The proton nmr spectrum consisted of a triplet (J = 7.0 cps) at δ 1.26 for the methyl and a quartet (J = 7.0 cps) at 2.45, with additional coupling detectable to the fluorines. The fluorine spectrum consisted of an AB quartet with ϕ^*_A −29.91, ϕ^*_B −36.91 (J_{AB} = 611 cps).

1-Chloro-1,1-bis(difluoramino)butane.—1-Chloro-1-nitrobutane (5.0 g, 0.0364 mol) was dissolved in a solution of 1.64 g (0.041 mol) of sodium hydroxide in 50 ml of water at 0–5° (2 hr) and 3.79 g (0.055 mol) of sodium nitrite was added. A 25% sulfuric acid solution (20 ml) was added slowly at 0–5°. A dark blue oil (6.2 g) separated and was stored overnight at −80° in 25 g of pentane.

The pentane solution was added to 10 ml of 20% fuming sulfuric acid and 27 g of refluxing difluoramine. After 4 hr the mixture was drained onto 100 ml of ice and pentane layer was separated. The aqueous layer was extracted with two 50-ml portions of methylene chloride. The combined organic solution was distilled to give 0.82 g of colorless liquid, bp 33–34° (35 mm). Gas chromatography (10 ft × $^1/_4$ in. column of 10% Ucon 50-HB100 on Fluoropak 80, 70°) was used to trap the major component (90% of the sample, 10% yield), identified as 1-chloro-1,1-bis(difluoramino)butane.

Anal. Calcd for $C_4H_7N_2F_4Cl$: C, 24.7; H, 3.60; N, 14.4. Found: C, 24.9; H, 3.89; N, 14.0.

The proton nmr spectrum consisted of an irregular triplet at δ 1.01 for the methyl, a multiplet at 1.78 (approximately a septet) for CH_3CH_2, and a multiplet at 2.24 for the other methylene. The fluorine spectrum consisted of an AB quartet, ϕ^*_A −30.42, ϕ^*_B −37.35 (J_{AB} = 609 cps). The infrared spectrum showed peaks in the NF region at (μ) 9.80 (m), 10.60 (s), 11.2–11.4 (s), 12.03 (m), and 12.30 (m).

Reaction of *n*-Octyl Nitrite with Difluoramine.—*n*-Octyl nitrite (5.0 g, 0.0314 mol) was added dropwise to 27 g of refluxing difluoramine. A purple solution was formed, which became colorless after 30 min. After 4 hr, difluoramine was removed and the residue was distilled to give 3.14 g (77% yield) of *n*-octanol, bp 54° (1 mm), infrared spectrum identical with that of an authentic sample.

Registry No.—Difluoramine, 10405-27-3; 1,1-dichloro-1-(difluoramino)butane, 19955-19-2; 1,1-dibromo-1-(difluoramino)butane, 19955-20-5; 1-bromo-1-difluoramino-1-fluoropropane, 19955-21-6; 1-bromo-1,1-bis(difluoramino)butane, 19955-22-7; α-bromo-α,α-bis(difluoramino)toluene, 19955-23-8; α,α-dibromo-α-(difluoramino)toluene, 19955-24-9; 1-chloro-1,1-bis(difluoramino)butane, 19955-25-0; α,α-dichloro-α-(difluoramino)toluene, 14092-53-6; 2-bromo-2,4,4-trinitropentane, 19955-54-5; 2-chloro-2,4,4-trinitropentane, 19955-55-6; 1-nitrocyclohexyl-N′-fluorodiimide N-oxide, 19955-56-7; 1-chloro-1,1-bis(difluoramino)propane, 19955-57-8.

Acknowledgment.—The author is indebted to Mr. F. J. Gerhart and Mr. H. F. Shuey for assistance in the synthesis work, to Dr. H. M. Nelson and Mr. L. A. Maucieri for nmr analyses, and to Mr. K. Inouye for elemental analyses.

Heterocyclic Ring-Closure Reactions. II.[1] Reactions of α-Mercapto Acids with Cyanogen[2a]

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The reaction of α-mercapto acids with cyanogen has been studied and shown to give 2-[(S-carboxyalkyl)-thioimidyl]-Δ^2-thiazolin-4-one in good yields. The reaction product undergoes unusual N-methylation in addition to esterification when treated with diazomethane and could be cyclized to afford bicyclic symmetrical 4,4′-diketo-Δ^2-bithiazolinyl, which could be converted into its dienol diacetate. Proof of structure has been obtained by X-ray crystallography and supporting evidence obtained from uv, ir, nmr, and pK_a determinations and dipole moment measurements.

Cyanogen reacts with mercaptans in the presence of catalytic amounts of *n*-butylamine at low temperature to yield S,S′-disubstituted dithiooxaldiimidates.[1,3] This is a general reaction for the preparation of dithiooxaldiimidic esters.

