[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Cyclopropyl Sulfones[1]

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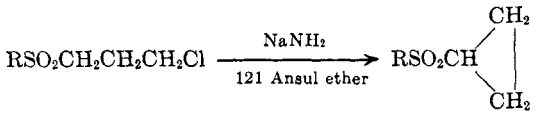
Several alkyl and aryl cyclopropyl sulfones have been prepared by γ-dehydrohalogenation and some of the chemical characteristics of the resulting products have been studied. Methyl cyclopropyl ketone was found to undergo cyclopropane ring opening when treated with sodium benzenethiolate.

Previous attempts[2] at preparing cyclopropyl sulfones have been unsuccessful except for the probable formation of 1,1-bis(ethylsulfonyl)cyclopropane[3] and the preparation of phenyl cyclopropyl sulfone.[4]

A common approach to cyclopropyl derivatives[5] involves a *gamma* elimination of hydrogen halide, where an α-hydrogen is activated by a carbonyl, nitrile, or other electron-withdrawing group. In view of the pseudo-acidity of the α-hydrogen of sulfones[6] this method was applied to γ-halopropyl sulfones, using sodium amide,[7] which had been found to be a suitable base for converting γ-chlorobutyronitrile into cyclopropyl cyanide.

Treatment of γ-halopropyl sulfones with sodium amide in 121 Ansul ether ($CH_3OCH_2CH_2OCH_3$) gave the desired cyclopropyl sulfones, where R is phenyl, *p*-tolyl,

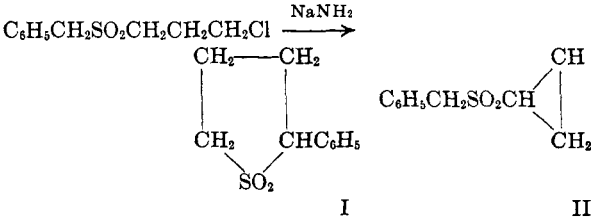


benzyl, methyl, and *t*-butyl. No phenyl cyclopropyl sulfone was obtained when diethyl ether was used as the medium. This preparation is similar to that recently reported by Zimmerman and Thyagarajan,[4] who used potassium *t*-butoxide in *t*-butyl alcohol.

The intermediate γ-hydroxypropyl sulfides, $RSCH_2CH_2CH_2OH$, were prepared by treating trimethylene chlorohydrin with sodium mercaptide, where R is phenyl, *p*-tolyl, benzyl, methyl, and *t*-butyl. Three different methods were used for the preparation of the γ-chloropropyl sulfides. Methyl and *t*-butyl γ-chloropropyl sulfides were prepared by the free radical addition of the corresponding thiol to allyl chloride. Phenyl and *p*-tolyl γ-chloropropyl sulfides were prepared by treating 1-bromo-3-chloropropane with the corresponding sodium thiophenoxide. The γ-chloropropyl sulfides, $RSCH_2CH_2CH_2Cl$, were also prepared by treating the corresponding alcohols with thionyl chloride in pyridine, where R is phenyl, *p*-tolyl, benzyl, methyl, and *t*-butyl. The γ-chloropropyl sulfones, $RSO_2CH_2CH_2CH_2Cl$, were prepared by oxidation of the corresponding sulfides with 30% hydrogen peroxide in glacial acetic acid.

The structures of the cyclopropyl sulfones were partially established by cleavage reactions. Phenyl and *p*-tolyl cyclopropyl sulfones were cleaved by lithium in methylamine,[8] to yield lithium cyclopropanesulfinate, which was converted into benzyl and methyl cyclopropyl sulfones upon treatment with benzyl chloride and methyl iodide, respectively. *t*-Butyl cyclopropyl sulfone was cleaved with sodium methoxide, by the method of Fenton and Ingold,[9] to give isobutylene (isolated as isobutylene bromide) and sodium cyclopropanesulfinate (isolated as benzyl cyclopropyl sulfone). Phenyl cyclopropyl sulfone was desulfurized by Raney nickel in refluxing ethanol to yield cyclopropane by the method of Mozingo and co-workers.[10]

2-Phenyltetrahydrothiophene-1-dioxide (I) was prepared to show its nonidentity with the compound described earlier as being benzyl cyclopropyl sulfone. This compound (I) might be expected to arise in the reaction of benzyl γ-chloropropyl sulfone with sodium amide; however, benzyl cyclopropyl sulfone (II) was the product isolated from the reaction mixture. The formation of a



(1) Abstract from the Ph.D. thesis of Lowell B. Lindy, Purdue University (1960).

