Less reactive dienophiles such as diethyl maleate, diphenylacetylene, and *p*-benzoquinone did not react with **1a**. Of the three vinylketene thioacetals examined in this study **1a** was the only one to give an adduct with maleic anhydride. Failure of **1b** and **1c** to react with maleic anhydride is presumably due to electronic and steric effects, respectively.

Experimental Section

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr discs for solids and pressed films for liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV.

Microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany.

Vinylketene thioacetals **1a** and **1b** were previously reported, while 2-[1-methyl-1-(1-cyclohexenyl)]methylene-1,3-dithiane (**1c**) was prepared in 87% yield from 1-acetyl-1-cyclohexene according to the general procedure described in ref 5.

The analytical sample was obtained by preparative tlc to yield **1c** as a colorless liquid: nmr ($CDCl_3$) δ 1.4–1.8 (m, 4), 1.9 (s, 3, CH_3C=), 1.9–2.2 (m, 6), 2.6–3.0 (q, 4, SCH_2), 5.34 (m, 1, vinyl H).

Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01. Found: C, 63.74; H, 7.89.

General Procedure for Reactions of 1a–c with Tetracyanoethylene.—Tetracyanoethylene was added to an equal molar amount of the vinylketene thioacetal in methylene chloride (3 ml per 2 mmol of **1**) at 25° and the solution was stirred for 15–30 min and evaporated.

2a.—The residue obtained after evaporation was washed with ether to afford the pure adduct in 71% yield: mp 169–170°; nmr ($CDCl_3$) δ 1.60 (d, 3, J = 7 Hz, CH_3CH), 1.90 (s, 3, C=C), 2–4 (m, 7, SCH_2CH_2 and CH_3CH), 5.6 (br s, 1, C=CH).

Anal. Calcd for $C_{15}H_{14}N_4S_2$: C, 57.29; H, 4.48; S, 20.40. Found: C, 57.43; H, 4.35; S, 20.53.

2b.—Purified adduct, mp 183°, was obtained in 83% yield by washing the material remaining after evaporation with ether: nmr ($CDCl_3$) δ 4.40 (s, 1, PhCH), 6.0 (m, 2, HC=CH), 7.45 (s, 5, Ph); mass spectrum m/e (rel intensity) 326 (12), 234 (100), 160 (42).

The analytical sample, mp 183°, was obtained by recrystallization from ether. *Anal.* Calcd for $C_{19}H_{14}N_4S_2$: C, 62.95; H, 3.89; S, 17.70. Found: C, 62.76; H, 3.87; S, 17.90.

2c.—The crude product was purified by preparative tlc on silica gel using ether as the developing solvent to yield white crystals, mp 168–169° (72% yield). The nmr spectrum was characterized by three broad, complex multiplets at δ 1.6–2.4, 2.5–3.2, and 3.3–4 and a doublet (J = 1–2 Hz) at δ 1.99 assigned to the allylic methyl group; mass spectrum m/e (rel intensity) 354 (26), 179 (20), 106 (100), 91 (31).

Anal. Calcd for $C_{18}H_{18}N_4S_2$: C, 60.98; H, 5.12; S, 18.09. Found: C, 60.97; H, 5.20; S, 18.02.

An authentic sample of the adduct of TCNE and **3** was prepared in the same fashion as the adducts of **1** in 77% yield: mp 155°; nmr ($CDCl_3$) δ 3.2 (br, 2, allylic CH_2), 4.3 (br, 1, PhCH), 6.0 (s, 2, vinyl CH), 7.4 (s, 5, Ph).

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90. Found: C, 74.22; H, 3.77.

Reaction of 1a with Maleic Anhydride.—A solution of 4.0 g (21.7 mmol) of **1a** and 2.1 g (21.5 mmol) of maleic anhydride in 50 ml of xylene was refluxed for 3 hr. The xylene solution was concentrated under vacuum. The crystalline adduct which resulted was filtered and washed with ether to yield 3.6 g (60%) of **4**: nmr ($CDCl_3$) δ 1.43 (d, 3, J = 7 Hz, CH_3CH), 1.87 (s, 3, CH_3C=), 1.9–2.2 (m, 2, SCH_2CH_2), 2.5–3.3 (m, 5, SCH_2 and CH_3CH), 3.5 (d, d, 1, J = 8, 5 Hz, HC=CO), 4.06 (d, 1, J = 8 HzHCC=O), 5.75 (br s, 1, C=CH).

