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THERMAL RACEMIZATION OF VARIOUS S-o-ANISYL S-PHENYL N-(SUBSTITUTED)SULFILIMINES

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Small electronic effects were discernible for rates of thermal racemization of various S-o-anisyl S-phenyl N-(substituted)-sulfilimines. The rate was retarded by the electron-withdrawing group on the nitrogen atom. A correlation was found further between the rate and the streching frequency (υ_{S-N}).

We reported earlier that optically active N-p-tosylsulfilimines undergo thermal racemization through pyramidal inversion. In comparing the rate of racemization of the sulfilimine with those of the analogous sulfoxide and sulfonium salt, one finds that these rates fall in the following sequence, i.e., sulfonium salt $\gg$ sulfilimine $\gg$ sulfoxide, approximately in the order of 10^{12}, 10^{7} and 1, respectively.[1] Also, Darwish and Tomilson found that S-ethyl S-methyl sulfonium phenacylide racemizes about 200 times faster than the corresponding sulfonium perchlorate.[2] These enormous rate differences among the above typical trivalent sulfur compounds each bearing a semi-polar linkage have been interpreted on the basis of the following three factors, i.e., (a) 2p-3dπ bond formation, (b) lone pair - lone pair electrons repulsion, and (c) electronegativity.[1-5] We have investigated the thermal racemization of various S-o-anisyl S-phenyl N-(substituted)-sulfilimines in order to understand the nature of various factors which effect the pyramidal inversion of the trivalent sulfur compound.[6]

Rates of racemization were measured at the temperature range 65-85°C by a polarimeter (Yanagimoto OR-10). The cell containing the 0.06-0.18 M solution was sealed after replacing air with dry nitrogen. All of the polarimetric rate constants

were of cleanly first order over a period of one to three half-lives. Except for the specific rotation, the product was completely identical to the starting sulfilimine, which was confirmed by TLC, IR and NMR analyses. The results are collected in Table.

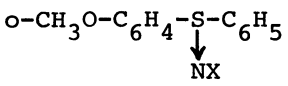
Since our experiments provide no evidence for carbon-sulfur and nitrogen-sulfur bond cleavages, the thermal racemization of these sulfilimines is considered to proceed by pyramidal inversion.[7)]

Electronic effects of the substituents on the nitrogen atom are small but quite noticeable and fall in the following order, p-CH_3O > p-CH_3 > p-H > p-Cl for p-(substituted)benzenesulfonylsulfilimines and $CH(CH_3)_2$ > CH_3 > C_6H_5 > CF_3 for N-acylsulfilimines. Log $k_{racemization}$ values of these N-sulfonyl and N-acyl derivatives were nicely correlated with σ and σ^* values, and small negative ρ and ρ^* (-0.31 and -0.22) values were obtained respectively. Namely, the electron-withdrawing group on the nitrogen atom retards the rate of pyramidal inversion.

The electron-withdrawing substituent on the nitrogen atom should reduce 2p-3dπ bond formation (a) of S-N bond which is formed by back donation from the nitrogen atom, and lone pair - lone pair electrons repulsion (b) between sulfur and oxygen at the transition state, because the electron density on the nitrogen atom is reduced by the electron-withdrawing substituent. Since both these effects reduce the energy barrier for the pyramidal inversion, they cannot account for all the observed substituent effects. Thus, the electronegativity effect (c) seems to be plausible. Namely, s character of the sp^3 lone pair electrons of the sulfur atom of the sulfilimine should be increased by such an electron-withdrawing(electronegative) substituent as p-Cl, and hence the pyramidal structure would be stabilized more.[8)] These subtituent effects are probably the first example to reveal the trivial but pronounced effect of the electronegativity on the pyramidal stability of the trivalent sulfur compounds.[9)] Since the difference of electronegativity due to the inductive effect of the substituent on the nitrogen atom of the sulfilimine is too small in comparison with that of the different atoms attached directly to the sulfur atom, the small difference of the rates due to the substituent on the nitrogen atom is quite rational.

