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CHEMICAL SHIFT NONEQUIVALENCE OF DIASTEREOTOPIC GROUPS IN SULFONIUM SALTS

Kiyosi Kondo and Kurt Mislow

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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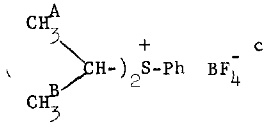
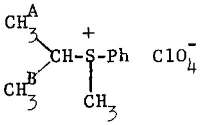
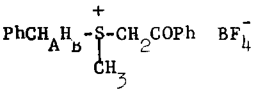
The present account is prompted by two recent communications (1,2) reporting on the detection of diastereotopic protons (3) in sulfonium ylids by n.m.r. Diastereotopic protons have previously been observed in a number of suitably substituted sulfur compounds: sulfices (4), sulfinates (5), sulfinamides (6), sulfide-borane adducts (7), and sulfoxides (7,8). Sulfonium salts are of considerable interest in current stereochemical studies (9) and in connection with our own work in this area we would like to report that simple sulfonium salts containing diastereotopic protons also exhibit the expected chemical shift nonequivalence.

Our findings are summarized in Table I. The seven sulfonium salts were prepared by the procedure (with slight modifications) of Franzen _et al_. (10); properties, yields and elemental analyses are given in Table II. As seen from inspection of Table I, the diastereotopic protons (H_A and H_B) in compounds 1-4 exhibit chemical shift nonequivalence under ordinary conditions of observation. The values of J_{AX} and J_{BX} in the isopropyl sulfonium salts 2 and 4 (X = methine proton) are the same as those reported (8) for isopropyl p-tolyl sulfoxide (J = 6.7 Hz).

The phenacyl sulfonium salts 5-7 are of special interest for they are members of the series studied by Ratts (1). Our finding that the diastereotopic methylene protons in 6 and 7 show apparent chemical shift equivalence (11) is in agreement with similar observations (1) on diethyl, di-_n_-propyl, and methyl _n_-propyl phenacyl sulfonium salts. However in 5, although the methylene protons of the benzyl group show apparent chemical shift equivalence in chloroform (singlet at τ 5.12 (1)), DMSO-d_6 (singlet at τ 5.20), and acetone-d_6 (singlet at τ 4.98), chemical shift nonequivalence is clearly manifested in solvent trifluoroacetic acid (Table I). The function of trifluoroacetic acid as a solvent medium capable of effecting the separation of signals is not yet understood, but since 5 recovered from the solution exhibits the same IR spectrum and m.p. as the original salt, and since the n.m.r. spectrum of 5 in CF_3COOD

TABLE I[a]

Compd. No.	Sulfonium Salt	Solvent	Chemical Shift (τ)	Multi-plicity[b]	Coupling Const. (Hz)
1	$(PhCH_AH_B)_2\overset{+}{S}-CH_3\ ClO_4^-$	DMSO-d_6	H_A 5.16 H_B 5.32	d d	13.0
2		DMSO-d_6	H^A 8.53 H^B 8.72	d d	6.8[d]
3	$(CH_3CH_AH_B)_2\overset{+}{S}-Ph\ \ ClO_4^-$	$CDCl_3$	H_A 6.08 H_B 6.20	m	12.5[e]
4		DMSO-d_6	H^A 8.52 H^B 8.73	d d	6.7[d]
5	 $PhCH_AH_B-\underset{CH_3}{\overset{+}{S}}-CH_2COPh\ \ BF_4^-$	CF_3COOH	H_A 5.13 H_B 5.24	d d	13.0
6	$(CH_3CH_AH_B)_2\overset{+}{S}-CH_2COPh\ \ ClO_4^-$	CF_3COOH	H_A 6.43[f] H_B	q	0
7	$(PhCH_AH_B)_2\overset{+}{S}-CH_2COPh\ \ BF_4^-$	CF_3COOH	H_A 5.21[g] H_B	s	0

a) All the spectra were measured on a Varian A-60A spectrometer using TMS as an internal standard. The concentrations of the solutions were in the range of 5-10%.

b) **d**, doublet; **m** ABX_3 multiplet; **q**,quartet; **s**, singlet.

c) Partial decomposition occurs in nitromethane as shown by the appearance of new peaks in the n.m.r. which become more intense with the passage of time. The salt is insoluble in chloroform.

d) Coupling constant between methyl and methine protons.

e) $J_{AX} \approx J_{BX} \approx 7.5$ Hz

f) Each line of the quartet is 1.7 Hz wide at half height. The τ-value refers to the center of the quartet.

g) The line width at half height is 2.0 Hz.

TABLE II

			Analyses (%)			
			Calcd.		Found	
Compd.No.	M.p. (°C)	Yield (%)	C	H	C	H
1	122	67	54.79	5.21	54.49	5.28
2	113	31	51.08	6.79	51.18	6.95
3	70	35	45.03	5.67	44.80	5.43
4	oil	53	45.03	5.67	44.84	5.82
5	131	81	55.83	4.98	55.88	5.03
6	123	23	46.68	5.55	46.67	5.54
7	149	36	62.86	5.04	62.95	5.00

is the same as that of **5** in CF_3COOH, it follows that enolization of **5** may be excluded as a source for the observed solvent effect. It is noteworthy, however, that the diastereotopic methylene protons in the phenacyl group of **5** exhibit apparent chemical shift equivalence (singlet at τ 4.90) even in trifluoroacetic acid.

The coupling constants in the sulfonium ylids are remarkably similar to those of the sulfonium salts. In ethyl or benzyl substituted compounds, the diastereotopic protons have $J_{AB} \approx$ 12-13 Hz and $J_{AX} \approx$ 7-8 Hz in all cases thus far investigated (1,2, present work).

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