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1,3-Dipole in Sulfilimine-Phosphine System. IV.*,[1] Preparations of Acid Anhydride, Amide, Ester and Thioester

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Complexes formed between N-arylsulfonylsulfilimines and triphenylphosphine, for example a couple of S,S-benzyl phenyl *p*-tosylsulfilimine and triphenylphosphine we call it SP-system for simplicity, were found to react with such compounds as carboxylic acids, alcohols, amines and acid anhydrides affording various interesting products. Among them, the reaction with carboxylic acids gave the corresponding anhydrides in substantial yields, and this reaction can be extended to prepare esters and amides. All these reactions can be explained by assuming the initial formation of a 1,3-dipole intermediate (sulfurane) between sulfilimine and triphenylphosphine.

Introduction

The reaction of N-arenesulfonysulfilimine with triphenylphosphine in the presence of water[1] or alcohol[3] was found to proceed through the formation of a sulfurane intermediate (**1**; a 1,3-dipole) as shown in Chart 1.

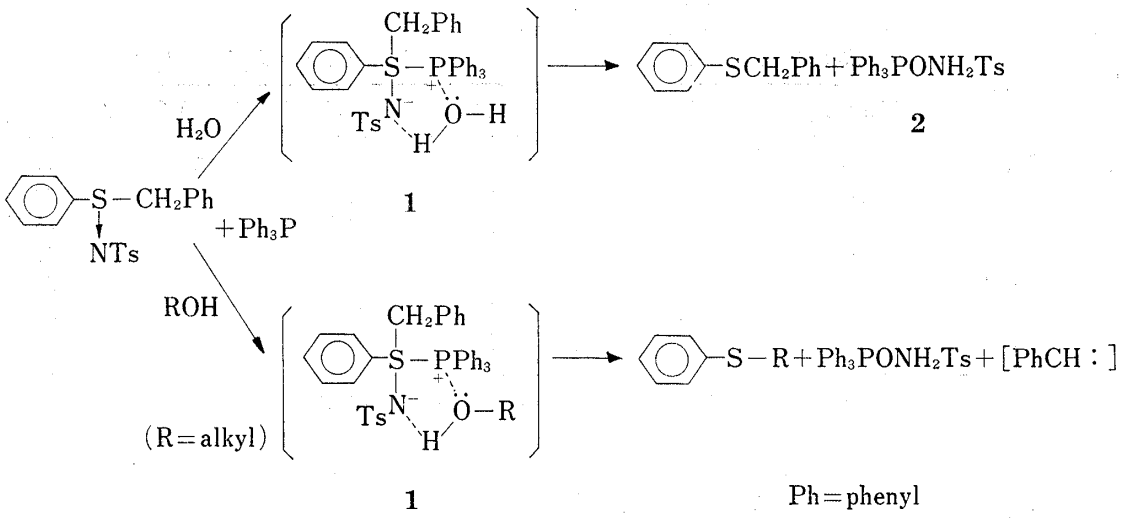


Chart 1

Inspection of the Chart 1 shows that the initial step of the reaction is a 1,3-dipolar addition which eventually leads to a dehydration. In order to obtain further information on this reaction, the SP-system was treated with various reagents.

When carboxylic acids were treated with the SP-system, a 1,3-dipolar addition took place affording the corresponding acid anhydrides in substantial yields. This means that the SP-system worked as an effective dehydrating reagent.

* Dedicated to the memory of Prof. Eiji Ochiai.

1) Part: III T. Aida, N. Furukawa, and S. Oae, *Chemistry Lett.*, **1973**, 805.

2) Location: *Sakura-mura, Niihari-gun, Ibaraki 300-31.*

3) T. Aida, N. Furukawa, and S. Oae, *Chemistry Lett.* **1974**, 121.

Earlier, Mukaiyama[4] and Yamazaki[5] reported a synthetic procedure for esters or amides using phosphorus compounds. Thus, it is interesting to see whether or not this SP-system can be extended to both esters and amides condensations. Actually, when the SP-system was treated with a mixture of carboxylic acids and alcohols or amines, the cross condensation reactions proceeded smoothly affording the corresponding esters or amides in high yields.

Meanwhile, the SP-system was found to react further with carboxylic acid anhydrides affording the corresponding thioester (3) almost quantitatively.

In this paper the results and scope of the reactions of novel this 1,3-dipolar system will be described.

