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Kinetic Studies of the Thiol-catalyzed Rearrangement of *N*-Phenylsulfonyl Thione *S*-Imide1)

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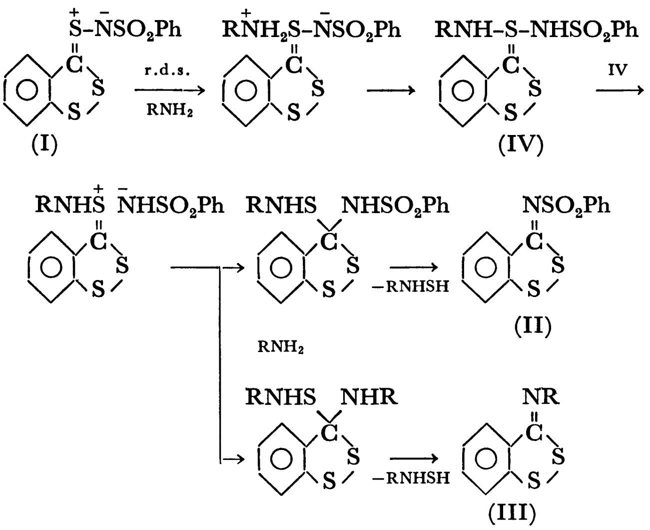
Synopsis. The *N*-phenylsulfonyl thione *S*-imide(I) of 1,2-dithiole-3-thione reacted catalytically with various thiols to afford the corresponding rearranged *N*-phenylsulfonyl-1,2-benzodithiole-3-imine(II) with the extrusion of the elemental sulfur together with a minor amount of reduced benzotrithione. A kinetic study of the rearrangement of I with thiobenzoic acid was performed, and a plausible mechanism is discussed.

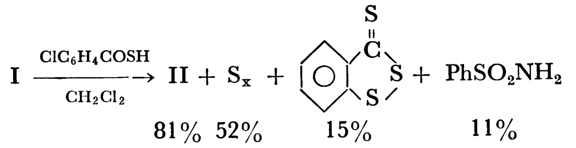
Recently we reported the reaction of I with a variety of amines to give the corresponding rearranged(II) and amine-exchanged(III) products. A detailed kinetic study of this reaction suggested that the rate-controlling step is the attack of amine on the tetravalent sulfur atom rather than on the carbon-3 of the thione *S*-imide(I) to give the addition complex(IV), which, in the subsequent step, yields an ion-pair that eventually collapses to give the products outlined below:



In this paper we wish to report our findings on an interesting rearrangement in which the thione *S*-imide(I) readily reacts catalytically with various thiols to afford mainly the same rearranged product(II) as in the amine-catalyzed rearrangement; however, the reaction was found to be quite different in its reaction mechanism from that with amines.

Results and Discussion

When I was treated with various inorganic sulfides, organic thiols, and thioacetic or thiobenzoic acid in CH_3CN or CH_2Cl_2 at room temperature, the precipitation of a yellowish, elemental sulfur was observed; furthermore, the rearranged product(II), benzotrithione, and the sulfonamide could be obtained.



The results of the product analyses are collected in Table 1. In order to focus our attention especially on the rearrangement of this hitherto unknown type, a kinetic study of the reaction between I and thiobenzoic acid was carried out in CH_3CN at about 20 °C. At the given initial thiobenzoic acid concentrations in the range of 1—5×10^{-5} mol/l, the reaction was found to follow strictly first-order kinetics with regard to the thione *S*-imide (I) up to more than half-lives.

The plot of the pseudo-first-order rate constants (k_{obsd}) thus obtained against the thiobenzoic acid concentrations showed a fairly good straight line in the 1—5×10^{-5} mol/l range, as shown in Fig. 1, while in the concentrations below this range the plot was found to shift the straight line upward. It seems likely that, in the range of high concentrations of thiobenzoic acid, the over-all reaction follows second-order kinetics essentially and that the reaction rate is not much affected by the occurrence of the reduction leading to the formation of benzotrithione and the

Table 1. Reaction of I with equimolar amounts of thiols at room temperature

Thiol	Solvent	Product (%)			
		II	S_x	Benzotrithione	$PhSO_2NH_2$
NaSH	$CHCl_3$	24.8	a	64.5	a
H_2S	$CHCl_3$	44	a	55	46
H_2S	CH_3CN	21.2	a	76.4	39.7
EtSH	CH_2Cl_2	63	33	20	a
p-ClC_6H_4SH	CH_2Cl_2	67	65	22	21
CH_3COSHb)	CH_2Cl_2	49	a	30	a
CH_3COSH	CH_2Cl_2	54	a	a	a
PhCOSH	CH_2Cl_2	78	50	15	8
PhCOSH	CH_3CN	71.5	60.4	17.5	14.5
p-$MeOC_6H_4COSH$	CH_2Cl_2	69	78	17	18
p-ClC_6H_4COSHc)	CH_2Cl_2	72	a	23	15
p-ClC_6H_4COSHd)	CH_2Cl_2	81	52	15	a
(*n*-PrO)$_2PS_2H$e)	CH_2Cl_2	52	a	38	a

a) Yields were not determined. b) Thirteen molar excess of thiol was used. c) One-third equiv. of thiol to I was used. d) In the presence of an equimolar amount of *p*-$MeC_6H_4SO_2NH_2$. e) Two molar excess of thiol.

