tions at 1488 cm^{-1}. Replacement of chloride ion for the methanesulfonate group did not result in any significant shifts in the positions of these two bands. Infrared spectra of the hydromethanesulfonate salts[3] as KBr pellets showed an absorption band at 1570 cm^{-1} for the >C=N group and at 1480 cm^{-1} for the $-NH_2$ group. A detailed analysis of the ^1H NMR spectra of the 2-imino-1,3-dithiolane hydromethanesulfonates is described in part 5 of this series.[14]

Experimental Section

Reagents. The *vic*-dithiocyanate adducts were prepared by thiocyanogen addition to the olefinic compounds as described in previous reports.[1,12] Ethylene dithiocyanate was a commercial sample supplied by Eastman Kodak.[15] Anion ion exchange resin AG 1-X4 (Bio-Rad Laboratories) was obtainable in analytical grade for the interchange of methanesulfonate and chloride anions.

Procedure. Examples of the Preparation of 2-Imino-1,3-dithiolane hydrogen Methanesulfonates and Chlorides. *cis*-4,5-Diethyl-1,3-ditholane-2-iminium Methanesulfonate from *erythro*-3,4-Dithiocyanatohexane 7. Compound **7** (1.0 g, 5.0 mmol) was added to a solution of 100 mg of water in 5 g of freshly distilled methanesulfonic acid. Upon heating the mixture to 60 °C the solid dithiocyanate dissolved and a vigorous evolution of carbon dioxide occurred. Aliquots were removed at frequent intervals as described in the text to test for completion of reaction. Upon completion of the reaction, coproduct **6** was removed as described below. The reaction mixture was then diluted with water and placed in a continuous extraction apparatus using ethyl ether as the extracting solvent. The product was extracted into ether which upon evaporation left a solid residue. The recovered salt was purified by recrystallization from methanol/ether and gave 1.15 g (85%): mp 132–134 °C dec; IR (KBr pellet) 2850, 1540, 1460, 1200, and 1050 cm^{-1}. Anal. Calcd for $C_8H_{17}NO_3S_3$: C, 35.4; H, 6.35; N, 5.15; S, 35.4. Found: C, 35.23; H, 6.34; N, 5.14; S, 35.7.

On the basis of this procedure, the hydromethanesulfonate salts of compounds **6, 8, 9,** and **11** were isolated and satisfactory spectral data and elemental analyses were obtained.

***trans*-4,5-Hexahydrobenzo-1,3-dithiolane-2-iminium Methanesulfonate from *trans*-1,2-Dithiocyanatocyclohexane 11.** Using the same procedure as described above, **11** was cyclized in 6.5 h to the title compound. However, the product could not be removed from the excess methanesulfonic acid by continuous extraction with ether. Exchange of methanesulfonic acid for volatile hydrochloric acid was simply attained by aqueous dilution of the crude methanesulfonic acid mixture after cyclization and elution through a column of AG 1-X4 resin (chloride form) and evaporation of the eluates. Comparison of the melting point and published spectral data[4] established the structure of this compound. By a similar technique the dithiocyanate **9** was also converted to the hydrochloride salt.

Ammonium methanesulfonate (**5**) precipitated upon addition of chloroform to the crude reaction mixture. The compound was isolated as a white, crystalline solid, purified by repeated washings with chloroform (mp 198–201 °C dec), and identified by IR (KBr pellet): 3100, 1920, 1200, 1050, 780, and 560 cm^{-1}. Anal. Calcd for CH_7NO_3S: C, 10.62; H, 6.19: N, 12.4; S, 28.5. Found: C, 11.04; H, 6.26; N, 12.38; S, 28.9.

Registry No.—**5,** 22515-76-0; **6,** 629-17-4; **7,** 30647-63-3; **8,** 61521-96-8; **9,** 61522-04-1; **10,** 55602-15-8; **11,** 30647-66-6.