The analytical sample was obtained by recrystallization from chloroform–ethanol, mp 114–115°.

Anal. Calcd for $C_{13}H_{16}O_3S_2$: C, 54.90; H, 5.67; S, 22.55. Found: C, 54.97; H, 5.46; S, 22.66.

Conversion of 4 to Methyl 2,3-Dimethyl-4-oxo-3-cyclohexenecarboxylate (6).—A solution of 500 mg (1.75 mmol) of **4** in 45 ml of methanol containing 5 ml of water and 1.05 g (3.9 mmol) of mercuric chloride was refluxed for 15 hr under nitrogen, cooled, and filtered through Celite. The Celite was washed thoroughly with methanol and the combined filtrates were evaporated. The residue (448 mg) exhibited peaks in the nmr at δ 3.7 attributable to a methyl ester and at 9.2 for the carboxylic acid. This product was taken up in 50 ml of methanol, several drops of sulfuric acid were added, and the solution was refluxed for 6 hr. The methanol was removed on the rotary evaporator and the product was taken up in methylene chloride. The solution was washed with water, dried ($MgSO_4$), filtered, and evaporated to yield 317 mg of **6**. The nmr spectrum of this product was identical with that of the purified product (190 mg, 58%) obtained by preparative tlc on silica gel with 75% ether–25% hexane. The nmr spectrum clearly showed that a mixture of epimers was present by the doubling of the $-OCH_3$ and CH_3CH signals: nmr ($CDCl_3$) δ 1.1 and 1.25 (2, d, J = 7 Hz, CH_3CH), 2.0 (2, d, CH_3C=C), 2.5–3 (m, CHC=O and CH_3CH), 3.70 and 3.75 (2, s, OCH_3), and 5.80 (br, s, vinyl H); mass spectrum m/e (rel intensity) 182 (18), 123 (100), 96 (65), 95 (28).

The analytical sample was obtained by preparative glpc on Carbowax at a column temperature of 200°.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.86; H, 7.72.

Registry No.—**1a**, 36744-60-2; **1b**, 36744-61-3; **1c**, 36736-49-9; **2a**, 36736-50-2; **2b**, 36736-51-3; **2c**, 36748-70-6; **3**–TCNE adduct, 36748-71-7; **4**, 36744-62-4; **6**, 36748-72-8.

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Ring Contraction in a Synthesis of 2-Piperazinemethanethiol[1]

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The reaction of the disodium salt of *N*,*N*′-ethylenebis-*p*-toluenesulfonamide (**1**) with 2,3-dibromo-1-propanol has recently been shown to give hexahydro-1,4-bis(*p*-tolylsulfonyl)-1*H*-1,4-diazepin-6-ol[2] (**2**) instead of 1,4-bis(*p*-tolylsulfonyl)-2-piperazinemethanol (**4**) as originally reported[3] and subsequently assumed by other investigators.[4,5] The error was confirmed[2] by a comparison of **2** with an authentic sample of **4** (which was prepared from ethyl 1,4-dibenzyl-2-piperazinecarboxylate[6] in three steps). The intermediacy of *N*-2,3-epoxypropyl-*N*,*N*′-ethylenebis-*p*-toluenesulfonamide in the formation of **2** was suggested.[2] The firm identity of **2** cast considerable doubt on the structures of intermediates and products in the re-

(1) This investigation was supported by U. S. Army Medical Research and Development Command (Contract No. DADA17-69-C-9033).

