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2-Substituted Imino-1,3-dithiolanes. Their Thermal Ring-isomerizations and Reactions with Epoxides[*1]

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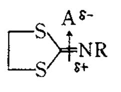
Thermal ring-isomerization and reactions with epoxides of 2-substituted imino-1,3-dithiolanes (I) were studied. The methylimino (Ia) and ethylimino derivatives (Ib) were found to be ring-isomerized to the corresponding 3-alkyl-1,3-thiazolidine-2-thione (V) at about 200°C, while the phenylimino compound (Ic) was not isomerized even under more drastic conditions. The influence of various additives including Lewis acids was also examined. In contrast to the oxygen analog of I, these imino compounds were not polymerized with Lewis acids, and catalysis of any additives on isomerization was not observed. The possibility that I thermally dissociated into methyl isothiocyanate and ethylene sulfide followed by their recombination to V would be excluded by the observation that the reaction of alkyl isothiocyanate with ethylene sulfide at 150°C afforded I in good yield. Reactions of I with epoxides were carried out regarding the isomerization mechanism. All these imino compounds reacted with epoxides to give the 2-oxazolidone derivatives (III) in good yield. Mechanisms of the ring-isomerization and formation of III have been suggested, and the difference in reactivity between I and its oxygen analog has been discussed.

In a previous paper[1] we reported that 1,2-dichloroethane reacted with sodium *N,N*-dialkyldithiocarbamate to result in the formation of 2-dialkylamino-1,3-dithiolanylium ions involving participation of the dithiocarbamate function as an internal nucleophile. In a similar way, 2-alkylimino-1,3-dithiolanes were obained by the reaction of 1,2-dichloroethane with sodium *N*-monoalkyldithiocarbamate in the presence of base. We were prompted to investigate the reactivities of 2-substituted imino-1,3-dithiolanes (I) in view of the following. (1) On the addition of acid catalysts (A) such as Lewis acids, the imino compounds are expected to form complex II, the structure of which resembles that of dithiolanylium ion III. The type of carbonium ions have been demonstrated to be the interesting reactive species.[2]

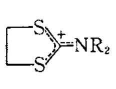
[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[1] T. Nakai, Y. Ueno and M. Okawara, *Tetrahedron Lett.*, **1967**, 3831; This Bulletin, **43**, 156 (1970).

[2] T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835.

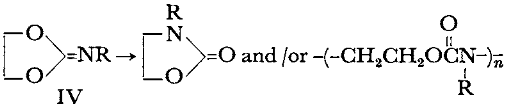


II



III

(2) Ring-isomerization³⁾ and ring-opening polymerization⁴⁾ of the oxygen analogs of I, *i. e.*, 2-substituted imino-1,3-dioxolanes (IV), have been reported. However, no information has been available on the imino-dithiolanes. Burkhardt has suggested that 2-benzoylimino-1,3-dithiolane considerably resists ring-isomerization as compared with oxygen analog.⁵⁾



IV

In the present work we studied the possibility of ring-isomerization or ring-opening polymerization of imino-dithiolanes (I) and their reactions with epoxides.

Results

Preparation of Imino-dithiolanes (I). 2-Methylimino- (Ia) and 2-ethylimino-1,3-dithiolane (Ib) were obtained in yields of 67 and 26%, respectively, by the reaction of 1,2-dichloroethane with the corresponding sodium *N*-alkyldithiocarbamate at 60°C in the presence of potassium carbonate. 2-Phenylimino-1,3-dithiolane (Ic) was obtained in 73% yield by the reaction of 2-dimethylamino-1,3-dithiolanylium perchlorate with aniline.²⁾

The infrared spectra of these imino compounds showed a strong absorption band around 1600 cm^{-1} due to the C=N group (Fig. 1). The NMR spectrum of Ia displayed a three-proton signlet at $\delta 3.10$ (*N*-methyl) and a four-proton multiplet in the region of 3.20—3.70 ppm (ring-methylene). (Fig. 2a). It is of interest that the ring-methylene protons of Ic appeared at 3.32 ppm as a singlet form.