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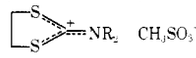
(2) Agricultural Research Service, U.S. Department of Agriculture.
(3) The *Chemical Abstracts* systematic name for structure **2** (R = H) is "cyclic ethylene dithioimidocarbamate hydrochloride". A convenient, acceptable name for 2,2-imino-1,3-dithiolane (ref 4) was adapted to the compounds reported in this paper. The methanesulfonate salts are accordingly termed hydromethanesulfonates. The alternative name applicable to the methanesulfonate of **4**, 2-imino-1,3-dithiolinium methanesulfonate, is descriptive of the carbonium ion (structure below) and reflects the reactivity toward



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(11) Preparations of *vic*-dithiols to be reported in a subsequent publication.
(12) L. S. Silbert, J. R. Russell, and J. S. Showell, *J. Am. Oil. Chem. Soc.*, **50,** 415 (1973).
(13) Dry hydrochloric acid dissolved in nonpolar solvents also failed to effect cyclization of adduct **1.** Under these conditions hydrochloric acid may be too weak an acid to function effectively as a catalyst or requires the presence of water to bring about cyclization.
(14) Part 5: R. J. Maxwell, P. Pfeffer, and L. S. Silbert, *J. Org. Chem.*, accompanying paper in this issue.
(15) Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.
(16) Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer.

Thiocyanations. 4. Cyclization of 1-Isothiocyanato-2-thiocyanates. A Stereospecific Route to the Preparation of 4,5-Thiazolidine-2-thiones[1,2]

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When 1-isothiocyanato-2-thiocyanates **2** are heated in ethanolic potassium hydroxide, they cyclize to 4,5-thiazolidine-2-thiones. It was found that 4,5-thiazolidine-2-thiones prepared in this manner are formed stereospecifically. The representative examples of adducts **2** cyclized to the heterocyclic derivatives are discussed and a mechanism based on the experimental observations is proposed.

vic-Dithiocyanates **1,** which are obtained by the trans addition[4,5] of thiocyanogen to olefins (eq 1), have long been useful intermediates for the preparation of thiiranes[6] **3** (eq 2) and, more recently, were effectively cyclized to 2-imino-1,3-dithiolane salts **4** (eq 3).[2] The isomeric adduct, 1-isothiocyanato-2-thiocyanate **2,** has been identified and isolated as a minor product of the thiocyanation reaction.[4,7] However, studies in this laboratory[8] have shown that the relative amounts of the two isomers **1** and **2** formed are solvent dependent so that either isomer may be prepared as the primary product (eq 1). The versatility of this reaction provides isomer **2** as a potential intermediate which could extend the utility of the thiocyanation reaction to other heterocyclic preparations.

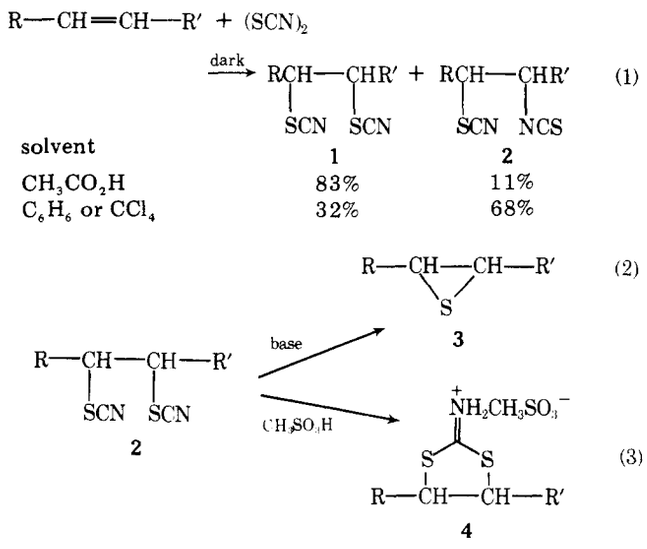
In contrast to the known base-induced cyclization of *vic*-dithiocyanates to form the three-membered thiirane ring[6] (eq

Table I. Yields and Stereochemistry of Thiazolidine-2-thiones from 1-Isothiocyanato-2-thiocyanates