Primary aliphatic amines react with cyanogen to yield symmetrically disubstituted oxamidines,[4] whereas secondary amines normally give only cyanoformamidines and under vigorous conditions oxamidine derivatives.[5] But when ethylenediamine and its C-alkyl derivatives are allowed to react with cyanogen the product obtained was characterized as bis(Δ^2-2-imidazolinyl).[6]

In the light of these results it was interesting to investigate the behavior of α-mercapto acids (**1**) with cyanogen, since the geminal mercapto and carboxylic acid groups could react separately or in conjunction. When 2 mol of mercaptoacetic acid (**1a**) were treated with 1 mol of cyanogen, a white crystalline product, henceforth referred to as the monocyclic product, was obtained. This substance analyzed for condensation of these three molecules accompanied by loss of 1 mol of water ($C_6H_6N_2S_2O_3$). This indicated that the expected diaddition product (**2a**) was formed but reacted further to afford a monocyclic product. Cyclization of **2a** can result in formation of **3a** having a five-membered ring or **4a** having a six-membered ring. When it is dissolved in water and treated with 5% aqueous sodium bicarbonate, carbon dioxide is liberated, indicating the presence of a strongly acidic function. It has a neutralization equivalent of 109 when titrated with sodium hydroxide (potentiometric titration) and has two acidic functions of apparent pK_a = 4.1 and 6.7 (50% acetone in water). It gives a red color when treated with a solution of ferric chloride, which indicates that the compound may be phenolic although there are other possibilities for complex formation with the various functional groups in either of the two structures. The

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[1] A. R. Martin and R. G. Ketcham, *J. Org. Chem.*, **31**, 3612 (1966).

[2] (a) Supported by National Institute of Mental Health Grant MH 08787. (b) A portion of the Ph.D. thesis of S. C. M. (c) To whom inquiries should be sent.

[3] H. M. Woodburn and C. E. Sroog, *J. Org. Chem.*, **17**, 371 (1952).

[4] H. M. Woodburn, B. A. Morehead, and C. M. Chih, *ibid.*, **15**, 535 (1950).

[5] H. M. Woodburn, B. A. Morehead, and W. H. Bonner, *ibid.*, **14**, 555 (1949).

[6] H. M. Woodburn and R. C. O'Gee, *ibid.*, **17**, 1235 (1952).

uv, ir, and nmr spectra do not distinguish unambiguously between the two structures **3a** or **4a**.

A 1-mol sample of the monocyclic compound (**3a** or **4a**) reacts with 2 mol of diazomethane and gives a product (**5a** or **6a**), mp 71–72°, which analyzes for $C_8H_{10}N_2O_3S_2$. The ir spectrum showed two peaks at 1740 and 1720 cm^{-1}, indicating two different carbonyl groups. Unexpectedly, there was no band at 3230 cm^{-1} corresponding to the imino N–H group. Disappearance of a group of small bands between 3000 and 2500 cm^{-1} indicated that the acid had been converted into the ester. The nmr spectrum of this ester in deuteriochloroform showed a singlet at 3.84 ppm (methylene group on the sulfur side chain, 3.88 ppm in the unmethylated compound), a singlet at 3.71 ppm (methyl ester), and another singlet at 3.06 ppm integrating for two, three, and three protons, respectively, and an AB quartet (J_{AB} = 16 cps) at 3.56 ppm assigned to ring methylene protons (3.92 ppm in the unmethylated compound) integrating for two protons. Disappearance of the =NH frequency in the ir spectrum coupled with appearance in the nmr spectrum of a singlet at 3.06 ppm integrating for three protons leads to the assignment of this signal to the $N-CH_3$ group.

The uv spectrum of this compound in ethanol showed an absorption maximum at 220 mμ (ε 7800) which is different from that of the parent compound. One would have expected the uv spectra to be similar since both contain the same chromophore. The differences might be explained if the carboxylic acid containing side chain were zwitterionic.

Further proof for concurrent N methylation and esterification was obtained from the reaction of diazomethane on the analogous monocyclic product (**3c** or **4c**) obtained from α-mercaptoisobutyric acid (**1c**) and cyanogen. In this case also two methyl groups are introduced although there is no possibility of enol formation, hence the possibility of O methylation of the enol is eliminated. All the above facts are consistent with either structure (**3a** or **4a**). In order to know more about this unusual N methylation some model compounds such as S,S′-dibenzyl dithiooxaldiimidate, S,S′-dimethyl dithiooxaldiimidate, and S,S′-dicarbomethyoxymethyl dithiooxaldiimidate were treated with diazomethane. In each case no reaction was observed and starting material was recovered. Therefore, no explanation can be offered for this N methylation accompanying esterification, except that the carboxylic acid group apparently facilitates the reaction. This suggests that the zwitterion may be required.

