PYROLYSIS OF N-*p*-TOLUENESULPHONYLSULPHILIMINES

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Abstract—Phenyl alkyl N-*p*-toluenesulphonylsulphilimines having β-hydrogens when heated to 130°, undergo elimination to give the corresponding olefins and phenyl-N-*p*-tolylsulphonyl sulphenamide in high yields. The rate of the thermal decomposition of several ethyl aryl N-arenesulphonylsulphilimines in benzene or DMSO solution between 60 and 100° were measured. The reaction obeys the first-order rate equation. The electron-withdrawing substituents on the phenyl group increased the rate, and the electron releasing substituents attached to the trivalent S atom decreased it ($\rho = +0.90$ in benzene and $+0.95$ in DMSO) while the opposite trend was observed in the effects of the *para* substituents on the phenyl ring attached to the sulphonyl group ($\rho = -0.60$ in benzene). Large kinetic isotope effects were also observed ($k_H/k_D = 3.03$ in benzene and 3.53 in DMSO). Activation enthalpies and entropies were found to be 26.9, 25.7 Kcal/mole and -5.4, -13.3 e.u. in benzene and DMSO respectively. The results indicate that the elimination proceeds through an intramolecular cyclic concerted process. The elimination of aryl alkyl N-*p*-toluenesulphonylsulphilimines usually proceed much more readily than those of the corresponding sulphoxides and sulphoximines. The relatively facile elimination is interpreted on the basis of the favoured conformation. The orientation in this Ei reaction is also discussed.

The physical properties and the configurations of N-*p*-toluenesulphonylsulphilimines have been established by spectroscopic studies[1] and the stereochemistry around the S atom.[2] The S(IV)-N bond of N-*p*-toluenesulphonylsulphilimine is now believed to be semipolar,[1] with the result that the facile Ei type pyrolysis takes place. similar to that of t-amine oxides[3, 4] and sulphoxides[5, 6] having β-hydrogens and a dipolar N—O or S—O bond to give a corresponding olefin via *cis*-elimination. In fact it was found that when N-*p*-toluenesulphonylsulphilimines were heated at 100–130° for several hours under nitrogen, olefins were produced in relatively high yields.[7] This paper describes the pyrolysis of several N-*p*-toluenesulphonylsulphilimines having β-hydrogens. the kinetic studies and their implications on the mechanism of the Ei reactions.
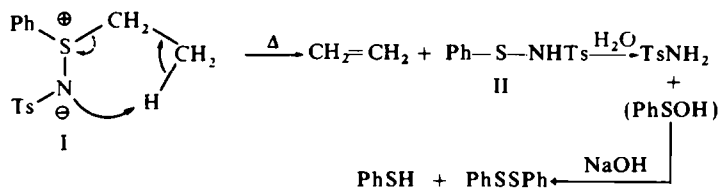
RESULTS AND DISCUSSION

The results obtained when alkyl N-*p*-toluenesulphonylsulphilimines having at least one β-H atom were heated at 100–130° are listed in Table 1.

Styrene was actually isolated and identified by IR and GLC, but the other olefins were converted to the dibromides and identified by comparing the GLC behaviours with those of the authentic dibromides. Ethyl phenyl N-*p*-toluenesulphonylsulphilimine (I) produced ethylene and from the residue, phenyl-N-*p*-toluenesulphonyl-sulphenamide (II) was isolated in 60% yield. The sulphenamide II, m.p. 113.5–115°. gave the characteristic IR and NMR spectra and a satisfactory analysis. Furthermore, hydrolysis of II gave *p*-tolylsulphonamide, thiophenol and diphenyl disulphide.
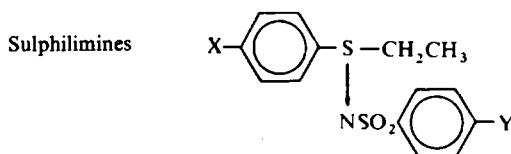
TABLE 1. THE PYROLYSIS OF N-p-TOLUENESULPHONYLSULPHILIMINES