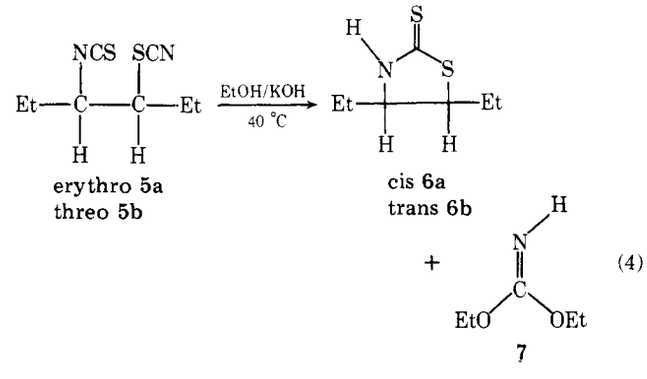
R—CH(SCN)—CHR′	R	R′	R—CH(S)—CH—R′	Yield, %
5a erythro	CH_3CH_2–	CH_3CH_2–	6a cis	70
5b threo	CH_3CH_2–	CH_3CH_2–	6b trans	60
8[a]	C_4H_9–	H	9a	85 {85
	H–	C_4H_9–	9b	85 {15
10 trans	$-C_4H_8-$		11 trans	60
12 erythro	C_8H_{17}–	C_8H_{17}–	13 cis	90
14 erythro	Ph	CH_3	15 cis	30
16	$-(CH_2)_8CO_2H$	H	17	50
18 erythro	$CH_3(CH_2)_7$–	$-(CH_2)_7CO_2H$	19 cis	60
20 threo	$CH_3(CH_2)_7$–	$-(CH_2)_7CO_2H$	21 trans	45

[a] 8 was an unseparable mixture of two positional isomers; however, the products of cyclization were separated to pure 9a and 9b.

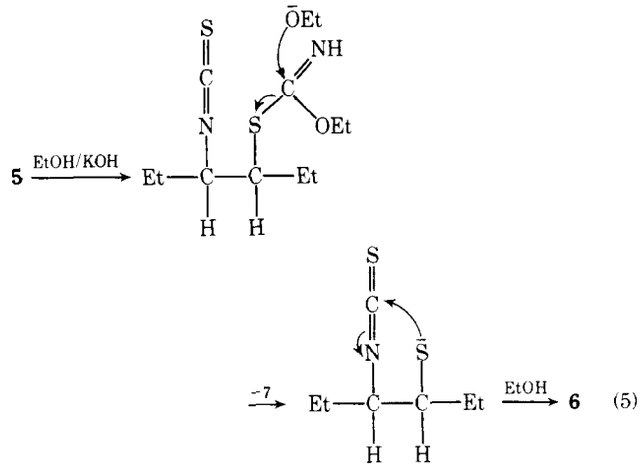
2), we have found that 1-isothiocyanato-2-thiocyanate adducts 2 cyclize in base to form the five-membered heterocycle 4,5-



thiazolidine-2-thione 6 as formulated in eq 4 for the erythro adduct **5a** and threo adduct **5b**. Diethyl imidocarbonate **7** was

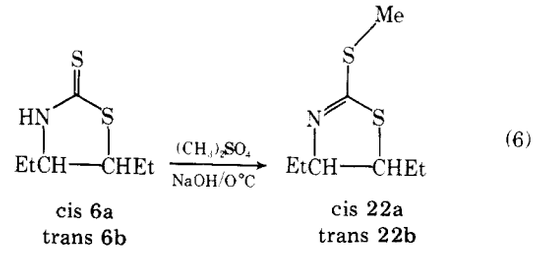


also isolated as the coproduct of this reaction and was identified by IR and NMR spectra and by comparison of its GLC retention time with that of an authentic sample prepared by an independent method.[9a,b] The isolation of coproduct **7** aided in establishing a mechanism for the cyclization of **5a** and **5b**. In the proposed mechanism shown in eq 5 initial attack by base on **5** occurs at the thiocyanate group and does not involve the asymmetric methine carbon atoms whose stereochemical identity is maintained in the product **6**. A series of aliphatic 4,5-thiazolidine-2-thiones listed in Table I was obtained in yields ranging from 45 to 90%, whereas the aromatic adduct



14 provided the corresponding **15** less efficiently.

