# Reaction of Dimethylsulfonium Methylide with Vinylic Sulfones. Formation of Aryl Cyclopropyl Sulfones

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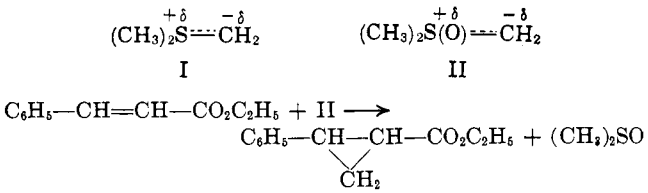
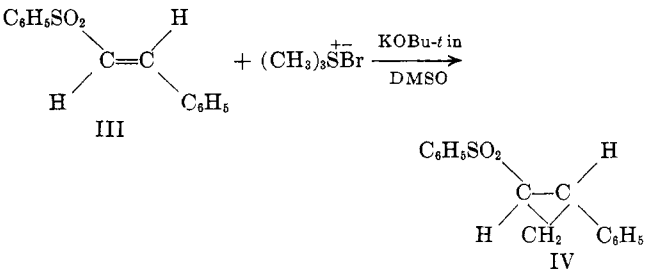
The formation of four new aryl cyclopropyl sulfones by the interaction of dimethylsulfonium methylide with vinylic sulfones is described.

The formation of substituted cyclopropanes from Michael-type acceptors and dimethylsulfonium methylide (I)[2] or dimethylsulfoxonium methylide (II)[3,4] is described in the literature and is shown as follows.

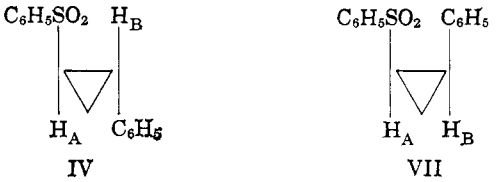


Although several types of "activated" olefins have been treated with sulfur ylides I and II there are no reports in the literature about like reactions with vinylic sulfones. Accordingly, the utility of dimethylsulfonium methylide (I) as a coreactant with vinylic sulfones for the synthesis of cyclopropyl sulfones (this comparatively new class of compounds having first been synthesized by an $\alpha,\gamma$-dehydrohalogenation approach[5]) was investigated.

Treatment of trimethylsulfonium bromide with *trans*-phenyl $\omega$-styryl sulfone (III) in the presence of potassium *t*-butoxide in dimethyl sulfoxide at room temperature afforded the adduct IV in 87.5% yield.



Strong evidence for the assignment of a *trans* configuration to compound IV was afforded by synthesizing the *cis* isomer VII by the method outlined below. Schoellkopf and his co-workers[6] have shown that phenylmercaptocarbene adds to olefins to form phenylmercaptocyclopropanes in good yields, *cis* products being favored. When phenyl chloromethyl sulfide (V) was allowed to react with potassium *t*-butoxide in the presence of excess styrene, 1-phenylmercapto-2-phenylcyclopropane (VI) was obtained and subsequently oxidized to the corresponding sulfone VII; the infrared absorption spectra of compounds IV and VII were consistent with that of related *trans*- and *cis*-cyclopropane derivatives, respectively.[7] The strongest evidence for the configurational assignments of IV and VII was offered by their nuclear magnetic resonance spectra. Analyses of the two spectra show that the coupling constants between $H_A$ and $H_B$ to be 5.6 c.p.s. for the isomer assigned the *trans* configuration and 8.3 c.p.s. for the *cis*



isomer. It has been established that *cis* protons on a cyclopropane ring have larger coupling constants than do *trans* protons.[8] The configurations of IV and VII are further supported by isomerizing *cis*-1-(phenylsulfonyl)-2-phenylcyclopropane (VII) to its *trans* isomer IV by means of potassium *t*-butoxide in dimethyl sulfoxide at room temperature. The n.m.r. and infrared spectra of the isomerized product are superimposable with the spectra of *trans* compound IV, obtained through the ylide reaction. The mixture melting point was not depressed.

