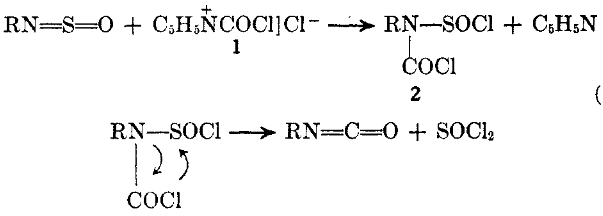
The catalytic effect of N,N-dimethylformamide in phosgenation reactions can be attributed to the rapid formation of chlorodimethylformiminium chloride $(\mathrm{Me_2\overset{+}{N}{=}CHCl]Cl^-})$, which in fact is the catalyst.[3] Chlorodimethylformiminium chloride is an exceedingly reactive electrophile, 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).



$$\mathrm{RN{=}S{=}O} + \underset{1}{\mathrm{C_5H_5\overset{+}{N}COCl]Cl^-}} \longrightarrow \underset{\underset{2}{\mathrm{COCl}}}{\mathrm{RN{-}SOCl}} + \mathrm{C_5H_5N} \qquad (3)$$

$$\underset{\mathrm{COCl}}{\mathrm{RN{-}SOCl}} \longrightarrow \mathrm{RN{=}C{=}O} + \mathrm{SOCl_2}$$

### 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.

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(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).

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## Reactions of Bis(trifluoromethyl)diazomethane with Perfluorothiocarbonyl Compounds

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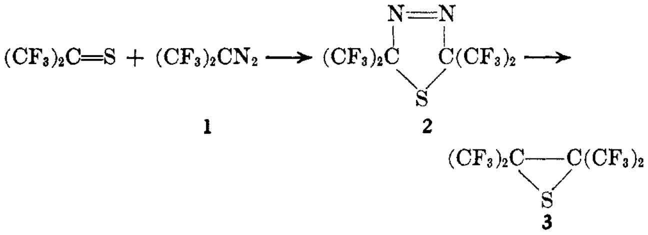
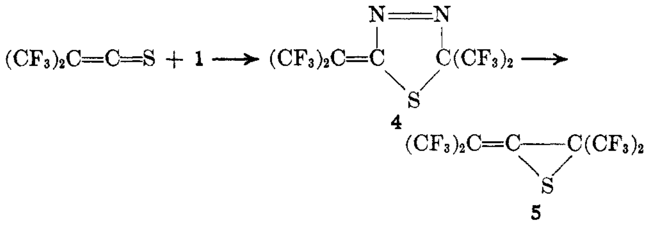
Several investigators have reported that diazo compounds react with thio ketones by loss of nitrogen to give episulfides.[1] It has been assumed that an unstable thiadiazoline is first formed as an intermediate,[1a] but there appears to be no report of the isolation or confirmation of such an intermediate.

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); $n^{25}\mathrm{D}$ 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°; $n^{25}\mathrm{D}$ 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)-

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(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.

diazomethane were mixed at −78° and allowed to warm slowly to room temperature. Distillation gave 3.57 g (96%) of **4** as a colorless liquid: bp 44–45° (20 mm); $n^{25}D$ 1.3622; $^{19}F$ nmr (neat) δ 57.3 ppm (q, $J$ = 8 Hz, 3 F), 63.2 (q, $J$ = 8 Hz, 3 F), 70.7 (s, 6 F); ir (liquid) 6.17 and 6.48 μ (C=C and N=N); Raman, 1630 and 1552 cm$^{-1}$; uv (isooctane) $\lambda_{max}$ 327 mμ (ε 4200).

*Anal.* Calcd for $C_7F_{12}N_2S$: C, 22.59; F, 61.27; N, 7.53; S, 8.61. Found: C, 22.89; F, 61.67; N, 7.67; S, 8.67.

**2,2-Bis(trifluoromethyl)-3-bis(trifluoromethyl)methylenethiirane (5).**—A 2.0-g sample of **4** was heated at reflux for 24 hr and then distilled to give **5** as a colorless liquid: bp 93°; $n^{25}D$ 1.3279; ir (liquid) 5.75 μ (C=C); uv (ethanol) $\lambda_{max}$ 239 mμ (ε 11,400), $^{19}F$ nmr (neat) δ 61.0 ppm (m, 3 F), 63.0 (q, $J$ = 6 Hz, 3 F), 67.4 (q, $J$ = 4 Hz, 6 F).

*Anal.* Calcd for $C_7F_{12}S$: C, 24.43; F, 66.25; S, 9.32. Found: C, 24.55; F, 66.32; S, 9.23.

