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A 1,3-DIPOLE IN SULFILIMINE-PHOSPHINE SYSTEM (II)1)

THE REACTION OF SULFILIMINE-PHOSPHINE SYSTEM WITH ALCOHOLS

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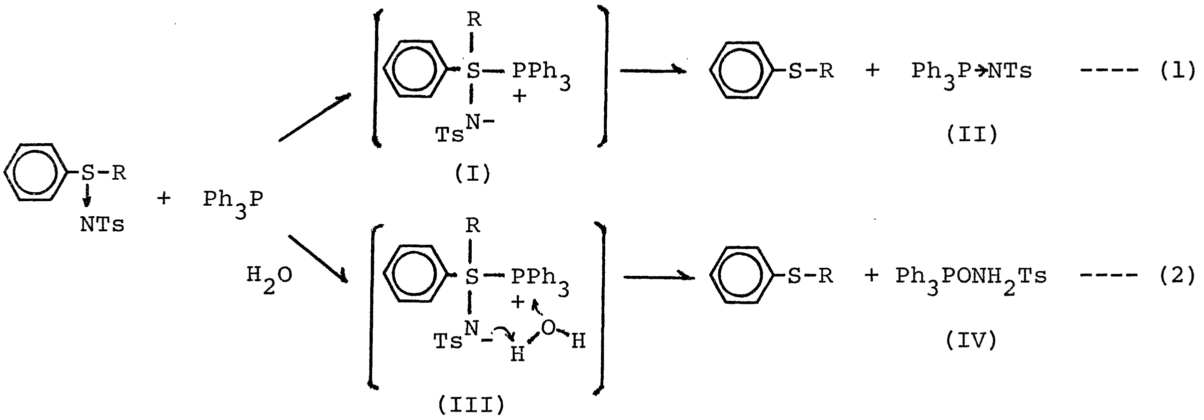
Alkyl phenyl N-p-tosylsulfilimine and phosphine react with various alcohols affording the phosphinimine(II) and the complex(IV) together with the reduced and alkyl-exchanged sulfides in which the alkyl groups come from the alcohols used. The results indicate the initial formation of a 1,3-dipole.

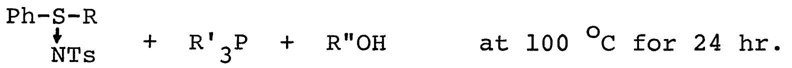
Recently we found that N-p-tosylsulfilimines are readily reduced by trivalent phosphorus compounds in DMF to afford the corresponding sulfides quantitatively1). The mechanism involves the initial nucleophilic attack by the phosphorus atom on the trivalent sulfur atom of the sulfilimine to give an intermediate(I) as shown below (eq. 1).



This reaction suggests that the sulfilimine-phosphine system may form a 1,3-dipole2), which then in the presence of a third component(1,3-dipolarophile) will lead to further reaction. Actually, when the above reaction was carried out in the presence of water, the reaction was accelerated and the product was the complex(IV), instead of phosphinimine(II) which was formed in the absence of water. As an extention of this reaction, N-p-tosylsulfilimine-phosphine system(SP-system) was treated with a third component such as alcohol, and found to work actually as a 1,3-dipole. In this communication, we describe the reaction of this unstable 1,3-dipolar system with alcohols.

Generally, the reaction was carried out with benzyl phenyl N-p-tosylsulfilimine (0.3 mmol), triphenylphosphine(0.4 mmol) and 2 ml of an alcohol in a sealed tube at 100 °C for 24 hr. Then the products were isolated and identified by means of spectroscopic and gas-chromatographic analyses. Furthermore, benzyl phenyl sulfide and triphenylphosphine did not react under the reaction condition, thus indicating that the SP-system forms a reactive intermediate. The products obtained are summarized in Table I.

Table I. Reaction of SP-system with Alcohols



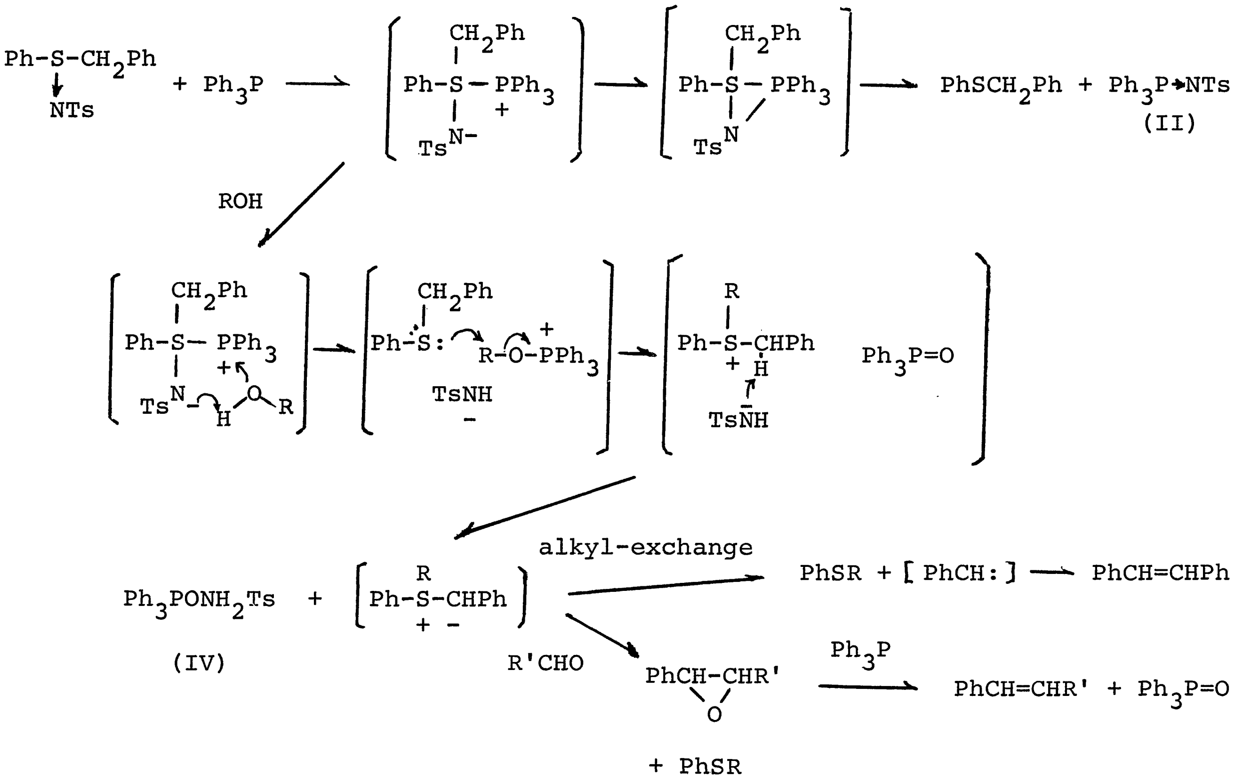
$$\underset{\mathrm{NTs}}{\overset{\downarrow}{\mathrm{Ph{-}S{-}R}}} + \mathrm{R'_3P} + \mathrm{R''OH} \quad \text{at } 100\ ^{\circ}\mathrm{C} \text{ for } 24 \text{ hr.}$$