A feasible mechanism for the reaction of dimethylsulfonium methylide (I) and vinylic sulfones is outlined in Chart I. The first step involves a Michael-type

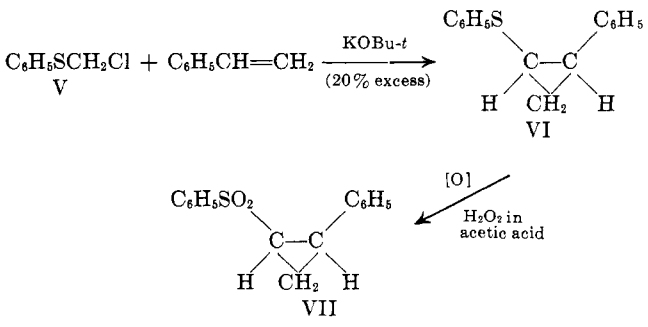
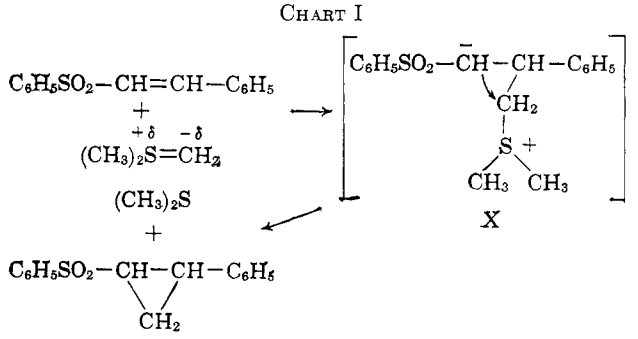


CHART I



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(2) V. Franzen and H. E. Driessen, *Tetrahedron Letters*, 661 (1962).

(3) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 3782 (1962).

(4) H. Koenig and H. Metzger, *Z. Naturforsch.*, [11] **18B**, 976 (1963); *Chem. Abstr.*, **60**, 9193 (1964).

(5) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).

(6) U. Schoellkopf and G. J. Lehman, *Tetrahedron Letters*, 165 (1962).

(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4263 (1961).

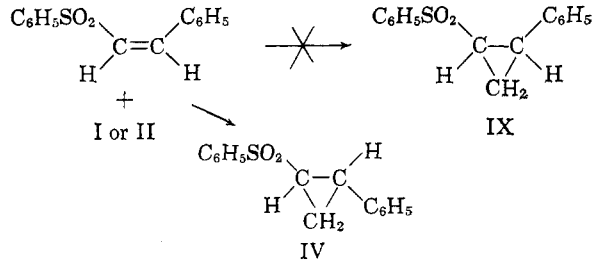
(8) (a) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); (b) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); (c) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963); (d) J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

TABLE I

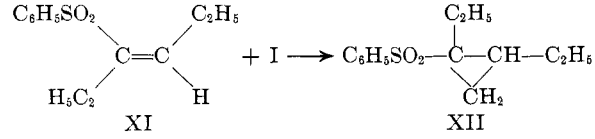
| Sulfone | Product | Yield, % |
|---|---|---|
| *cis*-$C_6H_5SO_2$—CH=CH—$C_6H_5$<br>*trans*-$C_6H_5SO_2$—CH=CH—$C_6H_5$ | $C_6H_5SO_2$, H, $C_6H_5$, $CH_2$ | 87.5 |
| *cis*-*p*-$CH_3$—$C_6H_4SO_2$—CH=CH—$C_6H_5$<br>*trans*-*p*-$CH_3$—$C_6H_4SO_2$—CH=CH—$C_6H_5$ | *p*-$CH_3$—$C_6H_4SO_2$, H, $C_6H_5$, $CH_2$ | 45 |
| $C_6H_5SO_2$, $C_2H_5$, $H_5C_2$, H | $C_6H_5SO_2$, H, $C_2H_5$, $CH_2$, $C_2H_5$ | 44 |
| *p*-$CH_3$—$C_6H_4SO_2$, $CH_3$, $H_3C$, H | *p*-$CH_3$—$C_6H_4SO_2$, H, $H_3C$, $CH_2$, $CH_3$ | 40 |
| *p*-$CH_3C_6H_4SO_2$, H, $CH_3$, $CH_3$ | | |

