Derivatives of 1,2-Dithiole-3-thiones. VII.[1] Study of Reaction of Thiocarbonyl *S*-Imide with Amines

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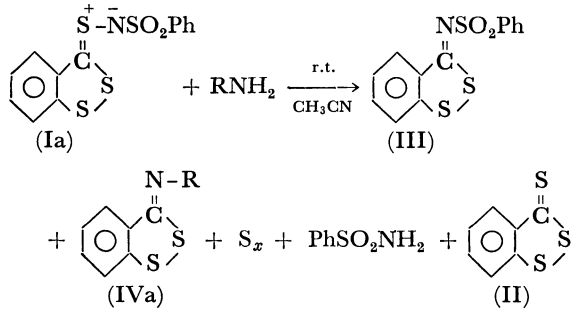
Thiocarbonyl *S*-imide of 4,5-benzo-1,2-dithiole-3-thione reacted with primary and secondary amines of various types to give both rearranged and amine-exchanged imines. By kinetical studies a plausible mechanism involving the addition and elimination of amine on the tetravalent sulfur atom was proposed.

Thiocarbonyl *S*-imides (>C=S̈⁺–N̈⁻–) are isoelectronic nitrogen-analogs of sulfines (>C=S̈⁺–Ö⁻) or thiocarbonyl ylides (>C=S̈⁺–C̈⁻<). Thiocarbonyl *S*-imides are thus expected to resemble sulfines or ylides in both chemical and physical properties. However, we have recently initiated the preparation of a stable thiocarbonyl *S*-imide of 1,2-dithiole-3-thione,[2] the characteristics of its chemistry not having been fully explored.

We wish to report detailed mechanistic aspects of the reaction of the thiocarbonyl *S*-imide (I) with various amines, in which a nucleophilic attack of amines on the sulfur atom at the initial step of the reaction is involved. As in the nucleophilic substitution on the divalent sulfur of sulfenyl chloride, the trivalent sulfur of sulfonium, or the tetravalent sulfur of sulfoxide or sulfilimine, the nucleophilic attack on the tetravalent sulfur atom of thiocarbonyl *S*-imide appears to proceed *via* a somewhat similar path.

Results

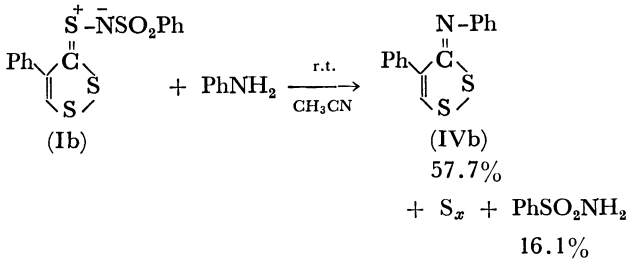
The reaction of the thiocarbonyl *S*-imide of 4,5-benzo-1,2-dithiole-3-thione (II) with an equimolar amount of a primary aryl or alkyl amine at room temperature in acetonitrile afforded the corresponding rearranged product, (*N*-benzenesulfonyl-4,5-benzo-1,2-dithiole-3-imine (IIIa)), the amine-exchanged product (*N*-aryl- or alkyl-4,5-benzo-1,2-dithiole-3-imine (IVa)), the benzenesulfonamide, elemental sulfur, as well as a small amount of the trithione:



Similarly, treatment of the *S*-imide (Ib) of 4-phenyl-1,2-dithiole-3-thione with aniline gave *N*,4-diphenyl-1,2-dithiole-3-imine (mp 166—167 °C) in a moderate yield.

Results for the reactions of the thiocarbonyl *S*-imide (I) with various amines, including secondary and tertiary amines, are summarized in Table 1.

In order to find the rate-determining step of the



reaction, a kinetic study was undertaken by observing the disappearance of the characteristic UV absorption band due to the thiocarbonyl *S*-imide at nearly 500 nm in acetonitrile, using about 15 mol excess amine, so as to keep the pseudo-first-order condition. The first-order dependence of the rate on the imide concentration was clearly observed. A typical run is given in Table 2.

