Tetrahedron Letters No. 33, pp.3109-3112, 1971. Pergamon Press. Printed in Great Britain.

The Alkaline Alcoholysis of N-p-Toluenesulfonyl Sulfilimine

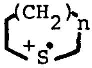
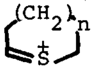
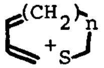
Haruyo Kobayashi, Naomichi Furukawa, Tetsuo Aida, Kenji Tsujihara,
and Shigeru Oae

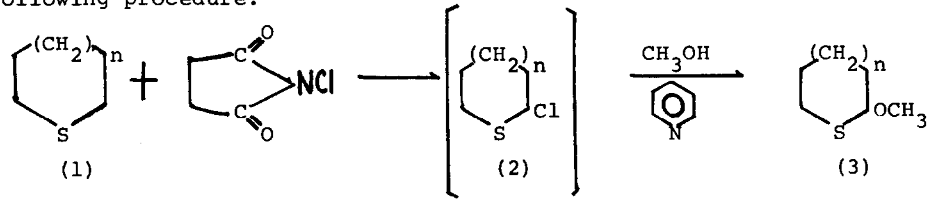
Faculty of Engineering, Osaka City University, Sugimoto-cho, Osaka, Japan

(Received in Japan 25 June 1971; received in UK for publication 14 July 1971)

Recently Cram et al[2)] reported that the reaction of p-tolyl methyl sulfilimine with hydroxide ion in methanol gives the corresponding sulfoxide in high yield. Based on stereochemical observation, the reaction was deduced to be a typical S_N2 reaction of the sulfur atom. Although the nucleophilic substitution reactions on the trivalent sulfur atom have been studied extensively[3)], the effect of ring size on the rate of substitution reaction on the sulfur atom has been investigated very little. We are interested in the nucleophilic substitution on the trivalent sulfur atom in cyclic sulfilimines especially as to the effect of ring size. Thus, various cyclic sulfilimines were prepared[4)] and subjected to the reaction with alkali hydroxide in methanol expecting to obtain the corresponding sulfoxides. However, instead of obtaining the sulfoxides, we found a new rearrangement reaction which leads to the formation of α-methoxy substituted sulfides in substantial yields. In this communication, we wish to present the nature and the scope of the novel rearrangement reaction.

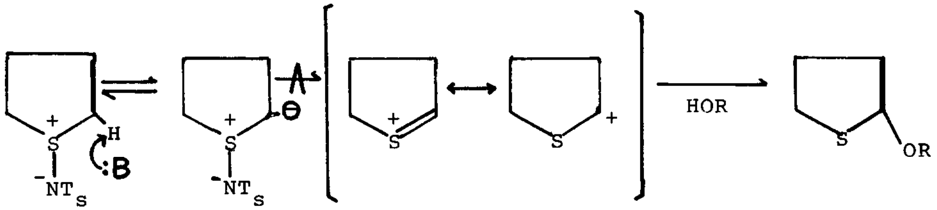
A typical run of the reactions is the following. N-p-Toluenesulfonyl-tetramethylene sulfilimine (15g) was dissolved in 200ml methanol containing 20 mole excess of potassium hydroxide at room temperature. Then, the solution was poured onto a large amount of ice water, and was extracted with chloroform. After drying, the solvent was evaporated. The oily product 6.0g(87%) obtained was distiled under reduced pressure giving pure 2.63g(38%) of α-methoxy tetramethylene sulfide, b.p. 44-45°C/15mmHg. Other N-p-toluenesulfonylsulfilimines were treated similarly with hydroxide ions in methanol and other alcohols.

The products were isolated by G.L.C. and identified by means of I.R.,N.M.R. and mass spectroscopic analyses. As shown in Table II, the I.R. spectra of the products show a typical strong absorption band at around $1100cm^{-1}$ that corresponds to the -C-O-C-streching. The N.M.R. data indicate the main product is α-alkoxy sulfides upon comparing their spectra with those of sulfides or sulfoxides. The mass spectra show molecular ion peaks at the corresponding molecular weights of the sulfides. Besides the molecular ions, all the spectra give strong peaks at P-31, P-33 which are those of    respectivelly. Furthermore, the structures of α-methoxy 5-7 membered cyclic sulfides were confirmed by comparing the spectroscopic data with those of the authentic samples which were prepared from the following procedure.[5)]



In order to examine the mechanism, the kinetic study on the reactions of N-p-toluenesulfonyltetramethylene sulfilimine and its 2,2,5,5,-tetradeuterated compound was carried out. The pseudo-1st order rate constants are $0.37x10^{-4}sec^{-1}$ (undeuterated) $0.34x10^{-1}$ sec^{-1} (tetradeuterated) at 30.1°C.Thus, kinetic isotope effect (k_H/k_D) is only 1.09. While the activation parameters are$\Delta H^{\ddagger}$=25.0Kcal, $\Delta S^{\ddagger}$=4.2 e.u. respectively. After 10% completion of the reaction the sulfilimine originally tetradeuterated was recovered and its deuterium content was found by N.M.R. to have decreased down to 85% from the original 95%. While the leaving group effect on the first order kintics was examined with N-p-substituted arylsulfonyl-tetramethylene sulfilimine where p-substituents are p-CH_3,H, p-Cl. The rate constants obtained were 0.34; 0.89; $1.98x10^{-4}sec^{-1}$ respectively.