(2) L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, **15**, 824 (1950).

(3) E. Rothstein, *J. Chem. Soc.*, 1560 (1940).

(4) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

(5) E. H. Rodd, *Chemistry of Carbon Compounds II*[A] Alicyclic Compounds, Elsevier Publishing Company, Amsterdam, 1953, p. 23–29.

(6) R. G. Pearson and R. L. Dillion, *J. Am. Chem Soc.*, **75**, 2439 (1953).

(7) J. B. Cloke, R. J. Anderson, J. Lachmamn, and G. E. Smith, *J. Am. Chem. Soc.*, **53**, 2791 (1931).

(8) W. E. Truce, D. N. Burdge, and D. P. Tate, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

(9) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 705 (1930).

(10) R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

cyclopropane ring in preference to a five-membered ring is not uncommon, as for example in the formation of methyl cyclopropyl ketone[11] from γ-chloropropyl methyl ketone. Compound I was prepared by treating 1-phenyl-1,4-dibromobutane with sodium sulfide (a general procedure for the preparation of tetrahydrothiophenes)[12] followed by oxidation with 30% hydrogen peroxide in glacial acetic acid.

The cyclopropyl sulfones did not react with potassium permanganate nor add bromine. The low resolution NMR spectrum of phenyl cyclopropyl sulfone (III) showed only three kinds of hydrogen atoms, aromatic, methylene, and tertiary.[4,13]

Ring opening reactions of cyclopropane derivatives have been discussed in terms of olefin-like properties. If the substituent on the ring is an electron-withdrawing group, the ring opening has been described[14] as being similar to additions to α,β-unsaturated ketones and to occur by base-catalyzed nucleophilic attack or by the attack of strong acids.

Base-catalyzed nucleophilic openings of cyclopropane rings are comparatively rare. Bone and Perkin[15] have shown that ethyl 1,1-cyclopropanedicarboxlate is attacked by ethyl sodiomalonate to give tetraethyl 1,1,4,4-butanetetracarboxylate. Kierstead, *et al.*[16] found that ethyl sodiomalonate reacted with ethyl 2-vinylcyclopropane-1,1-dicarboxylate to give ring opening similar to that described by Bone and Perkin.[15] We have encountered another example of this type. Methyl cyclopropyl ketone was found to react with sodium benzenethiolate to produce γ-(phenylmercapto)propyl methyl ketone (IV). The structure of ketone IV was established by its independent synthesis from sodium benzenethiolate and γ-chloropropyl methyl ketone, followed by a comparison of the corresponding sulfones. These three examples of base-catalyzed nucleophilic ring opening are somewhat reminiscent of the Michael addition.[17]

Strong acids have been shown by many workers to open cyclopropane rings which bear electron-withdrawing substituents.[14,18,19] A typical acid cyclopropane ring opening occurs on treating phenyl cyclopropyl ketone with refluxing hydrobromic acid to produce γ-bromopropyl phenyl ketone.[14]

In the attempt to open the ring in the cyclopropyl sulfones, phenyl cyclopropyl sulfone (III) was treated with refluxing 48% hydrobromic acid, refluxing 55% hydroiodic acid, 48% hydrobromic acid in glacial acetic acid,[18] the strong nucleophile, sodium benzenethiolate in refluxing ethanol, and the strong base, sodium *t*-butoxide in *t*-butanol. Sulfone III was recovered in each experiment in yields of 55%, 97%, 72%, 74%, and 89%, respectively. *p*-Tolyl cyclopropyl sulfone (V) was treated with 48% hydrobromic acid in glacial acetic acid and with sodium benzenethiolate in refluxing ethylene glycol; however, sulfone V was recovered in yields of 80% and 78%, respectively, and no other products were observed. The remarkable stability toward ring opening by strong acids as well as strong base and nucleophile, contrasts with the cleavage of 1,1-bis(ethylsulfonyl)cyclopropane to 1,1-bis(ethylsulfonyl)-3-iodopropane by hydroiodic acid.

