Pyrolysis of *S*-Alkyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimides with No β-Hydrogen Atoms

By **Tetsuo Aida, Naomichi Furukawa,*** and **Shigeru Oae,** Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki, Japan

S-Alkyl-*S*-phenyl-*N*-*p*-tosylsulphimides with no β-hydrogen atoms were thermally decomposed in sealed tubes at 180° in various solvents. The products obtained depended markedly on the solvent used. When pyrolysis of *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide was carried out in methanol, the major products were methyl phenyl sulphide, methyl phenyl sulphoxide, and toluene-*p*-sulphonamide. When dimethylformamide (DMF) or benzene was used as solvent, *N*-methyltoluene-*p*-sulphonamide and diphenyl disulphide were obtained in substantial yields. With dimethyl sulphoxide (DMSO), the main product was methyl phenyl disulphide which is considered to be formed by the reaction of *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide with DMSO. When alkyl aryl or diaryl sulphoxide was used as solvent, the sulphoxide or sulphimide was reduced to the corresponding sulphide accompanied by ammonium toluene-*p*-sulphonate in substantial yield. The distribution of products and the implication of this for the mechanism are discussed.

RECENTLY, the pyrolysis of *S*-alkyl-*S*-phenyl-*N*-arylsulphonylsulphimide with at least one β-hydrogen atom has been shown to proceed by intramolecular *cis*-elimination to give the corresponding olefin and phenyl *N*-arylsulphonylsulphenamide in high yield,[1] while the stereoselectivity [2] is higher than that for pyrolysis of the corresponding sulphoxide [3] or tertiary amine oxide.[4] However, the mechanism and products of the E_i reaction do not depend much on the nature of the solvents used. Sulphimides with no β-hydrogen atoms undergo pyrolysis in DMSO at 180° to afford unsymmetrical disulphides in substantial yield.[5] The pyrolysis of *SS*-dibenzyl-*N*-*p*-tosylsulphimide without solvent has been reported by Ash and his co-workers,[6] who isolated various compounds including *N*-benzyltoluene-*p*-sulphonamide. This indicates that migration of a benzyl group takes place from the sulphur to the nitrogen atom of the sulphimide. Thus, the combined results imply that the products of the pyrolysis of *N*-*p*-tosylsulphimide are varied by changing the reaction conditions. In order to understand further the nature of the pyrolysis of *S*-alkyl-*S*-phenyl-*N*-*p*-tosylsulphimide with no β-hydrogen atom, thermal decomposition was carried out in various solvents and the products were found to depend remarkably on the solvent used. The pattern of the pyrolysis of the *N*-*p*-tosylsulphimide with no β-hydrogen atoms can be divided into three classes: (i) pyrolysis in methanol in which nucleophilic substitution of the trivalent sulphur atom of the sulphimide is the major process, (ii) pyrolysis in benzene or DMF which involves the migration of the alkyl group from the sulphur atom to the imino-nitrogen atom of the sulphimide (Stevens-type rearrangement reaction), and (iii) pyrolysis in DMSO or other sulphoxides in which rearrangement and reduction are the two main pathways.

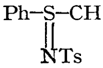
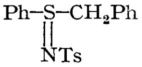
RESULTS AND DISCUSSION

Pyrolysis of Sulphimide in Methanol.—*S*-Benzyl- and -methyl-*S*-phenyl-*N*-*p*-tosylsulphimides were decomposed in methanol in sealed tubes at 180°. The products and yields obtained are listed in Table 1.

Inspection of the data shows that methyl phenyl sulphoxide and methyl phenyl sulphide are the major products in the case of the *S*-methyl-*S*-phenyl derivative while the *S*-benzyl-*S*-phenyl derivative gave benzaldehyde, *N*-benzyltoluene-*p*-sulphonamide, toluene-*p*-sulphonamide, and diphenyl disulphide. Since the reaction was carried out in anhydrous methanol, the oxygen atom in the sulphoxide formed in the reaction must originate from methanol. This means that the reaction involves substitution on the trivalent sulphur atom of the sulphimide. Recently, alkaline hydrolysis in