Thermal Ring-isomerization. Ring-isomerization of these imino-dithiolanes was undertaken by heating in a sealed tube in the presence or absence of an additives listed in Table 1. Among additives employed, $AlCl_3$, BF_3OEt_2, H_3PO_4 and $FeCl_3$ have been reported to be effective as catalysts for the ring-isomerization or the ring-opening polymerization of the oxygen-analogs IV.³,⁴⁾ It was found that Ia was ring-isomerized above 200°C into 3-methyl-1,3-thiazolidine-2-thione (Va) in 48% yield in the absence of an additive. The results are summarized in Table 1. Results indicate that any additives used neither increase the yield of Va nor lower the isomerization temperature. Ring-opening polymerization was not observed. These observations are in direct contrast to those of oxygen analogs IV. The infrared spectrum of the isomerized product Va showed no absorption band at 1600 cm^{-1} and a new band at 1500 cm^{-1} due to the –S–CS–N< structure (Fig. 1). The NMR spectrum of Va confirmed the structure (Fig. 2b).

TABLE 1. THERMAL RING-ISOMERIZATION OF 2-METHYLIMIMINO-1,3-DITHIOLANE (Ia) INTO 3-METHYL-1,3-THIAZOLIDIDINE-2-THIONE (Va) IN THE PRESENCE OF VARIOUS ADDITIVES

Reaction temp.: 200°C; time: 3 hr

Additive	Yield ,%
None	48
$AlCl_3$	47
$AlCl_3$*	0
BF_3OEt_2	41
H_3PO_4	46
H_2SO_4	23
$FeCl_3$	23
LiCl**	56
NEt_3	15

* 170—180°C; 60 min

** 230—240°C; 7 min

Similarly, the ethylimino derivative Ib was ring-isomerized to 3-ethyl thiazolidine-2-thione (Vb) in 66% yield in the absence of an additive. The structure was confirmed by elemental analysis

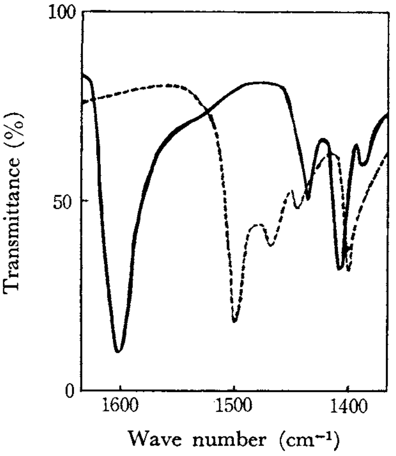


Fig. 1. The IR spectra.
——: 2-methylimino-1,3-dithiolane (Ia) (neat).
------: 3-methyl-1,3-thiazolidine-2-thione (Va) (KBr)

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3) K. Gulbis, M. Roth and N. Hamann, *Angew. Chem.*, **73**, 434 (1961).

4) T. Mukaiyama, T. Fujisawa, H. Nohira and T. Hyugji, *J. Org. Chem.*, **27**, 3337 (1962); T. Fujisawa, Y. Tamura, and T. Mukaiyama, This Bulletin, **37**, 797 (1964).

5) J. Burkhardt, R. Feinauer, K. Gulbis and K. Hamann, *Chem. Ber.*, **99**, 1912 (1966).

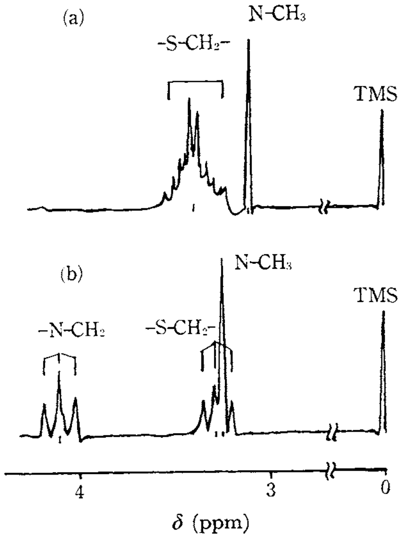
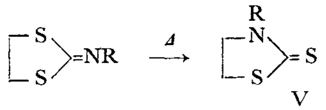