Assuming ring opening of cyclopropanes containing strong electron-accepting substituents involves nucleophilic displacement on a ring carbon *beta* to the substituent in its original (basic solution) or conjugate acid (acid solution) form, then the difference in behavior of the sulfone and carbonyl analogs may be due to a lower tendency toward protonation on the part of the sulfone group[20] and a lower stabilizing effect by a sulfone group on an incipient α-carbanion.[6] Presumably, two sulfonyl substituents sufficiently stabilize[6] an incipient carbanion to permit ring opening.[3]

EXPERIMENTAL[21]

γ-Hydroxypropyl sulfides. These sulfides (Table I) were prepared by the method described by Kirner and Richter.[22] In a typical preparation, γ-hydroxypropyl *p*-tolyl sulfide was prepared by adding 48 g. (0.50 mole) of trimethylene-chlorohydrin to 62 g. (0.50 mole) of *p*-toluenethiol which was dissolved in 200 ml. of water containing 22 g. (0.55 mole) of sodium hydroxide. The mixture was refluxed for 2 hr. and the product was extracted with ether. Distillation yielded 84.6 g. (0.465 mole) of *p*-tolyl γ-hydroxypropyl sulfide (b.p. 160–161°/10 mm., n_D^{20} 1.5684, lit.[23] b.p. 145–146°/2 mm.; 92% yield).

(11) G. W. Cannon, R. C. Ellis and J. R. Leal, *Org. Syntheses*, **31**, 75 (1951).

(12) D. E. Wolf and K. Folkers, *Org. Reactions*, **VI**, 443 (1951).

(13) The authors wish to express their gratitude to Mr. William Baitinger of this laboratory for the interpretation of the NMR spectra.

(14) E. P. Kohler and J. B. Conant, *J. Am. Chem. Soc.*, **39**, 1404 (1917).

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(20) (a) I. R. C. McDonald, R. M. Milburn and P. W. Robertson, *J. Chem. Soc.*, 2836 (1950). (b) D. C. Wimer, *Anal. Chem.*, **30**, 2060 (1958). (c) R. G. Laughlin, *J. Org. Chem.*, **25**, 864 (1960).

(21) The microanalyses were by Dr. C. S. Yeh and Mrs. B. Groten of the Purdue Chemistry Microanalytical Laboratory. The infrared spectra were run by Miss M. Haley and Mrs. W. Dilling of the Purdue Chemistry Infrared Laboratory with a Perkin-Elmer, infrared spectrophotometer, model 21. All boiling and melting points are uncorrected.

(22) W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.*, **51**, 3409 (1929).

TABLE I

γ-HYDROXYPROPYL SULFIDES, $RSCH_2CH_2CH_2OH$

R	B.P.	n_D (Temp.)	Yield, %
Phenyl[a,f]	140–141°/3.8 mm.	1.5763 (21.2)	68
p-Tolyl[b]	160–161°/10 mm.	1.5684 (21)	92
Methyl[c]	104–105°/30 mm.	1.4832 (30)	86
t-Butyl[d]	97–98°/10 mm.	1.4769 (17)	68
Benzyl[e]	154–155°/1.7 mm.	1.5637 (20)	88

[a] Lit.[22] b.p. 134–135°/2 mm., n_D^{20} 1.5813. [b] Ref. 23, b.p. 145–146°/2 mm. [c] Lit.[26] b.p. 105–105.5°/30 mm. [d] T. Hoshino and K. Yamagishi, *Chem. Abstr.*, **51**, 8779 (1957), b.p. 108–120°/11 mm. [e] J. L. Szabo and E. T. Stiller, *J. Am. Chem. Soc.*, **70**, 3667 (1948), b.p. 119.5°/1 mm. [f] This compound was prepared in a methanol medium.

