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Derivatives of 1,2-Dithiole-3-thione. II. Thermal Rearrangement of Iminothiocarbonyl Compounds.

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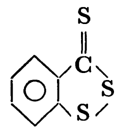
The synthesis[1] and cyclization mechanism[2] of thiocarbonyl ylides have recently attracted considerable attention. A solution of thiourea in chloroform reacts rapidly and exothermically with 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane, giving dicyanomethylene sulfonium dicyanomethylide in a high yield.[3] Certain thiocarbonyl compounds have been found to give the olefins by a similar treatment. The initial step of the reaction seems to be the formation of ylides, which collapses to a three-membered ring, giving rise to expulsion of sulfur to afford the final product.

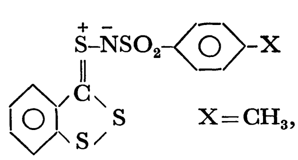
We have synthesized the terminal *N*-analog of thiocarbonyl ylide for the first time and found it to undergo similar rearrangement. This report deals with the nature of the thermal rearrangement of thiocarbonyl imines(B).[4]

Results and Discussion

When trithione(A) was treated with chloramine-B or corresponding substituted chloramines in methanol, thiocarbonyl imines(B) were obtained as red-colored precipitates in nearly quantitative yields.



(A)



X=CH_3, H, Br

(B)

When compound(B) (X=H) thus obtained was heated by refluxing in various solvents or kept standing at room temperature for a month without solvent, the rearranged imine (*N*-benzenesulfonyl-1,2-benzodithiole-3-imine)(C) was obtained. The analytical data are summarized in Table 1.

In order to clarify the mechanism of rearrangement we carried out kinetic measurements at about 60 °C. The rate of the rearrangement was followed by the disappearance of the absorption band due to thiocarbonylimine, appearing at 472—506 nm. In every case the reaction follows first-order kinetics. The relevant data are collected in Tables 2 and 3.

The marked change in rate with solvents indicates that the reaction rate sequence is not parallel at all with the ordinary polarity scale such as dielectric constant or dipole-moment. Instead, a relatively better correlationship can be found with $1/\lambda_{max}$ for the thiocarbonyl imine itself (Fig. 1). Accordingly, it should be pointed out that rearrangement involves a transition structure like the state of photoexcitation in

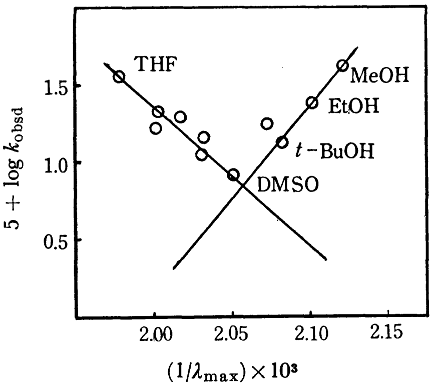
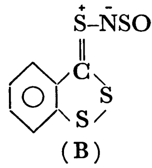
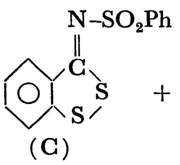
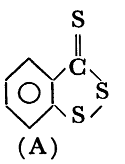


Fig. 1. Plot of log k_{obsd} vs. $1/\lambda_{max}$.

TABLE 1. PRODUCTS ANALYSIS

 (B)	 (C) +	 (A) +	$PhSO_2NH_2$ +	S_8 +	($+PPh_3$=S)
Solvent	Yield (%)				
Neat	86.2	8.1	6.1		
CH_3CN	85.5	8.1			
MeOH	31.9	67.5	67.5	31.9	
(CH_3CN)	(74.9)	(20.8)			(72.5)

Parenthesis indicates the reaction carried out in the presence of an equimolar quantity of triphenyl phosphine.

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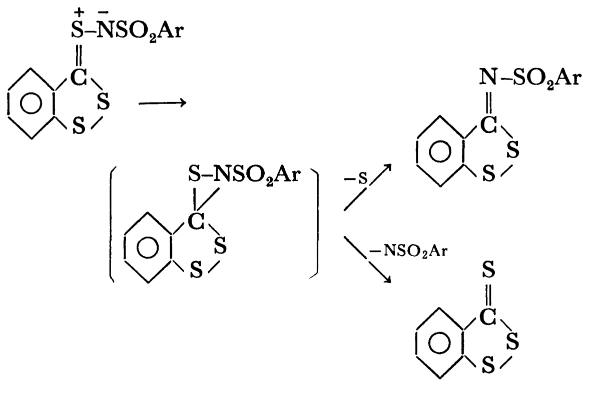
[1] E. B. Knott, *J. Chem. Soc.* **1955**, 916. B. H. Freeman, S. G. Harris, B. W. Kennedy, and D. Lloyd, *Chem. Commun.*, **1972**, 912.