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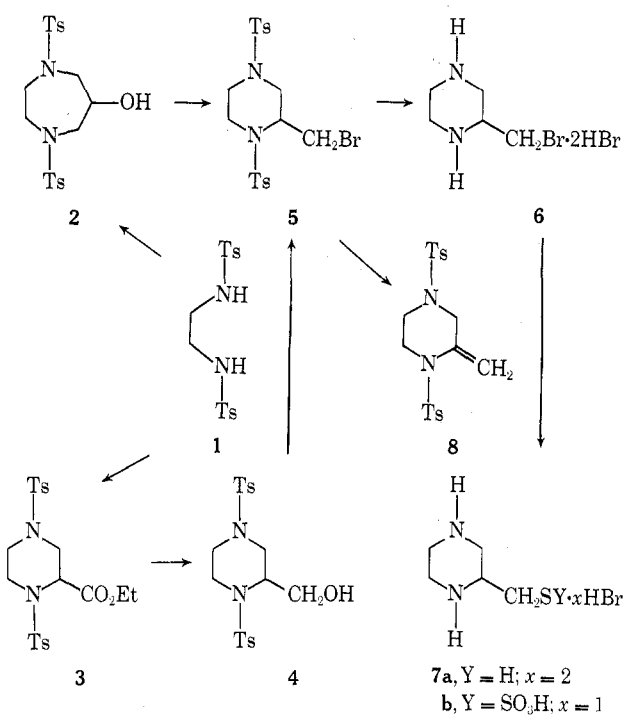
ported[4] synthesis of 2-piperazinemethanethiol dihydrobromide (**7a**) and the corresponding thiosulfate **7b**. The pmr spectrum of a sample of the hydroxy intermediate used in the synthesis of **7a,b** agreed with pmr data reported[2] for authentic **2**. These findings prompted an investigation of other structures in the sequence.

An unambiguous synthesis of **4** from **1** was performed, combining successively (1) the condensation[3a] of the preformed disodium salt of **1** with ethyl 2,3-dibromopropionate in *N,N*-dimethylformamide (DMF) and (2) the lithium aluminum hydride reduction[2] of the resulting ethyl 1,4-bis(*p*-tolylsulfonyl)-2-piperazinecarboxylate (**3**). Treatment of **4** with dibromotriphenylphosphorane[7] afforded 2-(bromomethyl)-1,4-bis-(*p*-tolylsulfonyl)piperazine (**5**), which, unexpectedly and fortuitously, was identical (melting point and mixture melting point, ir and pmr spectra) with the product obtained earlier[4] by the treatment of **2** (thought at that time to be **4**) with thionyl bromide.

The pmr spectrum was clearly consistent with **5**. Thus, it was shown that bromodehydroxylation of **2** with thionyl bromide resulted in ring contraction, similar examples of which effected with thionyl chloride[8] and with phosphorus tribromide[9] have recently been reported and for which activated aziridinium intermediates were proposed. The pmr spectrum of the thiol[4] derived from **5** *via* the detosylated bromide **6** was consistent with the originally assigned structure **7a**. In a resynthesis of **5** from **2**, dibromotriphenylphosphorane was shown to be an effective reagent for the rearrangement. An attempted alkylation of the sodium salt of 2-oxazolidinone[10] with **5** resulted in dehydrobromination; the isolated product was shown by elemental and spectral (pmr, mass) analysis to be 2-methylene-1,4-bis(*p*-tolylsulfonyl)-piperazine (**8**).



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Experimental Section[11]

Ethyl 1,4-Bis(*p*-tolylsulfonyl)-2-piperazinecarboxylate (3).—The disodium salt of **1** was prepared by the addition of pulverized **1**[4] (96.0 g, 0.260 mol) to a warm solution of sodium methoxide (28.0 g, 0.518 mol) in methanol (700 ml) and dilution of the resulting clear solution with ether (700 ml): yield 106 g (99%). The salt was suspended in DMF (500 ml), and a solution of ethyl 2,3-dibromopropionate (66.7 g, 0.256 mol) in DMF (500 ml) was added. The mixture was stirred at 90–110° for 3 hr, cooled, and added to water (12 l.). The precipitate that formed was recrystallized twice from ethanol to give **3**, mp 152.5–155° (lit.[2] mp 150.9–154.9°), in 83% yield (75.6 g).

