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A 1,3-DIPOLE IN SULFILIMINE-PHOSPHINE SYSTEM (III)[1)]

ACID ANHYDRIDE-, ESTER-, AND AMIDE-CONDENSATIONS BY SULFILIMINE-PHOSPHINE SYSTEM

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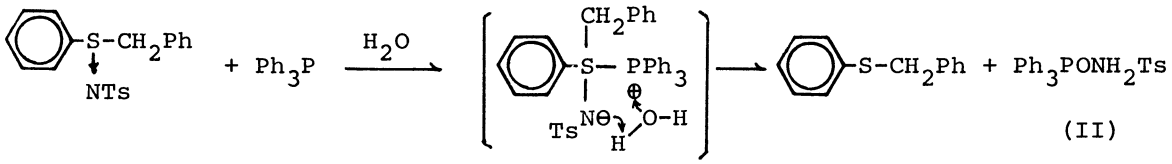
Alkyl phenyl N-p-tosylsulfilimine and triphenylphosphine reacted with various carboxylic acids affording their anhydrides. The reaction was successfully extended to an ester- or amide-condensation reaction. These results can be interpreted by the initial formation of a 1,3-dipole between the sulfilimine and the phosphine.

Recently we found that the reaction of N-p-tosylsulfilimine with triphenylphosphine in the presence of water[2)] or alcohol[1)] apparently proceeded via the formation of sulfurane intermediate(I)(a 1,3-dipole) as shown below.



(I) (II)

With an aim to obtain further information on the reaction this N-p-tosylsulfilimine -phosphine system(SP-system) was treated with carboxylic acid and found to work actually as a 1,3-dipole, namely, the corresponding acid anhydride was obtained in a substantial yield. This fact suggested that the SP-system works as an effective dehydrating system. Actually, when the SP-system was treated with a mixture of carboxylic acid and alcohol or amine, the condensation reaction proceeded smoothly affording the ester or the amide in a high yield.

In this communication we wish to describe the results and the scope of this 1,3-dipolar dehydrating system.

Typical run of the reaction is as follows: A mixture of benzyl phenyl N-p-tosylsulfilimine(3 mmol), triphenylphosphine(6 mmol), and 3 ml of acetic acid in 3 ml of benzene was heated in a sealed tube at 100°C for 12 hr. After the reaction the general work up process gave various products which were isolated and identified by GLC and spectroscopic analyses. Benzyl phenyl sulfide, phenyl thioacetate and a complex(II) were identified by comparing the spectroscopic behaviors with those of their authentic samples. The products and yields obtained are summarized in Table 1.

Table 1. Reaction of the SP-System with Carboxylic Acids

$$\underset{\underset{\text{NTs}}{\downarrow}}{\text{PhSCH}_2\text{Ph}} + \text{R'}_3\text{P} + \text{R"COOH}$$

R'	R"	Reaction Condition		Products and Yields(%)			
		Temp.(°C)	Time(hr)	$PhSCH_2Ph$	PhSCOR"	$(R"CO)_2O$	R'_3PONH_2Ts
n-Bu	Me	60	10	43	24	16	-*
Ph	Me	100	12	61	20	40	72
$CH_3C_6H_4$	Me	80	12	63	21	43	75
Ph	Et	100	12	65	20	46	67
Ph	n-Pr	100	12	63	20	42	70
Ph	i-Pr	100	12	66	21	44	74
Ph	Ph	100	12	55	45	5	50

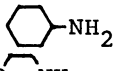
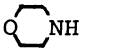
* $n\text{-}Bu_3PO$ and $TsNH_2$ were obtained separately in high yields.

Inspection of the results in Table 1 indicates the following feature of the reaction; (1) in all cases with the carboxylic acid a similar distribution of the products was obtained, namely, the original sulfide, thioester, acid anhydride and (II). (2) the formation of the sulfide and acid anhydride can be explained by the 1,3-dipolar addition reaction between the SP-system(I) and carboxylic acid, (3) the thioester may be derived via the similar 1,3-dipolar reaction of the acid anhydride with the SP-system. A control experiment of the reaction gave the corresponding phenyl thiocarboxylate almost quantitatively under the same reaction condition as shown in Table 1. Thus, the initial path of the reaction of the carboxylic acid and the SP-system seems to be the formation of its anhydride. As the yield of $PhSCH_2Ph$(corresponding to the total yield of acid anhydride formed in the reaction) was nearly equal to the summation of both yields of thiocarboxylate and acid anhydride isolated, it is suggested that the condensation of carboxylic acid with the SP-system proceeded

in high yields. (4) the formation of the acid anhydride from the corresponding carboxylic acid also suggests that the SP-system serves as a new dehydrating system and has a synthetic application for ester or amide. Recently, Mukaiyama et al.[3] and Yamazaki et al.[4] reported the synthetic method of ester or amide by means of phosphorus compounds. In order to ascertain this possibility the SP-system was treated with a mixture of carboxylic acid and alcohol or amine at 100°C for 12 hr. After the reaction, the products were separated and identified by their spectroscopic behaviors. The products and yields obtained are summarized in Table 2.