In order to obtain further information bearing on the question of formation of a five- or a six-membered ring, it was thought that, if a second ring could be closed, **3a** or **4a** would give rise to bicyclic product **7a** or **8a**, respectively. Although both structures are symmetrical, **7a** has free rotation around its central C–C bond whereas **8a** is more rigid; therefore, the former should have an appreciable dipole moment and the latter should have no dipole moment so long as the enol form does not exist in significant concentration. Molecular models of **8a** indicated that some of its conformations would have dipole moments. Thus one might be able to assign a structure to the condensation product of mercaptoacetic acid and cyanogen.

On refluxing the monocyclic product (**3a** or **4a**) with acetic anhydride for 10 min a white crystalline product, mp 152–175°, was obtained. Repeated crystallization from dioxane raised the melting point to 180–183°. Elemental analysis indicated the molecular formula $C_6H_4N_2S_2O_2$, resulting from loss of 1 mol of water in agreement with formation of a second ring. (Henceforth, this product will be referred to as the bicyclic product, **7a** or **8a**). At this stage considerable information on the bicyclic product (**7a** or **8a**) could be brought to bear on the question of formation of five- or six-membered rings. The fact that cyanogen reacts with mercaptoacetic acid to yield a monocyclic product, which under vigorous conditions loses a second mole of water to give a bicyclic product, suggests formation of first one and then a second six-membered ring. Once one six-membered ring was formed, subsequent closure of the second six-membered ring under similar conditions might be more difficult since it would give rise to a rigid fused bicyclic system. That is, the conformational requirements of the first six-membered ring would decrease the ease of formation of the second ring. In the case of the five-membered ring system, the existence of the first ring should have no obvious effect on formation of the second ring. The nmr data also favor a six-membered fused bicyclic structure (**8a**), since conformational differences in the geminal protons are more logically expected in the puckered six-membered ring compound than in the relatively more coplanar five-membered ring compound. The carbonyl frequency at 1775 cm^{-1} in the ir spectrum is in better accord with a five-membered bicyclic structure (**7a**), since the carbonyl frequency of five-membered cyclic ketones is observed between 1770 and 1800 cm^{-1}. Dipole moment data (2.6 D) are consistent with either **7a** or **8a**. If the dienol diacetate of the bicyclic compound could be prepared its nmr spectrum might indicate whether it is composed of five-membered rings (aromatic) or fused six-membered rings (less aromatic). The reaction of α-mercaptoisobutyric acid with cyanogen would yield a product incapable of enolization, whose dipole moment would indicate whether the product has five- or six-membered rings.

On refluxing the bicyclic product (**7a** or **8a**) with acetic anhydride and pyridine, a product (**9a** or **10a**), mp 215–26°, was obtained (Scheme I) which analyzed for $C_{10}H_8N_2O_4S_2$, indicating that two acetyl groups have been incorporated in place of the two enolic hydrogens.

The bicyclic product (**7c** or **8c**) from the α-mercaptoisobutyric acid–cyanogen reaction product (**3c** or **4c**) has a sharp melting point 109–110° and does not exhibit keto–enol tautomerism because of the replacement of geminal hydrogens by methyl groups. The dipole moment of this compound was found to be 3.2 D and could be best explained by the structure having free rotation around the central C–C bond. This is strong evidence that the bicyclic product has structure **7c**. However, the conformational differences for the methyl groups indicate that the rings are not flat, and that there may still be two six-membered rings.

For unequivocal assignment of structure, the dienol diacetate (**9b**) of the bicyclic product obtained from thiolactic acid and cyanogen was subjected to X-ray diffraction studies,[7] which conclusively proved that the

