Mechanism of the Reaction of *N*-Arylsulphonylsulphimides with Trivalent Phosphorus Compounds

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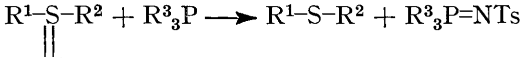
The reaction of *N*-arylsulphonylsulphimides with trivalent phosphorus compounds in dimethylformamide (DMF) gave the original sulphide and phosphinimine. The kinetic studies revealed that the rate of the reaction of *S*-aryl *S*-methyl *N*-*p*-tosylsulphimide with triphenylphosphine follows the second-order kinetic equation $v = k_2[\text{Sulphimide}][Ph_3P]$, and the activation parameters for the reaction were $\Delta H^\ddagger$ 26.9 kcal mol^{-1} and $\Delta S^\ddagger$ −8.8 cal mol^{-1} K^{-1}. Hammett ρ values of the reaction p-$XC_6H_4S(NSO_2C_6H_4Y$-$p)R$ + (p-$ZC_6H_4)_3P$, are ρ_X +3.7, ρ_Y +0.6 ($R = CH_3$), and ρ_Z −1.3 ($R = PhCH_2$). These observations suggest that the reaction proceeds *via* initial nucleophilic attack of the phosphine on the sulphinyl sulphur atom of the sulphimide. Addition of water or alcohol to the reaction mixture changed both the products and kinetic results. The reaction in alcohol gave, besides the original sulphide, an alkyl-exchanged sulphide in which the alkyl group is derived from the alcohol used. All these observations can be explained by assuming the initial formation of a 1,3-dipolar sulphurane intermediate between the sulphimide and triphenylphosphine.

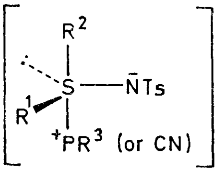
In the course of a study of nucleophilic substitution on the trivalent sulphur atom of the *N*-arylsulphonylsulphimide, the sulphimide was found to react readily with nucleophiles affording products of various types.[1] As an extension of these reactions *N*-arylsulphonylsulphimides were allowed to react with trivalent phosphorus compounds in various solvents. The reaction gave the original sulphide (1) and the phosphinimine (2) nearly quantitatively.



$$R^1\text{–}\underset{\underset{NTs}{\|}}{S}\text{–}R^2 + R^3{}_3P \longrightarrow R^1\text{–}S\text{–}R^2 + R^3{}_3P{=}NTs$$

(1) (2)

The products formed in this reaction are similar to those of the reaction with cyanide ion.[2] Thus, both reactions appear to proceed *via* similar reaction mechanisms, *i.e.* through the initial formation of pentacovalent sulphurane intermediates such as (3).[3]



(3)

This paper describes the results obtained for the reaction of *N*-arylsulphonylsulphimide with various trivalent phosphorus compounds and the reaction mechanism was discussed.

RESULTS AND DISCUSSION

Reaction of N-*Arylsulphonylsulphimide with Various Trivalent Phosphorus Compounds*.—The reactions were carried out in a sealed tube with three mol. equiv. of phosphorus compound to that of the sulphimide. The products and yields are summarized in Table 1.

Inspection of the data in Table 1 indicates that *S*-alkyl-*S*-aryl-*N*-arylsulphonylsulphimides reacted with the phosphorus compounds to afford as major products the original sulphide and the phosphinimine quantitatively except in the case of sulphimides having at least one β-hydrogen atom which undergo an E_i reaction.[4] In the case of the phosphite [*i.e.* $(EtO)_3P$], the product distribution was more complicated than that of the reaction with the phosphine. When the reaction was carried out with triethyl phosphite and *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide, reduction took place to afford benzyl phenyl sulphide, triethyl phosphate, *NN*-dimethyl-(*p*-tosylaminomethylene)amine (4), diethyl *N*-ethyl-*N*-*p*-tosylphosphoramidate (5), and ethyl phenyl sulphide. Although it is difficult to postulate a plausible mechanism, the first step in the reaction is considered to be the formation of the iminophosphorane (6) which undergoes Wittig-type reaction with DMF [path (a)], Arbuzov-type rearrangement [path (b)], and alkylation [path (c)] respectively. The alkylation is considered to proceed through the consecutive formation of the intermediates, the sulphonium salt (7) and the sulphonium ylide (8).

Thus, all the reactions in Table 1 seem to proceed *via* the same intermediate (3) and involve an imino-group transfer reaction from the trivalent sulphur atom of the sulphimide to the trivalent phosphorus atom of the phosphine.

Kinetics and Hammett Correlation.—Kinetic experiments were carried out for the following reaction: p-$XC_6H_4S(NSO_2C_6H_4Y$-$p)R$ + (p-$ZC_6H_4)_3P$. The results obtained indicate that the rate of the reaction can be correlated well with the second-order kinetic equation (i).

$$v = k_2[\text{Sulphimide}][\text{Phosphine}] \qquad \text{(i)}$$

The activation parameters ($R = CH_3$) were $\Delta H^\ddagger$ 26.0 kcal mol^{-1} and $\Delta S^\ddagger$ −8.8 cal mol^{-1} K^{-1} ($X = Z = H$, $Y = CH_3$).