$$\overset{Ph}{\underset{R}{>}}S \overset{+}{\longrightarrow} \overset{-}{N}Ts$$

R	mp(°C)	temp (°C)	time (hours)	olefin	yield (%)
—CH₂CH₃	98·5–99	120–130	2	CH₂=CH₂	70
—CH(CH₃)₂	115–116	120–130	2	CH₃CH=CH₂	80
—C(CH₃)₃	101 (decomp)	100–110	2	(CH₃)₂C=CH₂	85
—C(CH₃)(H)(CH₂CH₃)	85–86	120–130	2	CH₂=CH—CH₂CH₃	53
				CH₃—CH=CH—CH₃	27
—CH₂CH₂Ph	137–138	120–130	2	Ph—CH=CH₂	60

$$
\begin{array}{c}
\text{(I)} \quad \xrightarrow{\Delta} \quad CH_2{=}CH_2 + Ph{-}S{-}NHTs \xrightarrow{H_2O} TsNH_2 \\
\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (II) \quad\quad + \\
\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (PhSOH) \\
\\
PhSH + PhSSPh \xleftarrow{NaOH}
\end{array}
$$

The kinetic study of the elimination reaction was carried out with the N-p-toluene-sulphonylsulphilimines listed in Table 2 which includes some of their physical properties.

TABLE 2.

Sulphilimines $X-\bigcirc-S-CH_2CH_3$ with $NSO_2-\bigcirc-Y$

X	Y	mp (°C)	λ_{max}(mμ)	ε_{max}
H	CH₃	98·5–99	227	17400
CH₃	CH₃	89–90	230	21200
OCH₃	CH₃	95·5–96·5	240	19800
Br	CH₃	113·5–114·5	233	24000
NO₂	CH₃	118–119	231	17700
H	H	50.–51	222	15000
H	Br	108·5–109	236	18600
H	—CD₃	98–98·5	227	17400
p—CH₃C₆H₄—S(→O)—C₂H₅		bp. 142–143/5 mmHg		
p—CH₃C₆H₄—S(→NH)—C₂H₅		42–43	225	11200

The elimination reactions of several ethyl aryl-N-*p*-toluenesulphonylsulphilimines were carried out in benzene and in dimethyl sulfoxide at temperatures that ranged from 60 to 100° and the change of absorbance of the UV spectra of unreacted sulphilimines separated from the reaction mixture was followed. The reaction was found to follow a good first-order kinetic relationship. The results obtained are listed in Table 3.

The reaction is accelerated when X is an electron-withdrawing group or Y is an electron releasing group, or both. The effects of substituents on the phenyl rings attached to the S (IV) atom and S (VI) atom are illustrated in Fig. 1.
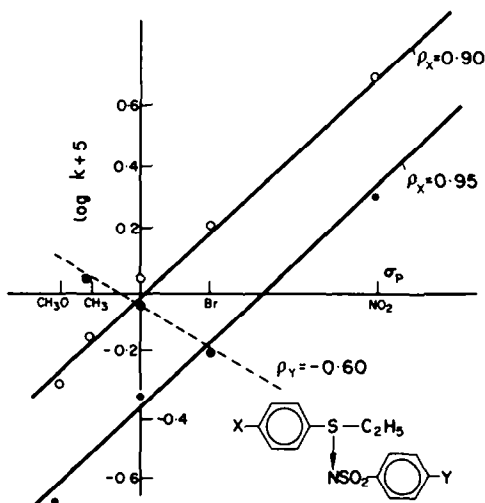

Fig 1. The substituents effects on the phenyl rings attached to the S (IV) atom and S (VI) atom
⊙ : for X in benzene at 80·3°
● : for X in DMSO at 90·3°
◎ : for Y in benzene at 80·3°

Plot of log k values *vs* σ values gives a good straight line for each series with slopes of $\rho_x = -0.90$ (in benzene) or -0.95 (in DMSO) and $\rho_y = -0.60$ (in benzene). respectively. This indicates that both the fissions of S(IV)-C bond and the abstraction of a β-hydrogen by the N atom participate in the rate determining step of the reaction both in benzene and in DMSO.

This is supported with the fact that the values of kinetic isotope effects observed in both benzene and DMSO are considerably large ($k_H/k_D = 3.03$ and 3.53 respectively. Table 3).

