406 (molecular ion); pmr (DMSO-d_6) ~ δ 2.36 (s, 3, CH_3), 2.43 (s, 3, CH_3), 2.8–3.8 (pair of triplets, 4, NCH_2CH_2N), 3.22 [s, 2, $NCH_2C(N)<$], 5.1 (d, 2, $>CH_2$), 7.1–7.7 (m, 8, aromatic CH). *Anal.* Calcd for $C_{19}H_{22}N_2O_4S_2$: C, 56.14; H, 5.45; N, 6.89. Found: C, 56.22; H, 5.27; N, 6.70.

The structure assigned to the previously described[4] **2-piperazinemethanethiol hydrobromide (7a)** was confirmed by pmr (D_2O, DSS internal standard) data: ~δ 2.8–3.2 (m, 2, CH_2S), 3.1–4.1 (m, 7, NCH).

Registry No.—5, 36748-77-3; **7a,** 36748-78-4; **8,** 36748-79-5.

Acknowledgment.—The authors are indebted to Dr. W. C. Coburn, Jr., and members of the Molecular Spectroscopy Section of Southern Research Institute for microanalytical and spectral data and to Mrs. Martha Thorpe for interpretation of pmr data.

A New High Yield Procedure for Thiocyanogen and Thiocyanates

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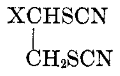
We report here a new high yield procedure for the preparation of thiocyanogen and thiocyanates, and the use of this procedure to synthesize three new haloalkylene bisthiocyanates.

The procedure consisted of the use of a two-solvent system (water and water-immiscible hydrocarbon) for the reaction between a thiocyanate salt and a halogen. The thiocyanogen formed in the aqueous phase was extracted into the hydrocarbon phase. With sodium thiocyanate and chlorine as the reactants, and toluene as the hydrocarbon solvent, 85–90% yields of thiocyanogen were routine. The thiocyanogen solution, after physical separation from the water phase and sodium chloride and without drying, could be used immediately or stored at reduced temperature for subsequent use.

The efficacy of this procedure was undoubtedly due to the presence of the water-immiscible phase during the generation of thiocyanogen, which extracted and preserved the thiocyanogen as it was formed. Until now, anhydrous conditions were generally considered to be essential for the satisfactory preparation of thiocyanogen.[1–3] Although aqueous systems (without a water-immiscible phase) have been tried, the conversions to thiocyanogen were not reported.[4–7]

Many well-known reactions of thiocyanogen have become economically feasible as a result of the two-solvent procedure, which depends on sodium thiocyanate and chlorine rather than the customary silver or lead thiocyanate, and bromine.

Also, a previously unknown reaction, the synthesis of haloalkylene bisthiocyanates,[8] has been carried out for the first time. The fluoro, chloro, and bromo analogs (**1**), crystalline solids with pungent odors, were prepared in good yield by the addition of thiocyanogen, prepared by the two-solvent procedure, to the corresponding vinyl halides, with diisopropyl peroxydicarbonate as the catalyst. Earlier attempts to add thiocyanogen to vinyl bromide and other halogenated olefins had been unsuccessful.[3]



$$\begin{array}{l} XCHSCN \\ | \\ CH_2SCN \end{array}$$

1, X = F, Cl, Br

Experimental Section[9,10]

Preparation of Thiocyanogen Solution.—Addition of 28.9 g (0.407 mol) of gaseous chlorine beneath the surface of a well-stirred mixture of 379 g of toluene, 50 g of water, and 64.9 g (0.800 mol) of sodium thiocyanate over a period of 1 hr with the temperature at 2–8° gave a mixture of yellow toluene layer and wet sodium chloride. After filtration, toluene wash of the cake, and physical separation of the water layer, 475 g of the upper toluene phase was obtained, containing 42.6 g of thiocyanogen, a 90% yield (iodimetric assay). The yellow solution, although wet, was moderately stable at reduced temperature. Thus, in 17 hr at 0–2°, the concentration of such a thiocyanogen solution fell from 0.57 to 0.54 *N*.

Chloroethylene Bisthiocyanate (CET).—To all of the above thiocyanogen solution at 0–5° was added the catalyst solution, 2.15 g (0.0104 mol) of diisopropyl peroxydicarbonate (PPG Industries, Inc.) in 13 g of toluene. After the apparatus was flushed with nitrogen, 28.6 g (0.457 mol) of vinyl chloride was added as a gas beneath the liquid surface at 0–5°. The solution was heated to 50° in 15 min and held at 50–57° for 2 hr. An exotherm lasting 20 min raised the temperature from 50 to 57°. Iodimetric titration showed that less than 2% thiocyanogen remained. The slurry was filtered to remove parathiocyanogen. The yellow filtrate contained 55.1 g of CET, a 77% overall yield based on sodium thiocyanate.

