the resulting solution resulted in a red powder, which was recrystallized from chloroform–methanol. The resulting red crystals (1.5 g, 68%) had mp 243–245 °C and analyzed correctly for $C_{23}H_{18}N_4O_4$: C, 66.66; H, 4.38; N, 13.52. Found: C, 66.80; H, 4.40; N, 13.27. The mass spectrum had a parent peak at *m/e* 414, M + 1 and M + 2 peaks at *m/e* 415 and 416, and peaks at *m/e* 413, 398, 397, 385, 384, 370, 368, 350, 339, 337, and 323. The IR spectrum (KBr) showed strong bands at 2920, 1600, 1575, 1565, 1530, 1385, 1335, and 1315 cm^{-1}. Strong visible maxima appeared at 476, 426, and 280 nm in Me_2SO, 478, 420, and 250 nm in chloroform, and 456, 412, and 247 nm in methanol. The ^1H NMR spectrum (Me_2SO-d_6) showed absorptions at δ 2.90 (6 H, s), 7.53 (5 H, m), 7.78 (5 H, m), 8.62 (1 H, d, J = 3 Hz), and 9.06 (1 H, d, J = 3 Hz). In $CDCl_3$ the spectrum showed absorptions at δ 2.95 (6 H, s), 7.66 (5 H, m), 7.96 (5 H, m), 8.76 (1 H, d, J = 3 Hz), and 9.22 (1 H, d, J = 3 Hz).

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Registry No.—**6a,** 56776-16-0; **6b,** 52066-17-8; **6c,** 60719-04-2; **7a,** 60719-05-3; **7b,** 60719-06-4; **8b/10b,** 60719-26-8; **8c/10c,** 60719-27-9; **11b,** 56776-17-1; **11c,** 56776-18-2; **16b,** 60719-07-5; **16c,** 60719-08-6; **19a,** 60719-09-7; **19b,** 60719-10-0; α-phenyl-*N*-methylacetamide, 6830-82-6; methylamine, 74-89-5; ethyl α-phenylacetimidate hydrochloride, 5442-34-2; dimethylamine, 124-40-3; 1,3,6,8-tetranitronaphthalene, 28995-89-3; TNB, 99-35-4; NBS, 128-08-5; 3,5-dinitrobenzophenone, 51911-74-1.

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Structural Studies of Organosulfur Compounds. 2.[1] Conformational Analysis of 2-Methoxy-*trans*-hexahydro-1,4-benzoxathianes

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The 2-methoxy substituent in the 1,4-oxathiane prefers the *equatorial* conformation where the $\Delta G°$'s range from −0.23 to −0.49 kcal/mol (axial ⇄ equatorial), in a number of solvents as determined by direct acid catalyzed equilibration of the diastereoisomeric 2-methoxy-*trans*-hexahydro-1,4-benzoxathianes.

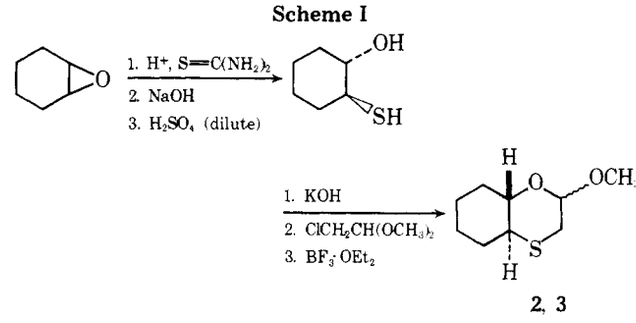
Recent reports indicate that the 2-methoxyl group in 1,4-oxathiane (**1**) may be slightly axial (56%)[2] or predominantly equatorial (75%)[3] in acetonitrile where presumably the anomeric effect,[4] van der Waals steric interactions, and the recently coined "hockey sticks" effect[2] collectively control its conformational preference. The conflicting results of these investigations[2,3] and other recent studies involving conformational predictions in some nucleoside derivatives of 1,4-oxathiane[5] have suggested the need for quantitative determinations of conformational energies of C-2 and possibly C-3 substituents in the 1,4-oxathiane system.