Thus, the above rate constants were nicely correlated with Hammett σ values giving the value of ρ=+2.0. Furthermore the rates of the 5-7 membered ring sulfilimines were found to fall in the following order, 7>5≫6. Based on these kinetic observations, this novel reaction appears to proceed through a E_{1cb} route via the initial fast proton removal and the subsequent rate determining cleavage of S-N linkage of the sulfilimine. The mechanism is shown as below.



References

1) Sulfilimine and Sulfoximine Part XI.
Part X, S.Oae, N.Furukawa and T.Yoshimura, Submitted to Bull.Chem.Soc. Japan, 1971

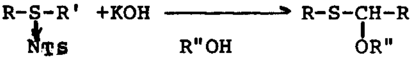
2) J.Day and D.J.Cram, J.Am.Chem.Soc. 87,4398(1965).
D.R.Rayner,D.M.von Scritz, J.Day and D.J.Cram, ibid.,90,2721(1968).
D.J.Cram,J.Day,D.R.Rayner,D.M.von Scritz,D.J.Duchamp and D.C.Garwood, ibid.,92,7369(1970).

3) E.Ciuffarin and A.Fava, Prog.Phys.Org.Chem.,6,81(1968).
Substitution reaction on sulfur atom is reviewed.

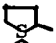
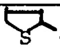
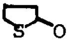
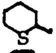
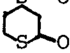
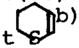
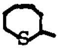
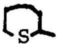
4) K.Tsujihara,N.Furukawa,K.Oae and S.Oae, Bull.Chem.Soc.Japan,42,2631(1969).

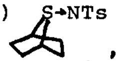
5) D.L.Tuleen and R.H.Benett,J.Heterocycl.Chem.,6,115(1969).

Table I [a)] The Products and Yield (%).



$$R-\underset{\downarrow\atop NTs}{S}-R' + KOH \xrightarrow[R''OH]{} R-S-\underset{\mid\atop OR''}{CH}-R$$

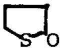
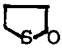
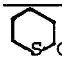
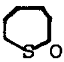
R"OH R R'	Me	Et	n-Pr	i-Pr
-(CH$_2$)$_4$-	 OMe(38)	 OEt(50)	 OPr(72)	 OPr-i(66)
-(CH$_2$)$_5$-	 OMe(30)  (13)	 OEt  b)		
-(CH$_2$)$_6$-	 OMe(35)	 OEt		
n-Bu, n-Bu,	n-Bu-S-CH(OMe)-Pr (41)			

-(CH$_2$)$_3$- (decomposed)   (no, reaction)

a) The reactions were carried out at room temperature for 2 days. The mole ratio of sulfilimine to KOH is 1:20. The products were all purified by G.L.C.. Besids α-alkoxy sulfide, p-toluene sulfonamide was obtained quantitatively.

b) Identified by comparing with the spectrum data of authentic sample.

Table II. The Spectrum of α-Alkoxy Sulfide.

	I.R.(cm^{-1})	N.M.R.(PPm) in Cl$_4$	Mass(m/e) %
 OMe	1090,1130, 1160.	1.6-2.4(m.4H)-C$\underline{H}_2$-C$\underline{H}_2$- 2.5-3.2(m.2H),C$\underline{H}_2$-S 3.22 (s.3H),O$\underline{Me}$ 5.0-5.2(m.1H),-C$\underline{H}<^{O}_{S}$	118(13.4) 87(24.8) 86(44.1) 85(100)
 OEt	1090,1110, 1150,1170,	1.15(t,J,7.5HZ,3H)-CH$_2$-$\underline{CH}_3$ 1.6-2.5(m.4H)-C$\underline{H}_2$-C$\underline{H}_2$- 2.5-3.1(m.4H),-C$\underline{H}_2$-S- 3.1-3.9(m.2H)-O-C$\underline{H}_2$CH$_3$ 4.9-5.4(m.1H),-C$\underline{H}<^{S}_{O}$	132(12.8) 88(7.85) 87(26.8) 86(44.4) 85(100)
 OMe	1065,1110, 1140,	1.4-2.2(m.6H)-C$\underline{H}_2$-C$\underline{H}_2$-C$\underline{H}_2$- 2.2-3.2(m.2H)-S-C$\underline{H}_2$ 3.35(S.3H)-OC$\underline{H}_3$ 4.2-4.4(m.1H)-C$\underline{H}<^{O-}_{S-}$	
 OMe	1060,1090, 1120,	1.4-2.3(m.8H)-(C$\underline{H}_2$)$_4$- 2.3-3.0(m.2H)-C$\underline{H}_2$-S- 3.29(S,3H)-O-C$\underline{H}_3$ 4.4(t,J.6HZ.1H)-C$\underline{H}<^{O-}_{S-}$	146(4.4) 115(6.0) 114(9.0) 113(100)