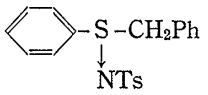
$$\underset{\underset{\text{NTs}}{\downarrow}}{\text{Ph-S-R}} + R'_3P + (R''CO)_2O \longrightarrow \underset{\mathbf{3}}{\text{Ph-S-COR''}} + R'_3POTsNHCOR''$$

Results and Discussion

Reaction of the SP-System with Carboxylic Acid

The SP-system (a pair of S,S-benzyl phenyl N-*p*-tosylsulfilimine and triphenylphosphine) was subjected to the reaction with various carboxylic acids. The products and yields are listed in Table I.

Table I. Reaction of the SP-System with Carboxylic Acid



$+ R'_3P + R''COOH$

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	—[a]
Ph	Me	100	12	61	20	40	72
p-Tol	Me	80	12	63	21	43	75
Ph	Et	100	12	65	20	36	67
Ph	*n*-Pr	100	12	63	20	42	70
Ph	iso-Pr	100	12	66	21	44	74
Ph	Ph	100	12	55	45	5	50

a) *n*-Bu_3PO and $TsNH_2$ were obtained separately in high yields.
Ph=phenyl

Inspection of the results in Table I indicates the following features of the reaction; (i) in all cases with the carboxylic acids a similar product distribution was observed, namely, the products were the original sulfides, thioester (3), acid anhydrides and the complexes (2), (ii) the yields of the sulfides were nearly equal to the total sum of those of thioesters and acid anhydrides. This means that the thioester is undoubtedly derived from the reaction of the SP-system with the carboxylic acid anhydride. Actually, a controled experiment of the reaction using the acid anhydride gave the corresponding thioester almost quantitatively under the same reaction condition listed in Table I (the detailed accounts of this reaction will be described in Chart 4). Thus, the initial pathway of the reaction of the SP-system with the carboxylic acid seems to be the formation of the corresponding anhydride which then reacts again with SP-system to afford thioester (3).

4) T. Mukaiyama, R. Matsuda, and M. Suzuki, *Tetrahedron Lett.*, **1970**, 1910.
5) N. Yamazaki, F. Higashi, and S.A. Kazaryan, *Synthesis*, **1974**, 436.

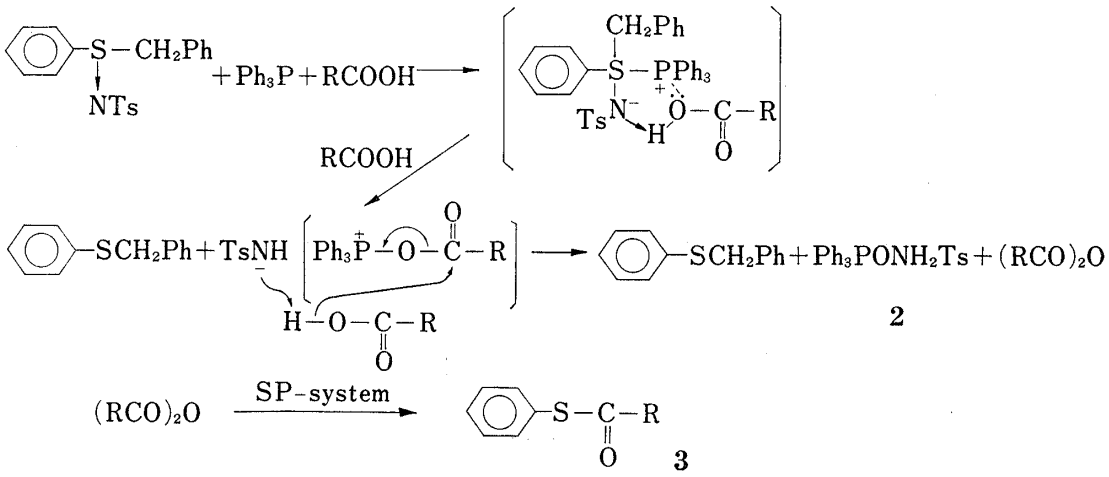


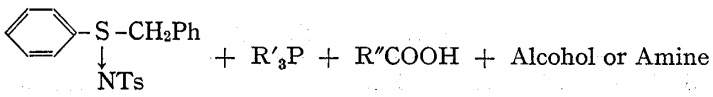
Chart 2

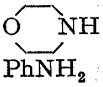
The formation of the sulfide and the acid anhydride can be rationalized by this Chart.