While conformational preferences of substituents derived from time-averaged intensive parameters (e.g., coupling constants and chemical shifts) of conformationally mobile systems and model systems are greatly influenced by the limitations of the models, direct chemical equilibrations of the appropriate model diastereoisomers (if practical) and direct observation of the conformers of conformationally mobile systems by NMR techniques are generally preferred[6] (Figure 1). However, solvent-dependent investigations are hampered by the inaccessibility of suitable solvents for low-temperature NMR determinations. In this report, we chose to put the conformational preference of the 2-methoxyl group in the 1,4-oxathiane system on a firm basis by determining its conformational free energy in a number of solvents by direct chemical equilibration of model diastereoisomers.

Results and Discussion

The diastereoisomers of 2-methoxy-*trans*-hexahydro-1,4-benzoxathiane (**2** and **3**) were envisioned as ideal models for the two chair conformations of 2-methoxy-1,4-oxathiane (**1**) since they would ensure conformational rigidity of the 1,4-oxathiane ring and allow for minimum distortions in the ring system. The compounds, **2** and **3,** were prepared by reacting a basic solution of *trans*-2-mercaptocyclohexanol, prepared from the addition of thiourea to cyclohexene oxide, with chloroacetaldehyde dimethyl acetal to afford the open chain acetal followed by condensation with boron trifluoride etherate (Scheme I). Separation of the stereoisomers was accomplished with spinning band column distillations, low-temperature crystallizations, and preparative gas chromatography (see Experimental Section).

Scheme I



2, 3

The stereochemistry of the C-2 methoxyl group in **2** and **3** was ascertained by ^1H NMR coupling constants and both proton and carbon chemical shifts. For example, the sample exhibiting the low-field "triplet" pattern for C-2 H at δ 4.75 ppm is suggestive of nearly equivalent vicinal couplings between the C-2 proton and the geminal C-3 protons. Application of the Karplus relationship to these couplings aided in

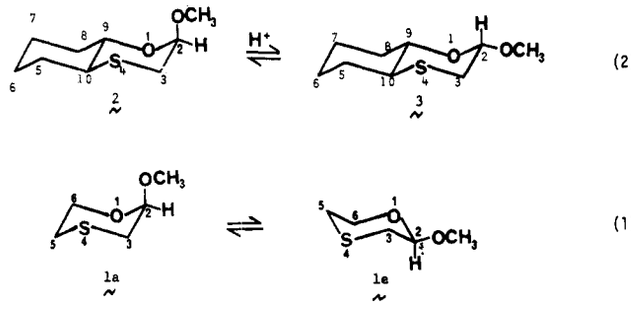


Figure 1.

Table I. Proton Chemical Shifts of *trans*-Hexahydro-1,4-benzoxathianes[a]

Compd	-OC-9 H	-S-C-10 H	C-3 H_e	C-3 H_a
trans-Hexahydro-1,4-benzoxathiane (4)[b]	3.28	2.65	2.37	3.10
2(a)-Methoxy-*trans*-hexahydro-1,4-benzoxathiane (2)	3.75	2.66	2.56	3.15
2(e)-Methoxy-*trans*-hexahydro-1,4-benzoxathiane (3)	3.41	2.56	2.51	2.75

[a] All NMR parameters were obtained as dilute solutions of the samp in deuteriochloroform ($CDCl_3$) with tetramethylsilane as internal reference. Chemical shifts (δ) are given in parts per million. [b] Unpublished observations with D. M. Frieze.

identifying the C-2 methoxyl group as axial. This "triplet" pattern was resolved, with an in-house modification of LACOON III,[7] into two coupling components of $^3J_{ee}$ = 1.93 and $^3J_{ea}$ = 2.45 Hz which could also be identified in the AB portion (C-3) of the NMR spectrum. The substance exhibiting the low-field doublet of doublets pattern at δ 4.55 ppm for C-2 H was assigned the other isomer, **3**. The magnitude of the C-2–C-3 vicinal coupling constants (J_{aa} = 8.63 and J_{ae} = 2.37 Hz)[7] supported this assignment.