TABLE 1

Pyrolysis of *S*-alkyl-*S*-phenyl-*N*-*p*-tosylsulphimides in methanol at 180°

Sulphimide	*T*/°C	*t*/h	Product and yield (%)			
 $\mathrm{Ph{-}\underset{\underset{NTs}{\|}}{S}{-}CH_3}$	180	30	$\mathrm{PhSCH_3}$ 32	$\mathrm{PhS(O)SH_3}$ 46	$\mathrm{TsNH_2}$ 87	PhSSPh 5
 $\mathrm{Ph{-}\underset{\underset{NTs}{\|}}{S}{-}CH_2Ph}$	180	20	$\mathrm{PhSCH_2Ph}$ 6	$\mathrm{PhS(O)CH_2Ph}$ Trace	$\mathrm{TsNH_2}$ 60	
			PhSSPh 67	PhCHO 8	$\mathrm{TsNHCH_2Ph}$ 26	

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

[2] K. Tsujihara, K. Harada, N. Furukawa, and S. Oae, *Tetrahedron*, 1971, **27**, 6101.

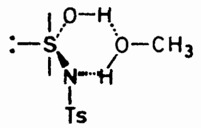
[3] C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810; D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, 1969, **34**, 4115; C. R. Johnson, *Quart. Reports Sulfur Chem.*, 1969, **4**, 33.

[4] A. C. Cope, T. T. Foster, and P. H. Towle, *J. Amer. Chem. Soc.*, 1949, **71**, 3929; A. C. Cope and E. R. Trumbull, *Org. Reactions*, 1960, **11**, 367.

[5] K. Tsujihara, T. Aida, N. Furukawa, and S. Oae, *Tetrahedron Letters*, 1970, 3415.

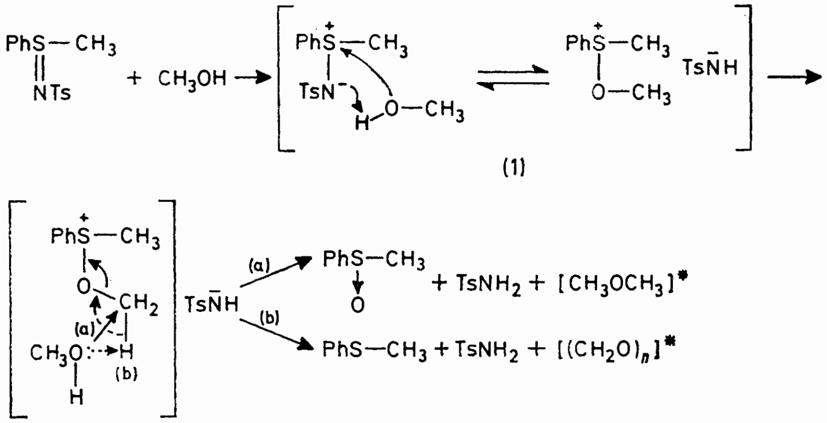
[6] A. S. F. Ash, F. Challenger, T. S. Stevens, and J. L. Dunn, *J. Chem. Soc.*, 1952, 2792; H. Kise, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, 1972, **37**, 1125.

methanol has been suggested to proceed *via* a six-membered cyclic transition state or intermediate as shown in Scheme 1.



Scheme 1

For the pyrolysis in methanol no alkali was used. Thus, an S_N2 type reaction would be unlikely. However, the process leading to the products may be visualized if one assumes initial protonation at the imino-nitrogen atom of the sulphimide and subsequent formation of a sulphoxonium salt (1) which eventually decomposes to the corresponding sulphoxide and the sulphide as shown in Scheme 2.



* Undetected.

Scheme 2

Pyrolysis of Sulphimide in Benzene or DMF.—Pyrolyses of *S*-benzyl- and -methyl-*S*-phenyl-*N*-*p*-tosylsulphimides were carried out in benzene or DMF in sealed tubes at 180° and the products obtained are listed in Tables 2 and 3.

