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Ei REACTION OF SULPHILIMINES AND RELATED COMPOUNDS

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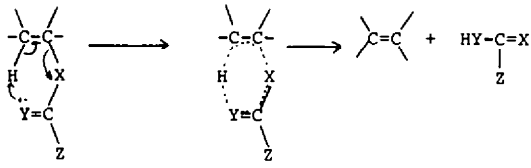
Abstract—Ei reaction of tertiary amine oxides, i.e. the Cope elimination and that of sulphoxides, are briefly reviewed. N-p-Tosylsulphilimines also undergo facile Ei reaction upon heating and the stereospecificity of the reaction is better than that of the corresponding sulphoxides and even somewhat better than that of the tertiary amine oxides.

A general outlook on research on the Ei reactions of sulphilimines and the mechanism of the reaction are discussed in comparison with those of similar Ei reactions which proceed via 5-membered cyclic transition states.

INTRODUCTION

Pyrolysis of alkyl acetates and xanthates, in which the alkyl group has at least one β-hydrogen, gives olefins via a 6-membered cyclic transition state, and the pyrolysis of xanthates is known to be the Chugaev reaction.[1] In this reaction the two groups leave at the same time and coplanarity is not required; however a *cis*-elimination product is obtained.

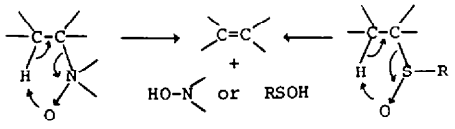


Y=O, Y=S

X=O, X=S

Z=alkyl, Z=OR

Similarly pyrolyses of tertiary amine oxides[2] and dialkyl or alkyl aryl sulphoxides[3] also give olefins via *cis*-elimination involving a 5-membered cyclic transition state, in which five atoms make up a rigid coplanar ring.



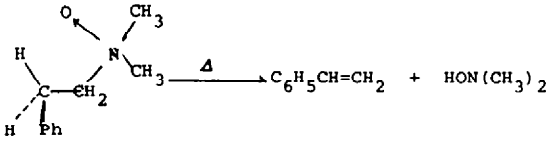
These reactions are highly *cis*-stereospecific, and hence have been used to prepare tailor-made olefins of desired geometries. Sulphilimines were also recently found to undergo a similar Ei reactions[4] and the mechanism of its Ei reactions has been studied somewhat extensively through kinetic and stereochemical investigations. Generally the Ei reaction which proceeds via a 5-membered cyclic transition state (Scheme 2) proceeds at markedly lower temperatures than that via a 6-membered transition state (Scheme 1).

The pyrolysis of tertiary amine oxides is especially facile and some undergo Ei reaction even at room temperature when dissolved in dipolar aprotic media. N-p-Tosylsulphilimines usually pyrolyze at around the refluxing temperature of benzene. One advantage of Ei process with sulphilimines is the easy preparation of N-p-tosylsulphilimines, most of which are obtained nearly quantitatively[5] in crystalline forms by treating sulphides with chloramine-T in hydrolytic solutions, and can be used for further reactions without any purification. Thus, the Ei process of N-p-tosylsulphilimines is probably more convenient than that of tertiary amine oxides (the Cope elimination) and sulphoxides. Recently Ei reaction of selenoxides has been applied for preparation of olefins because of its facile elimination even under cooling[6] despite the toxicity of the starting materials. However, the markedly high reactivity of selenoxides does not seem to have encouraged any detailed mechanistic investigation of the Ei reaction though the usefulness of the reaction has been well accepted.

In this review, we would like to deal briefly the mechanistic aspects of Ei reactions of tertiary amine oxides, sulphoxides and mainly that of sulphilimines somewhat in detail. The scopes and limitations of these reactions will also be mentioned briefly.

THE COPE ELIMINATION

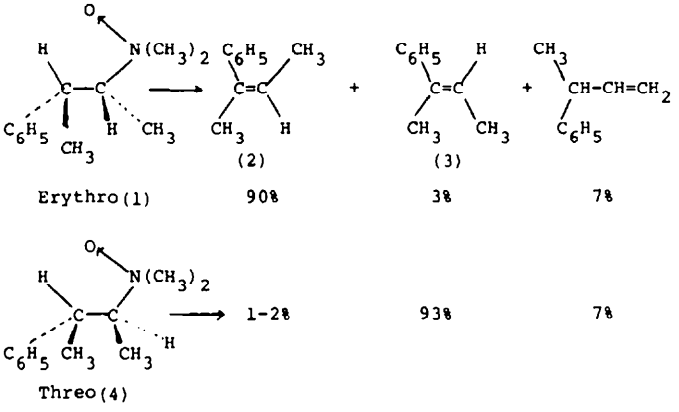
Tertiary amine oxides decompose thermally and give olefins and hydroxylamines, and the reaction is called the Cope reaction, named after the discovery of the synthetic utility of this reaction by Cope *et al.*[2] who first pyrolyzed dimethyl(β-phenylethyl)amine oxide at 80–115°C as shown below.