The Ester- and Amide-Condensations by the SP-System

The formation of the acid anhydride from the corresponding carboxylic acid also suggests that the SP-system does serve as a dehydrating system, and hence can be applied for the syntheses of esters and amides. In order to ascertain this possibility, the SP-system was treated with a mixture of carboxylic acids and alcohols or amines. The results obtained are listed in Table II.

Table II. Ester and Amide Condensations by the SP-System



R′	R″	Alcohol or Amine	Reaction condition		Products and yields (%)		
			Temp. (°C)	Time (hr)	$PhSCH_2Ph$	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	*n*-Pr	$PhCH_2CH_2OH$	100	12	97	90	83
n-Bu	*n*-Pr	$PhCH_2CH_2OH$	60	10	83	79	—*a*)
Ph	Ph	$PhCH_2OH$	100	12	99	93	80
Ph	Ph	$PhCH_2CH_2OH$	100	12	98	95	93
Ph	*n*-Pr	$PhNH_2$	100	12	93	86	87
n-Bu	*n*-Pr	$PhNH_2$	60	10	86	63	—*a*)
Ph	*n*-Pr		100	12	99	80	88
Ph	*n*-Pr		100	12	98	84	91
Ph	Ph	$PhNH_2$	100	12	97	71	86
Ph	Ph	PhNH(Me)	100	12	95	68	93

a) *n*-Bu_3PO and $TsNH_2$ obtained separately in high yields.

Inspection of the results in Table II indicates clearly that the products formed in almost quantitative yields are the original sulfides, esters or amides and the complexes (**2**). Thus, the present system worked effectively as a dehydrating system, and moreover the yields of these condensed products were quite high. This means that the SP-system has further synthetic applicability for various condensations.

Although it is difficult to determine the reaction mechanism, the following scheme may be proposed on the basis of these observations (Chart 3).

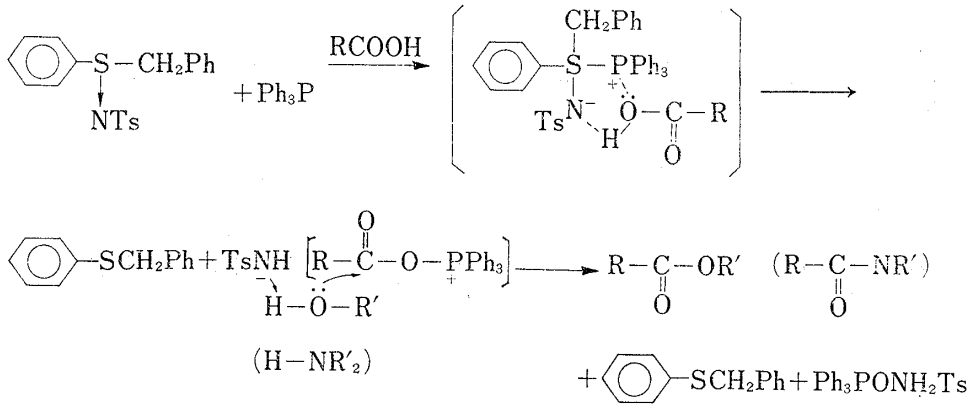
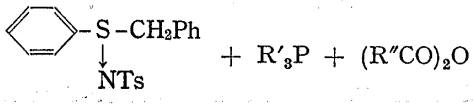


Chart 3

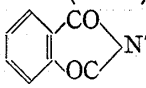
Reaction of the SP-System with Carboxylic Acid Anhydride

As shown in Table I, the SP-system was assumed to react with the carboxylic acid anhydride affording the corresponding thioester. In order to ascertain this, the reaction of the SP-system with various carboxylic anhydrides was investigated. The results obtained are summarized in Table III.

TABLE III. Reaction of the SP-system with Carboxylic Acid Anhydride



at 100° for 12 hr

R′	R″	Products and yields (%) PhSCH$_2$Ph	PhSCOR″	PhCH$_2$OCOR″	Others
Ph	Me	trace	75	5	R′$_3$PONH(COR″)Ts(58)[a]
Ph	Ph	5	82	10	
n-Bu	Me	7	56	—	R′$_3$PO(quant.), TsNH(COR″) (64)
Ph		87	0	0	R′$_3$PO (quant.),  NTs (76)[b]
Ph		97	0	0	R′$_3$PO (82)
n-Bu		83	0	0	R′$_3$PO (72)

a) This compound was prepared authentically from Ph_3PO and $TsNHCOCH_3$ by a fusion.
b) It was prepared authentically from potassium phthalimide and *p*-tosylchloride in DMF solution.

