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The Elimination Reaction of N-Sulfonylsulfilimine

S. Oae, K. Tsujihara and N. Furukawa
Faculty of Engineering Osaka City University, Sumiyoshiku, Osaka, Japan

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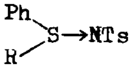
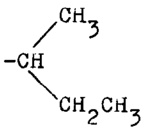
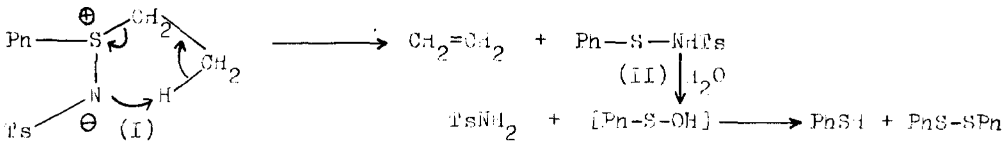
Like the pyrolysis of t-amine oxides which is known as Cope reaction[1)] sulfoxides with a β hydrogen are also known to undergo cis-elimination upon pyrolysis.[2)] Meanwhile, our spectroscopic study suggests that sulfur-nitrogen bond of N-sulfonylsulfilimines is of dipolar nature more so than sulfur-oxygen bond of sulfoxides[3)]. Accordingly, N-sulfonylsulfilimines with a β hydrogen are expected to undergo a similar and perhaps facile cis-elimination reaction like t-amine oxides and sulfoxides. In fact, we have found that when N-sulfonylsulfilimines were heated at 100 ~ 130°C for several hours under nitrogen stream olefins were produced in a relatively high yields.

The results obtained are listed in Table I.

Table I. The Pyrolysis of N-p-tolylsulfonylsulfilimines 

R	mp(°C)	temp(°C)	time(hours)	olefin	yield(%)
$-CH_2CH_3$	98.5—99	120—130	2	$CH_2=CH_2$	70
$-CH(CH_3)_2$	115—116	120—130	2	$CH_3CH=CH_2$	80
$-C(CH_3)_3$	101(decomp)	100—110	2	$(CH_3)_2C=CH_2$	85
 $-CH(CH_3)CH_2CH_3$	85—86	120—130	2	$CH_2=CH-CH_2CH_3$	48
				$CH_3-CH=CH-CH_3$	32
$-CH_2CH_2Ph$	137—138	120—130	2	$Ph-CH=CH_2$	60

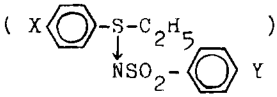
Among these olefins, styrene was actually isolated and identified from IR and GLC, and the other olefins were converted to the dibromides which were identified and determined by comparing the GLC behavior with those of the authentic dibromoolefins. When ethyl phenyl-N-p-tolylsulfonylsulfilimine (I) was heated in refluxing toluene for 2 hours ethylene was produced. From the residue, phenyl-N-p-tolylsulfonylsulfeneamide (II) was actually isolated in 60 % yield. The sulfeneamide (II), m.p. 113-115°C, gives the characteristic infrared spectra (ν N-H 3255, νs SO_2 1165, νas SO_2 1300 cm^{-1}) and the satisfactory analysis of carbon, hydrogen, and nitrogen. Furthermore, hydrolysis of sulfeneamide (II) gives p-tolylsulfoneamide, thiophenol and diphenyl disulfide.



The rates of elimination reaction of several ethyl aryl-N-sulfonylsulfilimines were measured in benzene and dimethyl sulfoxide as solvent. The reaction follows good first-order kinetics. The results obtained are listed in Table II. The rate of elimination reaction in benzene is about six times larger than that in DMSO. This may be due to that N-sulfonylsulfilimine having dipolar sulfur-nitrogen bond would tend to assume more readily the cyclic configuration in a non-polar solvent such as benzene than in a dipolar solvent, DMSO, which would solvate the compound by intermolecular dipolar interaction. This would be supported by larger entropies of activation in benzene ($\Delta S^{\ddagger}= +1.2$ esu) than that in DMSO ($\Delta S^{\ddagger}= -6.8$ esu).