Fig. 2. The NMR spectra.
(a): 2-methylimino-1,3-dithiolane (Ia) (CCl_4)
(b): 3-methyf-1,3-thiazolidine-2-thione (Va) (CCl_4+CDCl_3)

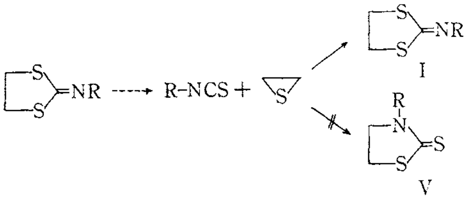
and spectroscopic methods.



Ia: $R=CH_3$
b: $R=C_2H_5$

The phenylimino derivative (Ic), however, did not ring-isomerize and only the starting material was recovered almost quantitatively after heating at 200 or 250°C.

Reactions of Isothiocyanates with Ethylene Sulfide. Isolation of a small amount of methyl isothiocyanate during the distillation of Ia suggests that Ia may thermally dissociate into the isothiocyanante and ethylene sulfide. In order to examine the possibility that V might be formed through recombination of these dissociated fragments, the reaction of isothiocyanate with ethylene sulfide were carried out in the presence of triethylamine at 120—140°C in a sealed tube. Methyl isothiocyanate reacted with ethylene sulfide to give Ia (not Va) in 40% yield. When the reaction temperature was raised to 200—220°C, Va was formed probably *via* the ring-isomerization of Ia formed. Similarly phenyl isothiocyanate afforded Ic in 83% yield.



These observations indicate that the isomerized product V is not formed directly from the isothiocyanate and ethylene sulfide.

This fact is in agreement with the observation that isocyanate reacts with epoxides to give 2-imino-1,3-dioxolanes (IV), in some instances followed by the subsequent ring-isomerization to the 2-oxazolidones.[6]

Reactions of the Imino-dithiolanes with Epoxides. Recently Russian chemists have reported that the 2-phenylimino-1,3-dithiolane (Ic) reacted with epoxides at 80—90°C to afford the 2-oxazolidone derivatives (VI),[7] the details of which have not been accessible. The fact that the phenylimino derivative, which did not ring-isomerize, reacted with epoxides under the mild condition leads us to a further study on the reaction of other imino-dithiolanes with epoxides.

2-Methylimino-1,3-dithiolane (Ia) reacted with propylene oxide and epichlorohydrin at 90°C in the presence of triethylamine to produce 5-methyl-(VIa) and 5-chloromethyl-2-oxazolidone (VIb), respectively, in yields of 64% and 67%. The structure of product VI was determined by elemental analysis and spectral data (IR and NMR). The infrared spectra of VIa and VIb showed the characteristic band of the oxazolidone-carbonyl group at

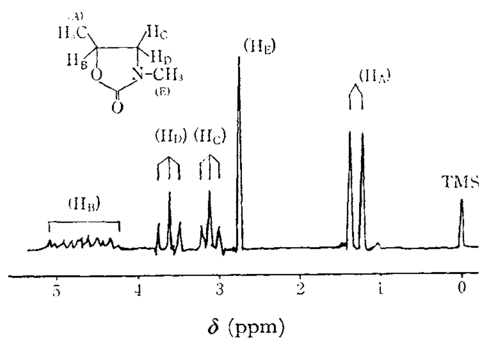
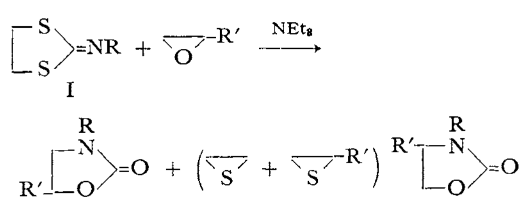


Fig. 3. The NMR spectrum of 3,5-dimethyl-2-oxazolidone (CCl_4).



