Cyclooctyl Mercaptan (1).—The general procedure of Urquhart, Gates, and Connor[11] was used to prepare this compound. To a solution of 15.2 g of thiourea in 150 ml of absolute ethanol was added 38.2 g of cyclooctyl bromide and the resulting solution was refluxed for 48 hr. To the cooled solution was then added 120 ml of 10% sodium hydroxide solution and the mixture was refluxed for an additional 2 hr. The mercaptan layer was separated and the neutralized aqueous layer extracted with three 100-ml portions of benzene and the benzene extracts were dried over sodium sulfate. The benzene was removed by distillation through a Vigreux column under reduced pressure and the product was distilled through a semimicro column yielding 12.44 g (43%) of crude mercaptan, bp 31–34° (0.35 mm), $n^{24}D$ 1.4822–1.5034. A portion of this product was chromatographed on Merck activity II acid-washed alumina and eluted with petroleum ether (bp 35–60°) to yield pure cyclooctyl mercaptan. Further elution with petroleum ether yielded a fraction shown to be cyclooctyl ethyl ether by comparison of its infrared spectrum with that of an authentic spectrum. This ether usually contaminated the crude reaction product to the extent of about 10%. The pure mercaptan had bp 98–99° (20 mm), $n^{25}D$ 1.5076–1.5078. Its infrared spectrum had the characteristic mercaptan absorption[12] at 2540 cm^{-1}.

Anal. Calcd for $C_8H_{16}S$: C, 66.63; H, 11.18; S, 22.19. Found: C, 66.86; H, 11.17; S, 21.66.

Cyclooctyl Sulfide (2).—The method of Bost and Conn[13] was used in the preparation of this compound. To a solution of 6 g of sodium sulfide nonahydrate in 50 ml of absolute ethanol was added 9.6 g of cyclooctyl bromide and the resulting solution was refluxed for 20 hr. The solution was then cooled and 50 ml of water was added. The sulfide layer was separated, the aqueous layer was extracted with five 20-ml portions of petroleum ether, and the combined extracts were dried over sodium sulfate. After removal of the petroleum ether under reduced pressure with a rotary concentrator, the crude product was distilled through a semimicro column. A total of 2.6 g (41%) of product, bp 126–127° (0.25 mm), $n^{25}D$ 1.5250–1.5286, was obtained. An analytical sample of cyclooctyl sulfide had bp 126–127° (0.25 mm), $n^{25}D$ 1.5255.

Anal. Calcd for $C_{16}H_{30}S$: C, 75.53; H, 11.89; S, 12.58. Found: C, 75.22; H, 11.90; S, 12.58.

Preparation of Degassed Raney Nickel.—The procedure used was adapted from a similar one used by Hauptmann.[4] Commercial W-2 Raney nickel (Raney Catalyst Co., Chattanooga, Tenn.) was thoroughly washed with large portions of distilled water, ethanol, and finally reagent benzene. The wet Raney nickel was transferred to a Carius tube and the excess benzene was removed under reduced pressure. A 1500-G permanent magnet surrounding the outside of the Carius tube held the powdered nickel in place. The system was then evacuated to 1–2-mm pressure and heated to 150°. Heating was continued for at least 8 hr, after which the system was cooled and the vacuum was slowly released under nitrogen pressure. The degassed nickel was then poured into an empty reaction flask under nitrogen and a benzene solution of mercaptan or sulfide was added.

Desulfurization of Cyclooctyl Mercaptan.—A 1.10-g sample of cyclooctyl mercaptan dissolved in 35 ml of dry benzene was refluxed for 49 hr with about 10 g of degassed Raney nickel. The benzene solution was then decanted from the nickel and the nickel was carefully transferred to a Soxhlet extraction apparatus and continuously extracted with pentane for 96 hr. The pentane extracts and benzene solution were then combined and the benzene and pentane were removed by distillation. Distillation of the product mixture at 25–40° (10 mm.) yielded 698 mg (82%) of a mixture consisting of approximately 80% cyclooctane and 20% *cis*-cyclooctene. The small amount of residue contained no bicyclooctyl as determined by gc analysis on a silicon grease column heated to 230°.

Desulfurization of Cyclooctyl Sulfide.—A 1.10-g sample of cyclooctyl sulfide dissolved in 35 ml of dry benzene was refluxed with about 10 g of degassed Raney nickel for 48 hr. Separation of the reaction products was accomplished using the procedure described in the desulfurization of cyclooctyl mercaptan. Distillation of the product mixture at 25–40° (10 mm) yielded 200 mg (71% based on recovered sulfide) of a mixture of 7% cyclooctane and 93% *cis*-cyclooctene as determined by gc using an NMPN column at 30°. Chromatography of the high boiling residue on 20 g of Merck activity II acid-washed alumina and elution with pentane yielded 688 mg of a colorless oil. This material was shown to be unreacted cyclooctyl sulfide by the use of infrared and gas chromatographic techniques (silicon gum rubber at 300°). No other product could be isolated from the column chromatogram.

Registry No.—1, 20628-54-0; 2, 20628-55-1.

