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THE PREPARATION AND RACEMIZATION OF OPTICALLY ACTIVE SULFONIUM YLIDES. PART II. (+)-N-ACETYLETHYLMETHYLSULFIMIDE[1,2]

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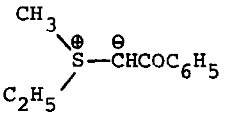
We have reported previously that the optically active ylide ethylmethylsulfonium phenacylide **1** undergoes thermal racemization, through pyramidal inversion, faster than the corresponding sulfonium salts and the sulfoxides.[1] The unexpectedly facile racemization of **1** prompted us to study the racemization of other optically active sulfonium ylides. We wish to report the preparation and racemization of the optically active N-acetylethylmethylsulfimide **2**[4] and of its protonated derivative, N-acetylaminoethylmethylsulfonium p-toluenesulfonate **3**.



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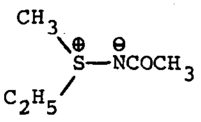

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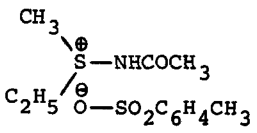

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Racemic **2** was prepared according to the method described by Kise, et al.[5] Optically active **2** $\left[[\alpha]_D^{25}+83°\text{ (c=0.42, acetone)}\right]$ was prepared by resolution of the corresponding (-)-dibenzoylhydrogen tartrate salt followed by treatment of the pure resolved salt with triethylamine in methylene chloride at 0°. The observed spectral properties of the resolved compound **2** were identical to those reported for the racemic **2**.[5] Treatment of optically pure **2** with p-toluenesulfonic acid monohydrate in acetone at 0° gave the sulfonium salt **3** [m.p. 66-67; $[\alpha]_D^{25}+4.2°$ (c=4.0, acetone); $\tau_{TMS}^{CDCl_3}$ 8.72 (t, 3H, J=7.5 Hz), 6.34 (q, 2H, J=7.5 Hz), 6.75 (s, 3H), 7.85 (s, 3H), 2.5 (q, 4H), 7.64 (s, 3H); ir. 1700, 1210, 1160 and 820 cm^{-1}].[6]

The racemization of 2 was accompanied by decomposition which resulted in the formation of N-(methylthio)acetamide.[7] The sulfonium salt 3 showed no appreciable decomposition in acetonitrile, whereas in ethanol ethyl methyl sulfoxide, ammonium p-toluenesulfonate and ethyl acetate were isolated. For a system in which the racemization is accompanied by decomposition, k_α represents the rate constant for the loss of optical activity and k_d represents the rate constant for the decomposition. The racemization rate constant, k_r, is given by $(k_\alpha - k_d)$, and in 2 and 3 racemization is assigned predominantly to pyramidal inversion.[8] The rate constants are summarized in Table I.

The activation enthalpies for racemization are 23.3 kcal for 1,[1] 34.1 kcal for 2, 29.2 kcal for 3 and 35-43 kcal for sulfoxides.[9] At 90° the racemization of 2 is ca. 10^6 times faster than the racemization of methyl p-tolyl sulfoxide, extrapolated from the data of Rayner, et al.[9] The stability of sulfoxides to racemization may be attributed to a) the greater electron repulsion between the unshared electron pairs on the sulfur and oxygen in the transition state for inversion as compared to the ground state, and b) the greater stabilization of the pyramidal ground state by p-dπ bonding than of the planar transition state. In 2, on the other hand, the lone pairs on nitrogen are delocalized by the carbonyl group,[10] leading to a weakening of the p-dπ bonding in the ground state, and consequently, to an increased rate of racemization as compared to sulfoxide. The racemization of the ylide 1 is even more facile than that of 2 in that at 90° 1 racemizes ca. 10^{11} faster than methyl p-tolyl sulfoxide, extrapolated from published data.[1,9] The facility with which 1 undergoes racemization may be explained in terms of a reduction of the electron repulsion between the lone pairs on sulfur and carbon due to rotation about the sulfur-carbon bond. Support for this explanation is provided by the fact that 3 (which is isoelectronic with 1) racemizes ca. 30 times faster than 2. In contrast, the ylide 1 racemizes ca. 200 times faster than the corresponding sulfonium salt since p-dπ bonding may stabilize the transition state for inversion in 1, but no such stabilization is possible in the case of sulfonium salt. Thus, while ylide 1 racemizes faster than the corresponding sulfonium salt and the sulfoxide, the ylide 2 is

Table I. The rate constants for the racemization of optically active 2 and 3.

Compound	Conc., M	Solvent	Temp., °C	k_α, sec^{-1}	k_d, sec^{-1}	k_r, sec^{-1}
2	0.0278	Acetonitrile	90.0	$(10.99 \pm 0.51) \times 10^{-7}$	$(5.07 \pm 0.21) \times 10^{-7}$[a]	5.92×10^{-7}
	0.0278	Acetonitrile	70.0	$(0.71 \pm 0.02) \times 10^{-7}$	$(0.35 \pm 0.02) \times 10^{-7}$	0.36×10^{-7}
	0.0408	2-Butanone	90.0	$(27.90 \pm 1.40) \times 10^{-7}$	$(15.62 \pm 1.40) \times 10^{-7}$	12.28×10^{-7}
3	0.0656	Acetonitrile	90.0	$(1.91 \pm 0.03) \times 10^{-5}$[b]	~0	1.91×10^{-5}
	0.0656	Acetonitrile	70.0	$(0.165 \pm 0.001) \times 10^{-5}$	~0	0.165×10^{-5}
	0.0328	Acetonitrile	90.0	$(1.850 \pm 0.030) \times 10^{-5}$	~0	1.850×10^{-5}
	0.0554	Ethanol	90.0	$(4.53 \pm 0.26) \times 10^{-5}$	$(1.911 \pm 0.17) \times 10^{-5}$[c]	2.620×10^{-5}

[a] k_d measured by glc and uv.

[b] Loss of optical activity measured on 2 generated from 3 by the addition of a calculated volume of 0.044 N $CH_3O^{\ominus}/CH_3OH$ solution to a measured volume of the solution from each ampoule in a given kinetic run. No racemization occurs during 3 → 2.

[c] k_d measured by glc.

intermediate between **3** and the corresponding sulfoxide.

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Notes and References

(1) Part I, D. Darwish, and R. L. Tomlinson, J. Amer. Chem. Soc., **90**, 5938 (1968).

(2) Address inquiries to K. R. Kopecky.

(3) Deceased April 15, 1973.

(4) For a related study see N. Furukawa, A. Harada and S. Oae, Tetrahedron Lett., 1377 (1972).

(5) H. Kise, G. F. Whitfield and D. Swern, J. Org. Chem., **37**, 1121 (1972).

(6) **3** gave satisfactory analysis.

(7) For a discussion of the thermolysis of sulfimides see H. Kise, G. F. Whitfield and D. Swern, J. Org. Chem., **37**, 1125 (1972).

(8) The other non-destructive process for racemization would involve the nitrogen-sulfur bond cleavage to give ethyl methyl sulfide and a nitrene, which could then reunite to give racemic **2**. This may be ruled out since neither ethyl methyl sulfide nor any of the insertion products of the nitrene was found in the reaction mixture.

(9) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordan and K. Mislow, J. Amer. Chem. Soc., **88**, 3138 (1966).

(10) The idea of lone pair delocalization is consistent with the spectral data, H. Kise, G. F. Whitfield and D. Swern, Tetrahedron Lett., 1761 (1971).