We examined further a possible correlation between the pyramidal inversion and the S-N bond charater. Interestingly, inspection of the results reveals that

Table. First Order Rate Constants of Thermal Racemization of S-o-Anisyl S-Phenyl N-(Substituted)sulfilimines at 75°C[a)]



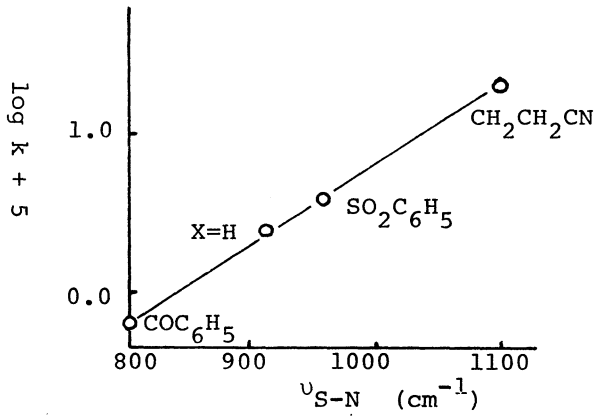
X	$[\alpha]_D^{25}$	T(°C)	$kx10^5(sec^{-1})$	k/k_H[b)]	υ_{S-N} (CCl_4)
H (1)	-61.3	75	2.2 ±0.03	1.0	907
CH_2CH_2CN (2)	-135	75	19.8 ±0.5	8.9	1091
$SO_2C_6H_5$ (3)	-77.2	75	3.61 ±0.04	1.6	950
COC_6H_5 (4)	-76	75	0.545±0.008	0.24	799[c)]
$SO_2C_6H_4CH_3$-p (5)	-94.8	75	3.72 ±0.05	1.7	964[c)]
$SO_2C_6H_4Cl$-p (6)	-73.8	75	3.06 ±0.05	1.4	963[c)]
$SO_2C_6H_4OCH_3$-p (7)	-32	75	4.38 ±0.10	2.0	957[c)]
$COCH_3$ (8)	-74	75	1.08 ±0.01	0.49	-[d)]
$COCH(CH_3)_2$ (9)	-145	75	1.21 ±0.05	0.54	-[d)]
$COCF_3$ (10)	-61.3	75	0.246±0.004	0.11	-[d)]

a) Rate constants were measured in 0.060 M chloroform solution.

b) Relative rate, X=H at 75°C as the standard.

c) Determined with KBr disks. d) Could not be assigned.

a decrease in frequency of infrared spectrum corresponds to decrease of the rate of the pyramidal inversion.[10)] It is demonstrated more clearly by plotting the rate constant (log k) against the streching frequency (υ_{S-N}) as shown in Figure.



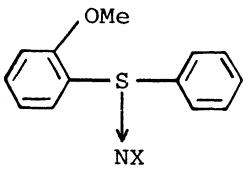


Figure. Correlation of rate constant with streching frequency.

Thus, the equation derived from the straight line shown in Figure, $\log k = 0.00547\ \upsilon_{S-N} - 9.63$, can predict the S-N streching frequency from the rate constant for racemization of other N-(substituted)sulfilimines, and vice versa.

References

1) N. Furukawa, K. Harada, and S. Oae, Tetrahedron Lett., 1972, 1377.

2) D. Darwish and R. L. Tomilson, J. Amer. Chem. Soc., 90, 5838(1968).

3) B. C. Menon and D. Darwish, Tetrahedron Lett., 1973, 4119.

4) D. Darwish and S. K. Datta, Tetrahedron, 30, 1155(1974).

5) S. J. Campbell and D. Darwish, Can. J. Chem., 52, 2953(1974).

6) The synthesis of these substances will be reported elsewhere.

7) J. B. Lambert, " Topics in Stereochemistry ", Vol. 6, ed. by N. L. Allinger and E. L. Eliel, John Wiley & Sons, Inc., New York, N. Y.(1971), p. 19.

8) C. C. Levin, J. Amer. Chem. Soc., 97, 5649(1975).

9) Mislow et al. have reported that the predominant influence upon pyramidal stability in phosphines and arsines appears to be due to the electronegativity of the ligand rather than to the conjugative effect.
R. D. Baechler and K. Mislow, J. Amer. Chem. Soc., 93, 774(1971).
R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, J. Amer. Chem. Soc., 94, 2859(1972).

10) J. A. Franz and J. C. Martin, J. Amer. Chem. Soc., 97, 583(1975).

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