VIa: $R=CH_3$; $R'=CH_3$
b: $R=CH_3$; $R'=CH_2Cl$
c: $R=C_6H_5$; $R'=H$

VII

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[6] K. Gulbis, G. Benzig, R. Maysenholder and K. Hamann, *Chem. Ber.*, **93**, 1975 (1960).

[7] V. S. Etilis, A. P. Sineokov and G. A. Razuvaev, *Zh. Obshch. Kim.*, **34**, 4018 (1964); *Chem. Abstr.*, **62**, 9132 (1965).

1700 cm^{-1}. The NMR spectrum of VIa completely supports the oxazolidone structure (Fig. 3). The possibility of structure VII could be eliminated based upon the results of systematic NMR studies of oxazolidone derivatives.[8]

Discussion

On the Mechanism of Ring-isomerization. Experimental results described above of the ring-isomerization of the imino-dithiolanes (I) are summarized as follows, comparing them with oxygen analogs IV;

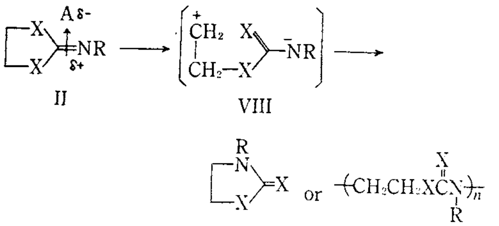
(1) 2-Alkylimino-1,3-dithiolanes were ring-isomerized to the thiazolidine-2-thione (V) under a severer condition than that for the oxygen analogs.

(2) Both the phenylimino- and the benzoylimino-dithiolane failed to be ring-isomerized, whereas their oxygen analogs with the same substituents isomerized more readily at lower temperatures.

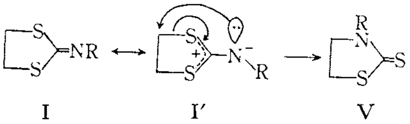
(3) Acid additives were ineffective or they resulted in lower yields of the isomerized products. This is significantly different from the case of the oxygen analogs.

(4) In all cases, polymeric materials were not obtained with any Lewis acids. This fact is in direct contrast with that of the oxygen analogs.

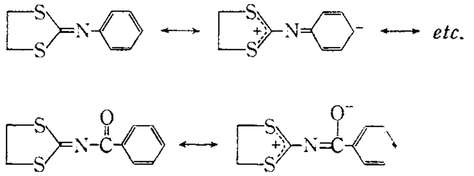
These fact substantially exclude the following mechanism involving carbonium ion VIII which has been accepted for both the ring-isomerization[3] and the ring-opening polymerization[4] of the oxygen analogs.



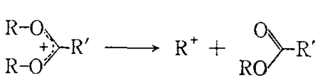
Thus we propose another possible mechanism for the ring-isomerization concerned, which involves concerted attack of the nonbonded electron pair of the nitrogen atom on the carbon atom of the ring-methylene through the S_N-2-like transition state.



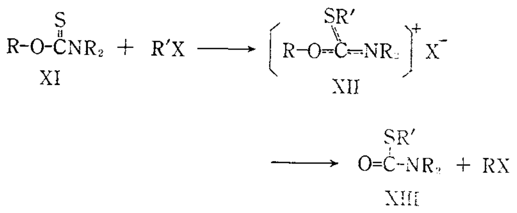
Structure I′ is more favorable than that of the ordinary imino compounds since the positive charge is more stabilized by the electron-donating character of the sulfur atoms. This fact is in agreement with the observation that 2-dialkylamino-1,3-dithiolanylium ions are considerably stable.[2] Although this unimolecular mechanism is sterically unfavorable and has not been completely established, this may explain the four experimental results described above. The electron density on the nitrogen atom is lowered either by the complex formation between the acidic additive and the imino compound (see (3)) or by electron delocalization to the other part of the molecule for 2-phenylimino-1,3-dithiolane (Ic) and the benzoylimino derivative shown below (see (2)).