The first-order dependence of k_{obsd} on the amine concentration is also shown in Fig. 1. The fact that the rate was found exactly proportional to the initial concentration of the amine indicates that at the rate-determining step of the reaction the attack of amine occurs on the sulfur atom without any concomitant base- or acid-catalyzed proton donation and/or removal. Namely, like the addition of primary amines to simple carbonyl compounds[3] the reaction is not the base-catalyzed nucleophilic substitution reaction. The sec-

TABLE 1. REACTION OF THIOCARBONYL *S*-IMIDE (I) WITH VARIOUS AMINES IN CH_3CN AT ROOM TEMPERATURE

Amine	IIIa	IVa	Sulfonamide	II	S_x
$ClC_6H_4NH_2$	13.0	75.5	72.4	6.0	99.6
$PhNH_2$	17.5 (0.0)[e]	60.0 (79.0)	44.6 (a))	13.6 (11.6)	a)
$MeOC_6H_4NH_2$	1.3	66.5	66.0	5.0	a)
t-$BuNH_2$[b]	6.3	95.0	88.1	0.0	a)
$C_6H_{11}NH_2$	3.3	64.3	88.5	7.6	a)
$ClC_6H_4NH_2$[c]	10.1	83.0	a)	a)	a)
$PhNHCH_3$	44.6	0.0	82.8	14.3	a)
Et_2NH	27.7	0.0	57.7	7.5	15.6
$PhN(CH_3)_2$[d]	35.2	0.0	a)	11.4	a)
Et_3N[d]	31.3	0.0	a)	42.4	35.3
$PhNHNH_2$	a)	83.8	98.2	6.7	a)

a) No further determination attempted. b) As solvent. c) Ten fold excess amine used. d) Twenty fold excess amine used. e) In the presence of an equimolar amount of *p*-toluenesulfonamide; this run indicates the absence of the anion-exchange during the formation of (III).

Table 2. Reaction of (Ia) with *p*-toluidine[a] at 24.8 °C in CH_3CN

$\log a/(a-x)$	Time, s	$1/t \cdot \log a/(a-x) = 10^3 k_{obsd}$
0.103	10	10.3
0.208	20	10.4
0.307	30	10.2
0.406	40	10.2
0.503	50	10.1
0.599	60	10.0
0.687	70	9.8

a) Fifteen equivalents.

Table 3. Substituent effect on the reaction rate in CH_3CN

Substituent, X[a]	$10^4 k_2$, $M^{-1} s^{-1}$ [c]
Br	6.87
H	6.47
CH_3	6.05
$\rho_X = +0.13$ (Y=CH_3)	
Substituent, Y[b]	$10^4 k_2$, $M^{-1} s^{-1}$ [c]
NO_2	no reaction
Cl	0.27
H	1.56
CH_3	6.73
CH_3O	33.1
$\rho_Y = -3.49$ (X=H)	

a) X: *para*-substituents of aryl groups in compound (Ia). b) Y: *para*-substituents in *para*-substituted anilines. c) reaction temperature 24.8 °C.

ond-order rate constants (k_2) can be easily obtained from the values of k_{obsd}, by dividing them by the concentration of amine. The resulting data are summarized in Tables 3 and 4. The second-order rate constants for the reaction of a few para-substituted thiocarbonyl *N*-benzenesulfonyl imides with *p*-substituted anilines are given in Table 3.

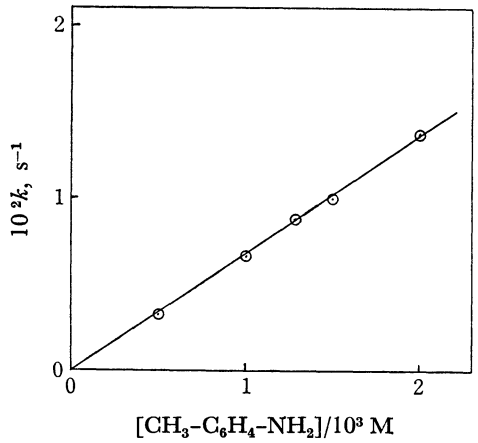
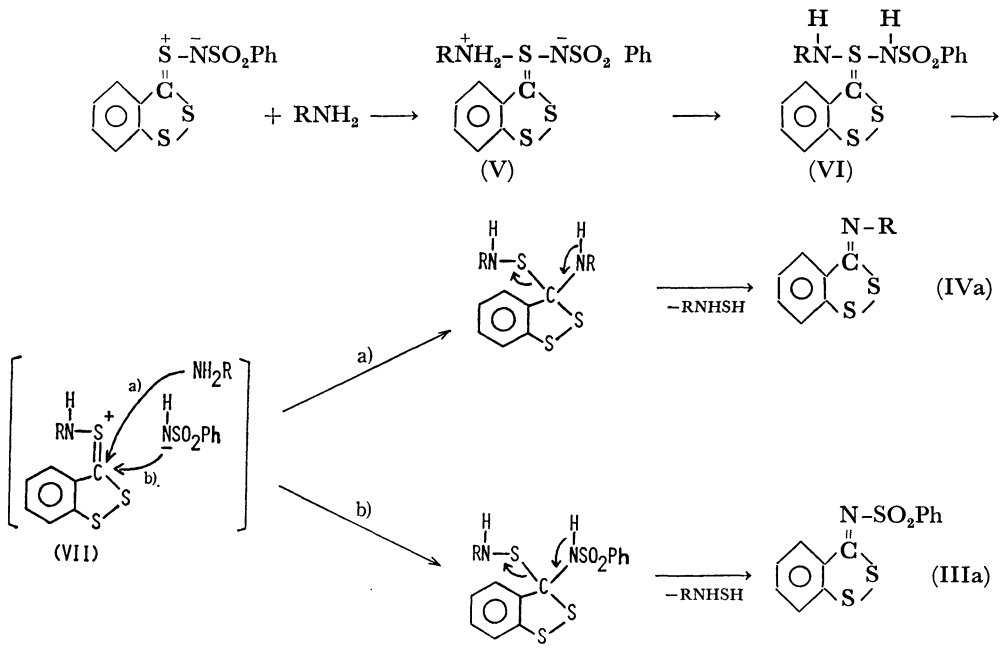


