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The Reaction of N-p-Tosylsulfilimine and Related Compounds with Thiophenolate Ion in DMF1)

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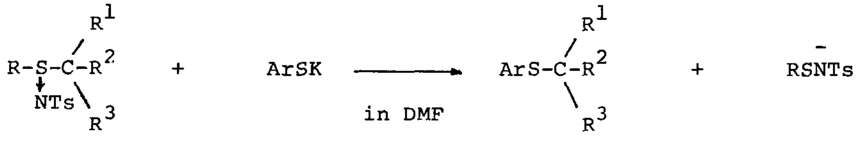
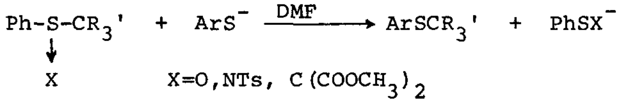
Recently we found that a number of N-p-tosylsulfilimines react with cyanide ion in DMSO or DMF affording the corresponding sulfides in nearly quantitative yields2). Based on the kinetic observations, the mechanism of the reaction is deduced to proceed via a typical S_N2 type substitution process involving the rate determining attack of CN ion at the sulfinyl sulfur.

Meanwhile, we also found that these sulfilimines react with other nucleophiles such as SCN^-, Ph_3P and PhSH, to give the corresponding sulfides via the S_N2 route similar to that with CN ion3). Similarly, the reaction of sulfoxides4) or sulfonium salt5) with PhSH has been known to yield the corresponding sulfides and the mechanisms of the reactions have been suggested to proceed by way of an S_N2 type substitution. In order to obtain further evidence to support the S_N2 type mechanism involving the nucleophilic center of the trivalent sulfur atom, sulfilimines and sulfoxides were subjected to react with thiophenolate ion in DMF solution. However, unexpectedly the reaction of sulfilimines with thiophenolate ion gave the following interesting products which are considered to arise from the S_N2 reaction on the carbon atom adjacent to the trivalent sulfur atom.



In this communication, we wish to report the scope and the mechanism of what appears to be a S_N2 type reaction on α-carbon of sulfilimines with thiophenolate ion. A typical run is as follows : p-Tolyl methyl-N-p-tosylsulfilimine (3m moles) was dissolved into 5 ml DMF containing 9 m moles of potassium thiophenolate. The solution was kept standing for 5 hours at room temperature. The usual work up of the reaction mixture show that the products were phenyl methyl sulfide, and disulfides, derived from N-p-tolyl-p-tosyl sulfeneamide and thiophenolate ion. All the other sulfilimines reacted similarly under mild condition such as room temperature in DMF and gave the corresponding substitution products on the α-carbon atom in nearly quantitative yields. Furthermore, when sulfoxides or S-ylids were subjected to the similar treatment, the reactions actually took place and gave the similar substitution products.



$$\text{Ph-}\underset{\substack{\downarrow\\ \text{X}}}{\text{S}}\text{-CR}_3' + \text{ArS}^- \xrightarrow{\text{DMF}} \text{ArSCR}_3' + \text{PhSX}^-$$

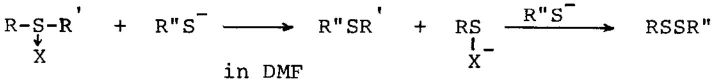
$$\text{X=O,NTs, C(COOCH}_3)_2$$

The products, yields and the reaction conditions are summerized in Table I.

In order to examine the mechanism of the reaction the kinetic study was carried out using N-p-tosyl-substituted-phenyl methyl sulfilimine. The results indicate that the rate of the reactions can be correlated well with the following 2nd order kinetic equation, i.e., Rate=k_2[Sulfilimine] [PhS$^-$] , up to 40% completion of the reaction. A typical value of k_2 for the reaction $[C_6H_5\overset{+}{S}(\overset{-}{N}Ts)CH_3 + C_6H_5S^-$ in DMF at $20.10 \pm 0.02°C]$ is 0.45×10^{-2} l $mole^{-1}$ sec^{-1} and the activation parameters are $\Delta H^{\ddagger}=17.8$ Kcal/mol, $\Delta S^{\ddagger}=-5.7$ e.u. respectively, while the observed Hammett ρ values for the reaction $[p\text{-}xC_6H_4\overset{+}{S}(\overset{-}{N}SO_2C_6H_4p\text{-}Y)CH_3 + C_6H_5S^-$ in DMF at $20.10 \pm 0.02°C]$ are $\rho x=+2.4$, and $\rho y=+1.2$, (see Table II,)

Apparently all these results indicate that the reaction is a typical S_N2 process involving the rate determining nucleophilic attack by thiophenolate ion on the α-carbon atom with N-p-tosylsulfeneamide as the leaving group. Thus, the whole scheme of the reaction may be illustrated as