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[1] (*a*) S. Oae, T. Aida, K. Tsujihara, and N. Furukawa, *Tetrahedron Letters*, 1971, 1145, 4255; (*b*) S. Oae, T. Aida, M. Nakajima, and N. Fukukawa, *Tetrahedron*, 1974, **30**, 947; (*c*) S. Oae, T. Aida, and N. Furukawa, *J.C.S. Perkin II*, 1974, 1231.

[2] (*a*) S. Oae, T. Aida, and N. Furukawa, *Internat. J. Sulfur Chem.*, 1973, **8**, 401; (*b*) T. Aida, M. Nakajima, T. Inoue, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Japan*, 1975, **48**, 723.

[3] C. R. Johson and J. J. Rigau, *J. Amer. Chem. Soc.*, 1969, **91**, 398; B. M. Trost and S. D. Ziman, *ibid.*, 1971, **93**, 3825; I. Kapovits and A. Kalman, *Chem. Comm.*, 1971, 649; J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 2341.

[4] S. Oae, K. Tsujihara, and N. Furukawa, *Tetrahedron*, 1971, **27**, 4921.

Table 1

Reaction of *N*-arylsulphonylsulphimide with trivalent phosphorus compounds [reaction (i)]

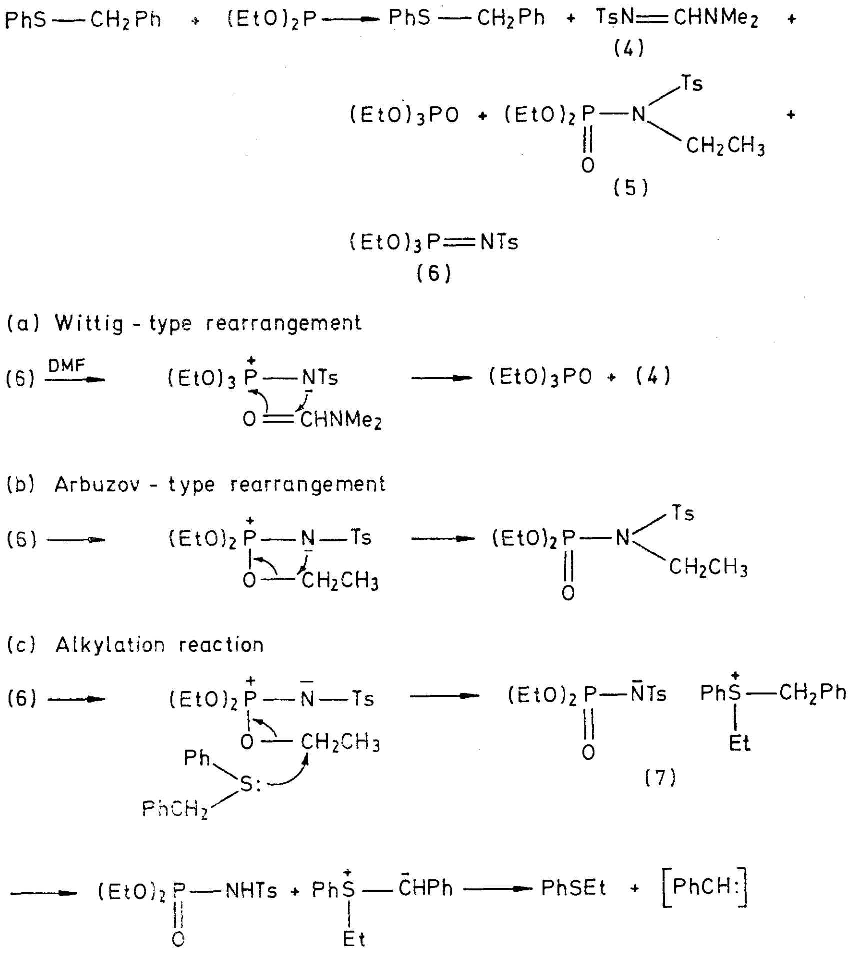
R^1	R^2	Ar	R^3	Reaction conditions Solvent	T/°C	t/h	Product and yield (%) R^1SR^2	$R^3_3P{=}NSO_2Ar$	Others
Ph	Me	p-MeC_6H_4	Ph	DMF	120	6	100	100	
Ph	Me	Cl	Ph	DMF	120	6	100	100	
Ph	Me	MeO	Ph	DMF	120	6	100	100	
Ph	Me	p-MeC_6H_4	Ph	DMSO	120	6	100	100	
Ph	Me	p-MeC_6H_4	Ph	Dioxan	120	10	100	100	
Ph	$PhCH_2$	p-MeC_6H_4	Ph	DMF	100	6	100	100	
Ph	Et [a]	p-MeC_6H_4	Ph	DMF	120	10	5		$CH_2{=}CH_2$, $TsNH_2$ (86), $(PhS)_2$ (37)
Me	Me	p-MeC_6H_4	Ph	DMF	120	10			Recovered (93)
$-[CH_2]_4-$		p-MeC_6H_4	Ph	DMF	120	10	6		Recovered (88)
Ph	Ph	p-MeC_6H_4	Ph	DMF	120	24			Recovered (100)
Ph	$PhCH_2$	p-MeC_6H_4	Bu^n	DMF	100	2	100	87	
Ph	$PhCH_2$	p-MeC_6H_4	EtO	DMF	130	48	45		PhSEt (50), R^3_3PO (60) $Me_2NH{=}NSO_2Ar$ (8), $R^3_2PON^{Et}{}_{Ts}$ (13)
Ph	$PhCH_2$	p-MeC_6H_4	PhO	DMF	130	48	53		$Me_2NCH{=}NTs$ (31), R^3_3OPO (64)
Ph	$PhCH_2$	p-MeC_6H_4 [b]	Ph	20% H_2O–DMF	120	6	100	30	Ph_3PONH_2Ts (45)