Table 2

Pyrolysis of *S*-alkyl-*S*-phenyl-*N*-*p*-tosylsulphimides in benzene at 180°

Sulphimide	*T*/°C	*t*/h	Product and yield (%)			
$\mathrm{Ph{-}\underset{\underset{NTs}{\|}}{S}{-}CH_3}$ [a]	180	20	$PhSCH_3$	PhSSPh	$TsNH_2$	$TsNHCH_3$
			16	65	18	9
$\mathrm{Ph{-}\underset{\underset{NTs}{\|}}{S}{-}CH_2Ph}$	180	20	$PhSCH_2Ph$	PhSSPh	$TsNH_2$	$TsNHCH_2Ph$
			Trace	89	4	34

[a] For reaction at 180° for 5 h 83% starting material was recovered.

The results indicate that both sulphimides gave the same kind of products, namely, the corresponding sulphide, diphenyl disulphide, *N*-alkyl (methyl or benzyl)-toluene-*p*-sulphonamide, and toluene-*p*-sulphonamide. *S*-Benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide gave a larger amount of the rearranged product than did the *S*-methyl-*S*-phenyl derivative. Although both sets of products are nearly the same, the reaction in DMF proceeds even under relatively mild conditions, and the yields of the products obtained increased considerably compared with those for benzene.

On the basis of the product analysis, the reaction is considered to be a Stevens-type rearrangement. As for the mechanism of the rearrangement, the Woodward–Hoffmann rules predict that ionic mechanisms are not allowed in such a thermal 1,3-rearrangement reaction.[7] A recent CIDNP investigation [8] showed that the Stevens rearrangement is not an ionic process and proceeds through recombination of radicals formed by homolytic cleavage of the bond between the 'onium atom and the sp^3 carbon atom.[9] Ando and his co-workers [10] also reported that the Stevens-type rearrangement of a sulphonium ylide proceeded through the radical mechanism shown in Scheme 3.

However, it should be noted that these CIDNP investigations do not completely rule out an ionic mechanism for the Stevens-type rearrangement, since the observation of CIDNP appeared mainly in the case of the benzyl derivative for which the benzyl group is considered to

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[7] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

[8] A. R. Lepley, 'Chemically Induced Magnetic Polarization,' Wiley, New York, 1973.

[9] U. Schollkopf, G. Ostermann, and J. Schossig, *Tetrahedron Letters*, 1969, 2619; U. Schollkopf, U. Ludwig, G. Ostermann, and M. Patsh, *ibid.*, p. 3415.

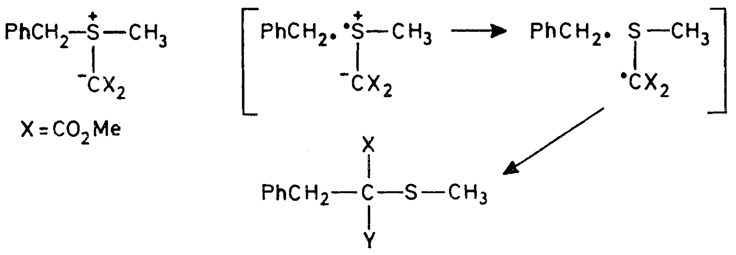
[10] W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Letters*, 1969, 1983.

facilitate homolytic cleavage. It has been found that *N-p*-tosylsulphimide readily gave the corresponding Stevens-type rearranged product by reaction with halide ions in dipolar aprotic solvents.[11] From product analyses and kinetic studies the reaction is considered to proceed through the initial formation of an alkyl halide produced by substitution on the α-carbon atom attached to the trivalent sulphur atom of the sulphimide (Scheme 4).

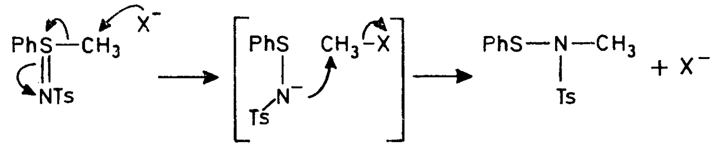
TABLE 3

Pyrolysis of *S*-alkyl-*S*-phenyl-*N-p*-tosylsulphimides in DMF

Sulphimide	*T*/°C	*t*/h	Product and yield (%)			
$\mathrm{Ph{-}\underset{\underset{NTs}{\Vert}}{S}{-}CH_3}$	180	5	$\mathrm{PhSCH_3}$	PhSSPh	$\mathrm{TsNH_2}$	$\mathrm{TsNHCH_3}$
			Trace	50	Trace	**51**
$\mathrm{Ph{-}\underset{\underset{NTs}{\Vert}}{S}{-}CH_2Ph}$	180	3	$\mathrm{PhSCH_2Ph}$	PhSSPh	$\mathrm{TsNH_2}$	$\mathrm{TsNHCH_2Ph}$
			Trace	58	Trace	**62**