Arrhenius plots for S.S-ethyl phenyl-N-*p*-toluenesulphonylsulphilimine are shown in Fig. 2.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 26·9 Kcal/mole and -5.4 e.u. in benzene and 25·7 Kcal/mole and -13.3 e.u. in DMSO respectively.

Meanwhile the rate of elimination in benzene is about six times greater than that in DMSO (Table 3). However. the enthalpy of activation in benzene is larger than that in DMSO and an unfavourable value for the reaction. Making up this disadvantage. the entropy of activation in benzene is larger by eight e.u. than that in DMSO. This may
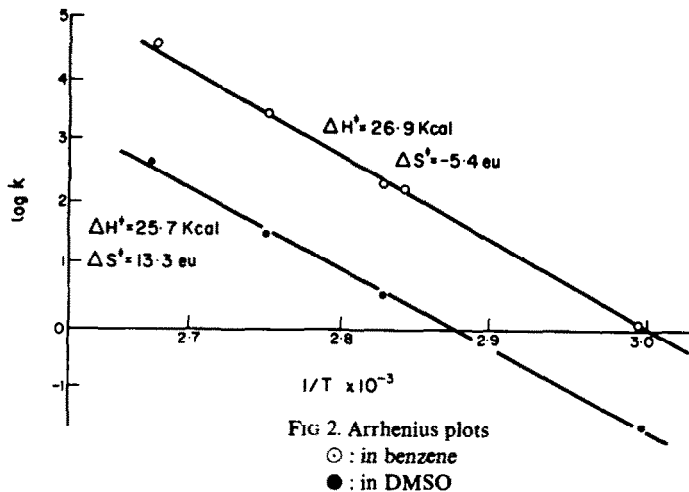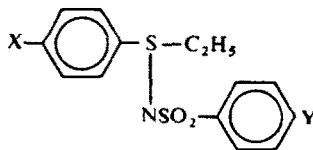
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FIG 2. Arrhenius plots
⊙ : in benzene
● : in DMSO

TABLE 3. RATES OF THE ELIMINATION REACTION OF N-SULPHONYLSULPHILIMINES

X	Y	conc (mol/l)	Temp (°C)	Solvent	$k(sec^{-1})$
H	CH_3	0·02	80·3	Benzene	$1·08 \times 10^{-5}$
		0·01	80·3		1·09 ,,
		0·01	60·3		0·108 ,,
		0·01	100·5		9·85 ,,
		0·01	80·3	DMSO	0·185 ,,
		0·01	60·3		0·0186 ,,
		0·01	9·03		0·449 ,,
CH_3	CH_3	0·01	80·3	Benzene	0·708 ,,
CH_3O	CH_3	0·01	80·3		0·483 ,,
CH_3O	CH_3	0·01	90·3	DMSO	0·198 ,,
Br	CH_3	0·01	80·3	Benzene	1·68 ,,
NO_2	CH_3	0·01	80·3		4·89 ,,
			90·3	DMSO	2·02 ,,
H	H	0·02	80·3	Benzene	0·906 ,,
H	Br	0·02	80·3		0·628 ,,
Ph—S—CH_2CH_3 ↓ NTs		0·01	80·3		0·356 ,,
			90·3	DMSO	0·127 ,,
p—T1—S—CH_2CH_3 ↓ O		0·02	80·3	Benzene	$< 10^{-8}$
p—T1, O, S, CH_3CH_2, NH		0·02	80·3		$< 10^{-8}$

be due to that the N-p-toluenesulphonylsulphilimine having a dipolar S-N bond would tend to assume more readily the favoured cyclic configuration in a non-polar solvent such as benzene than in a dipolar solvent, DMSO, which would solvate the compound by an intermolecular dipolar interaction (Fig 3).
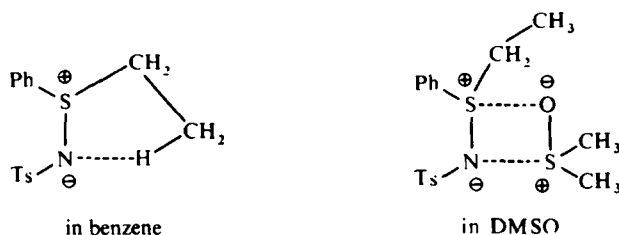
in benzene   in DMSO