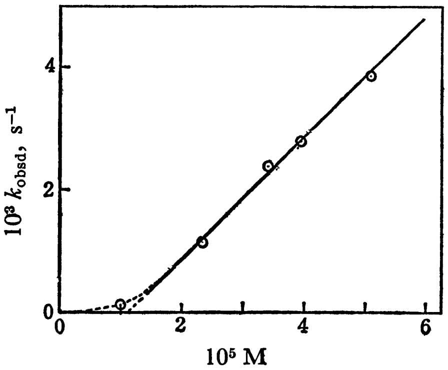


Fig. 1. Effect of acid concentration on the reaction at 1.0×10^{-4} mol/l of I in CH_3CN at 24.2 °C (X=H, Y=Cl).

Table 2. Rate constants for the reactions of *p*-substituted I[a] with *p*-substituted thiobenzoic acids[b] in CH_3CN at 24.2 °C

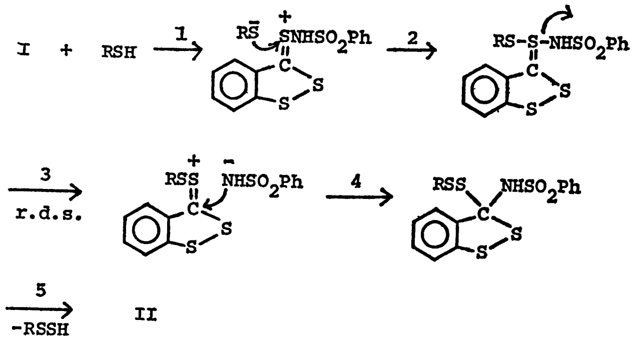
p-Substituent, X, in I[c]	*p*-Substituent, Y, in acid[d]	$10^3\,k_{obsd}$, s^{-1}
Br	Cl	7.59
H	Cl	3.90
Me	Cl	2.83
H	Cl	3.90[e]
H	H	2.40
H	Me	1.92
H	MeO	1.74

a) 10.0×10^{-5} mol/l. b) 5.06×10^{-5} mol/l. c) $\rho_X = +1.06$. d) $\rho_Y = +0.7$. e) $\Delta H^{\neq} = 11.9\pm1.0$ kcal/mol, $\Delta S^{\neq} = -8.0\pm3.0$ eu.

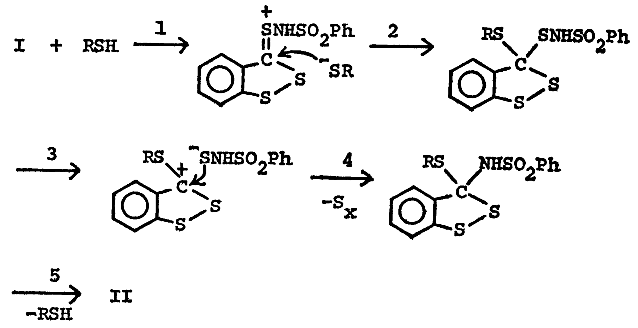
sulfonamide. The fact that I was recovered in a appreciable yield when I was treated with less than a one-fifth equiv. of thiobenzoic acid implies that the added acid was completely consumed by a side-reaction before the rearrangement was completed.

In order to clarify the mechanism, especially the rate-determining step of the reaction, the effects of the substituent and temperature on the rate were examined in CH_3CN as a solvent at the thiobenzoic acid concentration of 5×10^{-5} mol/l; the results are listed in Tables 2. An inspection of the data reveals that the *rho* values (ρ_X and ρ_Y) for the para-substituents, X in I and Y in thiobenzoic acid, are both positive, *i.e.*, 1.06 and 0.7 respectively. In sharp contrast to the previously reported reaction with amines ($\rho_X = +0.13$)[3] and phosphines ($\rho_X = +0.08$),[4] where the attack of the nucleophiles on the sulfur atom is considered to be rate-determining, the rate is very sensitive to the nature of the substituent(X). Thus, the fairly large value of ρ_X is fully consistent with Pathway I, as is shown below, when the reaction proceeds *via* the initial addition of thiobenzoic acid to the S–N moiety of I prior to the rate-controlling S–NSO_2 bond cleavage, eventually leading to the products *via* an ion-pair.

Another pathway involving the rate-determining nucleophilic attack of RS^- on the sulfur atom can readily be ruled out, since the activation energy for the reaction involving the rate-determining addition (Step 2 in Path I) would be low; it is estimated to be around 5 kcal/mol based on the activation energeis of 4±1 and 3±2 kcal/mol for the reactions with amines and phosphines respectively.



Path I.



Path II.

The large ρ_X value offers strong evidence against Pathway II, which proceeds through the rate-determining carbon attack. The HASB principle also seems to support the above conclusion, since a soft nucleophile(RS^-) tends to attack a soft electrophilic sulfur center rather than a hard electrophilic carbon center.[5]

Hence, the study of the effects of substituent and temperature on the rearrangement shows that both the large ρ_X value and an energy of activation as large as 12 kcal/mol are in accordance with the mechanism involving the S–N bond breaking in the rate-determining step.

Experimental

A typical run is as follows: to the imide(I)(339 mg, 1 mmol) in CH_2Cl_2, an equivalent thiol dissolved in the same solvent was added at room temperature. After 5 min, the solution turned yellow. The solvent was evaporated under reduced pressure, and then the residue was separated by preparative tlc using benzene. The yields thus obtained are listed in Table 1. The rate constants (k_{obsd}) were determined spectrophotometrically by the usual procedure.

References

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