Table 2. Ester- and Amide-Condensation by the SP-System[5]

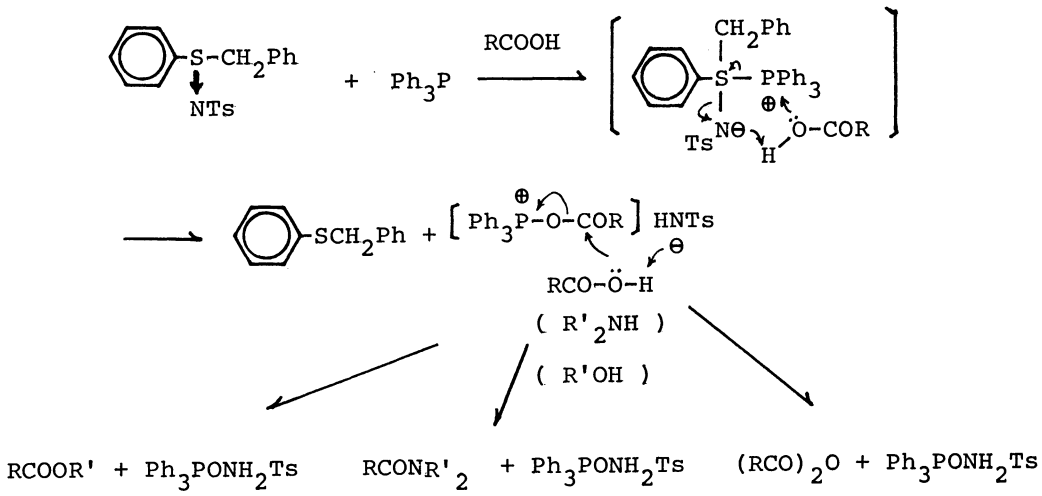
$$\underset{\text{NTs}}{\overset{\text{PhSCH}_2\text{Ph}}{\downarrow}} + \text{R'}_3\text{P} + \text{R"COOH} + \text{Alcohol or Amine}$$

R'	R"	Alcohol or Amine	Reaction Condition Temp.(°C)	Time(hr)	Products and Yields(%) $PhSCH_2Ph$	Ester or Amide	R'_3PONH_2Ts
Ph	Me	$PhCH_2OH$	100	12	98	96	80
Ph	Me	$PhCH_2CH_2OH$	100	12	95	88	85
Ph	Pr	$PhCH_2CH_2OH$	100	12	97	90	83
n-Bu	Pr	$PhCH_2CH_2OH$	60	10	83	79	-*
Ph	Ph	$PhCH_2OH$	100	12	99	93	80
Ph	Ph	$PhCH_2CH_2OH$	100	12	98	95	93
Ph	Pr	$PhNH_2$	100	12	93	86	87
n-Bu	Pr	$PhNH_2$	60	10	86	63	-*
Ph	Pr		100	12	99	80	88
Ph	Pr		100	12	98	84	91
Ph	Ph	$PhNH_2$	100	12	97	71	86
Ph	Ph	PhNH(Me)	100	12	95	68	93

* $n\text{-}Bu_3PO$ and $TsNH_2$ obtained separately in high yields.

The results indicate clearly that the products are the original sulfide, ester or amide and (II) in almost quantitative yields, and our present system effectively worked as a dehydrating system. Unlike the case of the reaction with carboxylic acid, the yields of these condensation products were in high yields and the corresponding acid anhydride could not be detected. It shows that the side reaction which takes place between acid anhydride and the SP-system affording the thioester was completely restrained, namely, the reactions of acid anhydrides with alcohols or amines proceeded faster than the side reaction or these cross condensation passed through another process without the formation of acid anhydride. Although, it is impossible to

distinguish between these two pathways, a plausible mechanistic scheme may be illustrated as follows. Further experiments on these new dehydrating system is now underway in these laboratories.



References

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2) T.Aida, N.Furukawa, and S.Oae, ibid., 805(1973).

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4) N.Yamazaki, F.Higashi, and S.A.Kazaryan, Synthesis, 436(1974).

5) These reactions were carried out in a sealed tube using 5 mmol of the SP-system and 1.5 mmol of carboxylic acid and alcohol or amine. The excess amounts of the SP-system reacted alone and gave the corresponding sulfide and phosphine imine (Ph_3P=NTs) in high yields, respectively.

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