Crystalline CET was recovered by removing the toluene solvent at reduced pressure, mp 46–46.5° (from ethanol). It was soluble in cold methanol, acetonitrile, methylene chloride and benzene, and hot ethanol, and difficulty soluble in hot water and petroleum ether (bp 30–60°).

Anal. Calcd for $C_4H_3ClN_2S_2$: C, 26.89; H, 1.69; N, 15.68; S, 35.89; Cl, 19.85. Found: C, 27.00; H, 1.60; N, 15.84; S, 35.84; Cl, 19.15.

Bromoethylene Bisthiocyanate (BET).—BET was prepared in 70% overall yield by the addition of 62.9 g (0.59 mol) of vinyl bromide to the same quantity of catalyst-containing thiocyanogen solution as above, followed by heating for 1 hr at 35–37°, filtration, and removal of solvent, mp 43.5–44° (from ethanol).

Anal. Calcd for $C_4H_3BrN_2S_2$: C, 21.53; H, 1.35; Br, 35.82; N, 12.56; S, 28.74. Found: C, 21.73; H, 1.25; Br, 36.19; N, 12.58; S, 28.45.

Fluoroethylene Bisthiocyanate (FET).—In order to contain the volatile vinyl fluoride, the reaction was carried out in an autoclave, within a glass liner. Excess vinyl fluoride (14.7 g,

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[1] G. B. Kauffman, G. E. Foust, and P. Tun, *J. Chem. Educ.*, **45**, 141 (1968).

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[3] A. Liermain, *Ann. Chim. (Paris)*, **9**, 507 (1954).

[4] (a) E. E. Stahly, U. S. Patent 3,308,150 (1967); (b) E. E. Stahly, U. S. Patent 3,314,983 (1967).

[5] (a) H. F. Pfann (to Koppers Co., Inc.), U. S. Patent 2,639,267 (1953); (b) H. F. Pfann (to Koppers Co., Inc.), U. S. Patent 2,639,291 (1953).

[6] H. P. Kaufmann (to I. G. Farbenindustrie Akt), U. S. Patent 1,859,399 (1932).

[7] J. H. Clayton and B. Baun (to the Manchester Oxide Co., Ltd.), U. S. Patent 2,212,175 (1940).

[8] Although the preferred Chemical Abstracts name for such a compound is haloalkylene thiocyanate, there is some precedent for either bis- or di- as a multiplying prefix (K. L. Loening, Chemical Abstracts Director of Nomenclature, private communication).

[9] All melting points are corrected. The ir spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. The nmr spectra were run on both the Varian A-60 and HA-100 instruments. The uv spectrum was recorded with a Cary 14 spectrophotometer.

[10] Thiocyanogen has been characterized as "probably highly toxic," See N. Irving Sax, "Dangerous Properties of Industrial Materials," 3rd ed, Reinhold, New York, N. Y., 1968, p 1160. No difficulty was experienced in this work, but the toluene solution of thiocyanogen should be considered irritating to the skin, and highly irritating to the eye.

0.32 mol) was added as a liquid to 190 g of frozen benzene solution containing 14.5 g of thiocyanogen and 0.8 g of catalyst at −80°. After heating for 2 hr at 40–54°, under a nitrogen pressure of 625 psi, venting, and removal of solvent, the residue was extracted with methylene chloride to provide a 57% overall yield of crystalline FET, mp 35.5–36° (from ethanol).

Anal. Calcd for $C_4H_3FN_2S_2$: C, 29.62; H, 1.86; F, 11.71; N, 17.28; S, 39.53. Found: C, 29.65; H, 1.57; F, 11.4; N, 17.08; S, 39.19.

Spectra.—The three haloalkylene bisthiocyanates had mostly similar ir spectra with the following bands in common: 2900 (s), 2150–2160 (s, sharp),[11] 1415–1425 (s), 1245 (s), 1150 (m), 900 (s), and 408 cm^{-1} (w). Distinctive bands were seen at 1300 (m), 1010 (m), and 632 cm^{-1} (m) for FET, 702 cm^{-1} (m) for CET, and 660 cm^{-1} (m) for BET.

CET had a weak absorption band in the near-ultraviolet region [ϵ_{243} 151 (in methanol)].