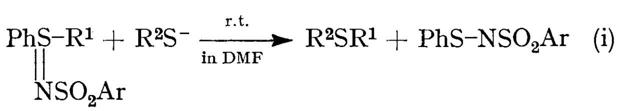
SCHEME 3



X = Cl, Br, or I

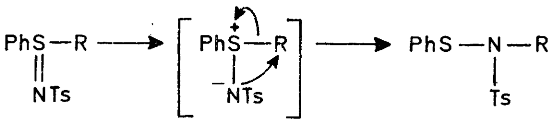
SCHEME 4

In general, nucleophilic substitution (i) at the α-carbon atom of an *N*-arylsulphonylsulphimide proceeds readily in a dipolar aprotic solvent.[12] Furthermore, the



$$\underset{\underset{\mathrm{NSO_2Ar}}{\Vert}}{\mathrm{PhS}}\mathrm{{-}R^1} + \mathrm{R^2S^-} \xrightarrow[\text{in DMF}]{\text{r.t.}} \mathrm{R^2SR^1} + \mathrm{PhS{-}NSO_2Ar} \qquad \text{(i)}$$

the imino-nitrogen atom of the sulphimide is considered to have nucleophilic character as does the oxygen of a sulphoxide [*e.g.* the Kornblum reaction (ii)].[13]



SCHEME 5

Although the detailed mechanism of the reaction cannot be deduced from these data only, an ionic mechanism (Scheme 5) seems favoured on the basis of the solvent effect observed for benzene and DMF, *i.e.* the rearrangement proceeded more readily in DMF than in benzene.

Pyrolysis of Sulphimides in Sulphoxides.—Pyrolysis in dialkyl sulphoxides. The products obtained from the pyrolysis of the *N-p*-tosylsulphimides in the dialkyl sulphoxides DMSO and tetramethylene sulphoxide are shown in Table 4. An interesting feature of the reaction is that unsymmetrical disulphides are always obtained in substantial yield. In addition to the unsymmetrical disulphide, diphenyl disulphide, paraformaldehyde, dimethyl sulphide, and toluene-*p*-sulphonamide were isolated and identified. Furthermore, when *S*-benzyl-*S*-phenyl- or *SS*-dibenzyl-*N-p*-tosylsulphimide was heated in DMSO, benzaldehyde was obtained nearly quantitatively. Diphenyl disulphide was formed in DMSO by the disproportionation of methyl phenyl disulphide. Thus, the initial yield of methyl phenyl disulphide should be >70%. In order to establish the origin of methyl group of the disulphide, *i.e.* whether the methyl group of the unsymmetrical methyl phenyl disulphide comes from the sulphimide or DMSO, *S*-methyl-*S*-phenyl-*N-p*-tosylsulphimide and diethyl sulphoxide were heated at 180° for 2 h, ethyl phenyl disulphide was obtained as the unsymmetrical disulphide. This indicates clearly that

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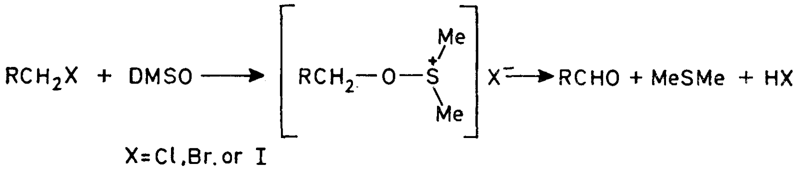
[11] N. Furukawa, T. Aida, and S. Oae, *Internat. J. Sulfur Chem.*, *A*, 1972, **2**, 181; S. Oae, T. Aida, and N. Furukawa, *J.C.S. Perkin II*, 1974, 1231.

[12] T. Aida, N. Furukawa, and S. Oae, *Tetrahedron Letters*, 1971, 4255; S. Oae, T. Aida, M. Nakajima, and N. Furukawa, *Tetrahedron*, 1974, **30**, 947.