(11) G. G. Urquhart, J. W. Gates, Jr., and R. Connor, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 363.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Second ed, John Wiley & Sons, Inc., New York, N. Y., 1958.

(13) R. W. Bost and M. W. Conn, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 547.

The Reaction of N-Sulfinylamines and N-Sulfinylsulfonamides with Carbonyl Chloride. A New Synthesis of Isocyanates

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The direct phosgenation of amine salts to isocyanates is well known; however, long reaction times are required because of the poor solubility of amine salts in organic solvents.[1] The facile reaction of amines and sulfonamides with thionyl chloride[2] provides a method of protection of the amino group, and the generated N-sulfinyl derivatives are easily soluble in organic solvents. Subsequent phosgenation could produce the corresponding isocyanate with regeneration of thionyl chloride. The over-all reaction is shown below (eq 1, 2).

$$RNH_2 + SOCl_2 \longrightarrow RN{=}S{=}O + 2\ HCl \quad (1)$$

$$RN{=}S{=}O + COCl_2 \longrightarrow RN{=}C{=}O + SOCl_2 \quad (2)$$

When carbonyl chloride is added to N-sulfinylaniline (N-thionylaniline) in *o*-dichlorobenzene at 180°, no reaction occurs. In contrast, facile conversion could be achieved in refluxing benzene (80°), provided that a catalytic amount of pyridine or N,N-dimethylformamide is added to the reaction mixture. The reaction is general, and aliphatic and aromatic amines as well as aromatic sulfonamides can be converted to the corresponding isocyanates (see Table I).

TABLE I[a]

CONVERSION OF N-SULFINYLAMINES AND N-SULFINYLSULFONAMIDES TO ISOCYANATES

$RN{=}S{=}O + COCl_2 \longrightarrow RN{=}C{=}O + SOCl_2$

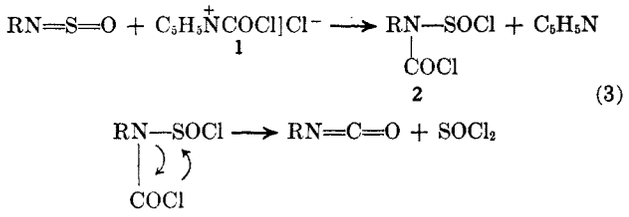
Registry no.	R	Scale, mol	Time,[b] min	Yield,[c] %	Bp, °C (mm)
103-71-9	C_6H_5	0.03	85	60	55–57 (16)
4083-64-1	$4\text{-}CH_3C_6H_4SO_2$	0.03	90	62	90–92 (0.5)
622-58-2	$4\text{-}CH_3C_6H_4$	0.03	120	67	88 (17)
104-12-1	$4\text{-}ClC_6H_4$	0.03	45	75	87 (8.5)
5416-93-3	$4\text{-}CH_3OC_6H_4$	0.03	300	73	102 (6.5)
3173-53-3	C_6H_{11}	0.035	630	61	76 (17)

[a] An amount of 5% (by weight) of pyridine was used as the catalyst. [b] The flow rate of carbonyl chloride was approximately 145 ml/min. [c] The yields are not optimal. Losses in distillation were encountered because of the small-scale experiments.

(1) W. Siefken, *Ann.*, **562**, 75 (1949).

(2) G. Kresze and W. Wucherpfennig in "Newer Methods of Preparative Organic Chemistry," Vol. V, Academic Press, New York, N. Y., 1968, p 113–115.

The catalytic effect of N,N-dimethylformamide in phosgenation reactions can be attributed to the rapid formation of chlorodimethylformiminium chloride ($Me_2\overset{+}{N}{=}CHCl]Cl^-$), which in fact is the catalyst.[3] Chlorodimethylformiminium chloride is an exceedingly reactive electrophile, and its reaction with N-sulfinyl derivatives to form 1:1 adducts has been reported recently.[4] In the case of pyridine, the 1:1 complex with carbonyl chloride (**1**) is believed to be the species which attacks the N=S=O bond to form compound **2**, which collapses to the reaction products (eq 3).



(3)

Experimental Section

The starting N-sulfinyl derivatives were prepared according to the literature procedures.[2]

Isocyanates. General Procedure.—The preparation of 4-chlorophenyl isocyanate demonstrates the general procedure followed in the synthesis of the isocyanates listed in Table I. To a refluxing solution of 5.2 g (0.03 mol) of N-sulfinyl-4-chloroaniline and 0.26 g of pyridine in 60 ml of benzene, carbonyl chloride was added over a period of 45 min, the progress of reaction being followed by infrared spectroscopy. The solvent was evaporated and vacuum distillation of the residue yielded 3.45 g (75.2%) of 4-chlorophenyl isocyanate, bp 87° (8.5 mm).

Instead of the pyridine, a 10% (by weight) amount of N,N-dimethylformamide can be used as catalyst, and the results are similar.

Registry No.—Carbonyl chloride, 75-44-5.

(3) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N. Y., 1968, p 82–83.

(4) Y. Ito, S. Katsuragawa, M. Okano, and R. Oda, *Tetrahedron*, **23**, 2159 (1967).