In conclusion, the difference in mechanism for ring-isomerization between the imino-dithiolanes and the imino-dioxolanes might be ascribed to the difference in stability between carbonium-ion like species IX and X. It has been accepted that the carbon-oxygen bonds in dialkoxycarbonium ions cleave more readily into the alkyl cation and the ester than the carbon-sulfur bonds in dialkoxythiocarbonium ions.[9]



This fact may be supported by the observation that the thioncarbamate XI reacts readily with alkyl halides to form triheterosubstituted carbonium ion XII followed by exclusive transformation into thiolcarbamate XIII.[9]



On the Mechanism for the Formation of 2-Oxazolidone Derivatives from Imino-dithiolanes and Epoxides. There are two possible mechanisms for the formation of the 2-oxazolidone

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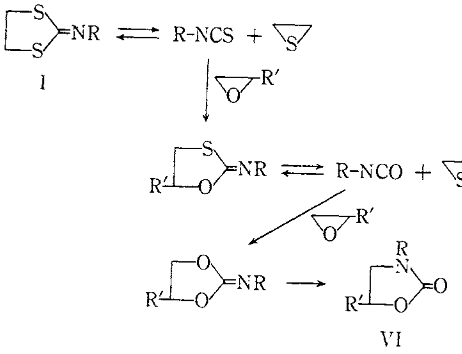
[8] J. E. Herweh, T. A. Fogjia and D. Swern, *J. Org. Chem.*, **33**, 4029 (1968).

[9] A. F. Schoberl and A. Waguer, "Houben-Wyle: Methoden der Organishen Chemie," Vol IX, George Thieme Verlag, Stuttgart (1955), p. 837.

derivative in the reaction of imino-dithiolane with epoxide.

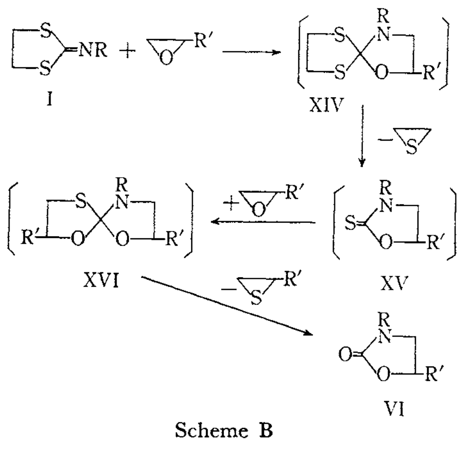
Firstly scheme A involves initial thermal dissociation of I into isothiocyanate and episulfide followed by a known subsequent reaction of isothiocyanate with epoxide giving 2-imino-oxothiolane. The imino-oxothiolane formed dissociates into isocyanate and episulfide followed by the reaction of isocyanate with epoxide to afford 2-imino-dioxolane, which, in turn, ring-isomerizes leading to the formation of VI.



Scheme A

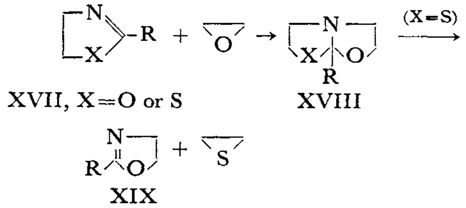
However, it is doubtful whether the dissociation of imino-dithiolane occurs at low temperatures such as 90°C. The fact that the formation of thioureas was not observed on treatment of Ia in the presence of excess aniline at 150°C, considerably reduces the possibility of occurrence.

The other mechanism, Scheme B, involves initial cycloaddition of epoxide to imino compound (I) followed by elimination of episulfide from the resulting spirocyclic compound (XIV), and then by further cycloaddition of epoxide to the thiocarbonyl group in oxazolidine-2-thione (XV) formed to yield another spirocyclic compound XVI. This, in turn, eliminates episulfide leading to the formation of VI.