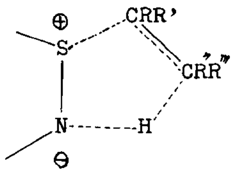
The effect of substituents on the phenyl rings attached to the S(IV) atom and S(VI) atom are shown in Fig 1. A plot of log k vs σ value gives straight lines with slops of +0.88 ($\rho x=0.88$) and -0.60 ($\rho Y=-0.60$) respectively. The kinetic isotope effect of β-hydrogens of ethyl group in ethyl-phenyl-N-p-tolylsulfonylsulfilimine is 3.03 in benzene solution.

Table II. Rates of the elimination reaction of N-sulfonylsulfilimines

()

X	Y	mp(°C)	temp(°C)	solvent	$k(sec^{-1})$
H	CH_3	98.5 — 99	80.3	benzene	1.08×10^{-5}
			60.3	"	0.108
			100.5	"	9.85
			80.3	DMSO	0.185
			60.3	"	0.0186
			90.3	"	0.449
CH_3	CH_3	89 — 90	80.3	benzene	0.708
CH_3O	CH_3	95.5 — 96.5	80.3	"	0.483
Br	CH_3	113.5 — 114.5	80.3	"	1.68
NO_2	CH_3	118 — 119	80.3	"	4.89
H	H	50 — 51	80.3	"	0.906
H	Br	108.5 — 109	80.3	"	0.628
$Ph\text{-}\underset{\underset{NTs}{\downarrow}}{S}\text{-}CH_2CD_3$		98 — 99	80.3	"	0.356
$p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}C_2H_5$		b5 142 — 143	80.3	"	$< 10^{-8}$
$p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{NH}{\downarrow}}{S}}\text{-}C_2H_5$		42 — 43	80.3	"	$< 10^{-8}$

These results indicate that the pyrolysis reaction of N-sulfonylsulfilimines is best represented by the cyclic internal concerted mechanism.



This internal cyclic elimination of N-sulfonylsulfilimines proceeds much more readily than the corresponding sulfoxides and sulfoximines. (See Table II)
The detailed accounts of this and further studies of this reaction will be reported soon from these laboratories.

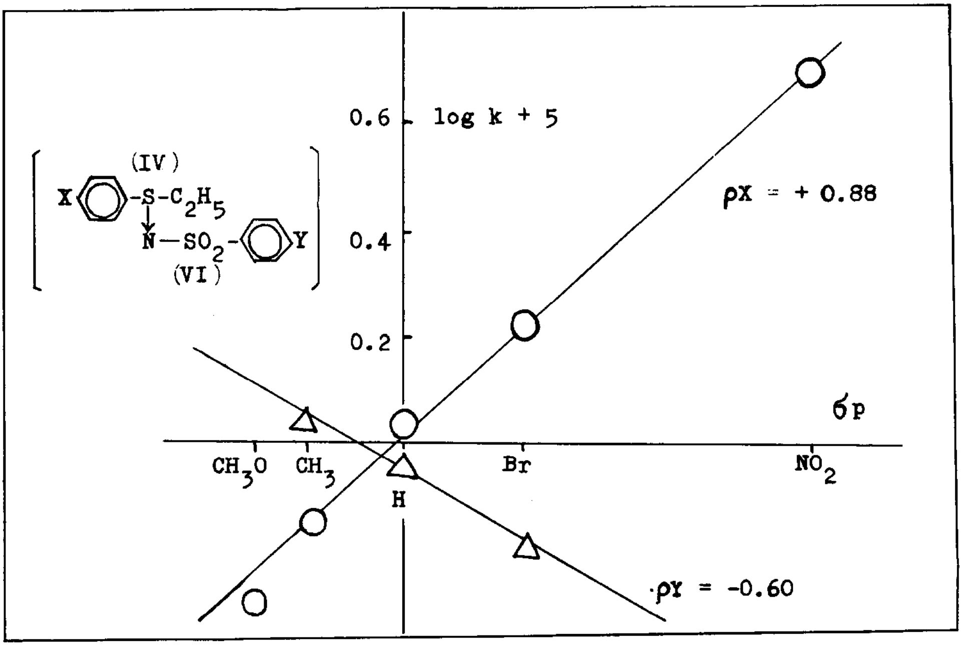


Fig 1. The substituent effects in the phenyl rings attached to the S(IV) atom and S (VI) atom in N-sulfonylsulfilimines.

○ : in the phenyl ring attached to the S(IV) atom

△ : in the phenyl ring attached to the S(VI) atom (at 80.3°C, 0.01 mol/l in benzene)

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