[13] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4113.

the methyl group comes from DMSO. Moreover, when isopropyl methyl sulphoxide and *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide were heated, methyl phenyl disulphide was obtained as the sole unsymmetrical disulphide.



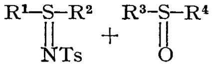
$$\mathrm{RCH_2X + DMSO} \longrightarrow \left[\mathrm{RCH_2{-}O{-}\overset{+}{S}(Me)_2}\right]\mathrm{X^-} \longrightarrow \mathrm{RCHO + MeSMe + HX} \qquad \text{(ii)}$$

$X = Cl, Br, or I$

The results indicate that the initial step is the formation of an ylide (2) by way of prototropic migration of the α-hydrogen atom, followed by the attack of the sulphoxide oxygen atom on the carbon atom of the sulphimide. Since the sulphoxide oxygen atom of DMSO is basic enough to attack an α-carbon atom,[13] the formation of the oxosulphonium intermediate (3) is considered reasonable. The final step is either attack of sulphoxide on the α-carbon atom or proton abstraction by toluene-sulphonamide anion of the thiosulphonium salt intermediate (4) giving both unsymmetrical disulphide and the aldehyde. The mechanism is depicted in Scheme 6.

TABLE 4

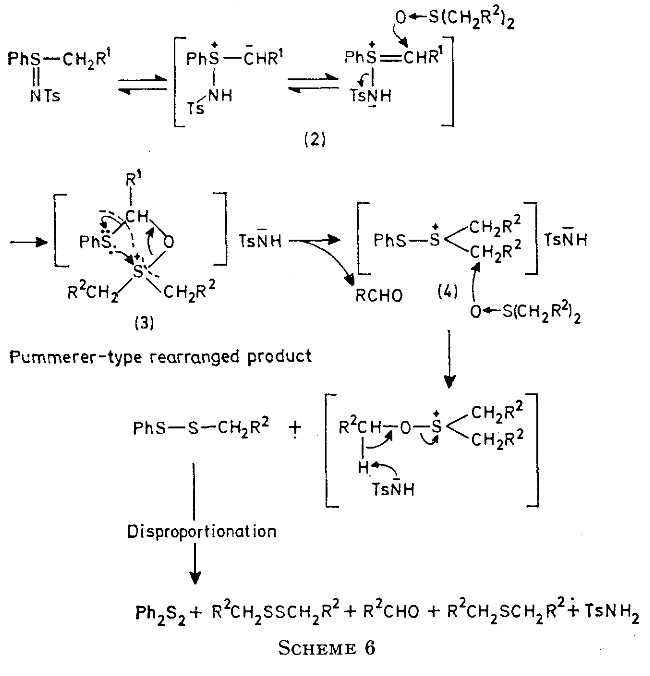
Pyrolysis of *S*-alkyl-*S*-phenyl-*N*-*p*-tosylsulphimides in dialkyl sulphoxides



$$\underset{\mathrm{NTs}}{\overset{\|}{\mathrm{R^1{-}S{-}R^2}}} + \underset{\mathrm{O}}{\overset{\|}{\mathrm{R^3{-}S{-}R^4}}}$$

					Product and yield (%)					
R^1	R^2	R^3	R^4	T/°C (t/h)	R^1SSR^3	R^1SSR^1	R^3SSR^3	R^1SR^2	R^3SR^4	Others
Ph	CH_3	CH_3	CH_3	180 (6)	45	15	36	10	61	$TsNH_2$ 30 $[CH_2O]_n$ 40
Ph	CH_3	Et	Et	180 (2)	51	10				$TsNH_2$ 55
Ph	$PhCH_2$	CH_3	CH_3	180 (6)	51	36				$TsNH_2$ 87 $[CH_2O]_n$ 28 PhCHO 9
$PhCH_2$	$PhCH_2$	CH_3	CH_3	180 (3)	37					$TsNH_2$ 38 PhCHO 99
p-ClC_6H_4	CH_3	CH_3	CH_3	180 (6)	41	13	16	11	45	$TsNH_2$ 43 $[CH_2O]_n$ 30
Ph	$PhCH_2$	CH_3	Pr^i	180 (2)	38					
Ph	Ph	CH_3	CH_3 [a]	180 (24)						

[a] 100% starting material recovered.