Proof of structure of the geometric isomers **6a** and **6b** was aided by the earlier study of Foglia et al.,[10] who synthesized the two compounds by an alternate procedure. They demonstrated with ^1H NMR spectroscopy that **6a**, the isomer with the larger methine coupling constant (J_{ab} = 6.8 Hz), was the cis isomer and that **6b** (J_{ab} = 4.2 Hz) was the trans isomer. Our IR and NMR spectra for these isomers agreed with those of Foglia; hence, the geometry of **6a** and **6b** was established. However, spectral comparison does not rule out the possibility of contamination of each isomer by small amounts of its geometric isomer. To establish the stereospecificity of the cyclization reaction, the crude reaction products **6a** and **6b**, from the cyclization of **5a** and **5b**, were each converted to the 2-methylthio-Δ^2-thiazoline derivative (eq 6). This sequence does



not alter the stereochemistry at the asymmetric carbon atoms of **6a** and **6b** so that no change in geometric configuration should occur in this reaction. The thiazoline derivatives **22a** and **22b** were obtained as volatile liquids. Each product was examined without further purification to prevent changes in composition during workup. It has been reported[11] that the IR spectra of thiazolines display an intense absorption at 1575

cm^{-1} which is ascribed to the C=N linkage of the thiazoline ring. The IR spectra of **22a** and **22b** showed this absorption. Foglia et al.[10] have reported that the GLC characteristics of isomeric thiazolines are analogous to those of the corresponding isomeric oxazolines[12] wherein the cis isomers for both series have longer relative retention times than the trans isomers. The crude products **22a** and **22b** were analyzed by GLC and each was found entirely free of the opposite geometric isomer. This indicates complete stereospecific cyclization of the precursors **5a** and **5b** to the thiazolidine-2-thiones **6a** and **6b**, respectively. From these results it may be inferred that the proposed trans addition of thiocyanogen to olefins in formation of 1-isothiocyanato-2-thiocyanates[4,5] is verified.

The cyclization of **5a** and **5b** to form **6a** and **6b** appears to be the only reported method for the stereospecific synthesis of both *cis*- and *trans*-thiazolidine-2-thiones. Other reports[10,13] indicate that while the *trans*-thiazolidine-2-thione may be obtained free of the cis isomer, the formation of the cis compound is accompanied by no less than 8% of the trans isomer.

Experimental Section

Melting points (uncorrected) were determined on a Kofler hot stage.[14] Infrared spectra were measured with a Perkin-Elmer Model 457 grating spectrophotometer. NMR spectra were recorded on a Jeolco C-60H spectrometer. Mass spectra were obtained with a Du Pont Model 21492 mass spectrometer. GLC analyses were carried out with an F&M Model 810 gas chromatograph.

Materials. *cis*- and *trans*-3-hexene and 1-phenylpropene were obtained from Chemical Samples Co., and their purity was established by GLC. 1-Hexene and cyclohexene were Phillips Petroleum products and were found to be 99+% pure. 10-Hendecenoic acid and *trans*-9,10-octadecenoic acid were prepared in this laboratory. Methyl *cis*-9,10-octadecenoate (99% purity) was purchased from Applied Science Labs. All solvents used in this study were reagent grade.

Preparation and Purity of 1-Isothiocyanato-2-thiocyanates. The procedures used to prepare these adducts have been reported elsewhere.[4,8] All of the 1-isothiocyanato-2-thiocyanates prepared were isolated from the product mixtures by silica gel chromatography as amber-colored, viscous oils. Analysis of these compounds by GLC confirmed their stereochemical purity. The IR spectra of these compounds are characterized by the intense absorption at 2150 cm^{-1} (s) for –SCN and at 2060 cm^{-1} (broad) for –NCS. A detailed analysis of the ^1H NMR spectra of **5a** and **5b** will be published elsewhere.[5]

Cyclization of 1-Isothiocyanato-2-thiocyanates. The 1-isothiocyanato-2-thiocyanate adduct (15 mmol) and KOH (2.0 g) in absolute ethanol (35 mL) were heated at 45 °C for 45 min. The reaction mixture was acidified with dilute HCl, extracted with $CHCl_3$, and dried over Na_2SO_4. After removal of solvent, the residue was purified by silica gel chromatography. The purity of samples, excluding **17**, **19**, and **21**, was determined by GLC.

