mixture was poured into water (200 ml) and then extracted with ether (200 ml) and dried ($MgSO_4$). Evaporation of the ether solution afforded white crystals of **15b**, mp 49.5–51.0° (from *n*-hexane).

Results of similar reactions including those of **6a** and **6b** with anhydrous alcohols are summarized in Table I.

The mass spectra of **15a** (75 eV) showed *m/e* (rel intensity) 243 (13), 141 (9), 105 (100), 101 (75), 87 (20), 77 (48), 59 (35), 55 (40); **15c** (30 eV) showed *m/e* (rel intensity) 288 (0.3, M^+), 257 (34), 141 (2), 115 (30), 105 (100), 101 (10), 77 (5), 59 (13). In general, intensities of molecular peaks of the ortho esters were very weak; the molecular peak of **15a** was not confirmed.

A.—Compound **6a** (from pentane) had nmr ($CDCl_3$) δ 1.20 and 1.58 (two s, 6, CH_3), 2.13 (s, 1, SO_2CH–), 3.12, 3.46 (two s, 6, OCH_3), 7.40–8.00 (m, 5, C_6H_5).

B.—Compound **6b** (from pentane) had nmr (CCl_4) δ 0.93–1.53 [m, 12, $-C(CH_3)_2$ and OCH_2CH_3], 2.13 (s, 1, $-SO_2CH$), 3.0–4.0 (m, 4, OCH_2), 7.54 and 7.92 (two m, 5, C_6H_5).

C.—**6b** and **8b** (17.32 g) were separated by fractional crystallization from pentane (300 ml); **6b** was less soluble.

D.—**8b** (from pentane) had nmr ($CDCl_3$) δ 1.13 (t, J = 7 Hz, OCH_2CH_3), 1.26 [s, $C(CH_3)_3$, area between 1.0 and 1.3, total

(5) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 196–198.

(6) For **16a** and **16c** see C. D. Hurd and L. L. Gershbein, *J. Amer. Chem. Soc.*, **69**, 2328 (1947). For **16b** see (a) O. Achmatowicz[2] and J. Michalski, *Rocz. Chem.*, **30**, 243 (1956); (b) P. Buckus, R. Stonite, and A. Buckiene, *Zh. Vses. Khim. Obshchest.*, **11** (4), 468 (1966).

(7) (a) B. Holmberg and E. Schjanberg, *Ark. Kemi. Mineral. Geol.*, A15, No. 20, 14 (1942) [(*Chem. Zentralbl.*, **I**, 388 (1943)]. (b) T. L. Gresham, *et al.*, *J. Amer. Chem. Soc.*, **74**, 1323 (1952).

(8) E. Larsson, *Trans. Chalmers Univ. Technol., Gothenburg*, **No. 35**, 3 (1944).

(9) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

weight 15], 3.37 (s, 2, SO_2CH_2), 3.60 (q, J = 7 Hz, 6, OCH_2CH_3), 7.59 and 7.59 (two m, 5, C_6H_5); nmr (CCl_4) shows shift of SO_2CH_2 to δ 3.14.

E.—**12** (from pentane) had nmr (CCl_4) δ 1.15 (t, J = 7 Hz, OCH_2CH_3), 1.25 [s, $C(CH_3)_3$, area 1.0–1.3, weight 12], 3.15 (s, 2, SO_2CH_2), 3.32 (s, 3, OCH_3), 3.63 (q, J = 7 Hz, 4, OCH_2CH_3), 7.55 and 7.90 (two m, 5, C_6H_5).

F.—**8a** (from pentane) had nmr (CCl_4) δ 1.23 [s, 6, $\cdot C(CH_3)_2$], 3.07 (s, 2, SO_2CH_2), 3.32 (s, 9, OCH_3), 7.48–7.83 (two m, 5, C_6H_5).

G.—**15a** was an oil ($n^{22}D$ 1.504) which decomposed on distillation. While satisfactory C and H analyses were not obtained, the spectra (ir, nmr, and mass) were consistent with assigned structure; nmr (CCl_4) δ 1.96–2.12 (m, 2, CH_2C), 2.92–3.06 (m, 2, SO_2CH_2), 3.10 (s, 9, OCH_3), 7.36–7.90 (m, 5, C_6H_5).

