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The Reactions of Cyclic Sulfilimines with Cyanide Ion and Phosphine: Evidence for Substitution on Trivalent Sulfur

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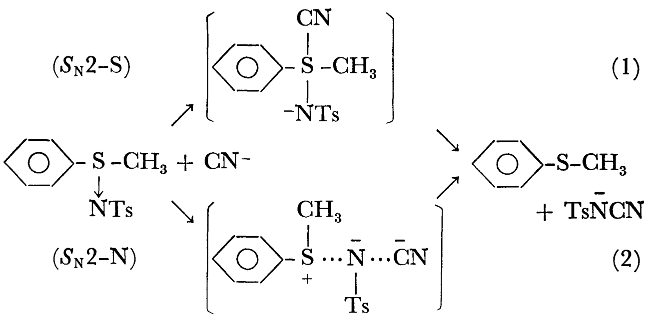
Synopsis. The effect of ring size on the reaction of *N*-*p*-tosylsulfilimine with such nucleophiles as CN^- and n-Bu_3P was investigated kinetically and compared with the effect on the reaction of the corresponding cyclic sulfonium salt. The results indicated that the S_N2–S process is more probable than the S_N2–N route.

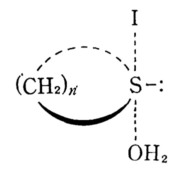
Recently, we found that the reaction of alkyl aryl *N*-*p*-tosylsulfilimines with such nucleophiles as CN^- and n-Bu_3P[1,2] afforded the corresponding sulfides in high yields. We postulated two pathways for the mechanism of this reaction the one involving an initial nucleophilic attack on the trivalent sulfur atom by CN^- or n-Bu_3P(S_N2–S), the other proceeding *via* a rate-determining nucleophilic attack on the imine-nitrogen atom(S_N2–N). These two mechanisms are shown in Scheme 1. Although the kinetic and steric observations seem to support an S_N2 attack on the sulfur atom[3] (S_N2–S), mechanism(2) cannot be ruled out. One way to make choice between these two mechanisms is to compare the effect of ring size on the rate of the nucleophilic substitution reaction of cyclic sulfilimines with that on the analogous reaction of the corresponding cyclic sulfonium salt. Since the following sulfonium salts are known to react with nucleophiles to afford the cyclic sulfides *via* an S_N2 attack on the methyl carbon, the small effect of ring size on reaction(3) should also be found in reaction path(2).



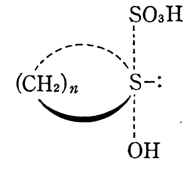
Scheme 1.

$$(\overset{\frown}{CH_2)_n\ S}{}^{+}\text{-}CH_3 + Nu \rightarrow (\overset{\frown}{CH_2)_n\ S} + CH_3\text{-}Nu \qquad (3)$$
$$(n=5,6,7;\ Nu=CN^-,\ n\text{-}Bu_3P)$$

In contrast, the effect of ring size would be substantial when the reaction proceeds *via* pathway(1) (S_N2–S), as in S_N2 attacks on sp^3 carbon atom[4] or in S_N2-like reactions of the trivalent sulfur atom.[5,6,7] In the reduction of cyclic sulfoxides by hydroiodic acid[8] which proceeds *via* the S_N2–S path, the reactivities fall in the following order: 5>7>6-membered rings, in keeping with the correlation between the reactivities and the steric effect for the transition complex (I). Johnson and his co-workers[9] also found a similar trend in the reaction of cyclic sulfoxides with sodium hydrogen sulfite, and postulated a transition state or an energetically contiguous intermediate (II) as shown below.



(I)



(II)

Thus, we have carried out the reaction of cyclic *N*-*p*-tosylsulfilimines and cyclic sulfonium salts with CN^- or n-Bu_3P in DMF (Table 1) and compared the effects of ring size (5, 6, and 7-membered rings) in these systems by means of competition reactions (Table 2).