[a] *S*-Alkyl-*S*-phenyl-*N*-arylsulphonylsulphimides having at least one β-hydrogen atom underwent an E_i reaction. [b] The reaction was carried out in aqueous DMF solution in a sealed tube.

The Hammett ρ values were ρ_X +3.7 ($R = CH_3$), ρ_Y +0.6 ($R = CH_3$), and ρ_Z −1.3 ($R = PhCH_2$) as shown in Table 2.

When the reaction of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide with tributylphosphine was carried out under the same reaction condition, the rate of the reaction increased *ca.* 700 times over that of triphenylphosphine, while the rate decreased below 10^{-5} times with triethylphosphite (Table 3).

These results suggest that the reaction proceeds *via*



Scheme 1

initial nucleophilic attack of the phosphine on either the trivalent sulphur atom or the imino-nitrogen atom in the transition state. However, recently we found that the reaction of sulphimide with phosphine or cyanide ion proceeds *via* substitution on the trivalent sulphur atom by means of the ring size effect of the sulphimide.[2b] In the reaction of sulphimide with thiophenoxide ion in which the thiophenoxide ion attacks the alkyl group, the ρ_X value (+2.4) was twice the ρ_Y value (+1.2).[1b] This seems reasonable, since the inductive effect is considered to be reduced by nearly half through an extra bonding atom such as an sp^3 carbon atom or sulphur atom. The ρ_Y/ρ_X ratio for the reaction of sulphimide with phosphine is somehow smaller than that of thiophenoxide ion. These observations may be rationalized by the following mechanism, *i.e.*, there is an equilibrium between the sulphimide–triphenylphosphine and sulphurane intermediate, and the rate-determining step is the subsequent intramolecular nucleophilic attack of the imino-nitrogen anion on the phosphorus atom. Then the Hammett ρ value should be the summation of those of the two steps (steps 1 and 2 in Scheme 2). Accordingly, the ρ_Y value will be somewhat smaller than that estimated from the ρ_X value, because the substituent effect for step 1 will compensate that of the others. Meanwhile, the transition state at step 2 results in two bond cleavages (S–P and S–N) and one bond formation (N–P), and hence the inductive effects of the substituent will cancel each other. Thus, the ρ_X value for step 1 should be little affected by that for step 2.

TABLE 2

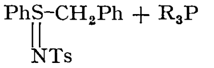
Kinetics of reactions of *N*-arylsulphonylsulphimides *p*-$XC_6H_4SR(=NSO_2C_6H_4Y$-*p*) with triarylphosphines (*p*-$ZC_6H_4)_3P$

R	X	Y	Z	T/°C	10^4k_2/l mol^{-1} s^{-1}
Me	H	Me	H	101.00 ±0.02	0.617 ± 0.015
Me	H	Me	H	110.00	1.103 ± 0.018
Me	H	Me	H	120.00	3.54 ± 0.08
Me	MeO	Me	H	110.10	0.115 ± 0.003
Me	Me	Me	H	110.10	0.220 ± 0.008
Me	Cl	Me	H	110.10	12.04 ± 0.21
Me	H	H	H	110.10	1.95 ± 0.05
Me	H	Br	H	110.10	2.49 ± 0.05
Me	H	*m*-NO_2	H	110.10	5.30 ± 0.15
$PhCH_2$	H	Me	MeO	101.50	83.0 ± 0.3
$PhCH_2$	H	Me	Me	101.50	17.22 ± 0.43
$PhCH_2$	H	Me	H	101.50	7.63 ± 0 14

$\Delta H^‡$ 26.0 kcal mol^{-1}; $\Delta S^‡$ −8.8 cal mol^{-1} K^{-1} (X = Z = H, Y = Me); $\rho_X = +3.7$; $\rho_Y = +0.6$; $\rho_Z = -1.3$.