FIG. 3. The specific solvation of DMSO

These results seem to indicate that the elimination reaction of the N-p-toluene-sulphonylsulphilimines is best represented by the cyclic internal concerted mechanism. This proceeds much more readily than the corresponding sulphoxide and sulphoxi-mine (Table 3).
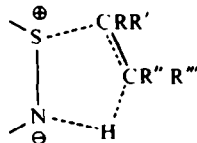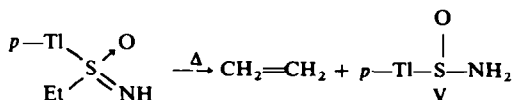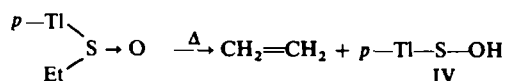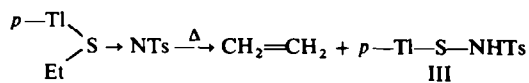
FIG. 4.

Ease and orientation of Ei *reaction*

Practically no systematic study on the ease and orientation of Ei reactions is available. except a brief DePuy's postulate concerning the ease of Ei reaction of 6-membered cyclic transition. According to his postulate, the stabilization of the leaving group controls the ease of the Ei reaction; namely, the Ei reaction occurs more readily when the leaving group is more stable.

Meanwhile the rates of the Ei reaction of ethyl-p-tolyl-N-p-toluenesulphonyl-sulphilimine, -sulphoxide and -sulphoximine were measured and the rate of sulphil-imine was found to be much faster than those of the corresponding sulphoxide and sulphoximine (Table 3).

The leaving groups in these Ei reactions are sulphenamide (III). sulphenic acid (IV) and sulphinamide (V) respectively.

$$p-Tl \diagdown$$
$$\diagup S \to NTs \xrightarrow{\Delta} CH_2=CH_2 + p-Tl-S-NHTs$$
$$Et \qquad\qquad\qquad\qquad\qquad\qquad\qquad III$$

$$p-Tl \diagdown$$
$$\diagup S \to O \xrightarrow{\Delta} CH_2=CH_2 + p-Tl-S-OH$$
$$Et \qquad\qquad\qquad\qquad\qquad\qquad IV$$

$$p-Tl \diagdown \quad O$$
$$\diagup S \diagup \xrightarrow{\Delta} CH_2=CH_2 + p-Tl-\overset{O}{\underset{}{S}}-NH_2$$
$$Et \diagup \diagdown NH \qquad\qquad\qquad\qquad V$$

Among these leaving compounds. the sulphinamide (V) is considered to be the most stable, however, the Ei reaction of the sulphoximine is very much slower than that of the sulphilimine and therefore the DePuy's theory cannot be applied in our system which deals with Ei reactions via the 5-membered cyclic transition complex. A comparison of the ease of Ei reactions of these compounds together with that of the corresponding t-amine oxide is listed in Table 4.

TABLE 4. THE COMPARISON OF Ei REACTION VIA FIVE MEMBERED CYCLIC TRANSITION

	$>\!\!\!N\!\to\!O$	$>\!\!S\!\to\!O$	$>\!\!S\!\to\!NTs$	$>\!\!S\!\overset{O}{\underset{NH}{\lessgtr}}$
Abstraction of β-H atom: pKa	4.21^9.	-0.488^{10}. (for methyl or dimethyl phenyl derivatives)	-1.96^{10}.	2.73^{11}
Fission of C–S or C–N bond; NMR shift of α-CH$_3$ (ppm)		2.69, (for methyl -p-tolyl derivatives)	2.81.	3.10
N–O. S–O or S–N Bond distance (Å)	1.3888^{12}.	1.531^{13}. (for dimethyl or trimethyl derivatives)	1.633^{14}. (for methionine $-$)	1.550^{15}
Rate constant of Ei (at 80°C. in benzene)	fast.	below 10^{-8}. (for ethyl p-tolyl derivatives)	0.7×10^{-5}.	below 10^{-8}
Distance between β-H atom and O or N atom (Å)	1.74.	1.94.	1.80.	1.85