Fig. 1. Dependence of reaction rate on amine concentration in CH_3CN at 24.8°.

Discussion

The products as well as their relative yields thus obtained (Table 1) indicate that the initial attack of amine on the tetravalent sulfur atom of thiocarbonyl *S*-imide moiety yields both the rearranged (III) and the amine-exchanged (IV) products as outlined in Scheme 1.

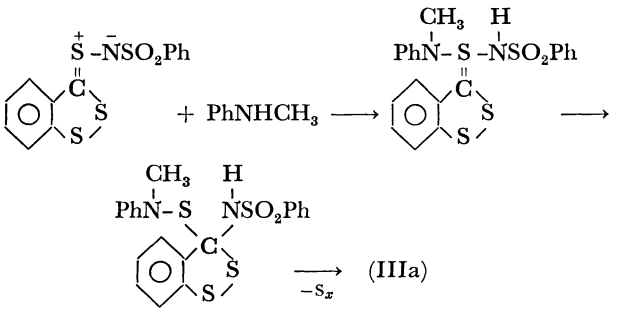
The initially formed dipolar intermediate (V) could break down through the symmetrical intermediate (VI) eventually to the ion pair (VII). Subsequently there are two competitive reactions: a) attack of a foreign amine molecule on the carbon-3, giving the amine-exchanged imine (IVa) upon elimination of RNHSH, and b) the intramolecular nucleophilic addition of the sulfonamide anion to the carbon-3, eventually leading



Scheme 1.

to the *N*-benzenesulfonyl imine (IIIa).

The above pathway does not contradict with the following finding that treatment of *N*-monomethylaniline with Ia afforded exclusively IIIa alone, since the second proton-transfer, which is required in the overall reaction sequence to form IVa, would be prohibited for any amine having only one proton on nitrogen atom.



Scheme 2.

As shown in Scheme 2, tertiary amines bearing no protic hydrogen attached to a nitrogen atom cannot be expected to react at all under similar conditions. In fact, a carefully purified tertiary amine, DABCO (pK_a=8.7), did not yield the rearranged product (IIIa). Anomalous results (Table 1) where treatment of Ia with 20 mol excess tertiary amines such as *N,N*-dimethylaniline and triethylamine gave the rearranged imine (IIIa) in yields similar to cases for secondary amines can be attributed to the contamination of a considerable amount of the corresponding secondary amines.

As one can see from Table 3 a straight line was obtained by plotting log k_2 values against the Hammett sigma values. The rho values of ρ_x=+0.13 and ρ_y=−3.5 were obtained for the respective reactions. Evidently, the reaction involves a nucleophilic attack of aniline molecule. The remarkably large and negative ρ_y value due to *p*-substituents on the nucleophile as well as the small ρ_x value due to *p*-substituents on the leaving group seem to suggest that this substitution is not a true S_N2 process. A more plausible mechanism would be one including the intervention of an unsymmetrical addition complex in which both the entering and the leaving groups are bound to the central sulfur atom of the intermediate of either trigonal bipyramid or square pyramid with or without involvement of 3d-orbitals.[4] Such a hypervalent intermediate involving the central sulfur atom has been reported in other substitution reactions[5] and in some cases isolated.[6] For example, the formation of a metastable addition intermediate at divalent sulfur was postulated in the reaction between triphenylmethylsulfenyl chloride and *n*-butylamine.[7] Evidence for the existence of the tetracoordinated sulfur complex as an intermediate has been reported by Givens and Kwart for chlorination of sulfenyl chloride[8] and by Trost *et al.* for the reaction of the sulfonium salts with organometallic compounds.[9]