Steric shifts arising from repulsive van der Waals interactions have been used extensively in NMR spectroscopy to support stereochemical assignments. In ^1H NMR this corresponds to downfield shifts of the interacting protons,[8] and in ^{13}C NMR upfield shifts of the appropriate carbon atoms.[9] Drieding molecular models show that when the C-2 methoxyl group and the C-9 proton are axial, they should experience severe nonbonding interactions. We noted that the C-9 proton in **2** is substantially deshielded (δ 3.75 ppm) on comparison with the same proton in both **1** and **4** (see Table I). On the other hand, the ^{13}C NMR spectra (Figure 2) show that C-9 of **2** experiences a substantial upfield shift of 9.78 ppm when compared to the C-9 atom in **3** (δ 82.37 for **3** and δ 72.59 ppm for **2**). In these anancomeric compounds, the C-2 atom of **2** responds similarly to the increase in steric congestion by exhibiting a higher field shift (δ 94.99 ppm) than the same carbon in **3** (δ 102.26 ppm) in accordance with previous observations on systems having similar functional groups.[12]

The chemical shifts of the axial and equatorial C-3 protons were also useful in corroborating the configurational assignment of the C-2 methoxyl group. In **3** and **4** the identity of the axial proton at C-3 is easily established since it should exhibit a relatively large coupling contribution from its axial neighbor at C-2 (8.83 Hz for **3** and 11.2 Hz for **4**). However, this scheme is not readily applicable in acetal **2** and since J_{ae} and J_{ee} are nearly identical assignments based on this coupling constant data would be less than conclusive.[13] The chemical shift of C-3

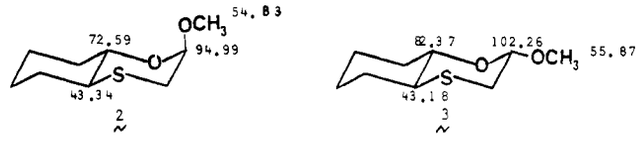


Figure 2. Partial assignments of carbons in **2** and **3**.

Table II. Solvent Dependent Conformational Free Energies of the 2-Methoxyl Group in 2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane (Axial ⇄ Equatorial)[a]

Solvent (ϵ)	K_{eq}	$-\Delta G_{30°C}$, kcal/mol
C_6H_{12} (2.02)	2.29 ± 0.04	0.49 ± 0.01
C_6H_6 (2.28)	1.94 ± 0.06	0.39 ± 0.02
CH_2Cl_2 (9.08)	1.47± 0.02	0.23 ± 0.01
CH_3CN (36.5)	1.61 ± 0.07	0.28 ± 0.03
CCl_4 (2.24)	1.94 ± 0.09	0.39 ± 0.03

[a] See Experimental Section for details of acid-catalyzed equilibration and methods of analytical analyses.

H_a (δ 3.10 ppm) in **4** is similar to that exhibited by the C-3 H_a (δ 3.15 ppm) in **2** which seems quite reasonable since the proton antiperiplanar to the methoxyl group may not be expected to be greatly influenced by the anisotropy of the methoxyl group. Similarly, the chemical shift of the C-3 H_e in **2** (δ 2.56 ppm) would be expected to remain unchanged in **3** since the anisotropic influence of the synclinal (gauche) methoxyl group would be approximately the same in each case. Thus, the C-3 proton at δ 3.15 ppm in **2** is assigned the axial conformation which is removed from the diamagnetic shielding environment of the axial methoxyl group. Collectively, these observations serve to confirm the 1,3-axial/equatorial relationship of the C-2 methoxyl group and the C-9 axial proton in **2** and **3**, respectively.