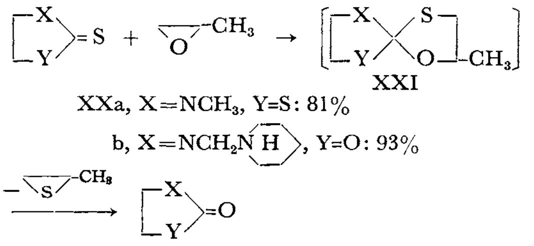


Scheme B

In support of the processes, I to XIV and XIV to XV, the following examples have been reported by Feinauer;[10] thia(or oxa)zolines (XVII) reacts with epoxide to yield the bicyclic compound XVIII *via* cycloaddition of epoxide to the *endo* C=N group, and in the case of X=S, loss of episulfide is followed leading to the formation of 2-oxazoline (XIX).



Little information on the reaction of the thiocarbonyl group with epoxides has been available in literature. In order to demonstrate the process XV→XVI→VI, we carried out the reaction of various thiocarbonyl compounds including oxazolidine-2-thione (XV) with epoxides. It was found that the thiocarbonyl group was readily converted to the corresponding carbonyl group in good yields presumably *via* spirocyclic adduct XXI as shown below. A detailed report on this type of reaction will be presented in a subsequent paper.[11]



XXa, X=NCH$_3$, Y=S: 81%

b, X=NCH$_2$N H , Y=O: 93%

We assume that the mechanism given in Scheme B is considered more likely for the reaction of imino-dithiolanes with epoxides.

Experimental

General. All melting and boiling points are uncorrected. The IR spectra were recorded with a Hitachi EPI-S2 spectrometer. The NMR spectra were determined with a Japan Electron Optics C-100 spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane as an internal standard.

Materials. Sodium *N*-monoalkyldithiocarbamates were prepared by the reaction of the aqueous solution of alkylamine with carbon disulfide in the presence of sodium hydroxide. 2-Dimethylamino-1,3-dithiolanylium perchlorate was obtained by a method reported.[1] Methyl isothiocyanate and ethylene sulfide were prepared by standard methods. Other reagents and solvents were commercial products and used after purification by standard methods.

2-Methylimino-1,3-dithiolane (Ia). To a suspension

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[10] R. Feinauer, *Angew. Chem. Int. Ed. Engl.*, **5**, 894 (1964).

[11] Y. Ueno, T. Nakai and M. Okawara, This Bulletin, **43**, 168 (1970).

of sodium methyldithiocarbamate (25.8 g, 0.20 mol) in absolute ethanol (200 m*l*), 1,2-dichloroethane (50 g, 0.50 mol) was added, and the mixture was then heated at 60°C for 1 hr. After cooling, a suspension of anhydrous potassium carbonate (27.6 g, 0.20 mol) in absolute ethanol (50 m*l*) was added, the reaction mixture was stirred at 60°C for further 4.5 hr, and the mixture was cooled followed by extraction with ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent was removed in reduced pressure. The residue was distilled giving a yellowish liquid (9.2 g, 35%); bp 79—81°C/0.45 mmHg; n_D (22°C) 1.6032. The IR and NMR spectra of Ia are given in Figs. 1 and 2a, respectively.

Found: C, 36.06; H, 5.30; N, 10.51%. Calcd for $C_4H_7NS_2$: C, 35.64; H, 5.39; N, 10.23%.

A higher boiling-point distillate obtained as a by-product was separated into 3-methylthiazolidine-2-thione (Va) and ethylene trithiocarbonate on column chromatography of active alumina.

The methylimino compound was also prepared by another method starting from methylamine and carbon disulfide. To a solution of carbon disulfide in ethanol, aq. methylamine solution was added drop by drop with vigorous stirring and cooling in an ice bath, where the temperature was kept below 30°C. The resulting clear orange-colored solution was added to 1,2-dichloroethane, and the mixture was stirred at 60°C for 1 hr. The yellowish solution was treated with concd. hydrochloric acid and the organic impurities were extracted with ether. An aqueous solution of potassium carbonate was added to neutralize the aqueous layer, and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent evaporated. Work-up gave the imino compound (Ia) in 67% yield.

2-Ethylimino-1,3-dithiolane (Ib) was prepared in 26% yield as in the case of Ia; bp 85—87°C/0.30 mmHg; n_D (27°C) 1.5839; IR (neat): 1595 cm^{-1} (C=N).