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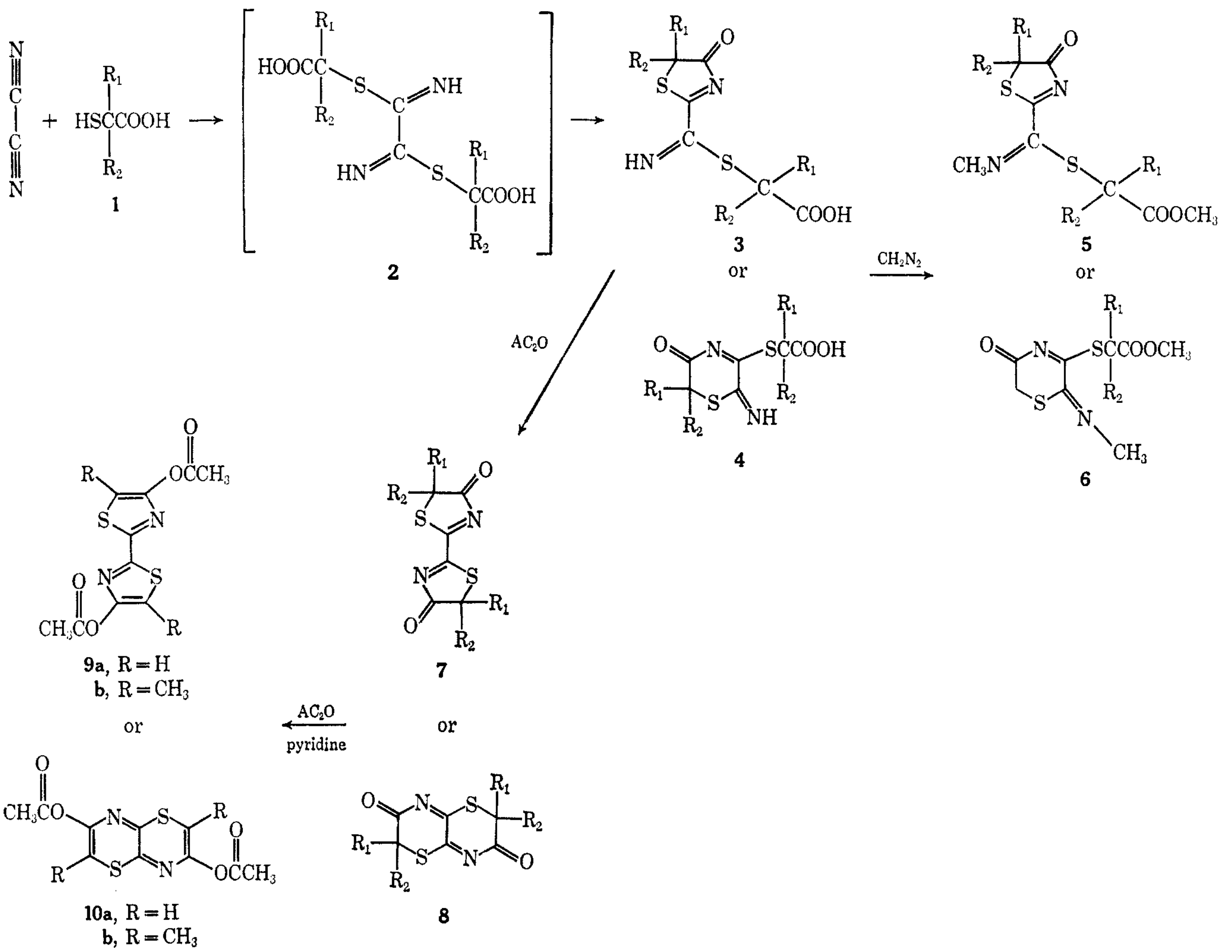
[7] X-Ray crystallographic studies were done by Dr. K. J. Palmer of Western Regional Research Laboratory, Albany, Calif., and will be published separately.

SCHEME I



a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

molecule has a center of symmetry and has two five-membered rings joined by a C–C bond, and is represented by structure **9b** (Figure 1). Thus it has been proved that the reaction of cyanogen and α-mercapto acids gives rise to a monocyclic product (**3a**) containing one five-membered ring which on treatment with diazomethane affords **5a** and on dehydration a bicyclic product (**7a**) having two five-membered rings is obtained, and that the dienol diacetate (**9a**) is a derivative of **7a**.

The results of the X-ray diffraction studies (Figure 1) have not only provided the proof of structure for the above compounds, but also supply confirmation for a number of structures proposed in the literature beginning in 1891. In each of these cases the same question of two five-membered rings or two fused six-membered rings exists. In none of these cases was an unequivocal proof of structure provided.

Forsell[8] reported that the thermal condensation of dithiooxamide with ethylenediamine affords bis(Δ^2-2-imidazolinyl) (**11**). The assignment of this structure was completely arbitrary. In a later publication[9] he commented that the product could also have structure **12** but concluded that this is highly improbable although possible. In 1944, Lehr and Erlenmeyer[10] condensed the dithioamide of adipic acid with ethylenediamine and obtained 1,4-bis(Δ^2-2-imidazolinyl)butane and concluded that Forsell's product was bis(Δ^2-2-imidazolinyl). They also condensed the dithioadipamide with α-bromoacetophenone and obtained α,ω-di[4-phenylthiazolyl-(2)]butane. Karrer and coworkers[11] condensed dithiooxamide with chloroacetone and on the basis of Lehr and Erlenmeyer's work[10] assigned structure **13** to the reaction product. In 1952, Woodburn and O'Gee reported that condensation of ethylenediamine with cyanogen yielded a product identical with **11** and, quoting Lehr and Erlenmeyer,[10] also assigned the structure bis(Δ^2-2-imidazolinyl). Forsell,[8,9] Lehr, and Erlenmeyer[10] and Woodburn and O'Gee[6] ignored the possibility of formation of **12** or a tautomer thereof.