***cis*-4,5-Diethylthiazolidine-2-thione (6a)** from *erythro*-3-isothiocyanato-4-thiocyanatohexane (**5a**) was isolated as a viscous oil. The product was identified by comparison of the IR and NMR spectra of the authentic compound prepared by an alternate procedure,[10] and by the preparation of the 3-*p*-nitrobenzoyl-*cis*-4,5-diethylthiazolidine-2-thione derivative, mp 93–94 °C (lit.[10] 93–94 °C).

***trans*-4,5-Diethylthiazolidine-2-thione (6b)** was obtained from *threo*-3-isothiocyanato-4-thiocyanatohexane (**5b**), and identified by comparison of its melting point, 58.5–59.5 °C (lit.[10] 59–60 °C), NMR, IR, and mass spectra with those of the authentic compound prepared by an alternate procedure.[10]

4-Butylthiazolidine-2-thione (9a) and 5-butylthiazolidine-2-thione (9b) were obtained from 1(2)-isothiocyanato-2(1)-thiocyanate (**8**). The adduct **8** was a mixture of two isomeric isothiocyanatothiocyanates. GLC of the product **9** showed two overlapping peaks in the ratio 85/15. Chromatography on a silica gel column completely separated the two components **9a** and **9b**, although an insufficient amount of **9b** was obtained for a satisfactory elemental analysis: **9a** mp 55–56 °C; **9b** mp 89–90 °C; **9a** NMR ($CDCl_3$) 9.3 (very broad, 2), 4.3 (broad, apparent pentuplet, 1), 3.6 and 3.2 (8 lines, 2), 2.4 (t, 2), and 1.3 ppm (s, 14); **9b** NMR ($CDCl_3$) gave spectrum similar to that of **9a** except that the methine protons superimposed upon the methylene protons (3.5–4.2 ppm, 3). **9a** Anal. Calcd for $C_7H_{13}NS_2$: C, 47.96; H, 7.48; N, 7.48; S, 36.58. Found: C, 47.92; H, 7.93; N, 7.65; S, 36.94.

***trans*-Hexahydrobenzothiazolidine-2-thione (11)** was obtained from *trans*-1-isothiocyanato-2-thiocyanatocyclohexane (**10**), and isolated as a solid which on recrystallization from benzene gave platelets, mp 174–175 °C (lit.[15] 173–174 °C).

cis-**4,5-Dioctylthiazolidine-2-thione (13)** from *erythro*-9-isothiocyanato-10-thiocyanatooctadecane (**12**) was recovered as a viscous oil. The IR and NMR spectra were identical with those obtained from the authentic compound.[10]

***cis*-5-Methyl-4-phenylthiazolidine-2-thione (15)** from *erythro*-1-isothiocyanato-2-thiocyanato-1-phenylpropane (**14**) was isolated as a solid and recrystallized from methylene chloride/benzene: mp 159.8–160.0 °C; IR (KBr) 3100 (NH), 1490 (CSNH), 1250, 1030 (C=S), 810, 690 cm^{-1}. Anal. Calcd for $C_{10}H_{11}NS_2$: C, 57.38; H, 5.30; N, 6.69; S, 30.63. Found: C, 57.60; H, 5.46; N, 6.52; S, 29.97.

4-(8-Carboxyoctyl)-thiazolidine-2-thione (17) from 10-isothiocyanato-11-thiocyanatohendecanoic acid (**16**) (isomeric purity not established) was recovered as a solid and recrystallized from hexane/ether: mp 100–102 °C; IR (KBr) 3230 (NH), 1695 (C=O), 1505 (CSNH), 1180, 1045 (C=S), 950, 840 cm^{-1}; NMR ($CDCl_3$) methine resonance (4.3 ppm), methylene (3.6 and 3.2). Anal. Calcd for $C_{12}H_{21}NO_2S_2$: C, 52.33; H, 7.68; N, 5.09; S, 23.28. Found: C, 52.53; H, 7.93; N, 4.94; S, 23.06.