γ-Chloropropyl sulfides. These sulfides (Table II) were prepared by three different methods. Method A consisted of treating the corresponding alcohol with thionyl chloride in the presence of pyridine.[22] In a typical example, γ-chloropropyl phenyl sulfide was prepared by dissolving 55 g. (0.33 mole) of γ-hydroxypropyl phenyl sulfide in 27 ml. of pyridine and slowly adding 42 g. (0.35 mole) of thionyl chloride while the reaction mixture was cooled by an ice bath. The ice bath was removed at the end of the thionyl chloride addition and the mixture was heated at approximate 60° for 2 hr. The black reaction mixture was poured into water and the product was extracted with chloroform. The chloroform extracts were washed well with water and distilled yielding 56.1 g. (0.301 mole) of δ-chloropropyl phenyl sulfide (b.p. 115–119°/3 mm., $n_D^{21.2}$ 1.5732, lit.[22] b.p. 116–117°/4 mm., n_D^{20} 1.5752; 91% yield).

TABLE II

γ-CHLOROPROPYL SULFIDES, $RSCH_2CH_2CH_2Cl$

R	Method	B.P.	n_D (Temp.)	Yield, %
Phenyl[a]	A	115–119°/3 mm.	1.5732 (21.2)	91
	B	114–115°/2.5 mm.	1.5720 (25)	80
p-Tolyl[b]	A	118°/2.3 mm.	1.5646 (21)	69
	B	116–118°/2 mm.	1.5634 (26)	80
Benzyl	A	167–168°/19 mm.	1.5622 (20)	70
Methyl[c]	A	70–75°/29 mm.	1.4874 (18)	56
	C	70–73°/30 mm.	1.4833 (30)	53
t-Butyl	A	103–107°/30 mm.	1.4775 (18)	58
	C	96–100°/30 mm.	1.4748 (20)	31

[a] Lit.[22] b.p. 116–117°/4 mm. [b] Ref. 23, p. 325, b.p. 127–128°/5 mm. [c] Lit.[26] b.p. 71.2°/29 mm.

Method B consisted of treating 1-bromo-3-chloropropane with the sodium thiolate.[24] γ-Chloropropyl phenyl sulfide was prepared by adding 158 g. (1.00 mole) of 1-bromo-3-chloropropane to a solution of 110 g. (1.00 mole) of benzenethiol and 77.5 g. (1.20 moles) of potassium hydroxide in 200 ml. of water. The resulting solution was refluxed for 4 hr. and the product was extracted with ether. Distillation yielded 148 g. (0.800 mole) of γ-chloropropyl phenyl sulfide (b.p. 114–115°/2.5 mm., n_D^{25} 1.5720, lit.[22] b.p. 116–117°/4 mm., n_D^{20} 1.5752; 80% yield).

Method C involved the free-radical addition of a thiol to allyl chloride.[25] γ-Chloropropyl methyl sulfide was prepared by irradiating a stirred mixture of about 70 g. (1.5 moles) of methyl mercaptan, 76.5 g. (1.00 mole) of allyl chloride in 200 ml. of carbon tetrachloride in a quartz flask with an ultraviolet lamp overnight. The excess mercaptan was removed by extraction with aqueous alkali, and the carbon tetrachloride layer was distilled yielding 61.2 g. (0.534 mole) of γ-chloropropyl methyl sulfide (b.p. 70–73°/30 mm., n_D^{23} 1.4875, lit.[26] b.p. 71.2°/29 mm., n_D^{20} 1.4833; 53% yield).

γ-Chloropropyl sulfones. In a typical preparation of these sulfones (Table III), 56.1 g. (0.300 mole) of γ-chloropropyl phenyl sulfide was oxidized with 200 ml. (about 2 moles) of 30% hydrogen peroxide in 200 ml. of glacial acetic acid. After adding the peroxide to an ice bath cooled solution of acetic acid of the sulfide, the mixture was heated 24 hr. on a steam bath and was poured into water. The oil, which separated on cooling, was induced to crystallize by scratching the walls of the container or was extracted and distilled when the oil failed to crystallize. γ-Chloropropyl phenyl sulfone was extracted with benzene and distilled yielding 50.8 g. (0.232 mole) of product (b.p. 173–174°/2 mm., $n_D^{21.2}$ 1.5463, lit.[27] m.p. 26°, lit.[24] m.p. 23–24°; 77% yield).