H.—**15b** (from nonane) had nmr ($CDCl_3$) δ 1.16 (t, J = 7 Hz, 9, OCH_2CH_3), 2.08–2.26 (m, 2, $-CH_2C$), 3.10–3.28 (m, 2, SO_2CH_2), 3.46 (q, J = 7 Hz, 6, OCH_2CH_3), 7.50–8.00 (m, 5, C_6H_5).

I.—**15c** (from nonane) had nmr (CCl_4) δ 1.10 (d, J = 6 Hz, 3, CH_3), 2.40–2.90 (m, 2, CH_2), 3.10–3.40 (m, 1, $-CH$), 3.18 (s, 9, OCH_3), 7.40–7.90 (m, 5, C_6H_5).

β-Phenylmercaptopivalic Acid (10).—Thiophenol (44.0 g, 0.4 mol) was added to a solution of potassium hydroxide (16.0 g, 0.29 mol) in ethanol (100 ml). The resulting solution was cooled (0°) and a solution of pivalolactone[10] (20.0 g, 0.2 mol) in dioxane (50 ml) was added dropwise (vigorous stirring under nitrogen). The mixture was maintained at 40° during the addition and the resulting solution was heated at 50° for 30 min. The resulting mixture was concentrated (until solid formed) and the mixture was dissolved in aqueous sodium bicarbonate (5%, 300 ml) and extracted with ether (300 ml total). Acidification of the alkaline solution gave **10** (37.8 g, 90% yield): mp 116–117°; nmr ($CDCl_3$) δ 1.30 [s, 6, $C(CH_3)_2$], 3.18 (s, 2, CH_2), 7.07–7.57 (m, 5, C_6H_5), 11.7 (br s, 1, COOH).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.68; H, 6.67.

β-Phenylsulfonylpivalic acid (11) was prepared (90% yield) by oxidation of **10** with hydrogen peroxide in acetic acid (80°, 4 hr): mp 147–148°; nmr ($CDCl_3$) δ 1.48 [s, 6, $C(CH_3)_2$], 3.52 (s, 2, CH_2), 7.63–7.97 (m, 5, C_6H_5), 10.1 (br s, 1, COOH).

Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; S, 13.23. Found: C, 54.26; H, 6.01; S, 13.42.

Ethyl β-phenylsulfonylpivatate (9b)w as prepared by esterification of **11** by a procedure adapted from that of Harrison and coworkers:[11] mp 56–57° (from ethanol–water); 85% yield; nmr (CCl_4) δ 1.25 (t, J = 7 Hz, OCH_2CH_3), 1.35 [s, $C(CH_3)_2$, area between 1.1 and 1.4, weight 9), 3.40 (s, 2, SO_2CH_2), 4.08 (q, J = 7 Hz, 2, OCH_2CH_3), 7.53–7.90 (m, 5, C_6H_5).

Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71; S, 11.86. Found: C, 57.77; H, 6.51; S, 11.98.

Methyl β-Phenylsulfonylpivatate (9a).—Reaction of **9b** (1.9 mmol) with sodium methoxide (50 mmol) in methanol (25 ml) at 0° for 2 hr resulted in ester interchange to give **9a** (mp 94–96°, 93% yield): nmr ($CDCl_3$) δ 1.43 [s, 6, $C(CH_3)_2$], 3.50 (s, 2, SO_2CH_2), 3.70 (s, 3, OCH_3), 7.65–7.98 (m, 5, C_6H_5).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; S, 12.51. Found: C, 56.03; H, 6.03; S, 12.72.