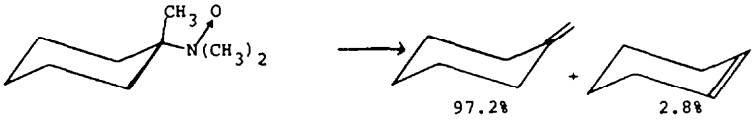
The pyrolysis is usually run at around 100°C, however when tertiary amine oxides are well dried or thermolysis is carried out in aprotic media, the Ei reaction proceeds smoothly at room temperature or even under cooling.[7] Apparently hydrogen-bonding reduces the basicity of N-oxide function to abstract proton from β-carbon. Similar retardations by hydrogen-bonding are

known in the pyrolysis of sulphoxides and sulphilimines though to smaller extents.

Stereospecificity is one of the highest among various pyrolyses leading to *syn*-elimination. Pyrolysis of *erythro* - dimethyl(3 - phenyl - 2 - butyl)amine oxides (**1**) gives predominantly *trans*-1-phenylbutene (**2**) and a minute amount of the *cis*-isomer (**3**) and another terminal olefin, while the *threo*-amine oxide (**4**) affords the *cis* olefin (**3**) predominantly.[8]

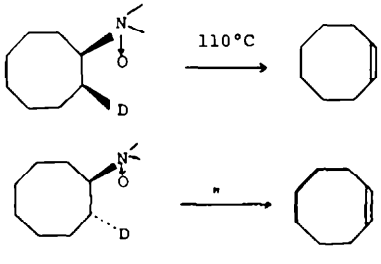


Pyrolysis of dimethyl(1-methylcyclohexyl)amine oxide gives predominantly methylenecyclohexane (97%) and a minute amount of the endo product.[9] In the thermal decomposition of esters and the Chugaev elimination the amount of the thermodynamically less stable *exo*-olefin does exceed more than 25% of all the olefins formed.[10]



Proper steric arrangements, in this case coplanarity and a right distance between β-hydrogen and the terminal oxygen atom of the N-oxide, are highly required in the transition state of the Cope elimination. This is true for other Ei reactions which proceed through 5-membered cyclic transition states. Formation of 65% 2-menthene and 35% 3-menthene in the pyrolysis of dimethylmenthylamine oxide is also in contrast with the result of the Chugaev reaction of the same system in which 2-menthene is the major product.[11]

A similar and more interesting example is the pyrolysis of *cis* and *trans*-N,N-dimethylcyclooctylamine oxides-2-d_1 shown below.[12]

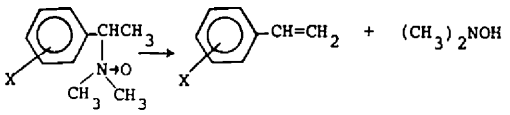


In the *trans*-derivative, the deuterium and the oxygen atoms are not in the same plane in the stable conformer and too far apart to be removed together, while there is a competition between the *cis*-D and the *cis*-H for Ei reaction in the coplanar positions. From the amount of the residual deuterium, the kinetic isotope effect $k_H/k_D = 3.5$ is obtained. As compared to many other proton-removal reactions which proceed via 5-membered cyclic transition states, this value of H-D kinetic isotope effect is an average (and probably nearly maximum) value. Thus, the Cope elimination of this 8-membered cyclic system appears to be a nearly concerted process. Dramatic differences of rates were observed in the Cope eliminations of cyclic systems, the largest being 2.5×10^5 between the most reactive cyclodecyldimethylamine oxide and the least reactive cyclohexyl derivative.[13] Variation of rates with ring sizes is due mainly to the difference in energy to assume *syn-peri*-planar transition state and partly to the difference of strain of the ring which reflects on the ratio of *cis*- and *trans*-isomeric products, *cis*- and *trans*-cycloalkenes.

Among open-chain N-oxides, the structure of alkyl substituent has very little effect on the rate, the orientation of Ei being controlled nearly by the statistical factor, with exception of tertiary-butyl group even which accelerates the rate only two-fold when corrected for the number of β-hydrogens ($Et\text{-}\overset{\downarrow}{\underset{O}{N}}(Me)_2$ (**1**): $t\text{-}Bu\overset{\downarrow}{\underset{O}{N}}(CH_3)_2$ (**6**)), unlike E1 or E2 process.[14]

However, substitution of β-phenyl group increases the rate nearly 100 times which is the highest value of activation among various Ei processes. ($EtN\overset{\downarrow}{\underset{O}{Me_2}}$ (**1**): $PhCH_2CH_2N\overset{\downarrow}{\underset{O}{Me_2}}$ (**70**)). Thus, it looks as though the transition state of this Ei reaction of dimethyl phenylethyl N-oxide is of nearly carbanion type, due mainly to the markedly basic nature of the N-oxide function (pKa = 4.21). However, the magnitude of the activation by β-phenyl group is not as large as in the typical E2 reactions in solution [e.g. k(2-phenylethyl)/k(ethyl) = 530 for bromides and 650 for dimethylsulphonium salts, when corrected for the number of hydrogens].[15]