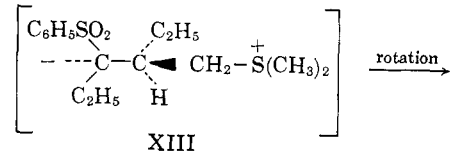
addition of ylide I to form a carbanion intermediate X, followed by internal displacement of the sulfide group to form the cyclopropane ring.

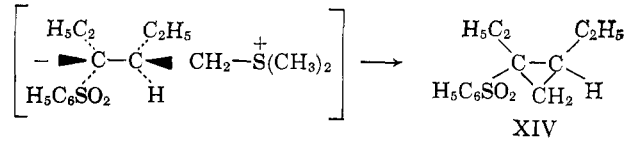
It was hoped that evidence for or against the stepwise character of this ring-forming reaction would be obtained through a study of the stereochemistry of the reaction between dimethylsulfonium methylide (I) and *cis*-phenyl ω-styryl sulfone (VIII). However, the facile isomerization of the *cis*-sulfone VII by the potassium *t*-butoxide needed to generate the ylide I from trimethylsulfonium bromide caused the results to be inconclusive. Only *trans*-1-phenylsulfonyl-2-phenylcyclopropane (IV) was obtained in nearly quantitative yield; similar results were observed with dimethylsulfoxonium methylide (II).




To preclude the complication of isomerization (*via* sulfonyl carbanions) dimethylsulfonium methylide (I) was treated with *trans*-3-phenylsulfonyl-3-hexene (XI), yielding 1-phenylsulfonyl-1,2-diethyl cyclopropane (XII) in 44% yield. The *cis* configuration of compound XII is tentatively suggested on the basis of the fact that it was cleaved by lithium in ammonia to yield, in addition to benzene, *cis*- and *trans*-diethylcyclopropanes in the relative ratio of 7.5:1, respectively. The cleavage is known to occur in cyclopropyl ketones with retention of configuration and optical activity.[9] The preferential formation of *cis* isomer can be explained in terms of nucleophilic displacement of dimethyl sulfide within the initially formed carbanion XIII to give the more stable isomer XIV in which the ethyl and bulky phenylsulfonyl groups are *trans* oriented. As indicated in Table I like results were obtained with *cis*- and *trans*-2-*p*-(tolylsulfonyl)-2-butenes (yields in this table are of recrystallized materials).




## Experimental[10]

*trans*-**Phenyl ω-Styryl Sulfide**.—The sulfide was prepared in an 83% yield by the method of Smith and Davis[11] from benzenethiol and phenylacetylene, b.p. 142–143° at 0.5 mm. (lit.[11] b.p. 155–60° at 1.0 mm.).

*trans*-**Phenyl ω-Styryl Sulfone (III)**.—To an ice-cold solution of 10.4 g. (0.047 mole) of *trans*-phenyl ω-styryl sulfide in 200 ml. of glacial acetic acid, was added dropwise 20 ml. of 30% hydrogen peroxide. After the addition, the mixture was refluxed for 1 hr. and then poured on crushed ice; the solid was filtered off. It was dried and recrystallized from 95% ethanol to give 7.6 g. (69% yield) of *trans*-phenyl ω-styryl sulfone, m.p. 73.5–75° (lit.[12] m.p. 74–75°).