1,1-Diphenylmercapto-2,2-dimethyl-3-phenylsulfonylcyclopropane (7).—Thiophenol (1.1 g, 10 mmol) was added to a solution of sodium ethoxide prepared from sodium (0.3 g, 13 mg-atoms) and absolute ethanol (25 ml). Dihalocyclopropane **5** (1.20 g, 4.3 mmol) was added and the mixture was stirred at 30° for 24 hr. The mixture was poured into water (25 ml) and the resulting mixture was extracted with chloroform (100 ml total) and washed with sodium hydroxide (10%, 15 ml) and then with water (25 ml). The extract was dried ($MgSO_4$) and concentrated to give nearly pure **7** (1.80 g, 98% yield): mp 138.5–140°; mp 139.5–141° from chloroform–hexane; nmr ($CDCl_3$) δ 1.70 and 1.88 [two s, 6, $-C(CH_3)_2-$], 2.95 (s, 1, SO_2CH-), 7.14 and 7.32 (two m, C_6H_5S-), 7.57 and 7.84 (two m, $C_6H_5SO_2-$, area between 7.1 and 8.0, weight 15).

Anal. Calcd for $C_{23}H_{22}O_2S_3$: C, 64.75; H, 5.20; S, 22.54. Found: C, 64.72; H, 5.10; S, 22.41.

1,1-Diphenylmercapto-2-phenylsulfonylcyclopropane (14a) was prepared from **13a** essentially as described above for **7**: mp 144–145.5° from chloroform–heptane; yield 100%; nmr ($CDCl_3$) δ 1.83–2.33 (AB portion of ABX, 2, $-CH_2-$), 3.17–3.42 (X portion of ABX, 1, SO_2CH), 7.24–8.00 (m, 15, C_6H_5-).

Anal. Calcd for $C_{21}H_{18}O_2S_3$: C, 63.28; H, 4.55; S, 24.13. Found: C, 63.09; H, 4.45; S, 24.00.

1,1-Diphenylmercapto-2-methyl-3-phenylsulfonylcyclopropane (14b) was prepared (74% yield, mp 94–96°) as described for **7**: mp 96.5–97.5° from chloroform–hexane; nmr ($CDCl_3$) δ 1.42–1.83 (d of d, 3, cis and trans CH_3), 2.04–2.68 (m, 1, $-CHCH_3$), 2.92–3.20 (d of d, 1, $-SO_2CH$, cis and trans), 7.17–8.00 (m, 15, aromatic H).

Anal. Calcd for $C_{22}H_{20}O_2S_3$: C, 64.04; H, 4.89; S, 23.31. Found: C, 64.03; H, 4.94; S, 23.54.

Conversion of 1,1-Dialkoxycyclopropanes and β-Phenylsulfonylorthopropionates to Alkyl β-Phenylsulfonylpropionates.—The cyclopropane ketals **6** and the ortho esters **8** and **15** were readily converted to β-phenylsulfonylpropionates (**9**, **16**) by action of hydronium ion or by treatment with Florisil. Typical experiments follow.

A.—A mixture of **8a** (0.27 g, 1 mmol), Florisil (2.5 g), and benzene (10 ml) was stirred at room temperature for 18 hr. The mixture was filtered (sintered-glass funnel), and the Florisil was washed with three 25-ml portions of chloroform. The combined organic solutions was dried ($MgSO_4$) and concentrated (rotary evaporator) to give essentially pure methyl β-phenylsulfonylpivalate (100% yield, mp 93–94°, mmp with material mp 94–96° was 93–94°).

B.—A mixture of **15a** (3.6 g, 0.013 mol), hydrochloric acid (3 ml, 12 N), and methyl alcohol (35 ml) was stirred for 19 hr at 25°. The solution was concentrated (rotary evaporator) and poured into water (200 ml) and then extracted with ether (200 ml). Evaporation of the dried ($MgSO_4$) ether extract gave **16a** (2.8 g, 94% yield, mp 74.5–75.5°): ir (Nujol) $\nu_{C=O}$ 1730 cm^{-1}; nmr ($CDCl_3$) δ 2.82 (t, J = 8 Hz, 2, CH_2CO), 3.48 (t, J = 8 Hz, 2, SO_2CH_2), 3.66 (s, 3, OCH_3), 7.52–8.00 (m, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30. Found: C, 52.42; H, 5.52.