The model compound (dithioadipamide) used by Lehr and Erlenmeyer for assignment of structure to the condensation product of Forsell is not as unique as dithiooxamide, while the latter has the possibility of form-

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[8] G. Forsell, *Ber.*, **24**, 1846 (1891).

[9] G. Forsell, *ibid.*, **25**, 2132 (1892).

[10] H. Lehr and H. Erlenmeyer, *Helv. Chim. Acta*, **27**, 489 (1944).

[11] P. Karrer, P. Leiser, and W. Graf, *ibid.*, **27**, 624 (1944).

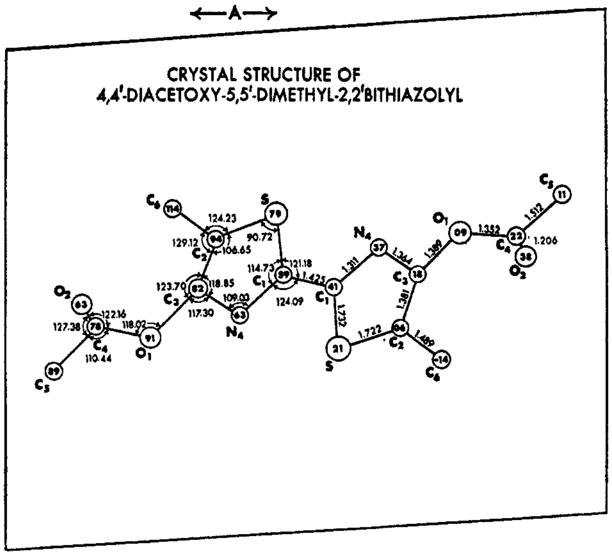
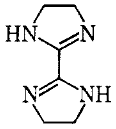


Figure 1.—The molecule has a center of symmetry. The angles are shown on the left side, the interatomic distances on the right. The number within each circle is the value of the y parameter. The unit cell dimensions are a = 13.125 Å, b = 4.830 Å, c = 10.995 Å, and β = 94.09°. Space group $P2_1/c$.

ing five- or six-membered rings the former can only form five-membered rings and hence is not compelling evidence for the formation of **11**. Therefore, the possibility of structures such as **12** cannot be ruled out. The same argument can be used in the assignment of structure to the condensation product of dithiooxamide and chloroacetone and the possibility of alternate structure **14** cannot be excluded.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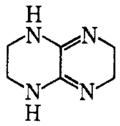
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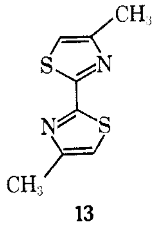
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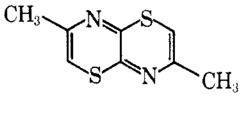
14

On mechanistic and structural grounds, the reaction of mercaptoacetic acid and cyanogen is not much different from that of ethylenediamine and cyanogen, and dithiooxamide and chloroacetone, hence the results in one case provide support for five-membered ring structures in the other similar cases. Thus the X-ray diffraction studies support formation of structures containing two five-membered rings.

Experimental Section[12,13]

Reactions of α-Mercapto Acids with Cyanogen (Synthesis of Monocyclic Products).—The procedure is the same as that reported earlier,[1,3] except that the reaction is carried out in ether instead of hexane because of the low solubility of α-mercapto acids in hexane.

2-[(S-Carboxymethyl)thioimidyl]-Δ^2-thiazolin-4-one (3a).—In a 300-ml three-necked flask, fitted with a Dry Ice-acetone condenser, a magnetic stirring bar, and a gas inlet tube cooled to −80°, were placed 18.4 g (0.2 mol) of mercaptoacetic acid, 2 drops of n-butylamine, and 200 ml of anhydrous ether. Cyanogen gas (5 g, 0.1 mol, previously frozen and weighed) was passed into the above solution. After addition of cyanogen was complete (20 min) the reaction mixture was maintained at −80° for 2 hr, and then allowed to warm to room temperature. At this stage the reaction became slightly exothermic and the reaction product precipitated as a white solid, which was collected, washed with ether, and crystallized from acetone or acetic acid to give 16.8 g (77%) of a white crystalline material: mp 164–165° dec; ir 3230 (NH), 3000–2400 (OH, CO_2H dimer), 1730 (ring C=O) and 1700 cm^{-1} (C=O of CO_2H); nmr (acetone-d_6) δ 4.4 (broad s, 2, NH and CO_2H), 3.92 (AB quartet, 2, J = 15.5 Hz, ring CH_2), and 3.88 (s, 2, S-CH_2); uv max (95% EtOH) 314 mμ (ϵ 7540) and 365 (10), 314 (7850, in acid), 365 (7900, in base); neut equiv (potentiometric titration), 109 (calcd 109); pK_a = 4.1 and 6.7 (50% aqueous acetone).