*cis*-**Phenyl ω-Styryl Sulfide**.—To a refluxing ethanolic solution of sodium benzenethiolate, prepared from 3.45 g. (0.15 g.-atom) of sodium, 16.5 g. (0.15 mole) of benzenethiol and 150 ml. of ab-

(9) F. J. Impastato and H. M. Walborsky, *J. Am. Chem. Soc.*, **84**, 4838 (1962).

(10) All melting and boiling points are uncorrected. The infrared spectra were run on a Perkin-Elmer Infracord or Perkin-Elmer Model 21 spectrometer. The n.m.r. spectra were obtained using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Microanalyses were performed by Dr. C. S. Yeh and Staff.

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

(12) H. G. Klein, Ph.D. Thesis, Purdue University, 1961.

solute ethanol, was added 15 g. (0.15 mole) of freshly distilled phenylacetylene. The mixture was refluxed in a nitrogen atmosphere for 16 hr., then cooled and poured on crushed ice. The crude product was filtered off and dried to give 28.65 g. (90% yield) of crude *cis*-phenyl ω-styryl sulfide, m.p. 41°. After several recrystallizations from methanol, the melting point rose to 45° (lit.[12] m.p. 44–45°).

***cis*-Phenyl ω-Styryl Sulfone.**—To a solution of 10.4 g. (0.048 mole) of *cis*-phenyl ω-styryl sulfide in 200 ml. of glacial acetic acid cooled in an ice bath, was added dropwise 40 ml. of 30% hydrogen peroxide. After the addition was completed, the mixture was refluxed for 1 hr. and then poured on crushed ice; the solid was filtered off and dried to give 10.0 g. (85% yield) of crude *cis*-phenyl ω-styryl sulfone, m.p. 62–63°. After two crystallizations from 95% ethanol, the product melted at 64–65° (lit.[12] m.p. 64–65°).

***cis*- and *trans*-1-Phenyl-2-(*p*-tolylmercapto)ethene.**—These compounds have been prepared from the peroxide-catalyzed addition of *p*-toluenethiol to phenylacetylene according to the known procedure.[13] *cis*-1-Phenyl-2-(*p*-tolylmercapto)ethene melted at 63.5–64.5° (lit.[13] m.p. 64.5°). *trans*-1-Phenyl-2-(*p*-tolylmercapto)ethene distilled at 154–158° at 0.6 mm. The compound when solidified melted at 44° (lit.[13] m.p. 44–45°).

***cis*-1-Phenyl-2-(*p*-tolylsulfonyl)ethene.**—To an ice-cold solution of 8.0 g. (0.036 mole) of *cis*-1-phenyl-2-(*p*-tolylmercapto)ethene in 75 ml. of glacial acetic acid was added 15 ml. of 30% hydrogen peroxide. The mixture was heated on a steam cone for 2 hr. and poured on crushed ice. The solid was filtered off and dried to give 9 g. (90%) of sulfone, m.p. 75–76°. Recrystallization from methanol gave 6.3 g. of sulfone, m.p. 77° (lit.[14] m.p. 76–77°).

***trans*-1-Phenyl-2-(*p*-tolylsulfonyl)ethene.**—The same procedure was used as in the preceding experiment. From 15 g. of *trans*-1-phenyl-2-(*p*-tolylmercapto)ethene, 12 g. of crude sulfone was obtained, m.p. 112–115°. After several recrystallizations from methanol, 7 g. of the sulfone was obtained, m.p. 120–121° (lit.[15] m.p. 121°).

***cis*-2-(*p*-Tolylmercapto)-2-butene.**—Using the procedure of Bordwell and Landis,[16] *cis*-2-(*p*-tolylmercapto)-2-butene was prepared in 50% yield from the lithium compound of *cis*-2-bromo-2-butene and *p*-tolyl disulfide, b.p. 75–77° at 0.5 mm., $n^{25}D$ 1.5574 (lit.[16] b.p. 67–69° at 0.3 mm.).

***cis*-2-(*p*-Tolylsulfonyl)-2-butene.**—The sulfone, prepared according to known procedure,[16] was obtained in 80% yield and melted at 52–53° (lit.[16] m.p. 52–53°).

