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The Facile Thermal Racemization of Optically Active Aryl Methyl Sulfilimines.

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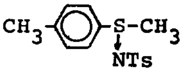
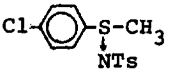
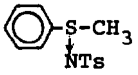
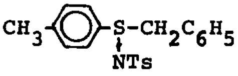
In the pyrolysis of threo-S-phenyl-S-1,1-diphenyl-2-methoxyethyl-N-p-tosylsulfilimine the olefine isolated was not found to be 100% cis but contained 5.5% trans isomer$^{1)}$. This stereochemical result appears to suggest the possibility of thermal racemization of the sulfilimine at either S atom or C atom or both during the reaction.

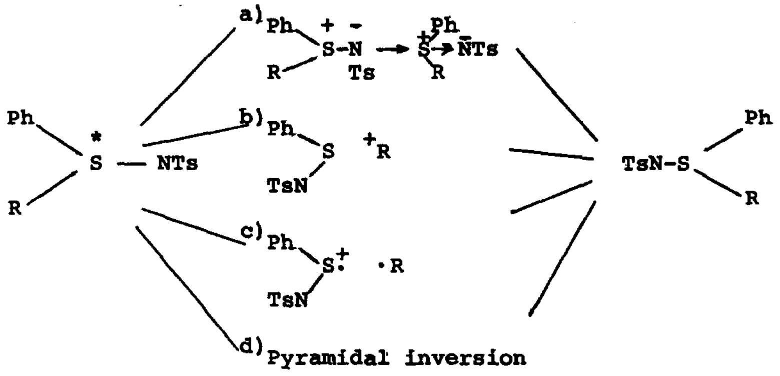
In order to examine the possibility of the thermal racemization of sulfilimines, several optically active aryl methyl sulfilimines were prepared and subjected to heating in a few solvents. Actually these sulfilimines were found to undergo an extremely facile thermal racemization upon heating. Therefore, we wish to report briefly the results of this facile racemization reaction and discuss its plausible mechanism. Optically active N-p-tosyl aryl methyl and benzyl p-tolyl sulfilimines were prepared from the corresponding active sulfoxide and N-sulfinyl p-tosyl amide in pyridine at 0°C according to the method by Day and Cram.$^{2)}$ The optically active products were identified by comparing their i.r. and n.m.r. spectra with those of the racemic compounds. The optical activity was measured with semi-automatic polarimeter (Yanagimoto OR-10). The racemization reaction was carried out by dissolving the sulfilimine in benzene, chloroform or ethanol in the temperature range of 90-120°C. The rate of racemization was followed polarimetrically and found to obey the first order rate equation. The first order rate constant k_{α} was obtained though the concentration of the sulfilimine was changed. T.L.C. i.r., n.m.r. spectra of the products indicated that the product was completely identical to that of the starting sulfilimine except the optical activity. The results obtained are summarized in Table I.

Table I. The rate constant (k_{α}) for the thermal racemization of sulfilimine

Sulfilimine	$[\alpha]_D$	m.p.	Reaction temp., (°C)	solvent	$k_{\alpha} \times 10^5 (sec^{-1})$
	-320° (C:1.6 acetone)	125 ~ 125.5	100	Benzene	7.08±0.14
			100	Chloroform	19.1±0.3
			100	Ethanol	6.47±0.06
 a)	-270° (C:1.6 acetone)	132.5 ~ 133.0	90	Benzene	1.81±0.06
			98	"	4.58±0.09
			100	"	5.30±0.01
			110	"	15.0±0.1
			100	Ethanol	5.55±0.07
	-64° (C:1.6 acetone)	125.5 ~ 126.6	100	Ethanol	8.82±0.08
	158.4° (C:1.0 acetone)	148.0 ~ 148.5	120	Benzene	60.0±3.0

a) Activation parameters were determined. $\Delta H^{\ddagger}$=27.9 Kcal/mole, $\Delta S^{\ddagger}$=-3.6 e.u.

From the results shown in the Table, the following characteristic features may be deduced: 1) Unimolecularity of the reaction; 2) No solvent polarity dependence; 3) No Hammett correlation with p-substituents; namely the rate sequence is H$>$P-$CH_3$$>$ P-Cl; 4) benzyl p-tolyl sulfilimine reacts nearly at a same rate as aryl methyl sulfilimine though the racemization of the benzyl phenyl sulfoxide is much faster than the aryl methyl sulfoxide.[3] The following few processes may be conceivable for the racemization.



The one via route a) can be ruled out since the kinetic data reveals that the rate depends only on the sulfilimine. Both routes b) and c) that involve the initial C-S bond fission, suggested earlier in the case of Ei reaction, can also be eliminated since the reaction did not depend on solvent polarity while there is no Hammett correlation between the rate and substituent effect. Moreover, if homolytic C-S or C-N bond fission would take place, the product distribution should be different from that of this experiment. However, the product identified after the reaction is only the original sulfilimine. Thus, free radical fission of C-S or C-N bond can be ruled out. The remaining and probably the only plausible one seems to be the pyramidal inversion d) which is known to be very sluggish in the thermal racemization of sulfoxide3) but facile with sulfonium salt4) or sulfonium ylide5). When the rate of the reaction is compared with that of a similar sulfoxide or a sulfonium salt, the ease of the racemization falls in the following sequence, sulfonium salt $\gg$ sulfilimine $\gg$ sulfoxide and the relative rate between these compounds is 10^{12}; 10^{7}; 1 (calculated roughly from the extraporated rates of 1-adamanthyl ethyl methyl sulfonium salt, methyl p-tolyl sulfilimine, and methyl p-tolyl sulfoxide respectively).

This enormous rate difference between the above three compounds can not be interpreted by the bond force constant of S-X linkage since no bond cleavage is involved in any of these three systems. Another possibility would be the difference of the abilities in forming intermolecular interaction such as dimerization[6] which arises from the semipolar nature of S-X bond. Then the sulfoxides should have the strongest interaction among these compounds and hence the pyramidal inversion would be retarded most. However the difference in molecular associations could not be so large as those for found in the activation energy. Therefore, this idea can not explain the difference. The other possibility is based on difference in the stabilities of the ground state pyramidal structures of these compounds due to the 2p-3d π bond formation by both donation from the electronegative X atom and the coulombic interaction between S(IV) and X. Then the sulfoxide oxygen has the highest electron density and hence would form the strongest 2p-3d π bond and its pyramidal structure would be stabilized most. Meanwhile the lone electron pair on the nitrogen atom of the sulfilimine would be pulled away by the sulfonyl group and hence the 2p-3d π bond of S-N group in the sulfilimine should be substancially weaker than S-O linkage, thus the pyramidal structure of the sulfilimine should not be as stable as that of the sulfoxide. Meanwhile the sulfonium compound can not form such a p-d π bond between S(IV) and C atom therefore the pyramidal structure should not be so stable. This last possibility may be the only compatible explanation for the difference in the case of racemization of these three trivalent sulfur compounds.

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