The diastereoisomers, **2** and **3**, were equilibrated by methods similar to those previously described for acid-catalyzed equilibrations of substituted 1,3-dioxanes.[15] The conformational free energy data in Table II clearly indicate that the 2-methoxyl group prefers the *equatorial* conformation in all of the solvents used in this study. These results disagree with those obtained by Zefirov et al.,[2] but support the findings of Buck et al.[3] The equatorial preference varies significantly with solvent but does not appear to correlate with solvent E_T (30) values[16] and only slightly with solvent dielectric (and only when acetonitrile is excluded).[17] These data indicate that the 1,3-nonbonding heteroatom interactions (presumably, hockey sticks effect[2]) between sulfur and oxygen appear to override the anomeric effect between the two acetal oxygens. Although this result is perhaps suggestive of an electronic perturbation involving sulfur and oxygen, it is substantially larger than originally viewed.[2]

Finally, conformational entropies (ΔS) for systems similar to those described here are often assumed to be zero (and in a number of cases this seems justified[18]), and it was of interest to examine ΔH and ΔS in view of the relatively small values for the conformational free energies obtained for the above equilibrium.[19] Acid-catalyzed equilibrations were performed for **2** ⇄ **3** at 22, 40, 60, and 80 °C, and a least-squares refinement of the equilibrium data gave ΔH and ΔS values for the equilibrium in cyclohexane solvent of −0.41 ± 0.03 kcal/mol and 0.25 ± 0.09 eu, respectively. Although ΔS is positive and small, perhaps implying a bit less rotational freedom in the axial conformation than in the equatorial, it is clear that ΔH dominates the conformational free energy.

The electrostatic contribution to ΔH appears to be quite visible as shown by the solvent dependence of the ΔG's. The data suggest that dipole–dipole interactions are more severe

in the axial isomer **2** and hence subject to some diminution in the more polar solvents making the axial form more favored. However, the fact that the ΔG's do not correlate well with E_T (30) values or solvent dielectric data may simply reflect solvent-induced differences in intramolecular dipolar interactions ($\Delta H_{dipolar}$) and energies of solvation (ΔH_{solv}) which represent significant components of $\Delta H_{electrostatic}$.[20]

In summary, sulfur clearly plays a unique role in determining the conformational preference of the C-2 methoxyl group in 1,4-oxathiane, particularly since in the absence of the sulfur atom in structurally similar systems (i.e., 2-methoxytetrahydropyrans), the axial methoxyl group is greatly preferred owing to the anomeric effect.[21]

Experimental Section

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube, and are uncorrected.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Proton magnetic resonance (^{1}H NMR) spectra were recorded on JEOL Model C-60 HL and Varian Model XL-100-12 NMR spectrometers. Carbon magnetic resonance (^{13}C NMR) FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. All FT spectra were obtained at ambient temperature (ca. 30 °C) and Fourier transforms were based upon 8K data points. The proton and carbon chemical shifts of samples as 5–30% (wt/wt %) deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si), and these values are considered accurate to ±0.01 ppm unless otherwise indicated. The coupling constants are given in hertz and are accurate to ±0.1–0.2 Hz unless otherwise specified. All relevant proton signals were simulated with an in-house modification of a LACOON III program.[7] ^{1}H NMR coupling patterns are designated as s = singlet, dd = doublet of doublets, bb = broad bands, and t = triplet.

Infrared spectra were obtained from samples as neat films and solutions, and were recorded on Perkin-Elmer Models 257 and 421 spectrophotometers with polystyrene (1601.4 cm^{-1}) as reference. Absorption intensities are shown as s = strong, w = weak, and m = medium.

Gas–liquid partition chromatography (GLC) analyses were performed on a Hewlett-Packard Model 5750B research gas chromatograph. A Varian Aerograph Series 2700 instrument was used for preparative separations.