***trans*-2-(*p*-Tolylmercapto)-2-butene.**—Starting from 11.5 g. (0.092 mole) of *p*-toluenethiol and 16.9 g. (0.12 mole) of 2-butyne, 11.25 g. (65%) of *trans*-2-(*p*-tolylmercapto)-2-butene, b.p. 80–81° at 1 mm., was obtained according to the method of Truce and Simms[14] (lit.[14] b.p. 83° at 2 mm.).

***trans*-2-(*p*-Tolylsulfonyl)-2-butene.**—To a solution of *trans*-2-(*p*-tolylmercapto)-2-butene (11.0 g.) in glacial acetic acid (110 ml.) at ice-cold temperature was added slowly with stirring 22 ml. of 30% hydrogen peroxide. The mixture was heated on a steam cone for 1 hr. It was then poured onto crushed ice, filtered, and dried under vacuum to give 9.2 g. of the sulfone, m.p. 45–46°. It was crystallized from alcohol, m.p. 47° (lit.[16] m.p. 46–47°).

***trans*-3-(Phenylmercapto)-3-hexene.**—To a solution of sodium ethoxide, prepared under nitrogen atmosphere, from 3.5 g. (0.15 g.-atom) of sodium in 50 ml. of absolute ethanol, was added 16.5 g. (0.15 mole) of benzenethiol. The solution was then added to 12.7 g. (0.15 mole) of 3-hexyne in a Carius tube flushed with nitrogen. The Carius tube was sealed and heated at 155–160° for 120 hr. After the reaction was completed, the sealed tube was cooled in Dry Ice and opened. The reaction mixture was poured in water and the oily layer was extracted with ether. The ethereal layer was dried over anhydrous magnesium sulfate. The ether was removed and the product was distilled to give 7.2 g. (38% yield) of *trans*-3-(phenylmercapto)-3-hexene, b.p. 68–70° at 0.4 mm.

*Anal.* Calcd. for $C_{12}H_{16}S$: C, 74.99; H, 8.32; S, 16.68. Found: C, 74.74; H, 8.70; S, 16.48.

***trans*-3-(Phenylsulfonyl)-3-hexene.**—*trans*-3-(Phenylmercapto)-3-hexene (4.8 g., 0.025 mole) was dissolved in 45 ml. of glacial acetic acid, cooled in an ice bath, and 15 ml. of 30% hydrogen peroxide was added dropwise to the cold, stirred solution. It was then heated on a steam cone for 1 hr. and poured on crushed ice. The oily layer was extracted with ether and the ethereal solution was washed with 20% aqueous sodium bicarbonate. The ethereal layer was dried over anhydrous magnesium sulfate and and the ether was distilled off. The residue on distillation gave 3.56 g. (65% yield) of *trans*-3-(phenylsulfonyl)-3-hexene, b.p. 124–126.5° at 0.3 mm., $n^{21}D$ 1.5016.

*Anal.* Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14; S, 14.30; mol. wt., 224. Found: C, 63.95; H, 6.80; S, 14.58; mol. wt., 227.

**Trimethylsulfonium Bromide.**—A mixture of dimethyl sulfide (24.8 g., 0.40 mole) and bromomethane (38.0 g., 0.40 mole) was heated in a sealed tube for 5 hr. at 80°. The Carius tube was cooled in Dry Ice and opened. The product was filtered, dried, and crystallized from methanol–ether, m.p. 201–202° (sealed tube), yield 50 g. (lit.[17] m.p. 200°, sealed tube).