[2] H. H. J. MacDonald and R. J. Crawford, *Can. J. Chem.*, **50**, 428 (1972). R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 1475 (1969). R. M. Kellogg, S. Wassenaar, and J. Buter, *Tetrahedron Lett.*, **1970**, 4689.

[3] W. J. Middleton, *J. Org. Chem.*, **31**, 3731 (1966).

[4] Derivatives of 1,2-dithiole-3-thione. I. S. Tamagaki and S. Oae, *Tetrahedron Lett.*, **1972**, 1159.

which the charge-separation initially existing completely disappears due to the charge-transfer photoexcitation.[5] The significant increasing change in entropies of activation on going from the reaction in THF to that in CH_3CN also implies that the extent of desolvation on proceeding from the initial state to the transition state is larger in the latter solvent. We can thus conclude that the rearrangement takes place through the initial ring closure to a three-membered thiaziridine ring, followed by the loss of sulfur. The following mechanism would be fully compatible with the negative ρ-value, *i.e.*, −0.56 (Table 3).



As for the reaction in protic solvents we see that the plot (Fig. 1) against solvent such scale as either $1/\lambda_{max}$ or E_T (not given here) displays a behavior essentially different from that of the reaction in aprotic solvents. The reaction is facilitated in more polar alcohols. The lower value of activation energy of 11 kcal/mol as compared with that in aprotic solvents (20 kcal/mol) would support the view that the reaction is brought by nucleophilic interaction of the oxygen atom of alcohol with the tetravalent sulfur atom of thiocarbonyl imine, giving a relatively large charge-separation. The slightly positive rho value of +0.13 also supports this.

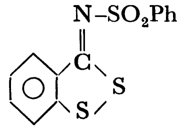
Experimental

Products. The thermal reaction was carried out by the following procedure. Thiocarbonylimine (339 mg, 1.0 mmol) was heated in various solvents or in neat until thiocarbonyl imine disappeared. The solvent was then evaporated *in vacuo* and the residual crystals were dissolved in a small amount of $CHCl_3$. The residue was chromatographed on silica gel using benzenel. The rearranged product obtained was purified by recrystallization from benzene. The yields of products are given in Table 1.

Table 2. Kinetic data for thermal rearrangement of thiocarbonyl imine (B) at 60.1 °C

Solvent	λ_{max} (nm)[a]	$10^4 k$, sec^{-1}
THF	506	3.28
DCE	500	1.52
Pyridine	499	2.05
$CHCl_3$	496	1.80
CH_3CN	493	1.08
CH_3NO_2	492	1.38
DMSO	488	0.78
n-BuOH	483	1.80
t-BuOH	480	1.29
EtOH	476	3.27
MeOH	472	3.90

a) The absorption band of thiocarbonyl imine in various solvents. DCE: dichloroethane.



Mp 176—177 °C, elemental analysis: Found: C, 50.65; H, 2.73; N, 4.55%. Calcd for $C_{13}H_9O_2NS_3$: C, 50.88; H, 2.93; N, 4.56%.

Kinetics. Thiocarbonyl imine (1.5 mg) was dissolved in 50 ml solvent. The solution was kept at 60.1 °C in a thermostat. Every ten minutes 3 ml of the solution was pipetted out and poured into the UV cell which was cooled previously in order to stop the reaction. The reaction rate was obtained by determining the intensity of UV spectra due to thiocarbonyl imine (493 mn in CH_3CN). The results are collected in Table 2.

Table 3. Effect of temperature and substituent at 60.1 °C

Solvent	E_a, kcal/mol	$\Delta S^{\neq}$, e.u.	Rho value
CH_3CN	23.8	3.8	−0.56
THF	20.2	−5.8	
MeOH	11.2	−46.1	+0.13

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[5] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253, 3267 (1958).