Anal. Calcd for $C_6H_6N_2O_3S_2$: C, 33.04; H, 2.77; N, 12.84; S, 29.34. Found: C, 33.36; H, 2.78; N, 12.76; S, 29.38.

2-[S-(2-Carboxyethyl)thioimidyl]-Δ^2-thiazolin-4-one (3b).—This product (monocyclic) could not be isolated in pure state from the reaction of thiolactic acid and cyanogen. It was always accompanied by 4,4'-dihydroxy-5,5'-dimethyl-2,2'-bithiazolyl (bicyclic). However, its presence was shown by treating this mixture with diazomethane whereby the monocyclic product was methylated and dissolved, whereas the unreactive bicyclic product remained behind. The N-methylated ester (**5b**) of the monocyclic product thus obtained could be characterized. The procedure described below is one which gave rise to the above-mentioned mixture.

Cyanogen gas (5 g, 0.1 mol) was passed into a stirred solution of 21.2 g (0.2 mol) of thiolactic acid and 2 drops of n-butylamine in 200 ml of anhydrous ether maintained at −80°. The reaction mixture was continuously stirred at −80° for 2 hr and then allowed to warm to room temperature. At this stage the colorless reaction mixture became pale yellow. On removing the ether under vacuum, there was obtained 24 g of solid, mp 190–220°. The heterogenous nature of the product could be observed by the presence of both yellow and white crystals. All attempts to separate the white product (presumably the monocyclic product) from yellow product (bicyclic) were unsuccessful, *e.g.*, fractional crystallization from a variety of solvents (benzene, acetone, ether, and ethanol) and chromatography on activated florisil and alumina (neutral).

5,5-Dimethyl-2-[S-(2-carboxyisopropyl)thioimidyl]-Δ^2-thiazolin-4-one (3c).—Into a stirred solution of 10 g (0.083 mol) of α-mercaptoisobutyric acid and 2 drops of n-butylamine in 100 ml of anhydrous ether maintained at −80° was passed 2.2 g (0.042 mol) of cyanogen gas. The reaction mixture was stirred at −80° for 2 hr and then allowed to warm to room temperature. Ether was removed on a rotary evaporator leaving behind a white crystalline product, mp 170–174°. Two crystallizations from methanol afforded 9.6 g (80%) of a white crystalline product: mp 177–178°; ir 3280 (NH), 3000–2400 (OH of COOH dimer), 1720 (ring C=O), and 1675 cm^{-1} (C=O of COOH); nmr δ 4.4 (broad, s, 2, NH and COOH), 1.96 (s, 3) and 1.73 (s, 3) (ring CH_3 groups), and 1.63 (s, 3) and 1.58 (s, 3) (side chain CH_3); neut equiv (potentiometric titration), 275.1 (calcd 274); pK_a = 4.1.

Anal. Calcd for $C_{10}H_{14}N_2O_3S_2$: C, 43.80; H, 5.15; N, 10.22; S, 23.35. Found: C, 43.98; H, 5.30; N, 9.99; S, 23.12.

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(12) Melting points were measured using a Thomas-Hoover capillary melting point apparatus, and are corrected. Elemental analyses were carried out by the micro-analytical laboratory of the University of California at Berkeley. The ultraviolet spectra were determined in 95% ethanol using a Carey Model-11 spectrophotometer. Absorption is reported in millimicrons, intensities as the molar extinction coefficient (ϵ). The infrared spectra were determined using a Perkin-Elmer 337 spectrophotometer. Potassium bromide was used for solids. The nuclear magnetic resonance spectra were measured in deuteriochloroform unless indicated otherwise, with tetramethylsilane as the internal standard, using a Varian A60-A spectrometer. Chemical shifts are reported as δ values (part per million); coupling constants (J values) are given in cycles per second. Potentiometric titrations were done on a Metrohm Herisau potentiograph at 25° in 50% aqueous acetone. Dipole moment measurements were made on a WTW dipolimeter DE01 using DLF-2 cells at 25° in dioxane. Calculations were done by the method of Kumler and Halverstadt[13] using an IBM 360 computer.

(13) I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2933 (1942).