**General Procedure for the Preparation of Cyclopropyl Sulfones.**—In a 100-ml., three-neck flask equipped with magnetic stirrer, dropping funnel, and nitrogen inlet tube, were placed trimethylsulfonium bromide (0.01 mole), vinyl sulfone (0.01 mole), and 20 ml. of dimethyl sulfoxide (distilled over calcium hydride). The mixture was stirred under a nitrogen atmosphere until the clear solution was obtained. Then the solution of potassium *t*-butoxide (0.01 mole) in 15 ml. of dimethyl sulfoxide was added dropwise at room temperature. After the addition was over, the reaction mixture was stirred further for 1 hr. and diluted with 250 ml. of water. The diluted reaction mixture was stirred until the solid was thrown out. The solid was filtered, dried, and crystallized from suitable solvents.

***trans*-1-(Phenylsulfonyl)-2-phenylcyclopropane (IV).**—From 2.44 g. (0.01 mole) of *cis*- or *trans*-phenyl ω-styryl sulfone, 2.25 g. (87.5%) of *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane was obtained according to general procedure. It crystallized from 95% alcohol, m.p. 96–97°.

*Anal.* Calcd. for $C_{15}H_{14}O_2S$: C, 69.70; H, 5.42; S, 12.40. Found: C, 69.41; H, 5.28; S, 12.24.

The infrared spectrum of *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane showed peaks at following wave lengths in μ: 3.40 (s), 6.30 (m), 6.72 (s), 6.98 (s), 7.30 (m), 7.70 (s, broad), 8.00 (w), 8.20 (w), 8.75 (s, broad), 9.05 (m), 9.25 (s), 9.55 (m), 9.80 (m), 10.10 (m), 10.95 (w), 11.20 (s), 11.70 (w), and 14.50 (s, broad).

**Preparation of Compound IV through Dimethylsulfoxonium Methylide.**—Trimethylsulfoxonium iodide[18] (2.20 g., 0.01 mole) was added in small portions to a nitrogen-blanketed, stirred suspension of 0.24 g. (0.01 mole) of sodium hydride (supplied as 55% dispersion in mineral oil by Metal Hydrides, Inc.) in 8 ml. of dimethyl sulfoxide. When the evolution of hydrogen had ceased, a solution of 2.44 g. (0.01 mole) of *cis*-phenyl ω-styryl sulfone in 5 ml. of dimethyl sulfoxide was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 1 hr. and diluted with 50 ml. of water. The solid residue was filtered and recrystallized from alcohol. *trans*-1-(Phenylsulfonyl)-2-phenylcyclopropane was obtained in 85% yield and melted at 95–96°. The mixture melting point with the compound, obtained from the interaction of dimethylsulfonium methylide and *trans*-phenyl ω-styryl sulfone, was not depressed.

***cis*-1-(Phenylsulfonyl)-2-phenylcyclopropane (VII).**—In a 500-ml., three-neck flask fitted with a stirrer and a dropping funnel was placed 75 ml. of styrene. Potassium *t*-butoxide (15 g., 20% excess then 0.075 mole) was added with stirring in small portions to styrene at −5°. Phenyl chloromethyl sulfide[19] (11.9 g., 0.075 mole) was added dropwise to the above mixture. After the addition was over, the mixture was stirred for 2 hr. and diluted with water. The oily layer was separated and dried over anhydrous calcium chloride. The styrene was distilled off and the residue was fractionated to give 6.63 g. (43%) of *cis*-1-(phenylmercapto)-2-phenylcyclopropane, b.p. 162–163° at 2 mm., $n^{20}D$ 1.6140.

The above sulfide (3.0 g.) was dissolved in 30 ml. of glacial acetic acid and 9 ml. of 30% hydrogen peroxide was added to the mixture at ice-cold temperature. The mixture was heated on a steam cone for 2 hr. It was then poured on crushed ice and the solid was filtered off and dried. *cis*-1-(Phenylsulfonyl)-2-phenyl-

(13) W. E. Truce, H. G. Klein, and R. B. Kruse, *J. Am. Chem. Soc.*, **83**, 4636 (1961).
(14) W. E. Truce and J. A. Simms, *ibid.*, **78**, 2756 (1956).
(15) E. P. Kohler and H. Potter, *ibid.*, **57**, 1316 (1935).
(16) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1596 (1951).
(17) H. Bohme and W. Krause, *Ber.*, **82**, 426 (1949).
(18) R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).
(19) O. Scherer and K. Fink, German Patent 845,511 (1952); *Chem. Abstr.*, **47**, 5442 (1953).

cyclopropane, crystallized from ethanol, m.p. 67–68°, was obtained in 83% yield.