The pKa value gives a measure of the basicity of the nucleophilic center and hence the ease of the abstraction of a β-hydrogen while the chemical shift of Me protons represents the ease of the fission of the S—C bond, since both the abstraction of a β-hydrogen by the polar O or N atom and the fission of the S—C bond participate in the transition state of the Ei reaction. A comparison of both the pKa values and the NMR chemical shifts of these compounds, however, cannot explain the fact that the Ei reaction of the N-p-toluenesulphonylsulphilimine is much faster than those of the corresponding sulphoxides or sulphoximines. Meanwhile, the bond distances of the S—O or S—N, namely the distances between a β-hydrogen and the polar O or N atom may control the ease of the Ei reaction. Thus the distance between a β-hydrogen and the polar O or N atom was estimated from the data of the X-ray analyses[12-15] of the di- or tri-methyl or methionine derivative (Fig 5).

The distances obtained for the t-amine oxide, the N-p-toluene sulphonylsulphilimine. the sulphoximine and the sulphoximide are 1.74, 1.80. 1.85 and 1.94 Å respectively and these distances are at least in a qualitative sense in agreement with the ease of the Ei reaction. However, it is difficult to explain why the sulphoximine. which has a larger basicity (5 pKa units) and only a 0.05 Å longer distance between a β-hydrogen and the polar N atom than N-p-toluene sulphonylsulphilimine, undergoes an Ei reaction very slowly as compared to the corresponding N-sulphonylsulphilimine.
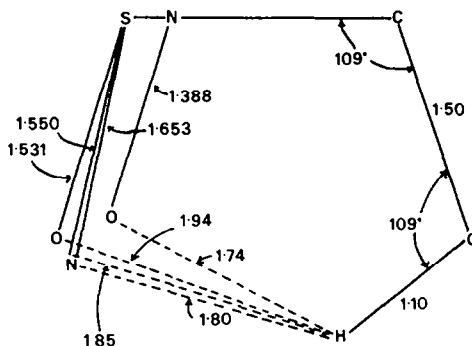
FIG 5. The distances between a β-hydrogen and the polar N or O atom.

This appears to indicate that not only the distance between a β-hydrogen and the polar N atom but also the direction of the lone pair on the N atom is responsible for the facile Ei reaction.

Meanwhile. data on the orientation of Ei reactions are so scant with only a few variations and no systematic study has been available.

The system chosen for this problem is sec-butyl phenyl-N-*p*-toluenesulphonyl-sulphilimine (VI) which has two different β-protons to generate 1- and 2-butene upon pyrolysis.
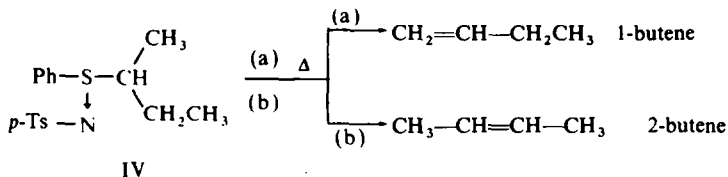
The sulphilimine (VI) was heated in sealed tubes under various conditions to complete the Ei reaction and the olefins formed were converted to the dibromides. The ratio of 1-butene to 2-butene was determined by measuring the amounts of the dibromides by GLC. The results obtained are listed in Table 5.

These results indicate that the ratio of 1-olefin to 2-isomer depends markedly upon the conditions of the Ei reaction. A similar phenomenon was observed in the Ei reaction of N,N-dimethyl-3-phenyl-2-butylamine oxide.[4] This may be due to the bulkiness of the leaving group proposed earlier by Brown *et al.*.[1b] in his steric strain

TABLE 5. THE ORIENTATION OF Ei REACTION OF SEC-BUTYL PENYL-N-*p*-TOLUENESULPHONYLSULPHILIMINE

Solvent	temp (°C)	time (hrs)	1-olefin	:	2-olefin
non-solvent	115–120	2	2·0	:	1·0
non-solvent	160–170	0·5	1·7	:	1·0
DMSO	115–120	5	1·5	:	1·0
Benzene	115–120	5	0·67	:	1·0