**Registry No.**—**1**, 684-23-1; **2**, 20728-38-5; **3**, 2375-87-3; **4**, 20708-15-0; **5**, 20728-39-6.

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## 1,2 and 1,4 Addition of Ethylene to Butadiene

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In a recent paper[1] Bartlett and Schueller report that at 175° the addition product of ethylene to butadiene consisted of 99.98% cyclohexene (CH) and 0.02% of a second product. Since this second product had the same retention time on two gas chromatographic columns as authentic vinylcyclobutane (VCB), they identify it as VCB. The conditions of the experiment were such that the product ratio, CH/VCB, is equal to the ratio of rate constants $k_{1,4}/k_{1,2}$ where $k_{1,4}$ and $k_{1,2}$ are the rate constants for formation from ethylene and butadiene of CH and VCB, respectively. The authors discuss the implications of this new reaction to the mechanism of the Diels–Alder reaction. It is the purpose of this paper to point out that there exist data in the literature from which the value of $k_{1,4}/k_{1,2}$ can be independently calculated.

The author feels the calculation is of interest both because it confirms Bartlett and Schueller product identification and because it provides new information, the temperature dependence of $k_{1,4}/k_{1,2}$.

It can easily be shown that $k_{1,4}/k_{1,2} = (k_{-1,4}/k_{-1,2})\ K_3$ where $k_{-1,4}$ and $k_{-1,2}$ are the rate constants for decomposition to ethylene and butadiene of CH and VCB, respectively, and $K_3$ is the equilibrium constant for the isomerization of VCB to CH. Using the tables given by Benson,[2] one calculates, *via* the group additivity method, that $\log K_3 = -1.604 + (25500/4.57\ T)$.

Uchizama, Tomioka, and Amano[3] report that $\log k_{-1,4} = 15.16 - (66200/4.575\ T)$. $k_{-1,2}$ has not been measured directly but it should be very nearly equal to the rate at which isopropenylcyclobutane[4] decomposes to ethylene and isoprene; *i.e.*, $\log k_{-1,2} = 14.64 - (51030/4.575\ T)$. This assumes that introducing a methyl group in a next nearest neighbor position does not change the rate of cyclobutane ring rupture. This assumption may be justified by comparing the rate constants of decomposition of methyl cyclobutane[5] and ethyl cyclobutane.[6] At 450° they are 7.6 × 10$^{-4}$ sec$^{-1}$ and 6.6 × 10$^{-4}$ sec$^{-1}$, respectively. Thus one calculates that $\log k_{1,4}/k_{1,2} = 1.08 + (10350/4.575\ T) = 3.97$ at 175°, in good agreement with Bartlett and Schueller's value of 3.7.

**Registry No.**—Ethylene, 74-85-1; butadiene, 106-99-0.

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[1] P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968).

[2] S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.

[3] M. Uchizama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, **68**, 1878 (1964).

[4] R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).

[5] M. N. Das and W. D. Walters, *Z. Physik. Chem.* (Frankfurt), **15**, 22 (1958).

[6] R. E. Wellman and W. D. Walters, *J. Amer. Chem. Soc.*, **79**, 1542 (1957).

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## Thiabenzenes. VI. Steric Factors Influencing the Stability of 2-Phenyl-2-thianaphthalenes

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The first thiabenzene prepared, the 1,2,4,6-tetraphenyl compound,[2a] was relatively unstable compared to others prepared later.[2b,c] While it failed to protonate readily like the phosphorabenzenes,[3] it rearranged to the isomeric thiopyran and reacted readily with oxygen. These differences in stability, as well as a difference in color, the unstable analog being purple while all the stable compounds were red-brown, was rationalized on the basis of a hypothesis that there was very little, if any, barrier to out-of-plane bending at phenyl–sulfur bond in these molecules due to relatively equal energy p$^3$ and sp$^2$ bonding geometry at the sulfur atom in thiabenzenes.[2b,c,3] This low barrier to bending was also offered as an explanation for the amorphous nature of these compounds as well as their remarkably broad absorbance of visible and ultraviolet radiation.

In order to test these theories further, we have now prepared two hindered analogs of the stable thiabenzene, 2-phenyl-2-thianaphthalene, by the following synthetic route, taking advantage of the fact that, while phenyllithium generally couples on the sulfur of thiopyrylium salts,[2] the Grignard reagent couples on carbon.

For the case of R = *t*-Bu, it was not possible to isolate the thianaphthalene IVb. Reaction mixtures for its preparation were deep wine red or purple (although the color faded in a day or so), but quenching with aqueous ammonium chloride gave the protonated form, Vb, as colorless crystals. This salt could be deprotonated only by base as strong as potassium ethoxide in DMSO, indicating a p$K_a$ in the range of 20–25.

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[1] Supported in part by a grant from the National Science Foundation, NSF GP-5269.

[2] (a) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962). (b) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963). (c) C. C. Price, M. Polk, and M. Siskin, *ibid.*, in press.

[3] G. Markl, *Angew. Chem.*, **75**, 168, 669, 1121 (1963).