***trans*-2-Mercaptocyclohexanol.** Thiourea (40.0 g, 500 mmol) was added to a solution of sulfuric acid (25.9 ml, 0.5 equiv, 500 mmol) in 300 ml of water while stirring at 0–5 °C (ice bath). Cyclohexene oxide (49.0 g, 500 mmol) was added dropwise to the acidic solution over a 90-min period with constant (vigorous) stirring. The suspension was allowed to warm to ambient temperature for ca. 1 h, then cooled to 0–5 °C, and the *S*-(*trans*-2-hydroxycyclohexyl)thiuronium sulfate was suction filtered. The aqueous filtrate was treated with 100–200 g of ammonium sulfate and additional thiuronium sulfate salt precipitated from the aqueous solution. The combined salts were dried in a vacuum desiccator to give 102 g (75%) or recrystallized from 50% ethanol to give 68–82 g (50–60%) of pure material, mp 312–314 °C (lit.[21] mp 310–325 °C).

A portion of the thiuronium sulfate (30.0 g, 110 mmol) was added to a solution of sodium hydroxide (9.2 g, 220 mmol) in 140 ml of water at 0–5 °C (ice bath). The resulting solution was allowed to stir at room temperature for 10 min, then poured over acidic ice water (ca. 5.3 ml, 110 mmol of sulfuric acid). The organic material was extracted with ethyl ether (3 × 100 ml) and the ethereal solution was dried ($MgSO_4$) and concentrated to dryness (rotary evaporator) to afford an oil (10.5 g, 70–72%). The oil was distilled under reduced pressure to give two major components. The low-boiling component (bp 29–37 °C, 0.035 Torr) was identified as cyclohexene sulfide (7.2 g, 69%) from comparison with published infrared data[22] and the remaining 3.3 g (31%) of the high-boiling component (bp 48–49 °C, 0.015 Torr) was identified as *trans*-2-mercaptocyclohexanol [lit.[23] bp 97–99 °C (15 mm)]: IR (neat film) 3400 (broad, OH), 2570 (weak, SH), 1504, 1120 (s), and 970 cm^{-1} (s).

***trans*-2-(Thioacetaldehyde dimethyl acetal)cyclohexanol.** A solution of *trans*-2-mercaptocyclohexanol (52.8 g, 400 mmol) in 200 ml of ethanol was added to a solution of potassium hydroxide (26.3 g, 400 mmol) in 500 ml of ethanol. The solution was stirred for 15 min, then a solution of chloroacetaldehyde dimethyl acetal (49.8 g, 400 mmol) in 100 ml of ethanol was added in one portion. The resulting solution was refluxed (16 h) and cooled to ambient temperature and the KCl was removed by filtration. The resulting filtrate was concentrated to dryness (rotary evaporator), diluted with water (150 ml), and washed with ether (3 × 100 ml). The combined ethereal solutions were dried ($MgSO_4$) and concentrated to dryness (rotary evaporator) to give an amber oil which was distilled under reduced pressure to afford a colorless oil (63 g, 71%): bp 97–99 °C (0.035 Torr); IR (neat film) 3450 (broad band, OH), 1452 (s), 1128 (s), 1071 (vs), and 970 cm^{-1} (s). On standing this material slowly cyclized to give an approximately equal distributon of **2** and **3**.

***trans*-2-Methoxyhexahydro-1,4-benzoxathianes.** A solution of *trans*-2-(thioacetaldehyde dimethyl acetal)cyclohexanol (61 g, 286 mmol) in 300 ml of anhydrous ether was stirred overnight with 4 ml of BF_3·OEt_2. The ethereal solution was washed with water (2 × 100 ml), dried ($MgSO_4$), and concentrated to dryness (rotary evaporator) to give a colorless oil. Distillation of the oil under reduced pressure gave 46.3 g (76% yield) of a colorless oil, bp 73–75 °C (0.05 Torr).