theory for the orientation of E_2 reactions. Namely, if there is no solvent the sulfilimine is considered to exist as a dimer or a trimer and the bulkiness would be the largest and hence the formation of 1-olefin is favoured as a result of a Hoffman type elimination. In DMSO, too, the bulkiness of the leaving group would be very large due to the specific solvation of DMSO to the dipolar sulphilimine group and hence the ratio of 1-olefin to 2-isomer is still large. In benzene, however, the dipolar sulphilimine would not be solvated strongly and hence the bulkiness of the leaving group would be the smallest and thus the 2-olefin become favoured as a result of a Zeitzev type elimination.
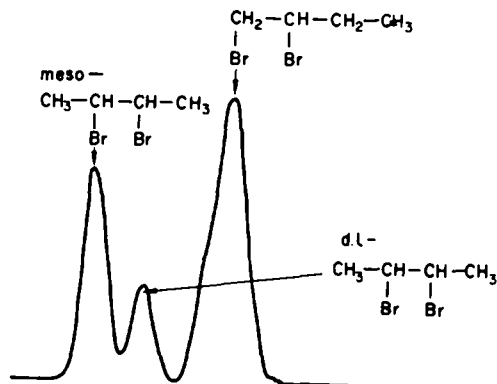
FIG 6. Typical behaviour of dibromides. The ratio of 1-olefin to 2-olefin was determined by measuring the amounts of meso and d.l-2,3-dibromides, by GLC.

EXPERIMENTAL

Syntheses of N-p-*toluenesulphonylsulphilimine.* Several S.S-aryl alkyl N-p-toluenesulphonylsulphilimines were prepared by the reaction of the corresponding sulphides with sodium p-substituted phenylsulphonyl chloramides as described.[17] The sulphides and chloramides were synthesized by ordinary methods. The m.ps of sulphilimines were listed in Tables 1 and 2.

Synthesis of ethyl-2,2,2-d₃-phenyl-N-p-toluenesulphonylsulphilimine

Tetradeuterioacetic acid. Dried malonic acid (8 g) was heated in heavy water (7 ml) at 80° for 1 hr and the water was removed under reduced pressure. This procedure was repeated for 3 times. Malonic acid labelled with deuterium was heated at 150° and the effluent was condensed. The fraction boiling between 105–116° was collected from the redistillation of this effluent, was dissolved in dry ether and dried over anhydrous silica. After removal of ether, the residue was redistilled. Tetradeuterioacetic acid. b.p. 112–116° was obtained (yield. 3·5 g).

Ethyl-2,2,2-d₃-alcohol. An ether soln of tetradeuterioacetic acid (3·5 g) was added dropwise at 0° to a stirred soln of LAH (4 g) in dry ether (80 ml) and the mixture was refluxed for 2 hr. Ice-water (5 ml) was added dropwise at 0° in order to hydrolyse unreacted LAH and then 10% HSO_4 aq (100 ml) was added. The ether layer was removed and the water layer was distilled and 70 ml distillate was collected. Ethyl-2,2,2-d₃-alcohol was obtained by repeated fractional distillation from the fraction boiling between 78·0–79·5° (yield. 2·0 g).

Ethyl-2,2,2-d₃-bromide. Ethyl-2,2,2-d₃-alcohol (2·0 g) was added to a cold mixture of 48% HBr (4·0 ml) and conc HSO_4 (2·0 ml) was added slowly. The mixture was heated at 65° for 3 hr and the direct-distillation was continued at the same time. The distillate was washed with 3 ml ice-cold 10% NaOH aq. and then with

5 ml ice-water. The product was dried over MgSO$_4$ and distilled. the distillate being collected in a dry receiver cooled in an ice-salt mixture. The yield of ethyl-2.2.2-d$_3$-bromide distilling between 38–40° was 1·5 g.

Ethyl-2.2.2-d$_3$-*phenyl sulphide.* Na (0·5 g) was dissolved in abs MeOH (20 ml) and then thiophenol (2·0 g) was added. Ethyl-2.2.2-d$_3$-bromide (1·5 g) was added slowly and the mixture was refluxed for 3 hr. Then the mixture was poured into ice-water, extracted with benzene, washed with water, dried over MgSO$_4$ and the solvent removed. yield of ethyl-2.2.2-d$_3$-phenyl sulphide boiling at 102–3°C/30mmHg was 1·3 g.