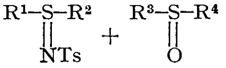
SCHEME 6

Pyrolysis in diaryl or alkyl aryl sulphoxides. In contrast to dialkyl sulphoxides, when *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide was heated with methyl phenyl or diphenyl sulphoxide, the mixture became deep blue or violet during the reaction and the main products were the sulphides which originated from both the sulphimide and the sulphoxide. In most cases, however, the sulphide obtained came from the sulphoxide. Unexpectedly, however, the ammonium salt of toluene-*p*-sulphonic acid was also isolated. The results are in Table 5.

Ammonium toluene-*p*-sulphonate and the sulphides which originate from either the sulphimide or the sulphoxide (or both) were obtained in substantial yield. The sulphimide was so thoroughly dried before use that the oxygen atom of ammonium toluene-*p*-sulphonate must come from the sulphoxide. Thus, the reaction of *S*-methyl-*S*-phenyl *N*-*p*-tosylsulphimide with methyl phenyl sulphoxide may suggest that the sulphoxide is reduced to the corresponding sulphide together with ammonium toluene-*p*-sulphonate as an oxidation product in which the hydrogen atom originates from the methyl protons of the sulphimide. The reaction of *SS*-diphenyl-*N*-*p*-tosylsulphimide with diphenyl sulphoxide did not proceed even under more severe conditions. This means that the hydrogen atom on the α-carbon of the sulphimide or the sulphoxide plays an important role in this reaction. It is interesting that the reduction proceeds readily in the case of either a sulphimide or a sulphoxide having an α-hydrogen atom even *e.g.* the reaction between *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide and diphenyl sulphoxide. Moreover, the reactions gave the same distribution and yields of both sulphides when carried out with either *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide and methyl *p*-tolyl sulphoxide or *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulphimide and methyl phenyl sulphoxide. A control experiment confirmed that the reduction did not proceed when either sulphimide or sulphoxide is absent. On the basis of these observations a plausible mechanistic scheme for the pyrolysis is illustrated in Scheme 7.

TABLE 5

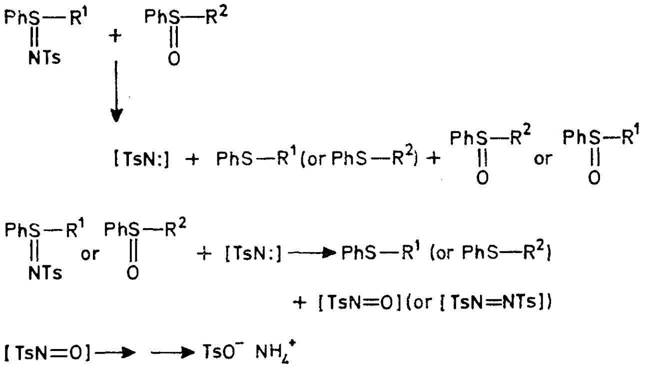
Pyrolysis of *S*-alkyl-*S*-phenyl-*N*-*p*-tosylsulphimides in diaryl or alkyl aryl sulphoxides [a]



$$\underset{\text{NTs}}{\overset{\|}{R^1\text{–S–}R^2}} + \underset{\text{O}}{\overset{\|}{R^3\text{–S–}R^4}}$$

R^1	R^2	R^3	R^4	T/°C (t/h)	Product and yield (%) R^1SR^2	R^3SR^4	$TsO^-NH_4^+$
Ph	CH_3	Ph	CH_3	180 (1.5)	73		27
Ph	$PhCH_2$	Ph	CH_3	180 (0.5)	0	80	32
Ph	Ph	Ph	CH_3	180 (6.0)	68	8	*b*
Ph	CH_3	Ph	Ph	180 (5.0)	0	78	*b*
Ph	$PhCH_2$	Ph	Ph	180 (3.0)	0	70	*b*
Ph	Ph	Ph	Ph [c]	180 (15.0)	0	0	0
Tol	CH_3	Ph	CH_3 [d]	180 (2.0)	33	21	*b*
Ph	CH_3	Tol	CH_3 [d]	180 (2.0)	19	40	*b*

[a] Reactions were carried out using an excess of sulphoxide and the yields were calculated on the basis of sulphimide consumed. [b] Though $TsO^-NH_4^+$ was detected, the yield was not determined. [c] Starting materials were recovered nearly quantitatively. The reaction was carried out using equimolar amounts of sulphimide and sulphoxide.