The nmr spectra were all consistent with the proposed structures. For BET and CET, the CH_2's were equivalent, giving only a doublet; the CH was a triplet. FET showed an extra coupling from the fluorine, so that the CH was a doubled triplet, and the CH_2 showed a slight nonequivalence. The CH and CH_2 peak positions and $CHCH_2$ couplings (absolute values) were as follows: BET, δ 5.27, 3.79 (J = 7.0 Hz); CET, δ 5.36, 3.70 (J = 6.7 Hz); FET, δ 6.10, $\sim$3.63 (J = 6.0 Hz). In addition, for FET the CHF coupling was 47.2 Hz.

Registry No.—Thiocyanogen, 505-14-6; CET, 24689-89-2; BET, 26799-59-7; FET, 26799-60-0.

Acknowledgment.—We thank Mr. N. B. Colthup, Mr. J. Koren, Dr. J. E. Lancaster, and Mrs. M. T. Neglia for their assistance in interpreting the ir, uv, and nmr spectra.

[11] Organic thiocyanates (RSCN) show a medium-strong sharp ir band at 2170–2135 cm^{-1} caused by the $C\equiv N$ stretch vibration. Organic isothiocyanates (RNCS) have a very strong broader ir band at 2150–2050 cm^{-1} caused by the out-of-phase $N{=}C{=}S$ vibration. See N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 201.

Preparation of the Diels–Alder Adducts of Methyl Vinyl Sulfone and Cyclopentadiene and of Their Dihydro Derivatives[1]

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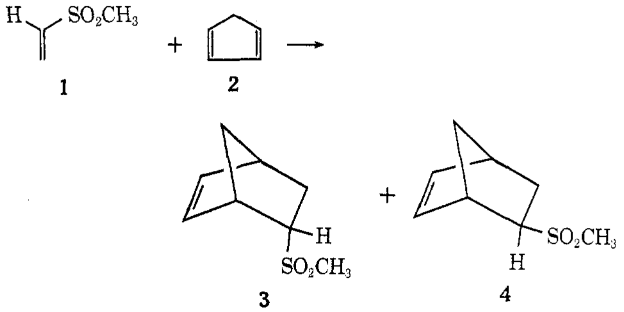
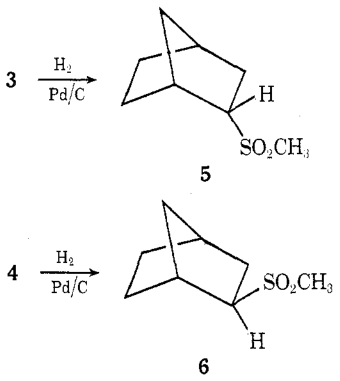
In the course of another problem[2] a need arose for relatively large quantities of the Diels–Alder adducts of methyl vinyl sulfone and cyclopentadiene and the corresponding dihydro derivatives and for a knowledge of the respective stereochemistries in each series. The methyl vinyl sulfone–cyclopentadiene reaction was investigated previously by Snyder,[3] but mention was made only of one adduct isomer, mp 55–56°, and no data or speculation concerning its stereochemistry were reported. Also, the addition of methyl mercaptan to norbornene followed by hydrogen peroxide oxidation has been reported by Davies[4] to afford only *exo*-2-methylsulfonylbicyclo[2.2.1]heptane.

The ambient temperature reaction of methyl vinyl sulfone (**1**)[5] with cyclopentadiene (**2**) was monitored by means of nmr, and the formation of two cycloadducts **3** and **4** was observed. Chromatography on silica gel afforded pure samples of each isomer. In accord with the endo rule[6] and on the basis of chemical shift data, the structure of the major cycloadduct, mp 55–55.5°, was assigned to the *endo*-methylsulfonyl isomer **3**. The $-SO_2CH_3$ nmr absorption of **3** is observed at a higher field than the corresponding absorption of the minor cycloadduct **4**, mp 41.5–42.5°. The shielding of endo protons or of protons attached to endo functional groups in bicyclo[2.2.1]hept-2-enes and inversely the deshielding of exo protons or of protons attached to exo functional groups are well-recognized phenomena.[7] However, care should be taken to ensure that these effects are due predominantly to the anisotropy of the double bond and not to that of the 5–8 σ bond.[8] Thus, removal of the double bond by hydrogenation should result in a downfield shift for the *endo*-methylsulfonyl hydrogens and an upfield shift for the *exo*-methylsulfonyl hydrogens.[7,8] The expected chemical shifts were indeed observed as can be seen in Table I. Further confirmation of the above structural assignments was obtained by comparison of the *exo*-methylsulfonyl isomer **6** with authentic material.[4] The two sulfones were identical in all respects.





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[1] Grants from The Research Corp. and The Petroleum Research Fund, administered by The American Chemical Society, are gratefully acknowledged.

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