TABLE 3

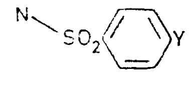
Relative rates of reactions of *N*-*p*-tosylsulphimide with trivalent phosphorus compounds



$$\underset{\displaystyle \| \atop \displaystyle NTs}{PhS}\text{–}CH_2Ph + R_3P$$

R	T/°C	10^3k_2/l mol^{-1} s^{-1}	k_{rel} (70°)
Bu^n	70 ± 0.02	5.29 ± 0.24	700
Ph	70 ± 0.02	7.5 × 10^{-3}	1
EtO	120 ± 0.02	10^{-3} [a]	10^{-5}

[a] This value was calculated from that of 101.5°.



Nu	ρ_Y / ρ_X
PhS^-	0·50
Ph_3P	0·16
CN^-	0·33

Effect of Addition of Water to the Reaction Mixture.— As shown in the product analyses (Table 1), the addition of water to the reaction mixture gave different products, *i.e.*, the corresponding sulphide quantitatively together with triphenyl-*N*-*p*-tosylphosphinimine (2) and complex (9). The yields of (2) and (9) varied with the change in water content. The phosphinimine (2) was not obtained from complex (9) and water under the reaction condition shown in Table 1. Therefore, compounds (2) and (9) arise *via* different reaction paths. The distribution of both (2) and (9) with the change in concentration of water was examined by i.r. analyses of the bands at 1 265 and 1 325 cm^{-1} which correspond to (2) and (9), respectively. The yield of (9) increased with an increasing amount of water in the reaction mixture.

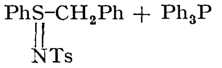
Ph_3PONH_2Ts

(9)

In order to understand the effect of water on the reaction rate, a kinetic study was carried out in H_2O–DMF of the reaction between *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide and triphenylphosphine. The apparent second-order rate constants were calculated from equation (i). The results are shown in Table 4, and indicate that the rate of reaction increases as the amount of water increases. If other reactions involving the water molecule at the transition state compete with the original reaction (step 2 in Scheme 2), equation (i) should be rewritten as follows. From Scheme 2, $v = k_2[SR] + k_3[SR][H_2O]^n$ and according to the usual steady state assumption equations (ii) and (iii) apply. If these reactions are competitive equations (iv) is obtained and if

TABLE 4

Effect of water at 98.7°



$$\underset{\displaystyle \| \atop \displaystyle NTs}{PhS}\text{–}CH_2Ph + Ph_3P$$

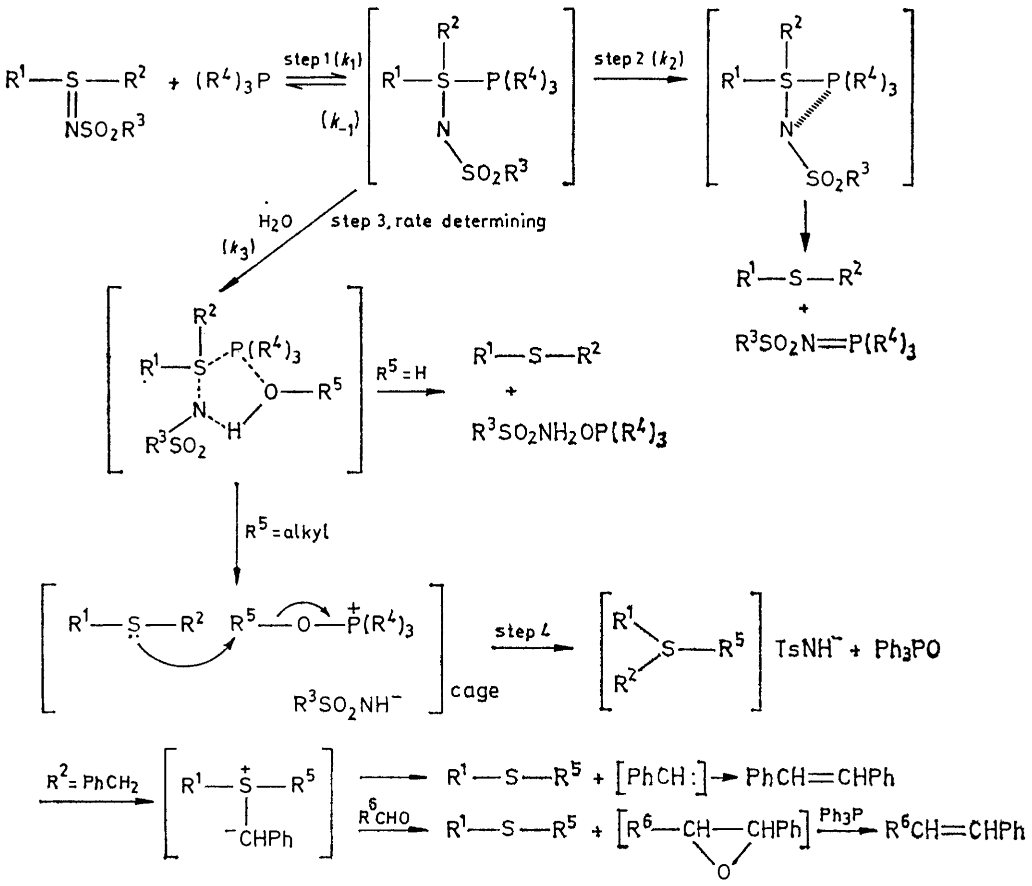
H_2O (vol %)	0.0	2.5	5.0	10.0 (D_2O)	20.0
10^3k_{app}/l mol^{-1} s^{-1}	0.86	1.27	1.76	3.7 (3.6)	11.0