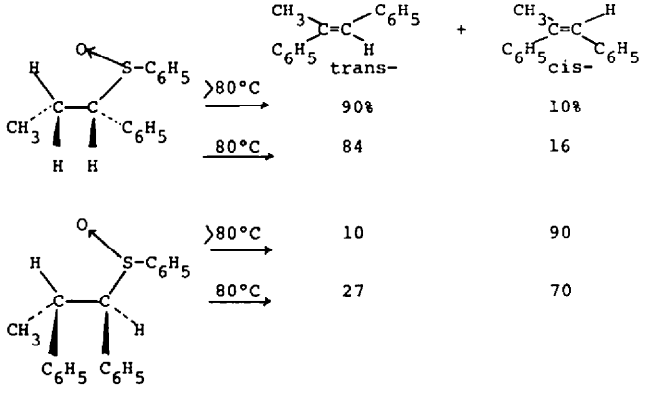
There is a recent investigation of the Cope elimination of 1-(p-substituted phenylethyl)dimethylamine oxides in solvents containing water.[16] The rates are shown to be nicely correlated by the Hammett equation with σ values of p-substituents and a large ρ-value of -6.5 was obtained. Furthermore, the entropy of activation was also found to be large i.e. $\Delta S^{+} = +32$ e.u., seemingly suggesting the possibility of El-like mechanism, though the rates are better correlated by σ-values than σ^{+}-values. Unfortunately there is no experiment on β-hydrogen-deuterium kinetic isotope effect to enable us to make a judgement on the mechanism of the elimination in detail.



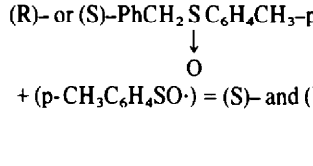
The Cope elimination perhaps has enjoyed the highest popularity among various Ei processes for tailor-made preparation of olefins because of the high stereoselectivity. Most tertiary amines can be oxidized to the corresponding amine oxides by 35% aqueous hydrogen peroxide and somewhat sterically hindered amines can be oxidized by more reactive peracetic acid or perphthalic acid. However, most tertiary amine oxides are hygroscopic and not very easy to handle in open atmosphere while the oxidation with peracids is tedious and sometimes dangerous, like other oxidations with peracids. Furthermore, molecules containing oxidation-sensitive functions cannot be used. The greatest drawback lies in the difficulty in the preparation of desired sterically hindered *tertiary* amine oxides due to the quaternary structure and sterically sensitive nature of amines. The lack of any good procedure to introduce amino group into molecules also limits the utility of this Cope elimination. Thus, the utilization of the Cope elimination has to be limited to the preparation of less sterically hindered olefins which however require high stereoselectivities.

PYROLYSIS OF SULPHOXIDES

In 1960, Cram and Kingsbury found that *erythro*- and *threo*-1,2-diphenyl-1-propylphenyl sulphoxides undergo *syn*-stereospecific thermal elimination of 80°C as shown below.[17]

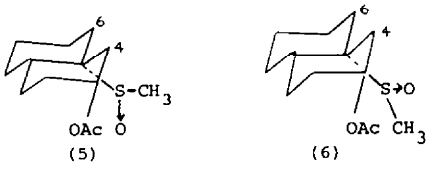


However, the stereospecificity is lost markedly at higher temperatures. For example, the *threo* isomer gives only 37% of the *cis* olefins at 120°C. Benzylic sulphoxides were later shown to be racemized at even below 100°C by the following homolysis.[18]



This facile homolytic racemization is undoubtedly responsible for the poor stereospecificity of the Ei reaction of 1,2-diphenyl-1-propylphenyl sulphoxides at above 80°C. Simple aliphatic sulphoxides do not racemize noticeably below 200°C and hence the stereochemistry is similar to the Ei process of the Cope reaction.

Pyrolysis of 3β - acetoxy(R) - 5α - menthylsulphinylcholestane (**5**) and the (S)-isomer (**6**) is interesting.[19] Here the difference is the configuration of oxygen and methyl group around the sulphur atom.