The approximately 50:50 mixture of stereoisomers (by ^{1}H NMR) was partially separated by distillation on a Nester-Faust adiabatic annular Teflon spinning band column. The equatorial isomer **3** could be obtained pure by distillation [bp 60–61 °C (0.25 Torr) which crystallized on standing] while the axial isomer **2** could only be obtained as a highly enriched mixture favoring the axial isomer. GLC separations of the mixtures on a 6 ft × 0.375 in. Al column packed with 20% FFAP on Chromosorb W (45/60 mesh) at 125 and 160 °C gave pure samples of both the axial and equatorial sulfides, **2** and **3**. The equatorial isomer could also be obtained in pure form by low-temperature crystallization from the pure mixture at ca. 0–5 °C. Continuous removal of the crystalline solid eventually gave a solution mixture composed of ca. 70% **2** and 30% **3**.

2(e)-Methoxy-*trans*-hexahydro-1,4-benzoxathiane (3): mp 42.5–44.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.02–2.04 (bb, 8 H, CH_2), 2.51 (dd, J_{gem} = 13.02, J_{ae} = 2.37 Hz, 1 H, SCH), 2.52 (bb, 1 H, SCH), 2.75 (dd, J_{gem} = 13.02, J_{aa} = 8.63 Hz, 1 H, SCH), 3.45 (bb, 1 H, OCH), 3.48 (s, 3 H, OCH_3), and 4.55 ppm (dd, J_{ae} = 2.37, J_{aa} = 8.63 Hz, 1 H, –OC**H**OCH_3); IR (CCl_4) 1450 (s), 1362 (s), 1338 (s), 1174 (s), 1152 (s), 1120 (s), 1065 (s), 985 (s), and 850 cm^{-1} (m).

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.56. Found: C, 57.37; H, 8.62.

2(a)-Methoxy-*trans*-hexahydro-1,4-benzoxathiane (2): mp 9.0–30.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.10–1.98 (bb, 8 H, CH_2), 2.56 (dd, J_{gem} = 13.62, J_{ae} = 2.45 Hz, 1 H, SCH), 2.66 (bb, 1 H, SCH), 3.15 (dd, J_{gem} = 13.62, J_{ee} = 1.93 Hz, 1 H, SCH), 3.44 (s, 3 H, OCH_3), 3.74 (bb, 1 H, OCH), and 4.75 ppm ("t", J_{ae} = 2.45, J_{ee} = 1.93 Hz, 1 H, OC**H**OCH_3); IR (CCl_4) 1448 (s), 1351 (s), 1130 (s), 1054 (s), and 987 cm^{-1} (s).

Anal. Found: C, 57.49; H, 8.60.

Equilibrations. Equilibrium concentrations were obtained by equilibrating weighted mixtures of **2** and **3** from both sides in five solvents at 30.0 °C in sealed ampules with Amberlyst-15 (a polystyrenesulfonic acid resin). GLC analyses were performed on primarily 6 ft and 10 ft × 0.125 in. (i.d.) stainless steel columns with 10% FFAP on Chromosorb W AW-DMCS (60–80 mesh) at 120–130 °C and 6 ft and 12 ft × 0.125 in. (i.d.) stainless steel columns with 10% XE-60 Nitrile on Chromosorb W HP AW DMCS (100–120 mesh) at 120–200 °C. Response ratios were measured from the areas obtained from weighed sample mixtures.

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Registry No.—**2,** 60861-03-2; **3,** 60895-17-2; cyclohexene oxide, 286-20-4; *S*-(*trans*-2-hydroxycyclohexyl)thiuronium sulfate, 60861-05-4; *trans*-2-mercaptocyclohexanol, 60861-06-5; *trans*-2-(thioacetaldehyde dimethyl acetal)cyclohexanol, 60861-07-6.