Reactions of Bis(trifluoromethyl)diazomethane with Perfluorothiocarbonyl Compounds

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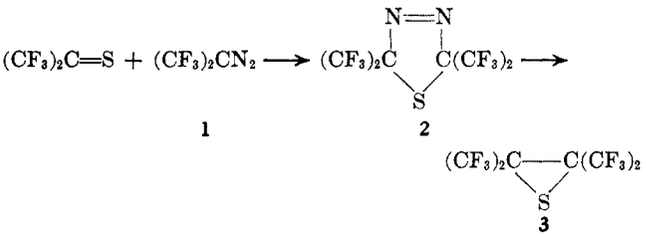
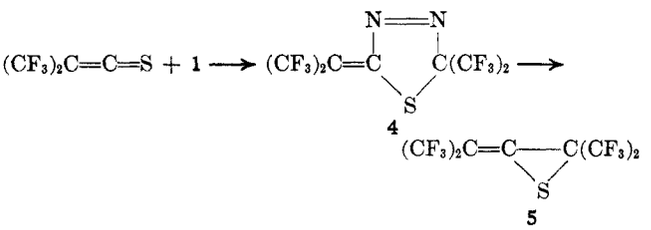
Several investigators have reported that diazo compounds react with thio ketones by loss of nitrogen to give episulfides.[1] It has been assumed that an unstable thiadiazoline is first formed as an intermediate,[1a] but there appears to be no report of the isolation or confirmation of such an intermediate.

We have found that bis(trifluoromethyl)diazomethane (**1**)[2] reacts readily with certain perfluorothiocarbonyl compounds to yield thiadiazolines, which can be isolated and characterized because of their stabilization by fluorine. Thus, **1** reacts with hexafluorothioacetone[3] to give the thiadiazoline **2**, which can be distilled at reduced pressure and is relatively stable at room temperature.



The ^{19}F nmr spectrum of **2** shows only a single absorption peak, indicating the symmetrical 1,3,4-thiadiazoline instead of the unsymmetrical 1,2,3-thiadiazoline. The thiadiazoline **2** is thermally unstable and can be decomposed with loss of nitrogen to give the known episulfide **3**[4] by simply refluxing it at its atmospheric boiling point for a few hours.

Bis(trifluoromethyl)thioketene[5] also reacts with **1** to give an adduct which is the thiadiazoline **4**. This



thiadiazoline is somewhat more stable than **2**, possibly because the N=N double bond is stabilized by conjugation with the C=C double bond. However, it can also be decomposed with loss of nitrogen to give the episulfide **5** by heating it to reflux for several hours at atmospheric pressure. We believe that **5** is the first example of an allene episulfide. The infrared double-bond absorption of compound **5** at 5.75 μ is appreciably shorter than that of compound **4** at 6.17 μ, apparently because of introduction of strain by the three-membered ring and loss of conjugation.

Experimental Section[6]

2,2,5,5-Tetrakis(trifluoromethyl)-1,3,4-thiadiazoline (2).—An 18.2-g sample (0.1 mol) of hexafluorothioacetone[3] was cooled to −30°, and 17.8 g (0.1 mol) of bis(trifluoromethyl)diazomethane[2] was added slowly with stirring. The blue color faded to yellow. The reation mixture was distilled at reduced pressure to give 33.0 g (92%) of **2** as a colorless liquid: bp 37° (50 mm); $n^{25}D$ 1.3202; ir (liquid) 6.24 μ (N=N?); ^{19}F nmr (neat) δ 68.5 ppm (s).

Anal. Calcd for $C_6F_{12}N_2S$: C, 20.01; F, 63.31; N, 7.78; S, 8.89. Found: C, 20.22; F, 63.16; N, 7.97; S, 8.51.

Tetrakis(trifluoromethyl)thiirane (3).—A 20.0-g sample of **2** was heated at reflux for 4 hr and the distilled to give 17.5 g (95%) of **3** as a colorless liquid: bp 91°; $n^{25}D$ 1.3164; ^{19}F nmr (neat) δ 59.9 ppm (s).

Anal. Calcd for $C_6F_{12}S$: C, 21.70; F, 68.65; S, 9.65. Found: C, 21.75; F, 68.68; S, 9.69.

2,2-Bis(trifluoromethyl)-5-bis(trifluoromethyl)methylene-1,3,4-thiadiazoline (4).—A 1.94-g sample (0.01 mol) of bis(trifluoromethyl)thioketene[5] and 1.78 g (0.01 mol) of bis(trifluoromethyl)-

(1) (a) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); (b) A. Schonberg and S. Nickel, *Chem. Ber.*, **64**, 2323 (1931); (c) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

(2) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 3617 (1966).

(3) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

(4) W. J. Middleton, U.S. Patent 3,136,781 (1964).

(5) M. S. Raasch, *Chem. Commun.*, 577 (1966).

(6) Fluorine nmr spectra were obtained with a Varian A56-60 spectrometer. Peak center positions for fluorine are reported in parts per million upfield from $CFCl_3$ used as an internal reference.