Inspection of these data indicates that the effect of ring size is a quite different in the two reactions. The effect of ring size on the reaction of sulfilimines with CN^- or n-Bu_3P is found to fall in the following order: 5>7>6-membered rings, whereas, for the sul-

TABLE 1. REACTION OF CYCLIC SULFILIMINE OR SULFONIUM SALT WITH NUCLEOPHILES[a)]

Nucleophile	Yield of cyclic sulfide (%)					
	$(\overset{\frown}{CH_2)_n\ S}\rightarrow NTs$			$(\overset{\frown}{CH_2)_n\ \overset{+}{S}}\text{-}CH_3\ ClO_4^-$		
	$n=4$	5	6	4	5	6
CN^-	quant	quant	78	quant	quant	quant
n-Bu_3P	quant	quant	81	quant	quant	quant

a) These reactions were carried out in DMF solution.

TABLE 2. RELATIVE REACTIVITIES OF CYCLIC SULFILIMINE AND SULFONIUM SALT[a)]

Nucleophile	Molar ratio of sulfide					
	$(\overset{\frown}{CH_2)_n\ S}\rightarrow NTs$			$(\overset{\frown}{CH_2)_n\ \overset{+}{S}}\text{-}CH_3\ ClO_4^-$		
	$n=4$	5	6	4	5	6
CN^-	15.0	1.0	13.0	0.7	1.0	1.5
n-Bu_3P	25.0	1.0	10.0	0.9	1.0	1.7

a) These reaction were carried out in DMF solution.

fonium salts only small differences of the reactivities were found. Therefore, we conclude that the reactions of sulfilimines with CN^- and n-Bu_3P proceed *via* route 1 and not *via* the S_N2–N route.

Experimental

Materials. *Cyclic* N-p-*Tosylsulfilimines*: All the cyclic *N-p*-tosylsulfilimines were prepared by the modified Mann-Pope reaction[10] from the corresponding sulfides and chloramine-T. For the five membered cyclic sulfide a commercial product was used without purification, while the six and seven membered ones were prepared by known methods.[9] All the cyclic *N-p*-tosylsulfilimines were identified by comparing their mp, IR and NMR spectra with those reported earlier.[10]

Cyclic Sulfonium Perchlorates: All the cyclic sulfonium perchlorates were prepared by treating the corresponding sulfides with methyl iodide and silver perchlorate in methanol solution.

Competitive Reaction of Cyclic N-p-*Tosylsulfilimine with Nucleophile*: A typical run was as follows. A mixture of each of the cyclic *N-p*-tosylsulfilimines(5, 6, and 7-membered cyclic sulfilimines, each 0.1 mmol) and NaCN (0.2 mmol) was dissolved in 4 ml of DMF and the whole solution was placed in a sealed tube. It was heated in a constant temperature oil bath at 100°C for 5 hr. The tube contents were then poured into ice-water and the sulfide formed was extracted with petroleum ether. The distribution of the sulfides was determined by gas chromatography; the molar ratio of 5 : 6 : 7-membered cyclic sulfides was 15.0 : 1.0 : 13.0.

Competitive Reaction of Cyclic Sulfonium Perchlorate with Nucleophile: A typical run was as follows. One ml of DMF solution containing all the cyclic sulfonium salts (5, 6, and 7-membered cyclic derivatives, each 0.1 mmol) and 1 ml of DMF solution of tri-*n*-butyl phosphine (0.2 mmol) were prepared. Both solutions were kept at constant temperature (100 °C) in an oil bath before mixing. The reaction was started by mixing the two solutions and continued for 3 hr. The reaction mixture was then poured into 5 ml of water and the sulfides formed were extracted with 1 ml of petroleum ether. The distribution of the sulfides formed in the reaction was determined by gas chromatography: The molar ratio of 5 : 6 : 7-membered cyclic sulfides was 0.9 : 1.0 : 1.7. The reaction of cyclic sulfonium perchlorates with NaCN was carried out at 100 °C for 1 hr and the distribution of sulfides formed in the reaction was determined as described above.

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