Reactions of Monocyclic Compounds with Diazomethane. 2-[N-Methyl-(S-carbomethoxymethyl)thioimidyl]-Δ^2-thiazolin-4-one (5a).—To an ice cold suspension of 2.2 g (0.01 mol) of **3a** in 15 ml of anhydrous ether was added an ethereal solution of diazomethane[14] (0.9 g, 0.021 mol) in small portions until evolution of nitrogen ceased and the solution acquired a pale yellow color. As reaction proceeds the suspended starting material dissolves and at the end a clear solution is obtained. The solvent was evaporated leaving behind a white crystalline product and an oil. The residue was dissolved in methanol and set aside for crystallization. On cooling it afforded 2.3 g (92%) of a white crystalline product, mp 69–71°. Two crystallizations from methanol afforded a product: mp 71–72°; ir 1780 (ring C=O) and 1700 (ester C=O), 1600 cm^{-1} (C=N); nmr δ 3.84 (s, 2, S-CH$_2$) and 3.71 (s, 3, methyl ester), 3.56 (AB quartet, 2, J = 16 Hz, ring CH$_2$), 3.06 (s, 3, N-CH$_3$); neut equiv (potentiometric titration), 247 (calcd 246); pK_a = 6.65.

Anal. Calcd for $C_8H_{10}N_2O_3S_2$: C, 39.23; H, 4.09; N, 11.38; S, 26.00. Found: C, 39.53; H, 4.36; N, 11.38; S, 25.60.

5-Methyl-2-[N-methyl-S-(2-carbomethoxyethyl)thioimidyl]-Δ^2-thiazolin-4-one (5b).—The reaction product of thiolactic acid and cyanogen (**3b**) (5 g) was suspended in 20 ml of anhydrous ether. To this suspension was added an ethereal solution of 0.42 g of diazomethane in small portions until the evolution of nitrogen ceased. As the reaction proceeded part of the mixture dissolved and part remained in suspension. The reaction mixture was filtered at this stage and a yellow product, mp 242–243°, was collected. This yellow product was identical in all respects with the bicyclic product (**7b**) obtained from cyanogen and thiolactic acid. The filtrate on evaporation afforded a crystalline product, mp 95–97°. This was recrystallized from methanol to afford 1.37 g of colorless needles, mp 98–99°, and represents 1.25 g of the corresponding unmethylated compound. On the basis of this yield of N-methylated ester, the percentage of monocyclic product in the mixture (5 g) was estimated to be 25%: ir 1780 (ring C=O), 1720 (ester C=O), 1610 cm^{-1} (C=N); nmr δ 4.07 (q, 1, J = 7 Hz, CH next to CH$_3$), 3.8 (s, 3, methyl ester), 3.71 (q, 1, J = 7 Hz, CH next to CH$_3$), 3.1 (s, 3, =NCH$_3$) and 1.63 (d, 3, J = 7 Hz, CH$_3$), 1.36 (d, 3, J = 7 Hz, CH$_3$).

Anal. Calcd for $C_{10}H_{14}N_2O_3S_2$: C, 43.80; H, 5.15; N, 10.22; S, 23.35. Found: C, 43.93; H, 5.40; N, 10.18; S, 23.50.

5,5-Dimethyl-2-[N-methyl-(S-carbomethoxyisopropyl)thioimidyl]-Δ^2-thiazolin-4-one (5c).—To an ice cold solution of 2.8 g (0.01 mol) of **3c** in 15 ml of anhydrous ether was added an ethereal solution of diazomethane (0.9 g, 0.021 mol) in small portions until gas evolution ceased and the solution became yellow. The solvent was evaporated leaving behind a white crystalline product. Two recrystallizations from methanol afforded 2.85 g (95%) of crystalline product: mp 120–121°; ir 1780 (ring C=O) and 1710 cm^{-1} (ester C=O); nmr δ 3.70 (s, 3, methyl ester), 3.06 (s, 3, =NCH$_3$), 1.96 (s, 3, CH$_3$) and 1.73 (s, 3, CH$_3$) (nonequivalent geminal methyl groups of the ring), 1.60 (s, 6, geminal methyl groups on side chain).

Anal. Calcd for $C_{12}H_{18}N_2O_3S_2$: C, 47.68; H, 6.00; N, 9.27; S, 21.96. Found: C, 47.52; H, 5.91; N, 9.02; S, 21.80.

Syntheses of Bicyclic Compounds. 4,4'Diketo-2,2'-Δ^2-bithiazolinyl (7a).—2-[(S-Carboxymethyl)thioimidyl]-Δ^2-thiazolin-4-one (4.36 g, 0.02 mol) was refluxed in 10 ml of acetic anhydride for 10 min. The reaction mixture was cooled and set aside for crystallization. It afforded 3.8 g (95%) of a white crystalline product, mp 152–175°. On repeated recrystallization from dioxane the melting point could be improved to 180–182°: ir 1775 cm^{-1} (ring C=O); nmr (pyridine-d_5) δ 4.2 (AB quartet, nonequivalent ring methylene protons) (deuterium oxide exchange resulted in disappearance of the AB quartet); uv max (95% EtOH) 314 mμ (ϵ 7850) and 365 (1700), 314 (8200 in acid), 365 (8100 in base); neut equiv (potentiometric titration), 100 (calcd 100.05); pK_a = 6.7; dipole moment 2.6 D.