A.—Reaction of **15b** (24 hr at 25°) gave **16b**: bp 143–144° (0.09 mm); 88% yield; ir (Nujol) $\nu_{C=O}$ 1725 cm^{-1}; nmr (CCl_4) δ 1.18 (t, J = 7 Hz, 3, CH_2CH_3), 2.62 (t, J = 8 Hz, 2, CH_2CO), 3.32 (t, J = 8 Hz, 2, SO_2CH_2), 4.00 (q, J = 7 Hz, 2, $-OCH_2CH_3$), 7.40–7.92 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 55.07; H, 5.73.

B.—Reaction of **15c** (1 hr at 25°) gave **16c**: mp 50–52°; 100% yield; ir (Nujol) $\nu_{C=O}$ 1720 cm^{-1}; nmr ($CDCl_3$) δ 1.35 (d, J = 6 Hz, 3, CH_3CH-), 2.80–3.30 (m, 2, CH_2), 3.60 (s, 3, OCH_3), 3.60–4.00 (m, 1, CH), 7.40–8.00 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.77; H, 6.14.

C.—Ester **16d** was obtained directly by reaction of **13b** with sodium ethoxide in ethanol (4 hr): mp 46–48° (94% yield); ir (Nujol) $\nu_{C=O}$ 1720 cm^{-1}; nmr (CCl_4) δ 1.00–1.40 (m, 6, CH_3CH_2 and CH_3CH), 2.60–3.10 (m, 2, SO_2CH_2), 3.36–3.68 (m, 1, CH), 3.97 (q, J = 7 Hz, 2, CH_2CH_3), 7.20–7.90 (m, 5, C_6H_5).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 55.70; H, 6.32.

Preparation of Acids 11, 16e, and 16f.—Cyclopropyl ketals (**6**), ortho esters (**8** and **15**), and alkyl β-phenylsulfonylpropionates (**9** and **16**) were readily converted to the corresponding acid by conventional acid- or base-catalyzed hydrolysis. Some typical examples follow.

A.—Acid **11** was isolated (a) by reaction of ketal **6b** in aqueous sodium hydroxide (100°, 4 hr) with subsequent acidification of the alkaline solution, 100% yield; (b) by reaction of ketal **6b** with hot 6 N hydrochloric acid (100°, 4 hr), yield 96%; (c) by alkaline hydrolysis of ortho ester **8b** (100°, 2 hr), 91% yield; (d) by alkaline hydrolysis of **9b** (100°, 2 hr), 86% yield; and (e) by reaction of **9b** with 6 N hydrochloric acid (100°, 2.5 hr, 96% yield.

B.—Reaction of alkyl β-phenylsulfonylpropionates with hydronium ion in alcohols at reflux gave a mixture of β-phenylsulfonylpropionic acids (**11**, **16e**, **16f**) and alkyl β-phenylpropionates formed by ester interchange.

A typical procedure is as follows. A mixture of the methyl ester **16a**, hydrochloric acid (3 ml, 12 N), and ethyl alcohol was heated at the reflux temperature for 4 hr, and was concentrated. There was obtained from the concentrate the ethyl ester **16b** (59% yield) and β-phenylsulfonylpropionic acid (40% yield), mp 123.5–124.5° (reported[7] mp 119–120°).

(10) Kindly supplied by Pioneering Division of the Textile Fibers Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

(11) H. R. Harrison, W. M. Haynes, P. Arthur, and E. J. Eisenbraun, see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 705.

Similar treatment of **16c** gave **16b** (60%) and α-methyl-β-phenylsulfonylpropionic acid (30% yield), mp 107–109° (reported[8] mp 113°).

Registry No.—**1**, 35347-56-9; **5**, 38434-93-4; **6a**, 38434-94-5; **6b**, 38434-95-6; **7**, 38434-96-7; **8a**, 38434-97-8; **8b**, 38434-98-9; **9a**, 38434-99-0; **9b**, 38435-00-6; **10**, 27943-35-7; **11**, 38435-02-8; **12**, 38435-03-9; **13a**, 38435-04-0; **13b**, 38435-05-1; **14a**, 38435-06-2; **14b**, 38435-07-3; **15a**, 38435-08-4; **15b**, 38435-09-5; **15c**, 38435-10-8; **16a**, 10154-72-0; **16b**, 10154-73-1; **16c**, 38435-13-1; **16d**, 38435-14-2; pivalolactone, 1955-45-9.