TABLE III

γ-CHLOROPROPYL SULFONES, $RSO_2CH_2CH_2CH_2Cl$

R	B.P. or M.P.	Yield, %
Phenyl[b,d]	173–174°/2 mm.	77
p-Tolyl[g]	72–73°[a]	88
Methyl[c,f]	135–136°/2.7 mm.	91
t-Butyl	74–75°[a]	60
Benzyl[e]	110–111°[a]	74

[a] Recrystallized from methanol. [b] $n_D^{21.2}$ 1.5463, n_D^{25} 1.5470. [c] n_D^{20} 1.4822. [d] Lit.[27] m.p. 26°; lit.[4] b.p. 137–140°/0.005 mm. [e] E. Rothstein, *J. Chem. Soc.*, 684 (1934), m.p. 96°; *Anal.* Calcd. for $C_{10}H_{13}ClO_2S$: C, 51.51; H, 5.59; Cl, 15.25. Found: C, 51.47; H, 5.85; Cl, 15.31. [f] Was obtained from the oxidation mixture by distilling it after the excess peroxide was destroyed with manganese dioxide. *Anal.* Calcd. for $C_4H_9ClO_2S$: C, 30.67; H, 5.75; Cl, 22.65. Found: C, 30.94; H, 5.95; Cl, 22.81. [g] *Anal.* Calcd. for $C_{10}H_{13}ClO_2S$: C, 51.60; H, 5.63; Cl, 15.24. Found: C, 51.66; H, 5.64; Cl, 15.48.

Cyclopropyl sulfones. The cyclopropyl sulfones (Table IV) were prepared by the γ-dehydrohalogenation of the corresponding γ-chloropropyl sulfones in 121 Ansul ether ($CH_3OCH_2CH_2OCH_3$) with sodium amide. In a typical preparation, 21.8 g. (0.100 mole) of γ-chloropropyl phenyl sulfone was added to a slurry of 5.9 g. (0.15 mole) of sodium amide in 70 ml. of 121 Ansul ether. Ammonia was observed coming off the vigorously stirred mixture, which became warm and turned brown. After maintaining it at about 60° for 2 hr. by occasional warming or cooling, the reaction mixture was poured into water and the product was extracted with ether and distilled.

An attempt to prepare phenyl cyclopropyl sulfone using diethyl ether as the medium proved to be unsuccessful and resulted in the recovery of γ-chloropropyl phenyl sulfone (74% recovery, b.p. 152–156°/1.5 mm., n_D^{24} 1.5459).

2-Phenyltetrahydrothiophene 1-dioxide. β-Benzoylpropionic acid[28] was converted to its ethyl ester (b.p. 139°/1 mm.) by treatment with ethanol and sulfuric acid and the water removed as a benzene-water azeotrope (70% yield). The ethyl ester was reduced by lithium aluminum hydride in

(23) E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publ. Co., Inc., 221 Fifth Avenue, New York, 1960, p. 307.

(24) A. Kretow and J. Toropova, *J. Gen. Chem. U.S.S.R.*, **7**, 2009 (1937).

(25) J. I. Cunneen, *J. Chem. Soc.*, 36 (1947).

(26) W. R. Kirner, *J. Am. Chem. Soc.*, **50**, 2446 (1928).

(27) G. Baddeley and G. Bennett, *J. Chem. Soc.*, 46 (1933).

(28) L. F. Somerville and C. F. Allen, *Org. Syntheses*, Coll. Vol. II, 81 (1943).