In our case, the marked solvent effect on the rate, *i.e.*, the faster rate in polar CH_3CN than in nonpolar THF by a factor of 3.6, and the large negative activation entropy (Table 4) indicate the existence of a rigid,

Table 4. Temperature effect on reaction rate in CH_3CN

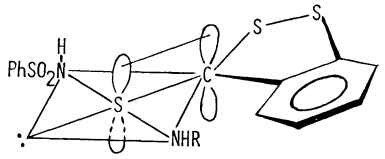
Reaction temp., °C	$10^4 k_2$, $M^{-1} s^{-1}$ a)
33.75	8.20
29.25	7.47
26.70	7.20
20.40	6.10

a) X=H, Y=CH_3; E_a=4.0 kcal/mol, $\Delta S^{\ddagger}$=−59.0 e.u.

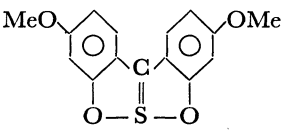
polar, and solvation-susceptible intermediate. Moreover, the activation energy of 4.0 kcal/mol implies that no bond cleavage takes place at the transition state. Thus, the intervention of a stable unsymmetrical intermediate (V) is more likely. The markedly small activation energy would eliminate the direct carbon attack where the activation barrier would be very large since the aromaticity ought to be destroyed. An insignificant increase in the rate of only less than two fold even by adding ten equimolar amounts of protic acid to aniline indicates also that the sulfonamide anion does not leave the reaction center at the transition state. If an S_N2 mechanism were in operation, a prior protonation should be required and the addition of acetic acid would result in a marked acceleration of the rate However, this was not found to be the case.

We may thus conclude that one more likely pathway should involve the initial formation of an unsymmetrical addition complex which, upon a stepwise proton switch from the aniline nitrogen of the charge-separated pentavalent intermediate to the sulfonamide nitrogen carrying the formal negative charge, gives a symmetrical complex that undergoes the subsequent cleavage of the old S–N bond to give the products shown in Scheme 1.

The addition complex could have a structure quite close to a square pyramid (VIII) where the attacking and leaving groups occupy *cis* or *trans* positions to each other, rather than a trigonal bipyramid. In fact, a structurally similar planar compound (IX),[10] isoelectronic around the sulfur atom, has recently been synthesized.



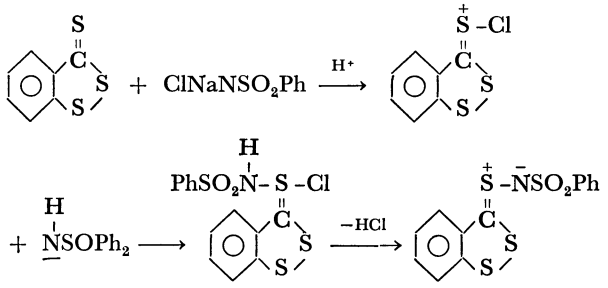
(VIIII)



(IX)

It should be emphasized that such a mechanism of the displacement on the sulfur atom is somewhat similar to that of the formation of the thiocarbonyl *S*-imide itself (I) from trithione and chloramine-B, where the reaction involves the initial formation of the chlorosulfonium-like salt followed by the displacement at the sulfur atom,[11] as was already established in detail

in the formation of the sulfilimine.[12]



Experimental

Materials. Thiocarbonyl *S*-imides were prepared by the method described previously.[2] To the benzotrithione dissolved in methanol was added a solution containing a slight excess of the *p*-substituted or unsubstituted chloramine with stirring at room temperature. After a few minutes red colored crystalline thiocarbonyl *S*-imide was filtered and washed with pure water and methanol. A typical reaction of thiocarbonyl *S*-imide with aniline is as follows: one equimolar amount of thiocarbonyl *S*-imide (Ia) (339 mg, 1 mmol) and *p*-chloroaniline (127.5 mg, 1 mmol) was mixed with stirring in acetonitrile at room temperature. After ten minutes the solvent was distilled off and residual crystals were dissolved in a small amount of $CHCl_3$. The solution was fractionated with thin layer chromatography on Kieselgel using benzene as an eluant. Each fraction was extracted with $CHCl_3$–EtOH (9 : 1), filtered off and evaporated. The product was purified by recrystallization from benzene or benzene-hexane. Physical properties and spectral data of thiocarbonyl *S*-imides and rearranged products are given in Tables 5 and 6, and analytical values of the rearranged products in Table 7.