The results in Table III show that the reaction with the acid anhydride can be divided into two types, namely, the one is the reaction with open chain derivatives (Class A) which give both the corresponding thioester (**3**) and the complex (**2**) in high yields, while the other is that with cyclic derivatives which give the original sulfide, triphenylphosphine oxide and N-*p*-tosyl dicarboxylic imide derivative (**4**) (Class B).

From the product distribution, the former reaction seems to be similar to that which proceeds *via* a 1,3-dipolar addition like the reaction with alcohol[3] as shown in Chart 4.

Although phenylcarbene or stilbene could not be detected in this reaction, the addition of benzaldehyde to the reaction mixture gave a small amount of stilbene. This may suggest that the sulfonium ylide (**5**) is formed during the reaction as an intermediate like the reaction with alcohol.[3]

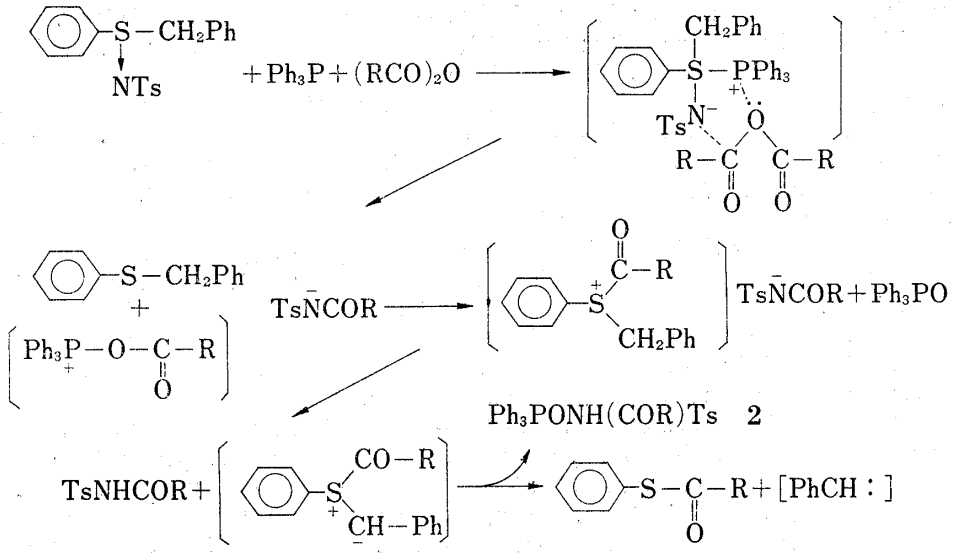


Chart 4 (Class A)

Meanwhile, in the case of the Class B, the products obtained were quite different from those of Class A; namely, the reduction of the sulfilimine to the corresponding sulfide took place almost completely accompanied with N-*p*-tosyldicarboxylic imide (**4**). The plausible reaction scheme for these reactions would be illustrated as shown in Chart 5.

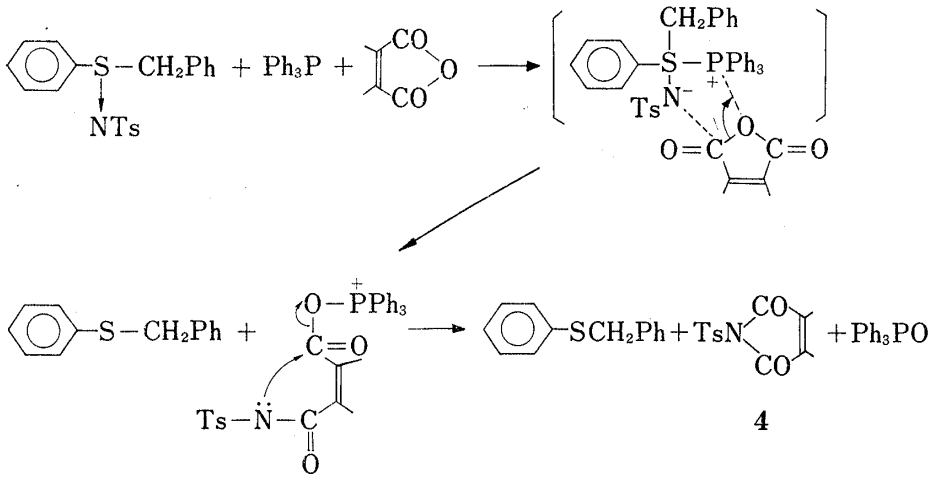


Chart 5 (Class B)