$$k_1[SI][Ph_3P] = k_{-1}[SR] + k_2[SR] + k_3[SR][H_2O]^n \quad \text{(ii)}$$

$$[SR] = k_1[SI][Ph_3P]/(k_{-1} + k_2 + k_3[H_2O]^n) \quad \text{(iii)}$$

$$v = k_1k_2[SI][Ph_3P]/(k_{-1} + k_2 + k_3[H_2O]^n) + k_1k_3[SI][Ph_3P][H_2O]^n/(k_{-1} + k_2 + k_3[H_2O]^n) \quad \text{(iv)}$$

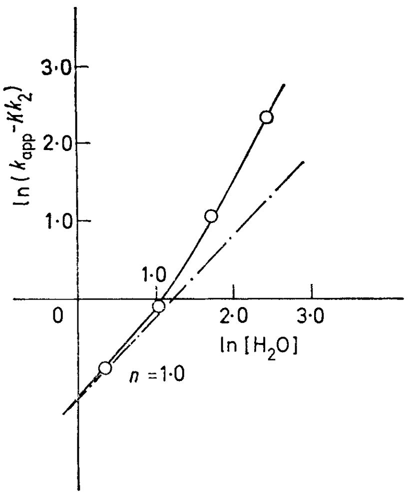
$$v = k_1k_2[SI][Ph_3P]/k_{-1} + k_1k_3[SI][Ph_3P][H_2O]^n/k_{-1} \quad \text{(v)}$$



SCHEME 2 The reaction mechanism

$k_2 + k_3[H_2O]^n \ll k_{-1}$ equation (v) applies. If $k_{app} = K(k_2 + k_3[H_2O]^n)$ equation (vi) is obtained. SR = sulphurane, SI = sulphimide, $K = k_1/k_{-1}$, k_{app} is the observed rate constant, and n the reaction order in water. From the data in Table 4 and equation (vi) the reaction order in water (n) was estimated by means of a graphical extrapolation method as 1.0 (Figure).

$$\log(k_{app} - Kk_2) = \log Kk_3 + n\log[H_2O] \qquad \text{(vi)}$$

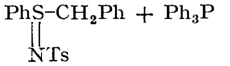


Effect of water on reaction between sulphimide and triphenylphosphine

An alternative explanation for the acceleration of the observed rate by water is a change in polarity of the solvent (solvent effect) and in fact the rate of the reaction seems to depend upon the polarity of the solvent (Table 5). The deviation from the n value at higher concentrations (Figure), *i.e.* the acceleration of step 2 in Scheme 2, may be due to the increasing polarity of the solvent. Meanwhile, the n value (*ca.* 1.0) suggests that the water molecule does participate in the rate-determining step, and thus, as shown in Scheme 2 there is an equilibrium between the sulphimide–phosphine and the sulphurane intermediate.

TABLE 5

Solvent effect at 98.7°



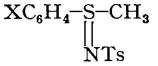
$$\underset{\text{NTs}}{\underset{\|}{\text{PhS}}}\text{-CH}_2\text{Ph} + \text{Ph}_3\text{P}$$

Solvent	k_2/l mol^{-1} s^{-1}	k_{rel}
Dioxan	0.39 ± 0.01	1.0
Benzene	1.21 ± 0.04	3.1
EtOH	5.13 ± 0.15	13.1
DMF	8.62 ± 0.14	22.1

Steric Effects.—The effect of steric hindrance on the reaction was also investigated. The results obtained are listed in Table 6. Inspection of the data reveals that *ortho*-substituents appear to accelerate the reaction, and the trend was remarkably, in the case of *o*-chloro-derivatives (*o* : *p* ratio 6.1), unlike the reaction with cyanide ion. The steric effect can be rationalized by Scheme 2, assuming that the second step (k_2) is accelerated by activation of the sulphurane intermediate due to steric repulsion between the bulky ligands and that this more than compensates for the unfavourable effect of the *ortho*-substituent on the first equilibrium.