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Heterocycles from *N*-Ethoxycarbonylthioamides and Dinucleophilic Reagents. 2. Five-Membered Rings Containing Two Heteroatoms at 1,3 Positions

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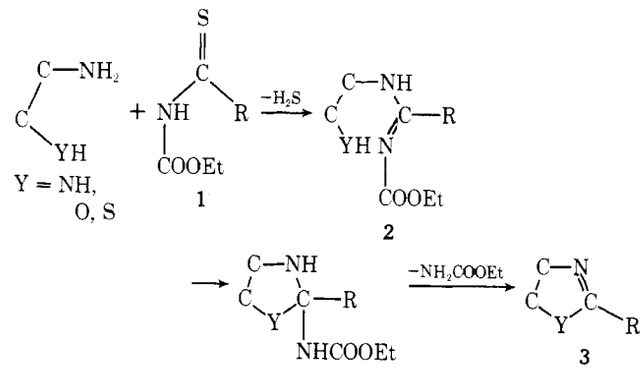
The reaction of *N*-ethoxycarbonylthioamides (1) with 1,2-diamines, amino alcohols, or aminomercaptans yields five-membered heterocyclic rings containing the thiocarbonyl carbon atom of 1 flanked by the two heteroatoms of the dinucleophilic reagent.

A recent study has shown that *N*-ethoxycarbonylthioamides (1) react with reagents possessing two adjacent nucleophilic sites (NH_2, NHR, OH) at both thiocarbonyl and carbonyl groups to form five-membered, carbonyl-containing heterocyclic rings. Thus reactions with hydrazines and hydroxylamines yield dihydro-1,2,4-triazolones and 1,2,4-oxadiazolones, respectively.[1] In view of these results, it was of interest to investigate the behavior of 1 toward reagents containing two nucleophilic groups separated by two or more positions. Were these reactions to proceed in the same manner as the previous ones, seven-membered or larger rings would be the anticipated products. A related study, however, has revealed that *S*-methyl derivatives of carbamates obtained by addition of alcohols to alkoxycarbonyl isothiocyanates react with 1,2- and 1,3-dinucleophilic reagents without participation of the ester group. Such reactions involving aliphatic 1,2- or 1,3-diamines result in formation of 2-alkoxycarbonyl derivatives of cyclic guanidines, whereas those with *o*-phenylenediamine lead to *N*-alkoxycarbonyl-2-aminobenzimidazoles.[2] On the other hand, it has long been known that primary thioamides react with ethylenediamine to form 2-substituted 4,5-dihydrothiazoles with elimination of H_2S and NH_3.[3]

Our investigation has shown that reactions of *N*-ethoxycarbonylthioamides (1) with 1,2-dinucleophilic reagents H_2NCCYH (Y = NH, O, S), in refluxing ethanol or tetrahydrofuran, proceed in complete analogy with the behavior of primary thioamides. The ester group is neither attacked by the reagent nor retained as side chain of the heterocyclic product. Instead, it is found in the reaction by-product, ethyl carbamate. On the basis of previous experience,[1] initial interaction between the thiocarbonyl of 1 and amino group of the reagent would be expected to result in elimination of H_2S and formation of a substituted amidine (2) as an intermediate. It now appears that this is followed by intramolecular addition of the second nucleophilic group YH to the C=N of 2 and elimination of ethyl carbamate. A five-membered, heterocyclic ring (3) is thus formed which is made up of the N–C–C–Y chain of the reagent and the thiocarbonyl carbon atom of 1.



This is a general reaction that *N*-ethoxycarbonylthioamides (1) undergo upon treatment with substances containing two primary amino, or a primary amino and a hydroxyl or mercapto groups on adjacent carbon atoms. Thus, treatment of 1 with 1,2-diaminoethane, 2-aminoethanol, and 2-aminoethanethiol yields 2-substituted 4,5-dihydroimidazoles (4), -oxazoles (5), and -thiazoles (6), respectively. Similarly, reactions with *o*-phenylenediamine, *o*-aminophenol, and *o*-aminothiophenol lead to 2-substituted benzimidazoles (7), benzoxazoles (8), and benzothiazoles (9) (Scheme I).