Experimental

Materials——N-Arylsulfonylsulfilimine: N-arylsulfonylsulfilimine was prepared from the corresponding sulfide and sodium salt of N-chloro-arylsulfonamide (*i.e.*, Chloramine-T) by the modified Mann-Pope reaction,[6] and identified by comparing the mp, infrared (IR) and nuclear magnetic resonance (NMR) spectrua with those reported earlier.[6]

Phosphorus Compounds: Triphenylphosphine was a commercial product which was recrystallized from ethanol twice. Tri-*n*-butylphosphine was also a commercial product which was distilled before use.

Carboxylic Acid and Acid Anhydride: All these reagents were commercial products which were purified by either distillation or recrystallization.

Alcohol: The commercial products were distilled after drying over CaO and used.

Amine: The commercial products were distilled under N_2-atmosphere after drying over CaH_2 and used.

Solvent: Dimethylformamide and dimethylsulfoxide were dried over CaH_2 and distilled before use. Benzene was purified by usual method.

6) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, **42**, 2631 (1969).

Reaction of the SP-System with the Carboxylic Acid——A typical run was as follows. A mixture of S-benzyl S-phenyl N-*p*-tosylsulfilimine (1.0 g; 3 mmole), triphenylphosphine (1.5 g; 6 mmole) and acetic acid (3 ml) was dissolved in 3 ml of benzene. The solution was heated in a sealed tube at 100° for 12 hr. Then, it was cooled down at room temperature, and allowed to stand overnight after adding 1 ml of petroleum ether. The crystalline material was filtered and washed well with petroleum ether (50 ml). The mixture of the filtrate and washings was concentrated carefully by evaporation of petroleum ether. From the concentrated mixture, benzyl phenyl sulfide (61%) and phenyl thioacetate (24%) were isolated. The phenyl thioacetate was authentically preparared from acetic anhydride and potassium thiophenolate. Although the corresponding acetic anhydride was detected by gas–liquid chromatography (GLC), it was very difficult to determine the yield because of the contamination with a large amount of acetic acid. Thus, the yield of acetic anhydride was determined by means of GLC after changing it to anilide derivative which was prepared by the reaction with aniline. As the corresponding anilide also came from the reaction of the thioacetate with aniline, the value obtained from GLC was recorrected by reducing the yield of the thioacetate from it.

All other experiments were carried out as described above.

Ester- and Amide-Condensations by the SP-System——A typical run was as follows. A mixture of S-benzyl S-phenyl N-*p*-tosylsulfilimine (2.0 g, 6 mmole), triphenylphosphine (1.5 g; 6 mmole), acetic acid (0.18 g; 3 mmole) and phenethyl alcohol (0.37 g; 3 mmole) was dissolved in 10 ml of benzene. The solution was heated in a sealed tube at 100° for 12 hr. Then, the solution was cooled down at room temperature and then allowed to stand overnight after adding *n*-hexane (2 ml). The crystalline products, the complex (Ph_3PONH_2Ts; 1.3 g, 95%) and triphenylphosphinimine ($Ph_3P{=}NTs$; 1.1 g, 85%) were isolated by column chromatography(silica gel, benzene). From the mixture of the mother solution and washings, *β*-phenethyl acetate (88%) and benzyl phenyl sulfide (95%) were obtained. The yields of these products were determined by GLC.

All other experiments were carried out as described above.

Reaction of the SP-System with Carboxylic Acid Anhydride——A typical run was as follows. S-Benzyl S-phenyl N-*p*-tosylsulfilimine (1.0 g; 3 mmole), triphenylphosphine (1.5 g; 6 mmole) and acetic anhydride (3 ml) were dissolved in 3 ml of benzene. The solution was heated in a sealed tube at 100° for 12 hr. The isolation and identification of the products were carried out as described above.