CHEMISTRY LETTERS, pp. 805-808, 1973. Published by the Chemical Society of Japan

REACTION OF N-p-TOSYLSULFILIMINE WITH TRIVALENT PHOSPHORUS COMPOUNDS

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The reaction of benzyl phenyl or methyl phenyl N-p-tosylsulfilimine with trivalent phosphorus compounds in DMF gave the original sulfide. From the kinetic study the reaction mechanism is proposed to proceed via the initial nucleophilic attack by phosphine to sulfinyl sulfur atom. Meanwhile, the addition of water to the solvent changed both the products and kinetic results.

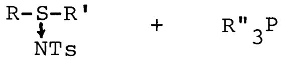
In the course of the study of the nucleophilic substitution reaction on trivalent sulfur atom, sulfilimines were found to react readily with nucleophiles affording various products$^{1)}$. As an extension of these, sulfilimines were subjected to react with trivalent phosphorus compounds. Actually, when sulfilimines were treated with phosphine in DMSO or DMF, the corresponding sulfides were obtained. Furthermore, addition of water was found to change both the products and the kinetic results.

In this communication, we wish to describe the results of the reaction together with the discussion of the mechanism.

A typical experiment is as follows; methyl phenyl N-p-tosylsulfilimine(3 mmol) was dissolved into 5 ml of DMF containing 6 mmol of triphenylphosphine. The mixture was heated for 6 hr at 120 °C. The usual work up of the reaction mixture showed that the products were methyl phenyl sulfide and triphenyl N-p-tosylphosphinimine in quantitative yields. The phosphinimine(mp 185-186 °C) was identified by elemental and spectroscopic analyses which were compared with those of the authentic sample$^{3)}$. The products obtained are summarized in Table I. Dialkyl or diphenyl sulfilimine did not react under the reaction conditions. In the case of phosphites as the nucleophiles the reaction required more drastic reaction condition than that for the phosphine and the product composition was also more complex as shown in Table I.

Furthermore, when benzyl phenyl sulfilimine was treated with triphenylphosphine in 20 % H_2O-80 % DMF solution, an interesting phosphorous compound, Ph_3PONH_2Ts(I), was obtained in 50 % yield. The yield of (I) increased with the increase of water content and in 10 % H_2O-90 % EtOH solution, (I) was the sole accompanied product besides the sulfide.

Table I. Reaction of Sulfilimine with Trivalent Phosphorus Compounds



$\underset{\underset{NTs}{\downarrow}}{R-S-R'} \quad + \quad R''_3P$

R	R'	R"	Reaction Condition			Products and Yields(%)		
			Solvent	(°C)	(hr)	RSR'	$R''_3P{\rightarrow}NTs$	Others
Ph	Me	Ph	DMSO	120	6	quant.	quant.	
Ph	Me	Ph	DMF	120	6	quant.	quant.	
Ph	Me	Ph	Dioxane	120	10	quant.	quant.	
Ph	CH_2Ph	Ph	DMF	100	6	quant.	quant.	
Ph	Et[a]	Ph	DMF	120	10	5	-	$CH_2=CH_2$, $TsNH_2$, $(PhS)_2$
Me	Me	Ph	DMF	120	10	-	-	recovd. (93)
$-(CH_2)_4-$		Ph	DMF	120	10	-	-	recovd. (88)
Ph	Ph	Ph	DMF	120	24	-	-	recovd. (quant.)
Ph	CH_2Ph	n-Bu	DMF	100	2	quant.	87	
Ph	CH_2Ph	EtO	DMF	130	48	45	-	$R''_2\underset{\overset{\|}{O}}{P}-N\genfrac{}{}{0pt}{}{Et}{Ts}$, $Me_2NCH=NTs$, $R''_3\underset{\overset{\|}{O}}{P}$
Ph	CH_2Ph	PhO	DMF	130	48	53	-	$Me_2NCH=NTs$, $R''_3P=O$
Ph	CH_2Ph[b]	Ph	20%-H_2O -DMF	120	6	quant.	40	Ph_3PONH_2Ts (45) (I)
Ph	CH_2Ph[b]	Ph	10%-H_2O -EtOH	120	6	83	-	Ph_3PONH_2Ts (quant.)

a) The alkyl phenyl N-p-tosylsulfilimines having at least one β-hydrogen atom undergo E_i-reaction.

b) The reaction was carried out in aqueous DMF or EtOH solution using a sealed tube.

(I) has mp 134-135 °C (recryst. from EtOH), elemental analysis, Found : C, 66.8; H, 5.12; N, 3.12; Calcd for $C_{25}H_{24}NO_3PS$: C, 66.8; H, 5.8; N, 3.15, IR(cm^{-1}) ; ν_{SO_2} 1315, 1160, $\nu_{P=O}$ 1120(H-bonded), ν_{NH} 3250, 3080(H-bonded). Although the structure of (I) has not been determined[4] it seems to be a molecular complex between phosphine oxide and tosylamine.