Ethyl-2.2.2-d$_3$-*phenyl-N-p-toluenesulphonylsulphilimine.* Ethyl-2.2.2-d$_3$-phenyl sulphide (1·3 g) and chloramine-T (3·0 g) were dissolved in MeOH (30 ml) and then a drop of AcOH was added. The mixture was warmed at 50° for 2 hr and then poured into a cold dil NaOH aq. The ppt was collected and recrystalised from MeOH. yield 1·8 g. m.p. 98–98·5°. The content of deuterium was found to be 88% of the theoretical amount from the measurement of its NMR spectrum.

The pyrolysis of N-p-toluenesulphonylsulphilimines

S.S-Aryl. alkyl N-p-toluenesulphonylsulphilimines having β-protons were heated at 120-130° for several hr under N$_2$ and the olefins formed were introduced with N$_2$ into bromine water and converted to the corresponding dibromides.

Identification of the products was done by comparing the GLC behaviour with that of the authentic dibromides.

The pyrolysis of ethyl-phenyl-N-p-toluenesulphonylsulphilimine

*The isolation and identification of phenyl-*N-p-*tolylsulphonylsulphenamide.* S.S-Ethyl. phenyl N-p-toluene-sulphonylsulphilimine (0·02 mole) was heated under reflux in toluene (50 ml) for 3 hr and the solvent was removed off under reduced pressure. The residue was recrystallised 3 times from EtOH-water yielding the sulphenamide. m.p. 113·5–115° (3·4 g). IR spectrum : v_{NH} 3255. v_sSO_2 1165. $v_{as}SO_2$ 1300 cm^{-1}; NMR spectrum : CH$_3$ 2·38(s). NH 6·85(s)ppm in CDCl$_3$. (Found : C. 55·78 : H. 4·70 : N. 4·98. Calcd. for C$_{13}$H$_{13}$NO$_2$S$_2$: C. 55 91 ; H. 4 66 ; N. 5·02 %).

The sulphenamide (1·5 g) was heated in dil NaOH aq at 100° for 5 hr and then acidified with H$_2$SO$_4$ and extracted with chloroform. The chloroform layer was washed with water. dried over MgSO$_4$ and concentrated. The residue after silicagel chromatography, yielded p-tolylsulphonamide, thiophenol and diphenyl disulphide (thiophenol 0·07 g. diphenyl disulphide 0·2 g. p-tolylsylphonamide 0·8 g).

Kinetic procedure of the pyrolysis of various N-p-toluenesulphonylsulphilimines

The kinetic experiments of all the aryl ethyl derivatives were carried out by following the change of absorbance of the UV spectra of unreacted sulphilimines separated from the mixture. A typical run was as follows.

The ampoules were flushed with dry N$_2$ and 2 ml of the benzene or DMSO solution of sulphilimines (0·01 or 0·02 mole/l) was added to each tube which was subsequently sealed. The tubes were placed in a constant temp bath at around 60–100°. and taken out at time intervals. The tubes were opened, the contents completely transferred by washing with 3 ml benzene 3 times into a separating funnel containing cold 1N NaOH (15 ml) and benzene (12 ml). The water-layer containing sulphenamide was removed and the benzene-layer was washed with 7 ml water 3 times. The benzene layer was dried over a constant weight of MgSO$_4$ and reduced to dryness carefully and dry air was passed through for 5 min. The residue was dissolved in pure MeOH and transferred quantitatively to a 25 ml volumetric flask. The MeOH soln was diluted to a suitable volume and the UV spectrum was taken.

The rate constant was obtained by the following equation.

$$k = 1/t \ln Co/C = 1/t \ln Ao/A$$

where k; the first-order rate constant (sec^{-1})

Co and C; the concentrations of unreacted sulphilimines at $t = 0$ and after t seconds respectively.

Ao and A; the absorbances at max of unreacted sulphilimines at $t = 0$ after t seconds respectively.

The typical kinetic run for ethyl phenyl-N-p-toluenesulphonylsulphilimine is given below.