Anal. Calcd for $C_6H_4N_2O_2S_2$: C, 36.01; H, 2.01; N, 14.00; S, 31.98. Found: C, 36.20; H, 2.19; N, 14.20; S, 31.98.

4,4'-Dihydroxy-5,5'-dimethyl-2,2'-bithiazolyl (7b).—Cyanogen gas (5 g, 0.1 mol) was passed into a stirred solution of 21.2 g (0.2 mol) of thiolactic acid and 2 drops of *n*-butylamine in 200 ml of anhydrous ether maintained at −80°. The reaction mixture was stirred at −80° for 2 hr and then allowed to warm to room temperature. The reaction mixture was then refluxed on a water bath for 30 min and ether removed at the water pump leaving behind a yellow solid. Two recrystallizations from dimethyl sulfoxide yielded 20 g (87%) of a yellow crystalline product: mp 242–243° dec; ir 3500–2500 (H bonded OH) and 1580 cm^{-1} (conjugated C=C); nmr (TFA) δ 2.20 (s, CH$_3$); neut equiv (potentiometric titration), 114 (calcd 114); pK_a = 6.7.

Anal. Calcd for $C_8H_8N_2O_2S_2$: C, 42.11; H, 3.53; N, 12.28; S, 31.56. Found: C, 42.28; H, 3.64; N, 12.20; S, 31.72.

4,4'-Diketo-5,5,5',5'-tetramethyl-2,2'-Δ^2-bithiazolinyl (7c).—5,5-Dimethyl-2-[S-(2-carboxyisopropyl)-thioimidyl]-Δ^2-thiazolin-4-one (2.8 g, 0.01 mol) was refluxed in 5 ml of acetic anhydride for 10 min and set aside for crystallization. On cooling it afforded 2.1 g (81.5%) of a white crystalline product, mp 105–108°. Two recrystallizations from benzene yielded a product of mp 109–110°; ir 1780 cm^{-1} (ring C=O); nmr δ 1.93 (s) and and 1.68 (s) (nonequivalent methyl groups); dipole moment 3.2 D.

Anal. Calcd for $C_{10}H_{12}N_2O_2S_2$: C, 46.88; H, 4.72; N, 10.93; S, 24.98. Found: C, 47.01; H, 4.78; N, 10.75; S, 24.72.

Syntheses of Dienol Diacetates. 4,4'-Diacetoxy-2,2'-bithiazolyl (9a).—4,4'-Diketo-2,2'-Δ^2-bithiazolinyl (1 g, 0.005 mol) was dissolved in a mixture of 3 ml of acetic anhydride and 1 ml of pyridine and gently refluxed for 30 min. On cooling it afforded 700 mg (50%) of a white crystalline product, mp 210–212°. Two recrystallizations from benzene afforded a product of mp 215–216°; ir 1750 (acetoxy C=O), 1210 cm^{-1} (C-O stretch); nmr δ 6.5 (s, 1, aromatic CH), 2 (s, 3, acetoxy CH$_3$); uv max (95% EtOH) 345 mμ (ϵ 25,200).

Anal. Calcd for $C_{10}H_8N_2O_4S_2$: C, 42.26; H, 2.84; N, 9.86; S, 22.52. Found: C, 42.21; H, 2.73; N, 9.71; S, 22.60.

4,4'-Diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl (9b).—4,4'-Dihydroxy-5,5'-dimethyl-2,2'-bithiazolyl (5 g, 0.02 mol) was dissolved in a mixture of 8 ml of acetic anhydride and 2 ml of pyridine and gently refluxed for 20 min. On cooling it afforded a white crystalline product, mp 240–241°. Two recrystallizations from benzene yielded a product of mp 242–243°; ir 1750 (C=O), 1210 cm^{-1} (C-O stretch); nmr δ 2.33 (s, 3, acetoxy group), 2.28 (s, 3, methyl); uv max (95% EtOH) 346 mμ (ϵ 25,300).

Anal. Calcd for $C_{12}H_{12}N_2O_4S_2$: C, 46.16; H, 3.87; N, 8.97; S, 20.50. Found: C, 46.24; H, 4.07; N, 9.14; S, 20.60.

Registry No.—Cyanogen, 460-19-5; **3a**, 19639-58-8; **3b**, 19639-59-9; **3c**, 19639-60-2; **5a**, 19639-61-3; **5b**, 19639-62-4; **5c**, 19639-63-5; **7a**, 19639-64-6; **7b**, 19639-65-7; **7c**, 19639-66-8; **9a**, 19639-67-9; **9b**, 19639-68-0.

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(14) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green & Co., London, 1956, pp 971 and 973.