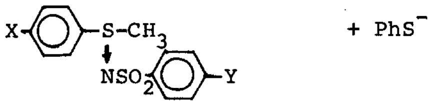
Table I. The Reaction of N-p-Tosyl Sulfilimine and Related Compounds with Thiophenolate ion.



$$R\text{-}\underset{X}{\underset{\downarrow}{S}}\text{-}R' + R''S^- \xrightarrow[\text{in DMF}]{} R''SR' + \underset{X^-}{\underset{|}{RS}} \xrightarrow{R''S^-} RSSR''$$

R	R'	X	R"	Reaction Condition			Product (%)		
				Temp. (°C)	Time (hr.)	R"SR'	RSSR"		$TsNH_2$
C_6H_5	CH_3	NTs	C_6H_5	r.t.	5	>95	78		82
C_6H_5	CH_3	NTs	p-$CH_3C_6H_4$	r.t.	5	>95		RSSR)	(R"SSR")
p-$CH_3C_6H_4$	CH_3	NTs	C_6H_5	r.t.	5	>95	24	8	18
p-ClC_6H_4	CH_3	NTs	C_6H_5	r.t.	5	>95	8	-	52
C_6H_5	Et	NTs	p-$CH_3C_6H_4$	r.t.	15	>95	3	51	
C_6H_5	i-Pr	NTs	p-$CH_3C_6H_4$	110	5	>95	trace	46	
C_6H_5	CH_2Ph	NTs	p-$CH_3C_6H_4$	r.t.	5	>95	2	54	78
C_6H_5	CH_2CH_2Ph	NTs	p-$CH_3C_6H_4$	r.t.	15	>95	3	49	
CH_3	CH_3	NTs	C_6H_5	110	21	60			
p-$CH_3C_6H_4$	CH_3	$C(COOMe)_2$	C_6H_5	r.t.	5	>95	20	6	16
C_6H_5	CH_2Ph	$C(COOMe)_2$	p-$CH_3C_6H_4$	r.t.	5	>95			
p-$CH_3C_6H_4$	CH_3	O	C_6H_5	110	21	13	4		8
C_6H_5	CH_2Ph	O	p-$CH_3C_6H_4$	110	21	10	3	trace	5
$p\text{-}CH_3C_6H_4\text{-}\overset{O}{\overset{\uparrow}{\underset{O}{\underset{\downarrow}{S}}}}\text{-}CH_3$			C_6H_5	110	21	3			
$p\text{-}CH_3C_6H_4\text{-}\overset{O}{\overset{\uparrow}{\underset{NH}{\underset{\Vert}{S}}}}\text{-}CH_3$			C_6H_5	110	21	17			
p-$NO_2C_6H_4S\text{-}CH_3$			C_6H_5	110	21	0	p-$NO_2C_6H_4SC_6H_5$ (13)		
$p\text{-}NO_2C_6H_4\overset{O}{\overset{\uparrow}{S}}\text{-}CH_3$			C_6H_5	110	21	0	p-$NO_2C_6H_4SC_6H_5$ (59)		
$p\text{-}NO_2C_6H_4\text{-}\overset{O}{\underset{NH}{\underset{\Vert}{S}}}\text{-}CH_3$			C_6H_5	110	21	0	p-$NO_2C_6H_4SC_6H_5$ (>95)		
p-$ClC_6H_4\text{-}S\text{-}CH_3$			C_6H_5	110	53	>95			

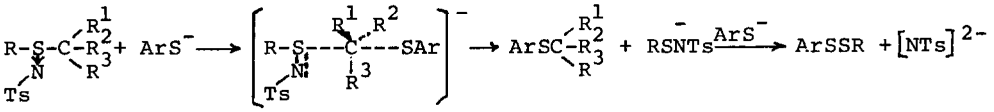
Table II.



in DMF at 20.10 ± 0.02 C

X	p-CH_3O	p-CH_3	H	p-Cl	
$k_2 \times 10^2$	0.071	0.161	0.45	1.11	ρ=+2.4
Y	p-CH_3	H	p-Br		
$k_2 \times 10^2$	0.45	0.61	0.96		ρ=+1.2

shown below.



Meanwhile, the change of the attacking site from trivalent sulfur atom to carbon atom by the change of the nucleophile may be explained by the Pearson's HSAB-rule6). Since thiophenlate ion is known to be a typical soft base according to the HSAB-rule, it is expected to attack the softer site of the substrate, while the trivalent sulfur atoms in such groups $\rangle S\rightarrow O$, $\rangle S\rightarrow N-$, and $\rangle\overset{+}{S}-\overset{-}{C}\langle$ are harder than α-carbon atom or divalent sulfur atom. Therefore thiophenolate ion is considered to attack preferentially at the α-carbon atom rather than the soft trivalent sulfur atom.

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