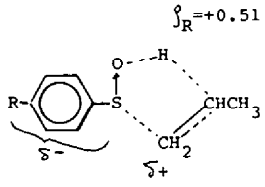
Pyrolysis of the conformer (**5**) gives rise to only elimination to the 4-position (86% 4-ene), while the latter (**6**) leads elimination predominantly to the 6-position (65% 5-ene and 20% 4-ene). Models indicate that the oxygen is near the 4-hydrogen in the former (**5**) and in the latter (**6**) it is near the 6-hydrogen. Here again the *syn*-coplanarity in the transition state appears to be the necessary requirement. However, the requirement seems to be less strict than the Cope elimination. For example, the yield of *endo*-cyclo-alkanes is markedly higher in the pyrolysis of sulphoxide than the Cope elimination of 1-substituted-1-ethylcycloalkyl derivatives.[20] Among cycloalkyl phenyl sulphoxides, the pyrolysis of cyclohexyl derivatives is slowest at 130°C and those of cycloheptyl and cyclopentyl sulphoxides are 25 and 120 times faster than the cyclohexyl derivative respectively at the same temperature, according to Kice and Campbell.[21]

Unlike the Cope elimination, the transition state of pyrolysis of sulphoxide appears to lie nearly El type, due mainly to the small basicity of sulphoxide function and relatively weak bond of C–S linkage. Indeed in the pyrolysis of 2-butyl propyl sulphoxide, elimination occurs predominatly on 2-butyl group.[22] However, the following example seems to support the Ei of substituted phenyl propyl sulphoxides to proceed via nearly an ideal

5-membered cyclic transition state. Namely, the rates are nicely correlated with the Hammett σ values and $\rho = 0.51$, while the activation parameters for the sulphoxide are ΔH^{+}; 25–28 kcal/mol, $\Delta S^{+} = -11.5 - -16$ e.u. Especially the relatively large negative value of entropy of activation is in accordance with the rigid 5-membered cyclic transition state.[23]

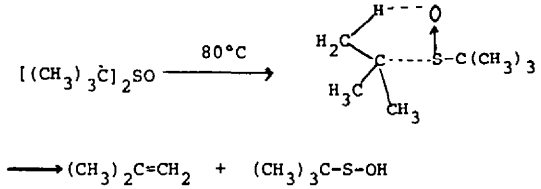
Table 1. Activation parameters for the pyrolysis of p-R-ArS(O)C_3H_7

p-R-ArS(O)C_3H_7	$\Delta H^{\ddagger}$ Kcal/mol	$\Delta S^{\ddagger}$ e.u.
R=H	25.9±1.9	-15.1±6.4
CH_3	27.2±2.3	-12.6±7.3
Cl	25.3±2.6	-16.0±8.2
NO_2	25.5±1.5	-14.3±4.8
OCH_3	27.9±2.1	-11.5±6.7



However, without any study on β-hydrogen-deuterium kinetic isotope effect and many more studies on the effects of substituents, structures and media, it is difficult to see the whole spectrum of the Ei reaction of sulphoxides.

The fate of the sulphoxide group in the pyrolysis is interesting to note, since it is related to the conversion of the penicillin sulphoxide to cephalosporin. Shelton and Davis were the first to demonstrate the incipient formation of tertiary-butylsulphenic acid in the pyrolysis of di-t-butylsulphoxide at 80°C by trapping the sulphenate with ethyl acrylate or methyl acetylenedicarboxylate and also by isolation of di-t-butylthiolsulphinate, dimerized product of the sulphenic acid.[24]



$\longrightarrow (CH_3)_2C{=}CH_2 + (CH_3)_3C\text{-}S\text{-}OH$

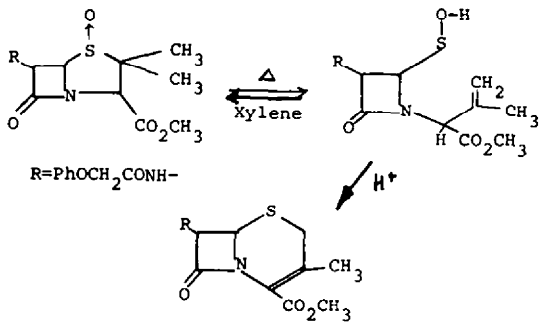
$(CH_3)_3CSOH + CH{\equiv}CH\text{-}CO_2C_2H_5$

$\longrightarrow (CH_3)_3C\text{-}\overset{\overset{O}{\|}}{S}\text{-}CH_2CH_2CO_2C_2H_5$

$2\,(CH_3)_3CSOH \xrightarrow[-H_2O]{} (CH_3)_3C\text{-}S\text{-}S\text{-}C(CH_3)_3$ (O)

A useful application of this reaction was found earlier by Morin *et al.* in the conversion of phenoxymethylpenicillin sulphoxide methyl ester to the corresponding cephalosporin.[25]

One advantage of the pyrolytic Ei reaction of the sulphoxides for organic synthesis is that sulphoxides can be prepared not only by oxidation of sulphides but also



by alkylating sodium dimsylate in DMSO or addition of dimsylate to a certain olefin as shown below.[26]

$$R\text{-}X + {}^{-}CH_2S(O)CH_3 \rightarrow R\text{-}CH_2S(O)CH_3$$

$$(C_6H_5)_2C{=}CH_2 + {}^{-}CH_2S(O)CH_3$$

$$\rightarrow CH_3S(O)CH_2CH_2\bar{C}(C_6H_5)_2$$

$$\xrightarrow{DMSO} CH_3S(O)CH_2CH_2CH(C_6H_5)_2$$

$$\xrightarrow[Ei]{} CH_2{=}CHCH(C_6H_5)_2.$$

A few conceivable drawbacks of this Ei reaction are that the temperature required for the reaction is relatively higher than those for both the Cope elimination and the pyrolysis of N-p-tosylsulphilimines while the stereospecificity is less rigid in this reaction than in the other Ei reactions which proceed via 5-membered cyclic transition states.