Solvent. Commercial acetonitrile was dried over phosphorus pentoxide and distilled just before use.

Kinetics. A typical procedure is as follows: thiocarbonyl *S*-imide (I) (3.39 mg, 0.01 mmol) was dissolved in 50 ml acetonitrile. *p*-Methylaniline (160.5 mg, 1.5 mmol) was also dissolved in 50 ml of the same solvent, the solution being diluted to one tenth of concentration. Both solutions were kept at 25 °C in a thermostat. Each solution (1.5 ml) was then mixed quickly in a UV cell which was also kept at the same temperature. Thus, the concentrations of thiocarbonyl *S*-imide and *p*-methylaniline at the initial reaction stage were 0.1 mmol/l and 1.5 mmol/l, respectively. Determination of the reaction rate was carried out as follows. The UV recorder was set at a certain wave length (490 nm due to thiocarbonyl *S*-imide). As soon as the reaction was initiated by mixing each solution, the recorder pen was started moving. Thus the chart obtained shows the decrease of thiocarbonyl *S*-imide concentration with time. The pseudo-first order rate constants were calculated by the integral form (2) of the differential equation (1), where a signifies the initial concentration of the thiocarbonyl *S*-imide reacted at a given time t from the start, while k is the pseudo-first-order rate constant.

$$\frac{dx}{dt} = k(a-x) \quad (1)$$

$$\ln\frac{a}{a-x} = kt \quad (2)$$

Table 5. Physical properties of thiocarbonyl *S*-imides and products

Imide, X	Mp (°C)	Imine, R	Mp (°C)
H	130	Cl-C_6H_4	124.5—125
CH_3	126—127	Ph	78—78.5
m-NO_2	129—130	PhNH	96—97
Br	137—139	*t*-Bu	oil
		C_5H_{11}	189—190

Table 6. IR spectral data of thiocarbonyl *S*-imides and products

Imide, X	cm^{-1}
H	1590, 1278, 1137, 1087, 969, 920, 760, 570
CH_3	1590, 1280, 1138, 1086, 969, 915, 828, 572, 550
m-NO_2	1589, 1540, 1354, 1282, 1152, 1112, 965, 928, 763, 577, 568
Br	1589, 1139, 1082, 968, 917, 758, 600, 568
Imine, R	
Cl-C_6H_4	1614, 1587, 1489, 1445, 1089, 918, 829, 763
Ph	1610, 1590, 1490, 1450, 1305, 1280, 1250, 1195, 1070, 925, 756
PhNH	3260, 1602, 1588, 1508, 1422, 1259, 1113, 952, 757, 740, 694
t-Bu	2980, 1620, 1365, 1210, 1070, 1025, 890, 755, 720
C_6H_{11}	2960, 2880, 1610, 1455, 1310, 1146, 1015, 983, 900, 740
(IVb)	3090, 1592, 1537, 1492, 1343, 1330, 1740, 1148, 890, 767, 700, 569

Table 7. Analytical values of products

Imine, R		%C	%H	%N
Cl-C_6H_4	Found:	56.14	2.90	4.89
	Calcd for $C_{13}H_8NS_2Cl$:	56.22	2.88	5.05
Ph	Found:	64.05	3.62	5.95
	Calcd for $C_{13}H_9NS_2$:	64.20	3.70	5.76
PhNH	Found:	60.57	3.99	10.85
	Calcd for $C_{13}H_{10}N_2S_2$:	60.47	3.88	10.85
t-Bu	Found:	59.58	6.24	5.90
	Calcd for $C_{11}H_{13}NS_2$:	59.11	5.83	6.28
C_6H_{11}	Found:	62.81	6.39	5.65
	Calcd for $C_{13}H_{15}NS_2$:	62.90	6.64	5.64
(IVb)	Found:	66.65	4.11	5.23
	Calcd for $C_{15}H_{11}NS_2$:	66.91	4.09	5.20

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