TABLE IV

CYCLOPROPYL SULFONES, $RSO_2CH\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix}$

R	M.P.	B.P.	Yield, %	Calcd. C	Calcd. H	Found C	Found H
Phenyl[a-c]	36–37.5°	130–135°/0.5 mm.	78	59.33	5.53	59.69	5.74
p-Tolyl[c]	65–66°		65	61.23	6.12	61.12	6.31
Methyl[c]	56–57°		24	40.00	6.67	40.16	6.97
t-Butyl[c]		89–90°/0.8 mm.	78	51.80	8.65	51.85	8.59
Benzyl[c]	82–83°	2.7 mm.	63	61.23	6.12	61.12	6.06

[a] Lit.[4] m.p. 35–36°. [b] NMR showed three kinds of hydrogen atoms, aromatic, methylene, and tertiary; molecular weight (calcd. 182, found 173) by Rast method; strong infrared absorption bands appeared at 6.95, 7.62, 7.78, 8.71, 9.20, 11.27, 12.05, 13.10, 13.70, 14.49, and 14.70 μ. [c] Failed to react with potassium permanganate or bromine.

diethyl ether to give 1-phenyl-1,4-butanediol which was crystallized from ether (m.p. 69–71°, lit.[29] m.p. 75°; 39% yield). The diol was converted to the dibromide by phosphorus tribromide (b.p. 123–125°/0.6 mm., n_D^{25} 1.5804, lit.[31] reports a colorless oil which turns dark on standing; 32% yield). The dibromide was treated with sodium sulfide nonahydrate in refluxing ethanol and 2-phenyltetrahydrothiophene (VI) was extracted with petroleum ether (b.p. 35–37°). Distillation yielded the tetrahydrothiophene VI (b.p. 64–70°/0.2 mm., n_D^{25} 1.5802, 54% yield).

2-Phenyltetrahydrothiophene 1-dioxide (1.1 g., 0.0056 mole) was obtained from the oxidation of 2.2 g. (0.013 mole) of tetrahydrothiophene VI in 10 ml. of glacial acetic acid with 4.4 ml. of 30% hydrogen peroxide and was recrystallized from methanol (m.p. 65–65.5°, 43% yield).

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.12. Found: C, 61.03; H, 5.88.

Cleavage of the cyclopropyl sulfones by lithium in methylamine. The general procedure of Burdge[30] was used in the cleavage of the cyclopropyl sulfones with lithium and methylamine. In typical cleavage, 6.0 g. (0.033 mole) of phenyl cyclopropyl sulfone was placed in a 1-l., three-neck flask equipped with a magnetic stirrer and Dry Ice condenser. About 100 ml. of methylamine was condensed in the flask. A thimble containing 0.55 g. (0.08 mole) of lithium was placed so that the refluxing methylamine would slowly dissolve the lithium and carry it into the reaction mixture. When all the lithium was added, methanol was added and the methylamine was allowed to evaporate overnight. Ether was added and 2.9 g. of white solid was obtained. The solid was dissolved in 50 ml. of water and 43 g. (0.03 mole) of methyl iodide was added. The resulting mixture was refluxed for 4 hr. and the product was extracted with ether. The residue, from the ether extract, was recrystallized from methanol yielding 0.6 g. (0.005 mole) of methyl cyclopropyl sulfone (m.p. 56–57°, 15% yield). The mixed melting point with methyl cyclopropyl sulfone (m.p. 56–57°) was 56–57°.

Phenyl cyclopropyl sulfone was cleaved by the above procedure and the white solid residue from the cleavage mixture was treated with benzyl chloride. Benzyl cyclopropyl sulfone (42% yield) was obtained (m.p. 82–83°).

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.21. Found: C, 61.58; H, 6.22.

p-Tolyl cyclopropyl sulfone was cleaved with lithium in methylamine by the above procedure. The white residue (assumed to be lithium cyclopropane sulfinate) from the reaction mixture was treated with benzyl chloride to produce benzyl cyclopropyl sulfone (m.p. 82–83°, 17% yield, recrystallized from methanol). The mixed melting point with benzyl cyclopropyl sulfone (m.p. 82–83°) was 81–83°.