R	R'	R"	Products and Yields(%)					
			PhSR	PhSR"	$R'_3P \rightarrow NTs$	R'_3PONH_2Ts	Others	
$PhCH_2$	Bu	Me	70	30	-			
$PhCH_2$	Ph	Me	57	35	-	85	$(PhCH_2)_2$ 3,	$(PhCH{=})_2$[c] 6
$PhCH_2$	Tol	Me	60	37	-	80	trace	" 5
Me[a]	Ph	Et	90	8	78	5	" -	" -
Me[a]	Ph	$PhCH_2$	64	16	52	8	-	trace[b]
$PhCH_2$	Ph	Et	80	20	63	14	" trace	" trace[b]
$PhCH_2$	Ph	n-Pr	88	11	71	8	" trace	" trace[b]
$PhCH_2$	Ph	n-Bu	97	3	85	-	-	-
$PhCH_2$	Ph	i-Pr	quant.	0	89	0		
$PhCH_2$	Ph	t-Bu	quant.	0	quant.	0		
$PhCH_2$	Ph	$PhCH_2$	quant.				" 8	" 15

a) p-Chlorophenyl methyl derivative was used.
b) It was detected by means of UV-spectroscopy.
c) trans-Stilbene.

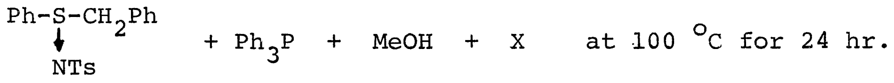
Inspection of the data reveals an interesting feature of this apparent reduction of the sulfilimines to the sulfides. Namely, the sulfides obtained are not only the benzyl phenyl derivative, but also the alkyl-exchanged sulfides in which the alkyl groups are originated from the alcohols used, while the ratio of the phosphinimine(II) and the complex(IV)[1] varies markedly. The product distribution seems to depend markedly upon the structure of the alcohol used. When methanol was used, (II) was not obtained but the complex(IV) was isolated as a sole phosphorus compound. The yield of (IV) decreased while that of (II) increased markedly with the increase of the bulkiness of alkyl group of the alcohol used. Thus in the case of i-PrOH or t-BuOH, there was no formation of the complex(IV) while phosphinimine(II) was obtained nearly quantitatively. The exchange of the alkyl group between the sulfide and the alcohol takes place undoubtedly during the course of the reaction. The ease of the exchange of alkyl group of the sulfide and the ratio of the phosphorus products formed can also be correlated well with the bulkiness of the alkyl group of alcohols. Another interesting observation is the isolation of trans-stilbene.

Apparently all these reactions may be explained on the basis of the initial formation of the transient 1,3-dipole involving a penta-coordinate sulfur intermediate followed by the addition of alcohol as a dipolarophile, thus affording benzyl phenyl sulfide and the phosphonium salt which in the subsequent step form the sulfonium salt before the completion of the reaction. The reaction scheme may be illustrated as shown below.



This mechanism may be supported from the following observations, namely, when the reaction was carried out in the presence of cyclohexene, the yield of the stilbene decreased markedly, while the addition of benzaldehyde increased the yield as shown in Table II.

Table II. Effects of the Addition of Third Components for the Formation of Stilbene and Bibenzyl



$$\underset{\displaystyle NTs}{\overset{\displaystyle Ph\text{-}S\text{-}CH_2Ph}{\downarrow}} + Ph_3P + MeOH + X \quad \text{at } 100\ ^{o}C \text{ for 24 hr.}$$

X	$PhCH_2CH_2Ph$ (%)	PhCH=CHPh (%)	Others
none	3	6	
cyclohexene (20%)	3	trace	
PhCHO (20%)	8	16	
p-TolCHO (20%)	0	0	p-TolCH=CHPh (16)

The structure of the corresponding stilbene derivative obtained suggests that a stilbene oxide is formed initially in the reaction3) of the sulfonium ylide with an aldehyde and then readily reduced by triphenylphosphine to the corresponding stilbene.4)

The formation of the sulfonium salt, though not isolated, would be responsible for the exchange of alkyl group of the sulfide and also for the addition of aldehyde or cyclohexene. Meanwhile, the formation of bibenzyl cannot be explained at the present experiment. Further works on these reactions are currently undergoing in these laboratories.

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