***cis*-4(5)-Octyl-5(4)-(7-carboxy)heptylthiazolidine-2-thione (19)** was obtained from *erythro*-9(10)-isothiocyanato-10(9)-thiocyanatooctadecanoic acid (**18**). The adduct **18** was a mixture of two positional isomers whose composition remained unchanged in the product **19**. The product was a solid which was recrystallized from acetone/hexane: mp 109–111 °C; neut equiv, calcd, 373.6, found, 370; IR (KBr) 3100 (NH), 1700 (C=O), 1495 (CSNH), 1175, 1010 (C=S), 810 cm^{-1}. Anal. Calcd for $C_{19}H_{35}NO_2S_2$: C, 61.08; H, 9.44; N, 3.74; S, 17.16. Found: C, 61.05; H, 9.73; N, 3.72; S, 17.20.

***trans*-4(5)-Octyl-5(4)-(7-carboxy)heptylthiazolidine-2-thione (21)** was obtained from *threo*-9(10)-isothiocyanato-10(9)-thiocyanatooctadecanoic acid (**20**). The adduct **20** was a mixture of two positional isomers whose composition remained unchanged in the product **21**. The product was a solid recrystallizable from acetone/hexane: mp 79–80 °C; neut equiv, calcd 373.6, found 370; IR (KBr) 3100 (NH), 1700 (C=O), 1495 (CSNH), 1160, 1000 (C=S), 875, 715 cm^{-1}. Anal. Calcd for $C_{19}H_{35}NO_2S_2$: C, 61.08; H, 9.44; N, 3.74; S, 17.16. Found: C, 61.00; H, 9.50; N, 3.74; S, 17.44.

Diethyl imidocarbonate was prepared by the procedure described by Nef[9a] using bromocyanogen and potassium hydroxide in ethanol at 0 °C: IR (CH_2Cl_2) 3340, 3365 (NH), 1650 (C=N), 1080, and 1025 cm^{-1}. The IR spectrum agreed with that obtained for **7**. Identical results were also obtained by comparison of the NMR spectra[9b] and GLC retention times of both samples.

2-Methylthio-*cis*-4,5-diethyl-2-thiazoline (22a) was prepared from *cis*-thiazolidine **6a** in accordance with the published procedure.[10] The IR spectrum of the crude reaction product was in complete agreement with the published values.[10] GLC analysis of this sample showed only one component.

2-Methylthio-*trans*-4,5-diethyl-2-thiazoline (22b) was prepared from *trans*-thiazolidine **6b** and dimethyl sulfate as described above. The IR spectrum agreed with the published values. GLC analysis of this sample showed one component having a shorter retention time than that of cis **22a**.

Registry No.—**5a**, 61522-02-9; **5b**, 61522-01-8; **6a**, 27787-21-9; **6b**, 27932-05-4; **8** isomer 1, 61522-04-1; **8** isomer 2, 61522-37-0; **9a**, 61522-38-1; **9b**, 61522-39-2; **10**, 61522-40-5; **11**, 61522-41-6; **12**, 50843-80-6; **13**, 27787-27-5; **14**, 60211-99-6; **15**, 61522-42-7; **16**, 61522-43-8; **17**, 61522-44-9; **18** isomer 1, 61522-45-0; **18** isomer 2, 61522-46-1; **19** isomer 1, 61522-47-2; **19** isomer 2, 61522-48-3; **20** isomer 1, 61522-49-4; **20** isomer 2, 61522-50-7; **21** isomer 1, 61522-51-8; **21** isomer 2, 61522-52-9; **22a**, 27787-25-3; **22b**, 27787-22-0; diethyl imidocarbonate, 2812-77-3.

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Thiocyanations. 5. Nuclear Magnetic Resonance Analysis of the Stereochemistry of α,β-Dithiocyanates and α-Isothiocyanato-β-thiocyanates[1,2]

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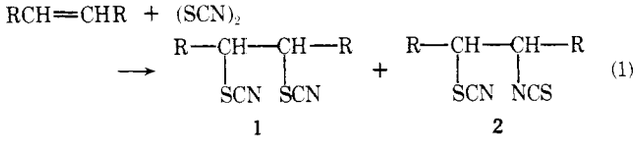
The stereochemical structures of 3,4-dithiocyanatohexanes as representative examples of aliphatic α,β-dithiocyanates could not be determined by direct conformational NMR analysis because of symmetry but were resolved by cyclization to and configurational analysis of their 2-imino-1,3-dithiolane salt derivatives. The aromatic 1,2-dithiocyanatophenylpropanes which have C–H asymmetry are subject to conformational analysis. Conformational analysis is also applicable to resolution of structures of the isomeric 3-isothiocyanato-4-thiocyanatohexanes.