2-(Bromomethyl)-1,4-bis(*p*-tolylsulfonyl)piperazine (5). A. From 4.—Dibromotriphenylphosphorane was prepared by the dropwise addition of a solution of bromine (1.92 g, 12.0 mmol) in acetonitrile (10 ml) to a partial solution of finely divided triphenylphosphine (3.14 g, 12.0 mmol) in acetonitrile (40 ml) at 10–15°. The mixture was allowed to warm to 25°, and **4** (4.24 g, 10.0 mmol) was added. The resulting solution was kept at 25–30° for 2 hr, refluxed for 2 hr, and allowed to cool. The cooled mixture, from which product had begun crystallizing, was treated with water (1.5 ml), stirred for ~10 min, and reheated to boiling. Water (~8.5 ml) was added to the hot solution until solid began forming, and the mixture was left to cool and stand overnight. The crystallized solid was collected and dried *in vacuo* (25–30°, P_2O_5). A small second crop was obtained from the filtrate diluted with water to incipient cloudiness. The two crops (3.47 and 0.37 g, mp of each ~200°) were combined and recrystallized from acetonitrile to give pure **5**, mp 204–206°, in 68% yield (3.29 g): pmr ($CDCl_3$) ~δ 2.0–2.5 (m, 8, includes CH_3 singlets at 2.40 and 2.44, and CH_2Br), 2.9–4.4 (m, 7, NCH), 7.1–7.8 (m, 8, aromatic CH). *Anal.* Calcd for $C_{19}H_{23}BrN_2O_4S_2$: C, 46.81; H, 4.75; N, 5.75. Found: C, 46.93; H, 4.86; N, 5.59. This compound was identical (melting point, mixture melting point, ir, pmr) with the product obtained earlier by the action of thionyl bromide on **2**, which had been erroneously assigned structure **4**.[4]

B. From 2.—Dibromotriphenylphosphorane (12.0 mmol) was prepared in acetonitrile (50 ml) for use *in situ* as described under A, and **2** (4.24 g, 10.0 mmol) was added. The mixture, which contained a small amount of insoluble solid, was stirred at 25–30° for 18 hr and was then refluxed for 6 hr, complete solution occurring shortly after heating was started. Examination of the reaction mixture during the 18-hr and 6-hr periods by thin layer chromatography [Merck silica gel H, ethyl acetate–benzene (1:1), iodine-vapor detection] showed the appearance of **5** during the heating period, but after 4 hr unchanged **2** was still present. The reaction solution was poured into water (200 ml), and the solid that formed was collected and dried *in vacuo* (25–30°, P_2O_5): wt 5.79 g, mp 130–138°. [A small amount (0.56 g) of solid that separated from the filtrate was identified as triphenylphosphine oxide.] Two recrystallizations of the crude solid from acetonitrile gave 1.44 g (29%) of pure **5**, mp 204–206°, whose identity was attested by a comparison (ir, tlc, melting point, mixture melting point) with **5** prepared from **4**. A work-up of the filtrate from the first recrystallization (precipitation by addition of water and recrystallization from acetonitrile) gave a slightly less pure crop (1.35 g, mp 202–204°), which increased the yield to 59%.

2-Methylene-1,4-bis(*p*-tolylsulfonyl)piperazine (8).—A solution of 2-oxazolidinone (0.435 g, 5.00 mmol) in DMF (10 ml) was added dropwise to a stirred suspension of sodium hydride (0.21 g of 57% dispersion in oil, 5.0 mmol) in DMF (8 ml). After 30 min, **5** (2.44 g, 5.00 mmol) and sodium iodide (0.1 g) were added. The mixture was stirred at 25–30° for 4 days, then poured into water to give **8**, mp 148–150°, in 62% yield (1.52 g). The analytical sample, mp 150.5–151.5°, was recrystallized successively from ethyl acetate and ethanol: mass spectrum *m/e*

(11) Melting points were determined with a Mel-Temp apparatus, ir spectra with a Perkin-Elmer 521 spectrometer, pmr spectra with a Varian XL-100-15 spectrometer, and mass spectra with a Hitachi Perkin-Elmer RMU-6D-3 spectrometer. Hexahydro-1,4-bis(*p*-tolylsulfonyl)-1*H*-1,4-diazepin-6-ol (**2**, from 2,3-dibromo-2-propanol) and 1,4-bis(*p*-tolylsulfonyl)-2-piperazinemethanol (**4**) were prepared by slight modifications of literature[2] procedures.

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.

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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]

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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(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.