Found: C, 40.19; H, 6.09; N, 9.34%. Calcd for $C_5H_9NS_2$: C, 40.81; H, 6.17; N, 9.52%.

2-Phenylimino-1,3-dithiolane (Ic) was prepared by the reaction of 2-dimethylamino-1,3-dithiolanylium perchlorate with aniline in 73% yield according to the procedure reported;2) mp 47—48°C (lit,2) 47—48°C); IR (KBr disk): 1570 cm^{-1} (C=N); NMR (CCl_4): δ 3.32 (s, CH_2S), 6.55—7.10 ppm (m, aromatic protons).

Ring-isomerization of Imino-dithiolane (I). Many attempts to isomerize Ia were made under various conditions as shown in Table 1. In the presence of aluminum chloride, imino-dithiolane Ia (1.3 g, 0.01 mol) and a small amount (*ca.* 0.1 g) of aluminum chloride were sealed in a tube. The tube was heated at 200°C for 3 hr in an oil-bath. After cooling, the tube was carefully opened and the reaction mixture was extracted several times with ether. The ethereal solution was evaporated *in vacuo*. Recrystallization of the residue from ether yielded 0.61 g (47%) of 3-methylthiazolidine-2-thione (Va); mp 68—69°C (lit,12) 68—69°C); UV: λ_{max} (H_2O) 265 mμ (lit,13) 265 mμ). The IR and NMR spectra of Va are given in Figs. 1 and 2b, respectively.

Found: C, 36.06; H, 5.30; N, 10.51%. Calcd for $C_4H_7NS_2$: C, 36.15; H, 5.31; N, 10.65%.

As in the case of Ia imino compound Ib was isomerized to 3-ethylthiazolidine-2-thione (Vb) in 67% yield in the absence of any additive; bp 155—157°C/2.5 mmHg; n_D (22°C) 1.625.

Found: C, 40.84; H, 6.34%. Calcd for $C_5H_9NS_2$: C, 40.81; H, 6.17%.

Ring-isomerization of Ic failed both under same conditions and at higher temperature (250°C), and only the starting material (Ic) was recovered.

Reactions of Isothiocyanates with Ethylene Sulfide. Methyl isothiocyanate (4.0 g, 0.055 mol), ethylene sulfide (3.0 g, 0.030 mol), and triethylamine (3.0 g, 0.03 mol) were heated in a sealed tube at 120—140°C for 3 hr. After cooling the tube was carefully opened. Distillation of the resulting mixture in the reduced pressure gave 2.7 g (41%) of 2-methylimino 1,3-dithiolane (Ia). The IR spectrum, the boiling point and the refractive index of this distillate were identical with those of the authentic sample.

In a similar fashion the reaction of phenyl isothiocyanate with ethylene sulfide gave 2-phenylimino-1,3-dithiolane (Ic) in 83% yield.

Reaction of Imino-dithiolane Ia with Epoxides. Imino-dithiolane Ia (2.0 g, 0.015 mol), propylene oxide (2.0 g, 0.034 mol) and triethylamine (0.1 g) were sealed in a tube. The tube was heated at 140—150°C for 7 hr in an oil-bath. After cooling the tube was carefully opened. Distillation of the reaction mixture gave 3,5-dimethyl-2-oxazolidone (VIa) in 64% yield: bp 90—95°C/1 mmHg (lit,14) 92°C/1.5 mmHg); IR (neat): 1700 cm^{-1} (C=O).

The reaction of Ia with epichlorohydrin was carried out at 90°C for 27 hr as in the case of propylene oxide, to give 3-methyl-5-chloromethyl-2-oxazolidone (VIb) in 67% yield; bp 94—96°C/0.3 mmHg; IR (neat): 1700 cm^{-1} (C=O).

Found: N, 9.36%. Calcd for $C_5H_8ClNO_2$: N, 9.14%.

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12) J. W. Batty, *J. Chem. Soc.*, **1949**, 786.

13) J. L. Grardway, *ibid.*, **1966**, 92.

14) A. B. Steele, U. S. 28668801 (1959).