Although the stereochemical structures of *vic*-dithiocyanate adducts were initially investigated by McGhie and co-workers,[4] our recent study of olefin thiocyanations emphasized the need for a reexamination of their structural assignments.[2]

On the basis of chemical evidence, McGhie and co-workers[4] proposed a trans addition of thiocyanogen to olefins to explain the reaction's stereochemistry; i.e., formation of erythro adducts from trans olefins and threo adducts from cis olefins. Their structural assignments for these adducts were based on the known pseudohalogen nature of thiocyanogen and on a comparison of a series of melting points of related isomeric dibromides, epoxides, and thiiranes. Such criteria are often inconsistent[4] and can be misleading; therefore, this approach to a determination of stereochemical assignments is provisional and not definitive for it is now recognized that the stereochemistry of electrophilic addition depends upon the structure of the olefin, the nature of the reagent, and the reaction conditions.[5]

McGhie[4] and earlier investigators[6] had examined only *vic*-dithiocyanate adducts as these were the sole products isolated from the addition of thiocyanogen to cis and trans olefinic compounds. However, more recently two independent investigations of the product distribution obtained by thiocyanations in acetic acid solution showed that formation of the *vic*-dithiocyanate adduct is accompanied by formation of several ancillary coproducts,[2,7] principally adduct **2**,



suggesting a further need for clarification of the reaction's stereochemistry.

A more direct and definitive method than chemical analysis of acquiring stereochemical determinations may be provided using NMR spectroscopy. However, a direct determination of the vicinal coupling constants is difficult for dithiocyanate adducts of aliphatic olefins because of their high degrees of symmetry. We undertook the present investigation to determine conclusively the stereochemical geometries of dithiocyanate adducts using *erythro*- and *threo*-3,4-dithiocyanatohexanes as the representative models. The stereochemical structures of the *vic*-dithiocyanate adducts were unequivocally confirmed by examination of the chemical shifts and the C-13 satellite spectra of their cyclic derivatives, the salts of 2-imino-1,3-dithiolanes. The coupling constants were also determined for the related erythro and threo isomers of 3-isothiocyanato-4-thiocyanatohexane and the 1,2-dithiocyanato-1-phenylpropane. The assignments were derived by correlation of the constants with the stereochemical conformations.

While our work was in progress, Guy and co-workers[7] reported assignments of several related dithiocyanate adducts. However, they did not report any NMR data or discuss the mode of analysis used that would allow independent confirmation of their assignments.

Results and Discussion

Configuration Assignment. In the earlier stages of this work differentiation of adducts **3** and **4** (eq 2 and 3) by NMR analysis was limited because of symmetry considerations. Therefore, a method of cyclic derivatization of **3** and **4** was developed whereby the stereochemistry of the asymmetric C–S bonds in these compounds was maintained. Cyclization would freeze the structures into a more limited and discrete number of conformations for each configuration. The desired derivatives of the erythro (**3**) and threo (**4**) forms of 3,4-dithiocyanatohexanes were accordingly obtained by facile cyclization to the corresponding 2-imino-1,3-dithiolane salts of methanesulfonic acid (**5** and **6**, respectively; eq 2 and 3).[8] The cyclization was smoothly attained in methanesulfonic acid as solvent–catalyst. No alteration of the precursor's C–S bonds at the point of carbon attachment in the alkane chain occurs since these asymmetric bonds do not participate in the reaction.

Chemical shifts of the salts **5** and **6** were obtained and the stereochemical assignments were proven by comparison with published assignments for known cyclic analogues (Table I). In each example the chemical shift of vicinal methine protons of the trans isomers appear ~0.2 ppm upfield relative to cis isomers. This difference has been noted for many cis–trans isomeric pairs of planar three- to five-membered ring com-