TABLE 6

Steric effect due to *ortho*-substituents



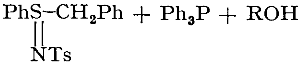
$$\mathrm{XC_6H_4{-}\underset{\underset{\displaystyle NTs}{\|}}{S}{-}CH_3}$$

$10^4k_2/\mathrm{l\ mol^{-1}\ s^{-1}}$

X	*ortho*	*para*	*ortho*/*para*
Me	1.55	1.10	1.5
Cl	72.7	12.0	6.1

TABLE 7

Reactions of sulphimide–phosphine system with alcohols (100°; 24 h)



$$\mathrm{Ph\underset{\underset{\displaystyle NTs}{\|}}{S}{-}CH_2Ph + Ph_3P + ROH}$$

	Product and yield (%)				
R	$\mathrm{PhSCH_2Ph}$	PhSR	$\mathrm{Ph_3P{=}NTs}$	$\mathrm{Ph_3PONH_2Ts}$	Stilbene[a]
Me	57	35		85	6
Et	80	20	63	14	Trace
$\mathrm{Pr^n}$	88	11	71	8	Trace
$\mathrm{Pr^i}$	100	0	100	0	0
$\mathrm{Bu^n}$	97	3	85		
$\mathrm{Bu^t}$	100	0	100	0	0

[a] The ratio of *trans*- to *cis*-isomer is *ca.* 2 : 1.

Reaction of N-p-*Tosylsulphimide with Triphenylphosphine in Various Alcohols.*—The data in Tables 4 and 5 reveal clearly that water plays an important role in forming the intermediate in the reaction of the sulphimide with triphenylphosphine. In order to understand the role of the hydrolytic solvent the reactions of the sulphimide with triphenylphosphine in various alcohols were investigated. The results obtained are summarized in Table 7.

Inspection of the data in Table 7 reveals an interesting feature of this apparent reduction of the sulphimide to the corresponding sulphide. The products obtained are benzyl phenyl sulphide and an alkyl-exchanged sulphide in which the alkyl group originates from the alcohol used, while the ratio of the phosphinimine (2) to complex (9) also varied markedly. The product distribution also depends upon the structure of the alcohol used. When methanol was used as solvent, (2) was not obtained, and (9) was isolated as the sole phosphorus product. The yield of (2) increased markedly with the increase in size of the alkyl group of alcohol used. In the case of propan-2-ol or t-butyl alcohol, there was no formation of (9), and (2) was obtained exclusively. Thus, the ease of exchange of the alkyl group of the alcohol and the ratio of the phosphorus compounds (2) and (9) can be correlated well with the size of the alkyl group. The exchange of the alkyl group between the sulphide and the alcohol took place during the reaction, since under the reaction conditions shown in Table 7, control experiments carried out with the original sulphide were unsuccessful.

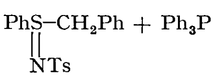
These observations suggest that the investigation of the molar ratio of the sulphides (γ value; exchanged sulphide/total sulphide) is useful in understanding the mechanism. The γ value varies with alcohol concentration and temperature (Tables 8 and 9).

If each of the sulphides has a common reaction intermediate (sulphurane) as in Scheme 2 the formation of the alkyl-exchanged sulphide proceeds through a bimolecular reaction (sulphurane and alcohol) at the product-determining step, and the reaction affording the original sulphide is unimolecular (*via* sulphurane). Thus, an increase in alcohol concentration or elevation of the temperature would facilitate exchange.

In order to confirm this assumption, the effect of substituent and the hydrogen–deuterium kinetic isotope effects on the γ value were examined. The results are listed in Tables 10 and 11.

TABLE 8

Alcohol concentration dependence

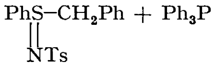


$$\mathrm{Ph\underset{\underset{\displaystyle NTs}{\|}}{S}{-}CH_2Ph + Ph_3P};\ \gamma = \frac{\text{Exchanged sulphide (\%)}}{\text{Total sulphide (\%)}} \times 100$$

EtOH–DMF (vol %)	100	60	30	10
γ	20.0	8.8	5.8	2.4

TABLE 9

Temperature dependence for reaction in EtOH



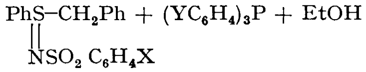
$$\mathrm{Ph\underset{\underset{\displaystyle NTs}{\|}}{S}{-}CH_2Ph + Ph_3P}$$

Temp. (°C)	80.0	100.0	133.0
γ	15.8	20.0	24.2

Inspection of the data in Tables 10 and 11 suggests that the electronic effect (*I* effect) on the sulphimide and fission of the alcoholic O–H bond play an important role in the product-determining step. These observations can be explained by assuming the formation of a sulphurane intermediate during the reaction. The more electron releasing the substituents (X and Y) the more favourable becomes the formation of the alkyl-exchanged sulphide.