Ph—S—CH$_2$CH$_3$
| 0·01 mole/l in benzene at 80·3 ± 0·05°
NTs
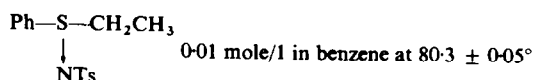
time (sec)	A	in (Ao/A)	k (sec^{-1})
0	0·681	—	—
1·50 × 10^4	0·576	0·167	1·11 × 10^{-5}
3·75 × 10^4	0·443	0·427	1·14
7.15 × 10^4	0·328	0·729	1·02
8·28 × 10^4	0·279	0·893	1·08

average $(1·09 \pm 0·04) \times 10^{-5}$

The pyrolysis of sec-butyl-phenyl-N-p-toluenesulphonylsulphilimine

S.S-sec-butyl. phenyl-sulphilimine was heated in a sealed tube without solvent or in benzene or DMSO soln at 115–120° or 160–170° for several hr. The tube was cooled and scratched with a file. While the top of this ampoule and the tube leading into bromine-water were bound with a rubber tube. the top of the ampoule was opened and the contents transferred into bromine-water to convert the olefins to the corresponding dibromoolefins. These were obtained by first extracting with ether. washing with cold dilute NaOH aq containing $Na_2S_2O_3$, then water and dried over $MgSO_4$ and final removal of ether.

REFERENCES

* Sulfilimines and Sulfoximine Part IX. Part VIII. S. Oae. M. Nakai. N. Furakawa and R. Kiritani. *Bull. Chem. Soc. Japan* submitted
[1a] K. Tsujihara. N. Furukawa and S. Oae. *Bull. Chem. Soc. Japan* **43**. 2153 (1970);
   [b] A. Kucsman. I. Kaporits. F. Ruff. *Acta Chem. Acad. Sci. Hung.* **40**. 75 (1964);
   [c] A. Kucsman. I. Kaporits. F. Ruff. *Tetrahedron* **22**. 1515 (1966)
[2] D. J. Cram. J. Day. D. R. Rayner. D. M. von Schriltz. D. J. Buchamp and D. C. Garwood. *J. Am. Chem. Soc.* **92**. 7369 (1970)
[3a] A. C. Cope. T. T. Footer and P. H. Towie. *Ibid.* **71**. 3929 (1944);
   [b] A. C. Cope and E. R. Trumbull. *Organic Reactions* Vol. 11. 361 (1960)
[4] D. J. Cram. M. R. V. Sahyun. and G. R. Knox. *J. Am. Chem. Soc.* **84**. 1734 (1962)
[5] C. A. Kingsbury. and D. J. Cram. *Ibid.* **82**. 1810 (1960)
[6a] D. W. Emerson. A. P. Craig. and I. W. Potts. *J. Org. Chem.* **32**. 102 (1967);
   [b] J. L. Kice and J. D. Campbells. *Ibid.* **32**. 1631 (1967);
   [c] J. R. Shelton. and K. E. Davis. *J. Am. Chem. Soc.* **89**. 718 (1967)
[7] S. Oae. K. Tsujihara and N. Furukawa *Tetrahedron Letters.* 2663 (1970)
[8] C. H. DePuy. and C. A. Bishop. *Ibid.* 239 (1963)
[9] P. Nylen. Tijdschr. K. Bergvesen. *Chem. Abstr.* **32**. 888 (1900)
[10] K. K. Andersen. W. H. Edmonds. L. B. Biasotti and R. A. Strecker. *J. Org. Chem.* **31**. 2859 (1966)
[11] S. Oae. K. Tsujihara and N. Furukawa. *Chem. & Ind.* 1569 (1968)
[12] A. Carn. G. J. Palenile. E. Goldish. and J. Donohue. *Acta. Crystr.* **17**. 102 (1964)
[13] R. Thomas. C. B. Shoemaker. and C. Eriks. *Ibid.* **21**. 12 (1966)
[14] A. Kalman. *Ibid.* **22**. 501 (1967)
[15] S. Neidle. and D. Rogers. *J. Chem. Soc.* 694 (1970)
[16a] H. C. Brown and O. H. Wheeler. *J. Am. Chem. Soc.* **78**. 2199 (1956);
   [b] H. C. Brown. I. Moritani. M. Nakagawa. *Ibid.* **78**. 2190. 2197. 2203 (1956)
[17] K. Tsujihara. N. Furukawa. K. Oae and S. Oae. *Bull. Chem. Soc. Japan* **42**. 2631 (1969)