Treatment of t-butyl cyclopropyl sulfone with sodium methoxide.[9] *t*-Butyl cyclopropyl sulfone (13 g., 0.080 mole) was mixed with 10.8 g. (0.20 mole) of sodium methoxide (Matheson). This paste was heated at 135 ± 5° for 28 hr. The gaseous products were trapped by a Dry Ice trap. Bromine in carbon tetrachloride was added to the material in the cold trap. Distillation yielded 2.4 g. (20% yield) of 1,2-dibromo-2-methylpropane (b.p. 66°/50 mm., n_D^{26} 1.5038, lit.[31] b.p. 62°/45 mm., n_D 1.5068). The residue in the reaction flask was dissolved in water and was extracted with ether. The ether extracts yielded 5.1 g. (0.031 mole) of *t*-butyl cyclopropyl sulfone. Benzyl chloride (6.3 g., 0.05 mole) was added to the water layer and the resulting solution was refluxed for 8 hr. Benzyl cyclopropyl sulfone (2.1 g., 0.011 mole) was extracted with ether, was recrystallized from methanol (m.p. 82–83°, 20% yield). The mixed melting point with benzyl cyclopropyl sulfone (m.p. 82–83°) was 82–83°.

Reaction of phenyl cyclopropyl sulfone with Raney nickel. Phenyl cyclopropyl sulfone was treated by the procedure of Mozingo *et al.*[10] to give cyclopropane. A flask containing 40–50 g. of Raney nickel, 6.0 g. (0.033 mole) of phenyl cyclopropyl sulfone and 100 ml. of 75% ethanol was heated, and cyclopropane (about 300 ml. of gas) was collected by displacing ethylene glycol from an inverted separatory funnel in a large beaker of ethylene glycol. The gas was collected in an evacuated tube which was cooled by liquid nitrogen. The infrared spectrum of the gas was identical with that of cyclopropane.[32]

Treatment of methyl cyclopropyl ketone with sodium benzenethiolate. Benzenethiol (5.5 g., 0.050 mole) was dissolved in 25 ml. of absolute ethanol which contained 0.1 g. (0.005 mole) of sodium. Methyl cyclopropyl ketone (4.2 g., 0.050 mole) was added and the resulting solution was refluxed for 3 hr. The mixture was distilled yielding methyl cyclopropyl ketone (0.6 g., 0.007 mole, b.p. 111°), benzenethiol (0.5 g., 0.005 mole, b.p. 53–54°/10 mm.) and γ-(phenylmercapto)propyl methyl ketone VII (4.7 g., 0.029 mole, b.p. 123–125°/0.7 mm., n_D^{25} 1.5557, 58% yield).

γ-(Benzenesulfonyl)propyl methyl ketone (VIII) was prepared by the oxidation of the above sulfide VII in glacial acetic acid with 30% hydrogen peroxide. Ketone VIII was recrystallized from methanol (m.p. 68.5–70°, 67% yield).

Independent synthesis of ketone VII and ketone VIII.

(29) T. R. Marshall and W. H. Perkin, *J. Chem. Soc.*, **59**, 891 (1891).

(30) D. N. Burdge, Ph.D. thesis (Purdue University, 1959).

(31) W. Evers, H. Rothrock, H. Woodburn, E. Stahley, and F. Whitmore, *J. Am. Chem. Soc.*, **55**, 1136 (1933).

(32) *Index of Compounds of the Catalog of Infrared Spectral Data of the American Petroleum Institute*, Research Project 44, June 30, 1956, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Serial No. 445.

α-Acetyl-γ-butyrolactone was prepared by the method of Johnson[33] (48% yield), and was converted into 5-chloro-2-pentanone by the procedure of Cannon, *et al.*,[11] in an 18% yield. Ketone VII was prepared by the treatment of 5-chloro-2-pentanone with sodium benzenethiolate (b.p. 125–126°/1.0 mm., n_D^{25} 1.5550, 57% yield). Ketone VIII was prepared as described before (m.p. 69–70.5°, 77% yield). The mixed melting point with previously described ketone VIII (m.p. 68.5–70°) was 67.5–69°.

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.37; H, 6.24. Found: C, 58.09; H, 6.28.

Treatment of cyclopropyl sulfones with acid. Phenyl cyclopropyl sulfone (6.0 g., 0.033 mole) was refluxed for 20 hr. in 20 ml. of 48% hydrobromic acid. The mixture was extracted with chloroform. Distillation of the chloroform extracts yielded 3.3 g. (55% recovery) of phenyl cyclopropyl sulfone (b.p. 124–129°/0.7 mm.). No other products were observed.