The Reactions of Bromothianaphthenes with Piperidine. A Reinvestigation[1]

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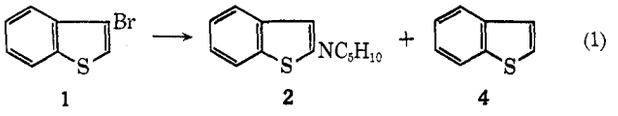
The reaction of 3-bromothianaphthene (**1**) with piperidine was reinvestigated and found to give primarily the normal (**3**) but also some of the cine-substitution product **2** which is also the only product from the reaction of 2-bromothianaphthene (**5**). The previously reported results can be rationalized by the effects of air, metals, and impure starting material on the reaction. 2,3-Dibromothianaphthene (**6**) also gives **2** under these conditions, probably *via* the bromamine **7** which was isolated under milder conditions, could be converted to **2** in high yield, and was synthesized from **2** *via* the iminium salt **9**. The diamine **8** was isolated in trace amounts from the reactions of **6** and **7** with piperidine. Possible mechanisms for some of these reactions are discussed.

Although five-membered hetarynes have been proposed as reaction intermediates for over 70 years,[2-4] closer examination[5,6] has invariably revealed these claims to be false.[7] One of those cases which has not been reexamined is the reaction of 3-bromothianaphthene (**1**) with piperidine, which, because it was reported[8] to give exclusively the cine (**2**) rather than the normal (**3**) substitution product (eq 1), might[4] involve



1 2 4 (1)

an elimination–addition mechanism *via* 2,3-dehydrothianaphthene. As part of the study of the reactions of halothiophenes[9-11] and halothianaphthenes[12-13] with bases a reexamination of the reactions of bromothianaphthenes with piperidine therefore was undertaken (Table I).

In agreement with the report of Brower and Amstutz[8] 2-bromothianaphthene (**5**) reacted cleanly with piperidine to give the normal substitution product **2** (expt 1). In contrast to this report (eq 1), however, the major product from 3-bromothianaphthene (**1**) was also that of normal substitution, 3-piperidinothianaphthene (**3**). A small amount of the 2 isomer (**2**) was found but thianaphthene (**4**) was not (expt 2). A possible explanation for this discrepancy may lie in differences in the reaction conditions and in the purity of the 3-bromothianaphthene (**1**). For example, when this reaction was repeated without precautions for removing air (expt 3), thianaphthene (**4**) was, as reported,[8] a minor product. Furthermore, when the starting material **1** was prepared, as reported,[8] by the direct bromination of thianaphthene,[14] substantial quantities of the 2 isomer (**2**) and thianaphthene (**4**) were present even after

TABLE I

REACTIONS OF BROMOTHIANAPHTHENES WITH PIPERIDINE

Expt	Reactant	Temp, °C (time, hr)	Products (yield, %)
1	**5**	220 (26)[a]	**2** (70)
2	**1**	250 (80)	**1** (73), **2** (2), **3** (15)
3	**1**	250 (80)[b]	**1** (60), **2** (5)
			3 (25), **4** (4)
4	**1**	250 (40)[a,c]	**1** (13), **2** (4)
			3 (67), **4** (9)
5	**1**	250 (40)[a,d]	**1** (70), **2** (1)
			3 (4), **4** (4)
6	**1**	250 (40)[a,e]	**1** (67), **2** (2)
			3 (15), **4** (4)
7	**6**	200 (15)	**2** (73), **8** (trace)
8	**6**	106 (60)[f]	**6** (71), **7** (5)
			2 (trace), **8** (trace)
9	**7**	180 (40)	**2** (83), **8** (trace)
10	**1** + **7** (1:1)	180 (40)	**2** (83),[g] **1** (70), **8** (trace)

[a] A Fischer and Porter aerosol compatibility tube with stainless steel valve was the reaction vessel. [b] No precautions for prior removal of air. [c] Valve top etched (see discussion). [d] 0.05 g of powdered Fe per 0.02 mol of **1**. [e] 0.05 g of $FeCl_3$ per 0.02 mol of **1**. [f] Reflux. [g] Based on added **7**.

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