In order to examine the reaction mechanism the kinetic study was carried out using the following systems, $[p\text{-}X\text{-}C_6H_4\overset{+}{S}(\overset{-}{N}SO_2C_6H_4\text{-}Y\text{-}p)R + (p\text{-}Z\text{-}C_6H_4)_3P]$.

The results indicate that the rates of the reactions can be correlated well with the following second order kinetic equation, rate = k_2[sulfilimine][triphenylphosphine] (1). A typical value of k_2 for the reaction, X = Y = Z = H, R = CH_3, in DMF at 110.1 ^{o}C, is 1.10×10^{-4} l/mol sec. The activation parameters(R = CH_3) are $\Delta H^{\ddagger}$ = 26.0 kcal/mol and $\Delta S^{\ddagger}$ = - 8.8 e.u. respectively. The Hammett ρ-values are ρ_x = + 3.7, ρ_y = + 0.6(R = CH_3) and ρ_z = - 1.3(R = $PhCH_2$). Furthermore when the reaction of benzyl phenyl sulfilimine and tri-n-butylphosphine was carried out, the rate of the reaction increased 700 times as that with triphenylphosphine while triethylphosphite decreased the rate down below 10^{-3} times. These results suggest that the reaction proceeds via the initial nucleophilic attack of phosphine on either the trivalent sulfur or the imino-nitrogen atom. Taking into consideration the results on sulfilimine[2)] and sulfoxide[5)], it may be concluded that the attacking site by phosphine should be the sulfur atom(in Scheme I-(a)).

As shown in the product analysis, the addition of water to the reaction mixture gave a different pattern of product distribution. Furthermore, the compound(I) was not obtained from the corresponding phosphinimine under the same reaction condition suggesting that the phosphinimine and (I) were obtained through a different reaction path. In order to understand the effect of water to the reaction rate, the kinetic study was carried out using benzyl phenyl sulfilimine with triphenylphosphine in H_2O-DMF solution. The apparent second order rate constants are calculated from the equation(1). The results obtained are shown in Table II.

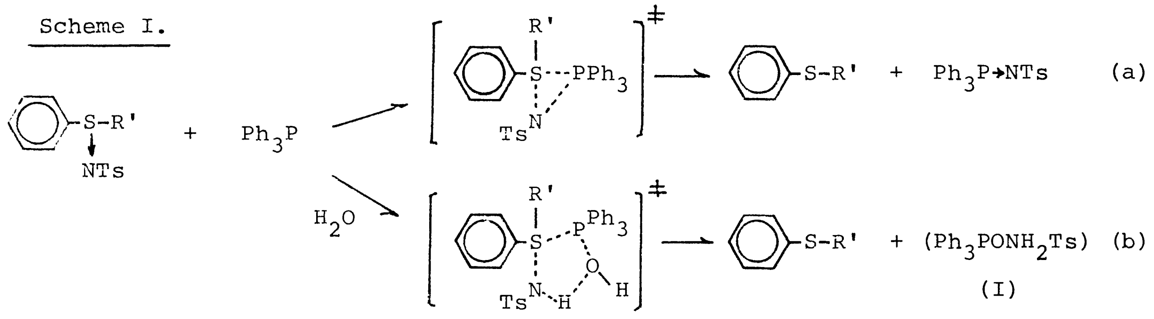
Table II. Effect of Water (at 98.7 ^{o}C)

H_2O (vol. %)	0.0	2.5	5.0	10.0	20.0
$k_{app} \times 10^3$ (l/mol sec)	0.86	1.27	1.76	3.7	11.0

The result indicates that the rate increases gradually, with increasing the amount of water. If it is assumed that some other reaction involving H_2O molecule at the transition state competes with the reaction shown in the following Scheme I-(b), the above equation should be rewritten as following; rate = k_{app}[sulfilimine][phosphine] = ($k_0 + k' [H_2O]^n$)[sulfilimine][phosphine], where k_0 is a second order rate constant in pure DMF solution, namely, $k_{app} = k_0 + k' [H_2O]^n$. Another alternative assumption of the effect of H_2O is that the change of polarity of the solvent which may accelerate the reaction by increasing the water content. The choice between these is necessarly further investigation. Meanwhile, the isotope effect k_{H_2O}/k_{D_2O} was determined, using D_2O-DMF solution, to be 1.02. This suggests that H_2O molecule does not act as a base, but rather a nucleophile toward the phosphorus atom.

Based on these results, the reaction is considered to proceed via the following mechanism(Scheme I).

Scheme I.



Further investigation on this reaction is now underway in these laboratories.

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(Received May 17, 1973)