*Anal.* Calcd. for $C_{15}H_{14}O_2S$: C, 69.70; H, 5.42; S, 12.40. Found: C, 69.44; H, 5.40; S, 12.52.

The infrared spectrum of *cis*-1-(phenylsulfonyl)-2-phenylcyclopropane showed peaks at following wave lengths in $\mu$: 3.40 (s), 6.30 (m), 6.75 (s), 7.00 (s), 7.35 (w), 7.70 (s, broad), 8.30 (s), 8.80 (s, broad), 9.10 (m), 9.25 (s), 9.50 (w), 9.80 (w), 9.95 (w), 10.05 (w), 10.95 (s), 11.0 (s), 12.05 (s), and 14.50 (s, broad).

**Isomerization of *cis*-1-(Phenylsulfonyl)-2-phenylcyclopropane (VII) to *trans*-1-(Phenylsulfonyl)-2-phenylcyclopropane (IV).**—In a 50-ml., three-neck flask equipped with magnetic stirrer, dropping funnel, and nitrogen gas inlet tube was placed a solution of *cis*-1-(phenylsulfonyl)-2-phenylcyclopropane (1.3 g., 0.005 mole) in 10 ml. of dimethyl sulfoxide. Potassium *t*-butoxide (200 mg.) in 15 ml. of dimethyl sulfoxide was added dropwise with stirring to the above solution at room temperature. The reaction mixture developed a reddish brown color. After the addition was complete, the mixture was stirred at room temperature for 2 hr. It was then poured in 200 ml. of ice-cold water and stirred until the solid was precipitated. The solid was filtered, dried, and crystallized from ethanol, m.p. 96–97°, yield 1.2 g. The mixture melting point of this compound with *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane, prepared through the sulfur ylid reaction, was not depressed. The infrared spectra were similar.

***trans*-1-(*p*-Tolylsulfonyl)-2-phenylcyclopropane.**—From *cis*- or *trans*-1-phenyl-2-(*p*-tolylsulfonyl)ethene (0.01 mole), *trans*-1-(*p*-tolylsulfonyl)-2-phenylcyclopropane was obtained according to general procedure in 45% yield. It crystallized from ethanol, m.p. 146–147°.

*Anal.* Calcd. for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.88; S, 11.76; mol. wt., 272. Found: C, 70.87; H, 6.15; S, 11.58; mol. wt., 265.

**1-(Phenylsulfonyl)-*cis*-1,2-diethylcyclopropane (XIV).**—In a 200-ml., three-neck flask equipped with dropping funnel, magnetic stirrer, and nitrogen gas inlet tube were placed 4.48 g. (0.02 mole) of *trans*-3-phenylsulfonyl-3-hexene, 3.15 g. (0.02 mole) of trimethylsulfonium bromide, and 35 ml. of dimethyl sulfoxide. The mixture was stirred until a clear solution was obtained. The solution of potassium *t*-butoxide (2.24 g., 0.02 mole) in 25 ml. of dimethyl sulfoxide was added dropwise with stirring at room temperature. After the addition, the reaction mixture was stirred further for 1 hr. and diluted with 200 ml. of water. The oily layer was extracted with ether and the ethereal layer was washed twice with 100-ml. portions of water. The ethereal layer was dried over anhydrous magnesium sulfate and the ether was removed. The residue on distillation gave 2.1 g. (44%) of 1-(phenylsulfonyl)-*cis*-1,2-diethylcyclopropane, b.p. 135–137° at 0.55 mm., $n^{29}D$ 1.5302.