Recently, an application of the pyrolysis of sulphoxides to organic synthesis, including the synthesis of some natural products has been published by Trost *et al.*[27]

PYROLYSIS OF SULPHILIMINES

N-p-Tosylsulphilimines can be readily obtained in crystalline forms nearly quantitatively by treating sulphides with chloramine-T in a proper pH region, and are easily handled.[28]

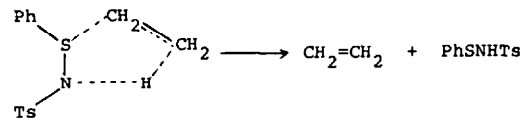
$$R\text{-}S\text{-}R' + TsN\bar{C}l \rightarrow R\text{-}\underset{\displaystyle Na^{+}}{\overset{\displaystyle \downarrow}{S}}\text{-}R'$$

$$\downarrow$$

$$NTs$$

Spectroscopic studies indicate that the S–N bond in N-p-tosylsulphilimines is more polarized than the S–O bond in sulphoxides.[29] Thus, N-p-tosylsulphilimines were found to be pyrolyzed under milder conditions than corresponding sulphoxides.[30] For example, S,S - ethyl - phenyl - N - p - tosylsulphilimine decomposes at least 10^3 times faster than ethyl phenyl sulphoxide at 80°C. The orientation of the pyrolysis of simple acyclic alkyl derivatives appears to be controlled by statistical factors, as illustrated by the ratio of 1-butene and 2-butene (nearly 3:2) in the pyrolysis of phenyl 2-butyl-N-p-tosylsulphilimine though it is more complicated as will be seen later.[31]

Meanwhile, the rates of pyrolytic elimination of sub-

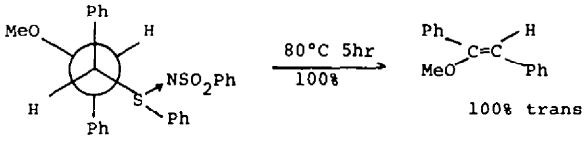


stituted ethyl-aryl-N-sulphonylsulphilimines follow first order kinetics.

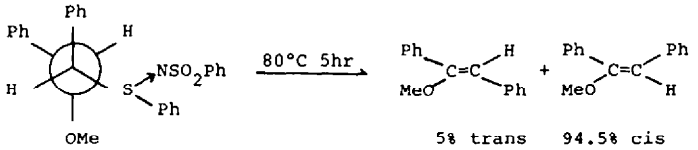
The stereochemistry of the pyrolysis of S-alkyl-N-sulphonyl-sulphilimines was investigated with both the *erythro*- and *threo*-isomers of S - phenyl - S - [1 - phenyl(2,2 - methoxy,phenyl - 1 - ethyl] - N - benzenesulphonylsulphilimines (7) and (8).[31] The pyrolysis of the *erythro*-isomer of the sulphilimine (7) gave only the *trans*-olefin quantitatively and hence the reaction is a completely stereospecific *cis*-elimination, whereas that of the *threo*-sulphilimine (8) gave the *trans*-olefin and the *cis*-olefin in the ratio of 1:17 in 80% of the total yield.[32] Thus, the reaction is not as stereospecific as that for the *erythro* isomer but a predominantly stereoselective *cis*-elimination similar to other *cis*-eliminations.[1]

that the transition state of this pyrolysis is of less carbanion character than that of the Cope elimination in the pyrolysis of alkyl - phenyl - N - p - tosylsulphilimine. However, α-phenyl group accelerates the rate by 10^3 fold, thus indicating the importance of S–C bond cleavage at the transition state of pyrolysis of the sulphilimine.[34] Substitutions of benzenesulphenyl, sulphinyl- and sulphonyl-groups at β-position increase the rate succesively as shown in the following Table.[35] The sizes of the activation parameters are quite similar to those of sulphoxides, ΔS^{+} values being a little larger than those of the sulphoxides.

Various N-sulphonylsulphilimines having substituents on two benzene rings were prepared and subjected to a kinetic study and following data were obtained.



Erythro-(7)



Threo-(8)

The first order kinetic rate of the pyrolysis of the *threo*-isomer (8), $(1.65 \pm 0.04) \times 10^{-4}\,sec^{-1}$, is slightly higher than that of the erythro-isomer (7), $(1.0 \pm 0.06) \times 10^{-4}\,sec^{-1}$. This is in contrast to the general trend in ordinary E2 reactions in which the rate of the *threo* isomer is usually smaller because of the large eclipsing effect by two bulky vicinal substituents at the transition state.[33] In the Ei reaction, however the cyclic conformations of both the *erythro*- and the *threo*-isomers are so rigid and strained that there is not much increase of steric strain as in the E2 reaction in going to the coplanar transition state, perhaps the *threo* being slightly favoured.