TABLE 10

Substituent effects

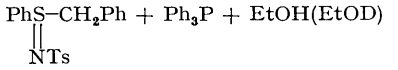


$$\underset{\mathrm{NSO_2\,C_6H_4X}}{\mathrm{PhS\!\!=}}\mathrm{-CH_2Ph + (YC_6H_4)_3P + EtOH}$$

X (Y = H)	*p*-Me	*p*-Br	*m*-NO_2
γ	20.0 ± 0.3	17.9 ± 0.3	16.2 ± 0.2
Y (X = Me)	*p*-H	*p*-Me	*p*-MeO
γ	20.0 ± 0.3	22.7 ± 0.2	29.5 ± 0.2

TABLE 11

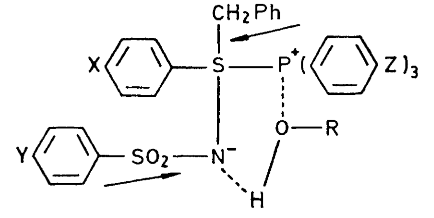
Isotope effect (EtOH–EtOD)



$$\underset{\mathrm{NTs}}{\mathrm{PhS}}\mathrm{-CH_2Ph + Ph_3P + EtOH(EtOD)}$$

Alcohol	EtOH	EtOD	γ_{OH}/γ_{OD}
γ	20.0	9.0	2.2

The participation of an alcohol molecule in the transition state may occur in a more concerted fashion than that in the case of water ($k_{H_2O}/k_{D_2O} = 1$).

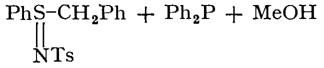


← = Direction of electron-releasing *I* effect

Another interesting observation was the isolation of *trans*- and *cis*-stilbene. When the reaction was carried out in the presence of cyclohexene, the yield of stilbene decreased markedly, while the addition of benzaldehyde to the reaction mixture increased the yield (Table 12).

TABLE 12

Effect of addendum for the formation of stilbene



$$\underset{\mathrm{NTs}}{\mathrm{PhS}}\mathrm{-CH_2Ph + Ph_2P + MeOH}$$

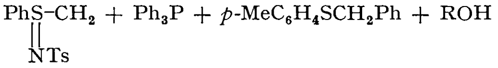
Addendum	*cis*-Stilbene (%)	*trans*-Stilbene (%)
None	3	6
Cyclohexene	Trace	Trace
PhCHO	8	16
p-MeC_6H_4CHO [a]	0	0

[a] *p*-$MeC_6H_4CH{=}CHPh$ was obtained; *cis*, 8%; *trans*, 16%.

The structure of the corresponding stilbene formed in the presence of aldehyde was confirmed by the use of *p*-tolylaldehyde; the olefin obtained was exclusively 1,2-diphenyl-1-*p*-tolylethylene. Phosphonium ylides (Wittig reagents) react with aldehydes to afford the corresponding olefin,[5] and sulphonium ylides also give an olefin produced by initial formation of an oxiran [6] and subsequent reduction by the phosphine.[7] Although it is difficult to distinguish between these reaction routes, these data strongly suggest the existence of either a phosphonium or sulphonium ylide intermediate during the reaction (Scheme 2). According to this mechanism, the cross-over reaction of the sulphide takes place during the formation of the sulphonium salt (step 4 in Scheme 2). However, as shown in Table 13 very little cross-over reaction took place under the reaction condition shown in Table 7 suggesting that the sulphonium salt is formed in a cage reaction.

TABLE 13

Effect of addition of sulphide



$$\underset{\mathrm{NTs}}{\mathrm{PhS}}\mathrm{-CH_2 + Ph_3P + \mathit{p}\text{-}MeC_6H_4SCH_2Ph + ROH}$$

ROH	MeOH		EtOH	
Sulphide	PhSMe	*p*-MeC_6H_4SMe	PhSEt	*p*-MeC_6H_4SEt
Yields (%)	33.4	1.6	18.7	Trace

EXPERIMENTAL

Materials.—N-*Arylsulphonylsulphimides.* All the *N*-arylsulphonylsulphimides were prepared from the corresponding sulphide and the sodium salt of the *N*-chloroarenesulphonamide by the modified Mann–Pope reaction.[8] They were identified by comparison of m.p.s and i.r. and n.m.r. spectra with those reported earlier.[8]

Trivalent phosphorus compounds. Triphenylphosphine was a commercial product twice recrystallized from ethanol. Tributylphosphine, triethyl phosphite, and triphenyl phosphite were also commercial products which were distilled before use. Tris-*p*-methyl(or-*p*-methoxy)phenylphosphine was prepared from the corresponding *p*-methyl(or-*p*-methoxy)bromobenzene and trichlorophosphine by the Grignard reaction, and recrystallized from ethanol.

Benzaldehyde and p-*tolylaldehyde.* Commercial products were distilled under nitrogen before use.

Solvents. DMF was dried over calcium hydride and distilled before use. All alcohols were purified by normal methods. Dioxan was purified by drying with metallic sodium and distilling.