*Anal.* Calcd. for $C_{13}H_{18}O_2S$: C, 65.55; H, 7.55; S, 13.46. Found: C, 65.76; H, 7.78; S, 13.16.

**Cleavage of 1-(Phenylsulfonyl)-*cis*-1,2-diethylcyclopropane by Lithium in Ammonia.**—Liquid ammonia (25 ml.) was condensed into a three-neck flask equipped with a Dry Ice condenser and a magnetic stirrer. Lithium wire (0.180 g., 0.025 g.-atom) was cut into small pieces and added to ammonia. After all the lithium had completely dissolved, the flask and the contents were cooled to about −75° by means of a Dry Ice–acetone bath and 1-(phenylsulfonyl)-*cis*-1,2-diethylcyclopropane (2.36 g., 0.01 mole) was added dropwise. After all of the compound had been added, the mixture was stirred at −75° for about 15 min. and the excess of lithium metal was decomposed by the addition of 5–7 ml. of methanol followed by the addition of 75 ml. of distilled water. The cleavage mixture was stirred vigorously until all the sulfinate was dissolved. *n*-Nonane (Phillips Yellow Label, 10 ml.) was added to the cleavage mixture and stirred for five min. The upper organic layer was analyzed by vapor phase chromatography, using column R (Ucon polyglycol LB-550-x) at 80°.

**1-(*p*-Tolylsulfonyl)-*cis*-1,2-dimethylcyclopropane.**—This was prepared in 40% yield according to the general procedure from either *cis*-2-(*p*-tolylsulfonyl)-2-butene or *trans*-2-(*p*-tolylsulfonyl)-2-butene. 1-(*p*-Tolylsulfonyl)-*cis*-1,2-dimethylcyclopropane distilled at 149–151° at 0.55 mm.

*Anal.* Calcd. for $C_{12}H_{16}O_2S$: C, 64.3; H, 7.14; S, 14.28. Found: C, 64.11; H, 7.20; S, 14.00.

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# Halogen and Nucleoside Derivatives of Acyclic 2-Amino-2-deoxy-D-glucose.[1,2] I

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2-Acetamido-3,4,5,6-tetra-*O*-acetyl-2-deoxy-D-glucose diethyl dithioacetal (I), and its 2-(2,4-dinitroanilino) analog (III) react with a stoichiometric amount of bromine to give acyclic 1-bromo derivatives (II and VI, respectively) by replacement of one ethylthio group by bromine. An excess of chlorine converts (III), with replacement of one ethylthio group, into a trichloro derivative having the structure (IV). The acyclic 1-bromo derivative (VI) reacts with alcohols, with replacement of the bromine atom by an alkoxy group, to give mixed acyclic monothioacetals (VII). Reaction of VI with 6-acetamido-9-chloromercuripurine gives substituted acyclic nucleoside derivatives (V) in good yield.

Acyclic halogen derivatives of aldoses have been described by Wolfrom and co-workers.[3,4] Bromination of penta-*O*-acetyl-D-galactose diethyl dithioacetal provides a convenient synthetic route[5,6] to penta-*O*-acetyl-1-bromo-1,1-dideoxy-1-ethylthio-D-galactose aldehydrol,[4] and the latter, together with the sirupy D-glucose analog, has been used in preparation of acyclic sugar nucleoside analogs.[7] Related derivatives have also been prepared[8] from penta-*O*-acetyl-1-bromo-1-deoxy-1-*O*-methyl-D-galactose aldehydrol,[6] or the chloro analog.[3] The present work describes the bromination of two diethyl dithioacetal derivatives of 2-amino-2-deoxy-D-glucose to give crystalline acyclic 1-bromo derivatives which are, to the best of our knowledge, the first acyclic 1-halogen derivatives of an amino sugar to be described. One of them has been transformed, by alcoholysis, into acyclic mixed acetal derivatives, and, by a conventional procedure,[7,8] into acyclic sugar nu-

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