The high stereospecificity of this pyrolysis not only indicates the pyrolysis to proceed via a concerted *cis*-elimination but also will be quite an advantage for sulphilimines to be used as a source for preparation of tailor-made olefins.

Unlike in the Cope elimination, the activation by β-phenyl group is very small, i.e. only 1.5 fold revealing

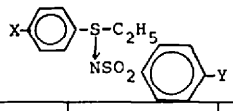
Substitution of an electron-withdrawing benzenesulphonyl group at β-position accelerated the rate by 500-fold, apparently facilitating the proton-removal and changing the transition state toward more nearly carbanion type. Yet the kinetic isotope effect, $k_H/k_D = 4.0$, is quite large suggesting the elimination to quite concerted.

The electron-withdrawing substituents on the phenyl ring attached to the trivalent S atom increase the rate and electron-releasing substituents decrease it ($\rho = +0.90$ in benzene and +0.95 in DMSO) while the opposite trend was observed in the effects of *para* substituent on the phenyl-ring of the sulphonyl group ($\rho = -0.60$ in benzene) respectively. These observations indicate that both the cleavage of S–C bond and the abstraction of a β-hydrogen by the N-atom participate in the transition state. Relatively large values of kinetic isotope effects ($k_H/k_D = 3.03$ in benzene and 3.50 in DMSO respectively) also support it. It is interesting to note that the rate of elimination in benzene is about 6 times larger than that in

Table 2. Relative rates of the pyrolysis of various sulphilimines

Sulphilimine	Rel. rate	$\Delta H^{\ddagger}$ Kcal/mol	$\Delta S^{\ddagger}$ e.u.
PhS(NTs)-CH_2CH_3	1.0	26.5	-5.8
PhS(NTs)-CH(Ph)-CH_3	10^3	20.8	-7.2
PhS(NTs)-CH_2CH_2Ph	1.5	-	-
PhS(NTs)CH_2CH_2SPh	7	26.8	-2.4
PhS(NTs)-CH_2CH_2SPh	15	26.6	-1.7
PhS(NTs)-CH_2CH_2SPh	4.8×10^2	20.4	-12.6

Table 3. Kinetic results of pyrolysis of

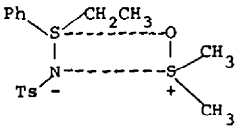


X	Y	Rel.rate	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H	H	1		
H	CH_3	1.19	26.9	-5.4
H	Br	0.69		
CH_3	CH_3	0.78		
CH_3O	"	0.58		
Br	"	1.87		
NO_2	"	5.55		
Ph-S-CH_2CD_3 (NTs)		0.39		
p-Tol-S-CH_2CH_3 (O)		10^{-3}		
p-Tol-S-CH_2CH_3 (O, NH)		10^{-3}		

ρ_X=0.90, ρ_Y=-0.60(in benzene)

ρ_X=0.95, (in DMSO at 90.3°C)

DMSO. However, the enthalpy of activation in benzene ($\Delta H^{\ddagger}$ = 26.9 kcal/mol) is larger than that in DMSO ($\Delta H^{\ddagger}$ = 25.7 kcal/mol) and disadvantage is more than compensated by the unfavorable entropy of this activation in DMSO (i.e. $\Delta S^{\ddagger}$ in benzene is −5.4 e.u. and $\Delta S^{\ddagger}$ in DMSO is −13.3 e.u.) due mainly to the dipolar interaction between the sulphilimine and DMSO as illustrated above.



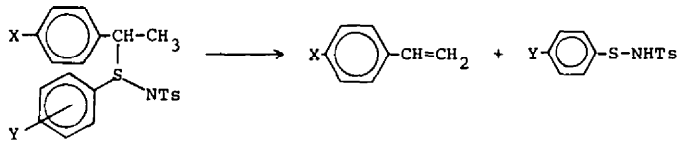
Since the earlier study indicated that substitution of α-phenyl group accelerated the rate by 10^3-fold. This large rate enhancement was thought to be due to the change of the transition state from an ideal *cis*-elimination to nearly El type. Thus, several substituted 1-phenylethyl phenyl-N-p-tosylsulphilimines were prepared and subjected to the kinetic study and the results are listed in Table 4.

Though the effects of substituents on α-phenyl group can be correlated with σ^+values to give $\rho = -0.20$, while those on S-phenyl group give a good straight line of $\rho_y = +0.90$ with σ values, the σ^+-value of −0.20 is too small for a nearly El-like transition state. Furthermore a substantial kinetic isotope effect, i.e. $k_H/k_D = 2.90$, clearly reveals that the reaction proceeds via an intramolecular concerted process.