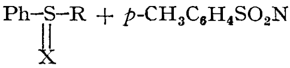
SCHEME 7

In this mechanism liberation of *p*-tosylnitrene is assumed. In order to confirm this assumption, the reaction of *p*-tosyl azide with sulphimide or sulphoxide was carried out under the reaction conditions shown in Table 5. The results obtained are listed in Table 6. Inspection of the data in Table 6 reveals that the reaction with *p*-tosyl azide gives products similar to those of the reaction of the sulphimide with sulphoxide. This supports the mechanism in Scheme 7.

The difference in reactivity of the sulphimide upon varying the structure of the sulphoxide may be explained by the differing nucleophilicity of the oxygen atom of these sulphoxides (nucleophilicity: dialkyl > alkyl aryl ≫ diaryl).[14] In the case of dialkyl sulphoxide nucleophilic attack on the α-carbon atom attached to the trivalent sulphur atom of the sulphimide takes place preferentially.

TABLE 6

Pyrolysis of *p*-tosyl azide at 170° for 3 h



$$\underset{\text{X}}{\overset{\|}{\text{Ph–S–R}}} + p\text{-}CH_3C_6H_4SO_2N_3 \; ^a$$

R	X	Product and yields (%) [b]
CH_3	O	$PhSCH_3$ (78); $TsO^-NH_4^+$ (13)
CH_3	NTs	$PhSCH_3$ (100); $TsO^-NH_4^+$ (trace)
Ph	O	PhSPh (86)

[a] Excess of sulphoxide or sulphimide was used. [b] The yield calculated on the basis of *p*-tosyl azide consumed.

EXPERIMENTAL

Materials.—N-p-*Tosylsulphimides.* All the *N*-*p*-tosylsulphimides used were prepared from the corresponding sulphide and the sodium salt of *N*-chlorotoluene-*p*-sulphonamide by a modified Mann–Pope reaction.[15] The m.p.s and i.r. and n.m.r. spectra are identical with those reported earlier.[15]

Sulphoxides. Dialkyl, alkyl aryl, and diaryl sulphoxides, with the exception of DMSO, were prepared by oxidation of the corresponding sulphide with bromine–acetic acid [16] and were identified by comparing their m.p.s, b.p.s, and i.r. and n.m.r. spectra with those reported earlier. DMSO was a commercial product which was dried over CaH_2 and distilled before use.

p-*Tosyl azide.* *p*-Tosyl azide was prepared from *p*-tosyl chloride and sodium azide, and purified by chromatography (silica gel–benzene).

Solvents. All the solvents were purified by the standard method.

Pyrolysis of Sulphimides in Methanol. *S*-Methyl-*S*-phenyl-*N*-*p*-tosylsulphimide (3 mmol) was dissolved in methanol (6 ml). The solution was heated in a sealed tube at 180° for 30 h. After the reaction, the tube was cooled with dry-ice–methanol and broken. Removal of the solvent left a light brown oil. The oils obtained were: methyl phenyl sulphide (32%), methyl phenyl sulphoxide (46%), diphenyl disulphide (5%), and toluene-*p*-sulphonamide (87%) (yields were determined by column chromatography), identified by comparing their g.l.c. behaviour and i.r. and n.m.r. spectra with those of authentic samples.

Pyrolysis of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide was carried out as above.

Pyrolysis of Sulphimides in Benzene.—Typically, *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide (3 mmol) was dissolved in benzene (6 ml). The solution was heated in a sealed tube at 180° for 20 h. The separation and identification of the products were carried out as described above.

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[14] K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, 1966, **31**, 2859.

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

[16] Beilstein Handbuch, Band **11**, p. 104.