Reactions of N-*Arylsulphonylsulphimides with Trivalent Phosphorus Compounds.*—As a typical run, a mixture of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (1.0 g, 3 mmol) and triphenylphosphine (1.5 g, 6 mmol) was dissolved in DMF (5 ml). The solution was heated in a sealed tube at 120° for 6 h, then cooled down in ice–water, and the contents were poured into water (50 ml). The solution was extracted with hexane (100 ml) and the crystalline precipitate which appeared was filtered. From the hexane extract, benzyl phenyl sulphide (0.6 g, 100%) and the excess of triphenylphosphine (0.6 g) were obtained. The crystalline precipitate was recrystallized from ethanol (1.3 g, 98%), m.p. 185—186°, and identified as triphenyl-*p*-tosylphosphinimine

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[5] D. J. Cram and G. S. Hammond, 'Organic Chemistry,' McGraw-Hill, New York, 1964, 2nd edn., p. 375.

[6] V. Franzen and H. E. Driesen, *Tetrahedron Letters*, 1962, 661.

[7] C. B. Scott, *J. Org. Chem.*, 1957, **22**, 1118.

[8] K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.

(Ph_3P=NTs) by comparison with an authentic sample.[9] Dimethyl-(*p*-tosylaminomethylene)amine was isolated from the reaction mixture by column chromatography (silica gel–benzene), ν 1 630 (C=N) and 1 340 and 1 150 (SO_2) cm^{-1} (Found: C, 52.7; H, 6.3; N, 12.7. Calc. for $C_{10}H_{14}N_2O_2S$: C, 53.1; H, 6.2; N, 12.4%). Diethyl *N*-ethyl-*N*-*p*-tosylphosphoramidate was also isolated by preparative g.l.c. as a light yellow oil and characterized on the basis of elemental analysis and spectral data (Found: C, 47.2, H, 6.9; N, 4.05. Calc. for $C_{13}H_{22}NO_5PS$: C, 46.6; H, 6.55; N, 4.2%). The complex Ph_3PONH_2Ts was identified similarly, m.p. 134—135° (from ethanol) ν 1 315 and 1 160 (SO_2), 1 120 (P=O), and 3 250 and 3 080 cm^{-1} (NH) (Found: C, 66.8; H, 5.1; N, 3.15. Calc. for $C_{25}H_{24}NO_3PS$: C, 66.8; H, 5.35; N, 3.1%).

Reaction of N-*Arylsulphonylsulphimide with Triphenylphosphine in Alcohol*.—As a typical run, a mixture of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (1.0 g, 3 mmol) and triphenylphosphine (1.5 g, 6 mmol) was dissolved in ethanol (5 ml). The solution was heated in a sealed tube at 100° for 24 h, the tube was cooled in ice–water, and broken. The contents were poured into water (50 ml), left at room temperature overnight, and extracted with hexane (100 ml). Removal of the solvent gave benzyl phenyl sulphide (80%), ethyl phenyl sulphide (20%), and a small amount of *trans*-stilbene (2%) which were isolated by preparative g.l.c. and identified by comparing their i.r. and n.m.r. spectra with those of authentic samples. The yields were determined by g.l.c. The mother solution gave a crystalline precipitate which upon column chromatography gave Ph_3P=NTs (63%) and Ph_3PONH_2Ts (14%).

Effect of Addition of Water (*I.r. Investigation*).—A mixture of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (1.0 g, 3 mmol) and triphenylphosphine (1.5 g, 6 mmol) dissolved in DMF–H_2O (19 : 1 v/v; 5 ml). The solution was heated in a sealed tube at 100° for 12 h, the tube was cooled to room temperature, and broken. The contents were poured into water (50 ml), and left at room temperature overnight. The crystalline precipitate which appeared was filtered and washed well with hexane. After drying and grinding, a fine powder was used for the i.r. spectroscopic determination (KBr method).

Kinetic Procedures.—A typical kinetic procedure was as follows. A DMF solution of *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide and triphenylphosphine was prepared, keeping the concentration of both components at 0.062 5M. To this solution was added 0.02M biphenyl as an internal standard for g.l.c. analysis. The solutions were mixed at room temperature and immediately divided into 10 portions each of which were sealed in an ampoule. The ampoules were heated in a constant temperature bath and taken out at intervals. After cooling the ampoule to dry-ice–methanol temperature, the contents were poured into water (5 ml) and extracted with n-hexane (2 ml). The extract was directly injected into the g.l.c. column (5% diethyleneglycol succinate on Celite; 1 m; 3 mm i.d.; stainless steel tube temperature 130°; H_2 flow 60 ml min^{-1}).

Effect of Addendum on the Formation of Stilbene.—A typical run was as follows. A mixture of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (1.0 g, 3 mmol) and triphenylphosphine (1.5 g, 6 mmol) was dissolved in methanol (5 ml) containing *p*-tolualdehyde (1 g). The solution was heated in a sealed tube at 100° for 12 h. The isolation and determination of stilbene were carried out as described above.

[5/2132 *Received*, 31*st October*, 1975]

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[9] H. Bock and W. Wiegrasse, *Angew. Chem.*, 1963, **75**, 789; J. E. Franz and C. Osuch, *Tetrahedron Letters*, 1963, 841.