Solvent effect was then examined by carrying out the pyrolysis of 1-phenylethyl phenyl-N-p-tosylsulphilimine and the data are summarized in Table 5.

In ethanol, the reaction proceeded very slowly and the yield of olefin was also low. Apparently hydrogen-bonding to the N-atom is quite strong and assists only the C–S bond cleavage but retards β-proton removal. Thus, there is a concurrent substitution besides the elimination and 1-phenylethyl ether, a substitution product, is obtained together with ethylene. The rate is also low in chloroform, due mainly to a weak hydrogen-bonding. In aprotic solvents, the rate of pyrolysis is not much affected by solvent. The change in polarity of the solvent from benzene (ϵ = 2.27) to nitrobenzene (ϵ = 34.6) or acetonitrile (ϵ = 37.5) changes the rate rather little. This seems to indicate that there is not much change in charge separation in going from the ground state to the tran-

Table 4. Effects of substituents in the pyrolysis of the following reactions in benzene at 25°C



X	Y	Rel.rate	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
			Kcal/mol	e.u.
H	H	1.0	20.8	-7.2
p-CH_3	H	2.24	22.6	-2.7
p-Cl	H	1.41	22.8	-2.1
p-NO_2	H	1.22	24.4	+3.2
H	p-Cl	1.28		
H	p-CH_3	0.65		
H	p-OCH_3	0.47		
Ph-$CHCD_3$ (S-NTs, Ph)		0.34	k_H/k_D=2.90	

ρ_X=-0.20 ρ_Y=+0.90

Table 5. Solvent effect on pyrolysis of 1-phenylethyl phenyl N-p-tosylsulphilimines at 40°C

Solvent	ε	$10^{-4}xk_1$ (sec^{-1})
Benzene	2.27	2.45
Toluene	2.38	5.41
Chlorobenzene	5.61	3.24
Nitrobenzene	34.6	2.29
CH_3CN	37.5	1.20
EtOH	24.3	not measured
$CHCl_3$	4.7	1.42

sition state. A possibility of homolytic C–S bond cleavage was ruled out, since there was no noticeable ESR signal in the pyrolysis while styrene placed in the reaction vessel did not polymerized under the reaction condition. Thus, the transition state for the pyrolysis of the 1-phenylethyl system is shifted toward nearly El type, yet the reaction undoubtedly proceeds via an intramolecular concerted Ei process.

The fate of sulphonylsulphilimine group is very clear, unlike that of sulphoxide. When ethyl - phenyl - N - p - tosylsulphilimine was pyrolyzed, phenyl - N - p - tosylsulphenamide was isolated in crystalline form, m.p. 113.5–115°C, over 60% yield beside ethylene. Thus, this is one way to prepare N-sulphonylsulphenamides.

EASE OF Ei REACTION AND ITS ORIENTATION

Among these Ei reactions which proceed via 5-membered cyclic transition states, anhydrous tertiary amine oxides decompose the fastest, then sulphonylsulphilimines, and the pyrolysis of sulphoxides is the slowest. Meanwhile, the rate of Ei of ethyl-p-tolyl sulphoximine was measured and found to be much slower.

In the Ei reactions which proceed via 6-membered cyclic transition states the stabilization of the leaving group is suggested by DePuy[36] to control the ease of the Ei reaction: namely the Ei reaction occurs more readily when the leaving group is more stable. The leaving group in these Ei reactions via concerted 5-membered cyclic transition state, are hydroxylamine, sulphenamide, sulphenic acid and sulphinamide, respectively. Among these leaving compounds, the sulphinamide is considered to be the most stable, however the rate of Ei reaction of the sulphoximine is the lowest. Thus, the DePuy's postulation cannot be applied to these systems which deal with Ei reactions via 5-membered cyclic transition states. Comparison of the ease of Ei reactions of these compounds together with other related data is listed in Table 6.[31]

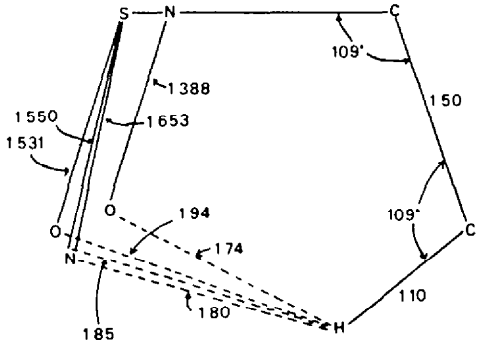
The basicity of the terminal nucleophilic center may give a measure of the ease of the Ei reaction. Indeed, relatively more basic N-carbamoylsulphilimines undergo somewhat facile decomposition,[37] while more basic free alkyl sulphilimines (pKa = 8.5) decompose at room temperature, forming olefins.[38]

$$\text{Ph–S–Et} \rightarrow \text{PhNHCONH}_2 + \text{CH}_2{=}\text{CH}_2.$$
$$\quad\downarrow$$
$$\quad\text{NHCONH}_2$$