N-Methyltoluene-*p*-sulphonamide was identified by comparing its m.p. 78—79° (from ethanol) (lit.,[17] 78—79°), and i.r. spectrum with those of an authentic sample.

Pyrolysis of the *S*-benzyl derivative was carried out as above.

Pyrolysis of Sulphimides in DMF.—Typically, *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (3 mmol) was dissolved in DMF (6 ml). The solution was heated in a sealed tube at 180° for 3 h. The products were separated and identified as described above. The yields were as follows: benzyl phenyl sulphide (trace), diphenyl disulphide (58%), *N*-benzyltoluene-*p*-sulphonamide (62%), and toluene-*p*-sulphonamide (trace).

Pyrolysis of *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide was carried out as above.

Pyrolysis of Sulphimides in DMSO.—Typically, *S*-methyl-*S*-phenyl-*N*-*p*-tosylsulphimide (3 mmol) was dissolved in DMSO (6 ml). The solution was heated in a sealed tube at 180° for 6 h. After the reaction, the tube was cooled to room temperature and broken and the contents were distilled into two fractions. From the first fraction, b.p. 100°, dimethyl sulphide and dimethyl disulphide were separated by means of preparative g.l.c. and identified by comparing their g.l.c. retention times and n.m.r. spectra with those of authentic samples. The other fraction, b.p. >100°, was poured into ice–water. The aqueous solution was extracted with ether and the ether layer washed well with water and dried (Na_2SO_4). After removal of the solvent, the residue was chromatographed. Methyl phenyl sulphide, diphenyl disulphide, and methyl phenyl disulphide were isolated by preparative g.l.c. and identified by comparison of the i.r. and n.m.r. spectra with those of authentic samples. Paraformaldehyde condensed on the cold part of the sealed tube. The yields were as follows: methyl phenyl disulphide (45%), diphenyl disulphide (15%), dimethyl disulphide (36%), dimethyl sulphide (61%), methyl phenyl sulphide (10%), toluene-*p*-sulphonamide (30%), and paraformaldehyde (40%).

Preparation of Methyl Phenyl Disulphide.—Diphenyl disulphide (3 g) was dissolved in chloroform (20 ml) and chlorine gas was bubbled into the solution at 0° for 2 h. From the reddish solution obtained, solvent was removed and chloroform (20 ml) was added. Methanethiol gas was bubbled into the solution with cooling in ice–water for 3 h. The solution was washed with 0.5N-aqueous sodium hydroxide solution and water and dried (Na_2SO_5). The evaporation of the solvent gave methyl phenyl disulphide, b.p. 89—92° at 3 mmHg, in 57% yield.

Disproportionation of Disulphides in DMSO.—Methyl phenyl disulphide (3 mmol) was dissolved in DMSO (6 ml) in a sealed tube and heated at 180° for 6 h. The tube was cooled to room temperature and broken and the disulphides were detected by g.l.c. The distribution of the disulphides is methyl phenyl disulphide (35%), diphenyl disulphide (62%), and dimethyl disulphide (54%).

Pyrolysis of Sulphimides in Methyl Phenyl Sulphoxide.—A mixture of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulphimide (3 mmol) and methyl phenyl sulphoxide (15 mmol) was placed in a sealed tube and heated at 180° for 0.5 h. The solution became deep violet. The mixture was left at room temperature overnight; ammonium toluene-*p*-sulphonate crystallized and was identified by comparing its m.p., 184—185°, with that of an authentic sample obtained from toluene-*p*-sulphonic acid and ammonia. After filtering off ammonium toluene-*p*-sulphonate, the residue was chromatographed on silica gel with benzene as eluant; benzyl phenyl sulphide was obtained in 80% yield accompanied by brown tar.

Pyrolysis of Tosyl Azide in Methyl Phenyl Sulphoxide.—*p*-Tosyl azide (3 mmol) was dissolved in methyl phenyl sulphoxide (3 ml) and heated at 170° for 3 h in a sealed tube. The reaction proceeded vigorously generating nitrogen gas and the solution turned brown. The mixture was chromatographed on silica gel with benzene as eluant. Methyl phenyl sulphide and ammonium toluene-*p*-sulphonate were obtained in 78 and 13% yield, respectively.

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[17] Ref. 17, p. 105.