Phenyl cyclopropyl sulfone (4.0 g.) was refluxed in 55% hydroiodic acid for 2 hr. The hydroiodic acid was evaporated and the residue yielded 3.9 g. (98% recovery) of starting material (n_D^{21} 1.5496, starting material $n_D^{21.5}$ 1.5516).

Phenyl cyclopropyl sulfone (4.0 g.) was dissolved in 20 ml. of acetic acid and 48% hydrobromic acid[18] was added until the solution became milky. Acetic acid was added to make the mixture homogeneous. The mixture was allowed to stand at room temperature for 3 days and on a steam bath for 1 day. Water was added and the mixture was extracted with ether. Distillation yielded 2.9 g. (72% recovery) of starting material (b.p. 125–130°/1 mm.). The infrared spectrum was identical with phenyl cyclopropyl sulfone.

(33) Wm. L. Johnson, U. S. Pat. 2,443,827 [*Chem. Abstr.*, 43, 678 (1949)].

p-Tolyl cyclopropyl sulfone was treated by the above procedure of Fuson and Baumgartner[18] and starting material was recovered (80%, m.p. 64–65.5°).

Treatment of cyclopropyl sulfones with sodium benzenethiolate and sodium t-butoxide. Phenyl cyclopropyl sulfone (5.0 g., 0.027 mole) was refluxed for 24 hr. in 50 ml. of absolute ethanol which contained 1 g. (0.04 mole) of sodium and 3.0 g. (0.027 mole) of benzenethiol. Most of the ethanol was removed and water was added. An oil was extracted with ether and distilled, yielding 3.7 g. (74% recovery) of phenyl cyclopropyl sulfone (b.p. 136–141°/2 mm.). The infrared spectrum was identical with phenyl cyclopropyl sulfone.

p-Tolyl cyclopropyl sulfone (5.0 g., 0.026 mole) was refluxed for 46 hr. in 25 ml. of ethylene glycol which contained 1.7 g. (0.030 mole) of potassium hydroxide and 2.8 g. (0.025 mole) of benzenethiol. Water was added and crystals formed (3.9 g., 78% recovery of starting material, recrystallized from methanol, m.p. 65–66°).

Phenyl cyclopropyl sulfone (10 g., 0.055 mole) was added to 100 ml. of *t*-butyl alcohol which contained 2.3 g. of sodium and the resulting solution was heated at 70 ± 5° for 60 hr. Water was added and the product was extracted with ether. Distillation yielded 8.9 g. (89% recovery) of phenyl cyclopropyl sulfone (m.p. 33–34°).

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[2]]

The Reactions of Thiolsulfinates with Triphenylphosphine, Triphenylarsine, and Triphenylstibine[1]

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Triphenylphosphine reacts smoothly and rapidly with alkyl or aryl thiolsulfinates at room temperature to yield triphenylphosphine oxide and disulfide. Triphenylarsine and triphenylstilbine react similarly with aryl thiolsulfinates to yield disulfide and the corresponding oxide or dihydroxide but require more drastic conditions and the reaction does not occur with alkyl thiolsulfinates.

This study was made with the aim of finding new chemical methods for distinguishing thiolsulfinates and thiolsulfonates from the corresponding disulfides. The reactions of tertiary phosphines and phosphites toward sulfur,[3] episulfides,[4] epoxides,[5] and particularly thiolsulfonates[6] suggested a study of the reactions of the triaryl derivatives of some of the group V elements with thiolsulfinates.

We have found that triphenylphosphine reacts rapidly and smoothly with alkyl or aryl thiolsulfinates at room temperature to yield triphenylphosphine oxide and the corresponding disulfide in nearly quantitative yields: When a solid aryl thiolsulfinate such as phenyl benzenethiolsulfinate or *p*-tolyl *p*-toluenethiolsulfinate is mixed with an equimolar quantity of triphenylphosphine in the solid state, the mixture liquifies in a few minutes with the evolution of heat followed by crystalliza-

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