Tetrahedron Letters No.16, pp. 1145-1148, 1971. Pergamon Press. Printed in Great Britain.

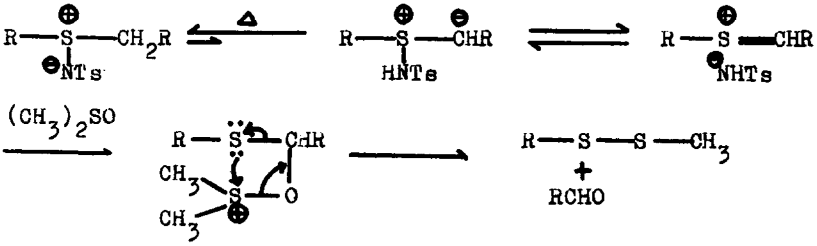
The Reaction of N-Sulfonyl Sulfilimine with Cyanide Ion in DMSO

S. Oae, T. Aida, K. Tsujihara and N. Furukawa

Faculty of Engineering, Osaka City University, Sugimotocho, Osaka, Japan

(Received in Japan 14 January 1971; received in UK for publication 19 March 1971)

Recently we reported that N-sulfonyl sulfilimines having α-protons react with DMSO or diethyl sulfoxide at elevated temperature giving unsymmetric disulfides in substantial yields.1) The mechanism of the above reaction is postulated to involve the initial formation of an equilibrium mixture of ylide and ylene followed by the nucleophilic attack by sulfoxide oxygen.



If the reaction proceeds by way of the above mechanism the addition of cyanide ion, a good carbon nucleophile, is expected to give α-cyanosulfide. When N-sulfonyl sulfilimines were actually heated with sodium or potassium cyanide in DMSO or DMF, the major product was the original sulfide instead of α-cyanosulfide. Besides cyanide ion thiophenol, thiophenolate anion, triphenyl phosphine and thiocyanate anion were also found to react with sulfilimines giving rise to the corresponding sulfides nearly in quantitative yields. In this communication, we wish to report this new reduction of N-sulfonyl sulfilimine with nucleophilic reagents and discuss its mechanism.

The reaction was carried out by heating a mixture of sulfilimine and metal cyanide in DMSO or DMF at various temperatures for 1∼2 hrs. After the reaction, the reaction mixture was poured into water. The products were isolated and identified by comparing their IR, NMR and GLC behaviors with those of the authentic compounds separately prepared. The results and reaction conditions are summarized in Table I.

The results reveal that the yield of the sulfide depends very much on the structure of the sulfilimine. Diphenyl sulfilimine does not react and is completly recovered even after heating at high temperature for a prolonged period. Aryl methyl or aryl benzyl sulfilimine gives the corresponding sulfide quantitatively, however, the yield decreases in the case of dimethyl or dibenzyl sulfilimine and byproducts such as nitrile and aldehyde are formed substantially. Meanwhile, N-tosyl urea was found among the products and identified by comparing it with the authentic sample, prepared from urea and toluene sulfonamide with sodium hydroxide.2) The product analysis indicates that the reaction is likely to proceed through the initial attack of cyanide anion on the sulfinyl sulfur atom. In the subsequent step the substitution of tosylamide group on the cyano carbon atom is considered to take place to give the final products, i.e., the sulfide and N-tosyl cyanamide. The latter product is then hydrolyzed to N-tosylurea. The above reaction route which involves the initial attack by cyanide ion on the sulfur atom, seems to be supported by the following observations ; 1) N-Sulfonyl sulfilimine reacts with various nucleophiles such as PhS^-, Ph_3P and ^-SCN similarly all giving the sulfide as shown in Table I. 2) The kinetic study was carried out using a few N-tosyl-p-substituted phenyl methyl sulfilimines. The results indicate that the reaction can be correlated by the usual 2nd order kinetic equation i.e., $\text{Rate}=k_2[\text{sulfilimine}][{}^{\ominus}\text{CN}]$, namely, first order dependence on both the sulfilimine and cyanide ion respectively.