Therefore, within the same sulphilimine derivatives, the basicity does give a measure of the Ei reaction. However, comparison of both the pKa values and the NMR chemical shifts of these four different compounds in the Table 6 cannot explain the fact that the Ei reaction of the N-p-tosylsulphilimine is much faster than those of the corresponding sulphoxides or sulphoximines. Meanwhile, the bond distances between the terminal nucleophilic centre and β-hydrogen may control the ease of the Ei reaction. The distance obtained for tertiary amine oxides,[39] N-p-tosylsulphilimine[40] (data from methionine derivative), sulphoximine[41] and sulphoxide,[42] are 1.74, 1.80, 1.85 and 1.94 Å, respectively and are at least in a qualitative sense in keeping with the ease of the Ei reaction, however not in quantitative sense. The distance between a β-hydrogen and the polar N or O atom is definitely important but the direction of the lone pair on the terminal atom, the basicity and the bond strength of C–S or C–N linkage are also responsible for the facile Ei reaction.

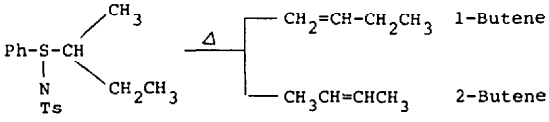
Table 6. The comparison of Ei reaction via 5-membered cyclic transition state

	$\rangle N\rightarrow O$	$\rangle S\rightarrow O$	$\rangle S\rightarrow NTs$	$\rangle S(=O)=NH$
pKa	4.21	-0.488	-1.96	2.73
NMR of α-CH_3 (δ)		2.69	2.81	3.10
Bond Distance(Å) (N–O, S–O, S–N)	1.3888	1.531	1.633	1.550
Ei Reaction Rate (80°C in benzene)	fast	10^{-8}	0.7×10^{-5}	10^{-8}
Distance toward β-H(Calculated) Å	1.74	1.94	1.80	1.85



The distances between a β-hydrogen and the polar N or O atom.

In the early experiment with 2 - butyl - phenyl - N - p - tosylsulphilimine in benzene the orientation of olefin formation, i.e. the ratio of 1-butene and 2-butene, was suggested to be controlled by statistical factors. However, a more careful examination under a few different conditions revealed that the ratio of 1-olefin to 2-isomer in the following reaction depends markedly on the conditions of the Ei reactions as seen in the data in Table 7.



A similar phenomenon was observed in the Cope elimination of N,N-dimethyl-2-phenyl-2-butylamine oxide.[43]

In benzene the dipolar sulphilimine is not solvated strongly and also not dimerized and the bulkiness of the leaving group would be the smallest. Thus, the 2-olefin becomes favoured as a result of a Zaitzev-type elimination. However, in DMSO which slows down the rate of pyrolysis and also without solvent, the sulphilimine is apparently associated or dimerized. Thus the leaving group becomes so bulky and hence the formation of 1-olefin is favoured as a result of a Hofmann type elimination according to the earlier postulation of Brown *et al.*[44]

One advantage in synthetic utilization of the pyrolysis of the sulphilimine is the facile preparation of N-sulphonylsulphilimines. Since the reaction of alkyl phenyl and dialkylsulphilimines with chloramine-T is sterically quite insensitive.[45] One can prepare N-sulphonylsulphilimines with S-alkyl substituents of varying bulkiness. The initial attack of chloramine-T is with chlorocation on bivalent sulphur which is known to be more susceptible than ordinary olefinic double bond.[46] Therefore, the Mann–Pope reaction, i.e. the conversion of sulphides to sulphilimines by treatment with chloramine-T ought to be applied to olefinic sulphides. Another unique feature is that most N-p-tosyl-sulphilimines are crystalline and readily purified into anhydrous state by recrystallization from non-aqueous media. Unlike amine oxides or sulphoxides, the N-sulphonylsulphilimines are not hygroscopic and readily handled. However, the most characteristic features of the Ei process of the sulphilimines is the extremely high stereospecificity of the *cis* elimination, which is not surpassed by any other similar Ei process known in the literature. In order to maintain high stereospecificity of the Ei reaction, the pyrolysis should be conducted at a lowest temperatures possible, since S-alkyl-S-p-tolyl-N-p-tosylsulphilimines are known to racemize thermally through pyramidal inversion at 80–100°C and the racemization on the sulphur atom should deteriorate the stereospecificity of the Ei reaction.[47]

Table 7. Orientation of Ei reactions of phenyl sec-butyl-N-p-tosylsulphilimines

Solvent	Temp. °C	Time (hr)	1-Olefin	2-Olefin
Non-solvent	115–120	2	2.0	1.0
"	160–170	0.5	1.7	1.0
DMSO	115–120	5	1.5	1.0
Benzene	115–120	5	0.67	1.0

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