Table I The Reaction of N-Sulfonyl Sulfilimine with ^{-}CN and Other Nucleophiles

$R-\overset{\bullet}{\underset{\bullet NTs}{S}}-R'$

R	R'	Reaction Condition		Products and Yield (%)	
		Temp. (°C)	Time (hr)	Sulfide R-S-R'	Other Products
C_6H_5,	CH_3 a)	100	1	>95	$TsNH_2$(8), $TsNHCONH_2$(47)
p-$CH_3C_6H_4$,	CH_3	100	1	>95	$TsNHCONH_2$
p-ClC_6H_4,	CH_3	70	3	>95	
p-$NO_2C_6H_4$,	CH_3	70	3	73	
p-$CH_3OC_6H_4$,	CH_3	70	3	>95	
$C_6H_5CH_2$,	C_6H_5 a)	r.t.	3	>95	$TsNHCONH_2$(31)
"	" b)	100	3	>95	$TsNH_2$(52)
$C_6H_5CH_2$,	$C_6H_5CH_2$	60	1	57	C_6H_5CHO(36), $C_6H_5CH_2CN$(41)
CH_3,	CH_3	100	2	49	$TsNHCONH_2$
i-Pr,	i-Pr[3]	100	2	3	$CH_3Ch=CH_2$, $((CH_3)_2CHS)_2$(37)
$-(CH_2)_5-$[4]		100	2	trace	recovered(94)
$-(CH_2)_6-$		100	2	16	recovered(65)
C_6H_5,	C_6H_5	100	4	0	recovered(>95)
"	"	180	24	0	" (81)
$C_6H_5CH_2(\overset{\bullet}{N}Ts)\overset{\bullet}{S}C_6H_5$ + PhSNa		100	2	>95	PhSSPh, $TsNH_2$
" + PhSH		100	2	>95	PhSSPh(90) $TsNH_2$
" + KSCN		100	2	94	
" + Ph_3P c)		100	2	>95	Ph_3PNTs(92)

The mole ratio ; sulfilimine / Nucleophiles except Ph_3P =1/3

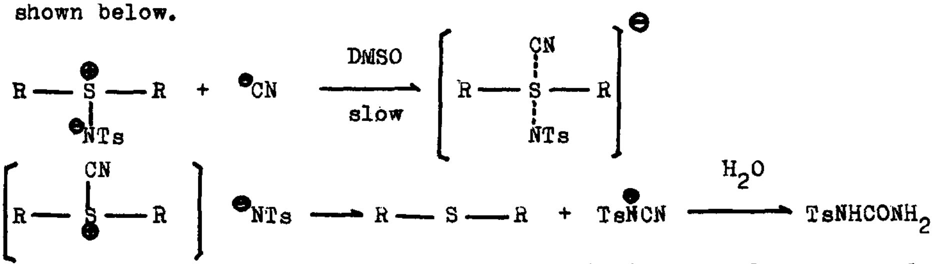
a) Solvents used were both DMSO and DMF.

b) Methanol was used as a solvent. The products were an original sulfide and p-$TsNH_2$. A lower boiling product detected by G.L.C. was probably CH_3OCN.

c) The mole ratio ; sulfilimine / Ph_3P=1

As a typical example, the observed value of k_2 for $(C_6H_5\overset{\oplus}{S}(\overset{\ominus}{N}Ts)CH_3$ + $^{\ominus}CN$ in DMSO at 70°C) is 0.98×10^{-4} l $mole^{-1}$ sec^{-1} and the activation parameters are $\Delta H^{\ddagger}=22.3$Kcal/mol, $\Delta S^{\ddagger}=-7.3$ e.u. respectively while the Hammett ρ value is +0.92.

Apparently all these results indicate that the reaction proceeds through the typical Sn2 reaction mechanism on the sulfur atom involving the rate determining nucleophilic attack by cyanide ion on the sulfur atom. Thus the whole scheme of the reaction may be illustrated as shown below.



The reaction is quite interesting, since it is not only a new reduction method of sulfilimine but also impling that the sulfilimine can serve as another useful compound to study the nature of the substitution reaction on the sulfur atom.

References

Sulfilimine and Sulfoximine VII ; VI, see reference 1.

1) K. Tsujihara, T. Aida, N. Furukawa and S. Oae, Tetrahedron Letters, 1970, 3415.

2) U.S.S.R., P. 12805, C.A., 55, 35236 (1961).

3) In this case, Ei reaction is favored over the substitution reaction.

4) When cyclic sulfilimines are heated into DMSO, decomposition takes place. Therefore the best result is obtained at 100°C. The thermal decomposition of cyclic sulfilimines will be reported soon.

5) An alternative pathway, namely the initial attack of cyanide anion on the nitrogen atom of sulfilimine forming both sulfide and N-tosyl cyanide seems to be ruled out since in the case of 6 and 7 membered sulfilimines, the former compound was hydrolyzed 100 times slower than the latter. The Sn2 type reaction on the sulfur atom of the ring S-compound will be published by S. Oae and S. Tamagaki.