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N. M. R. SPECTRA OF S-YLIDS. SULFUR BONDING AND MAGNETIC NONEQUIVALENCE

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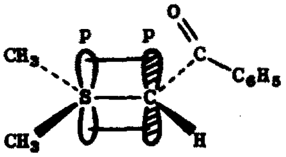
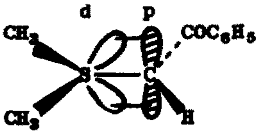
The types of structures which are associated with large values of magnetic nonequivalence of methylene protons have recently been of interest (1). In our work with sulfonium ylids we have discovered such nonequivalence, which is of surprising magnitude, in groups bonded to sulfur. These results are reported here due to the implications concerning sulfur bonding and geometry in sulfur ylids.

In a previous paper (2) concerning the N.M.R. spectra of a series of 2-(dimethylsulfuranylidene)acetophenones (I), the SCH_3 proton resonances are reported as singlets ($CDCl_3$) near τ 7.0. There is, consequently, no cis-trans isomerism involving p-p overlap which could cause restriction of rotation about the S-C bond. Such restricted rotation should give rise to two nonequivalent methyl groups (see Ia). Rapid rotation around the CH_2-$S(CH_3)_2$ bond, an alternate explanation for the equivalence, with planar or tetrahedral sulfur is ruled out due to the fact that the equivalence remains at -65°. The sulfur atom must be hybridized as it is in sulfonium salts; p^3 with an unshared electron pair in an s-orbital (3). The



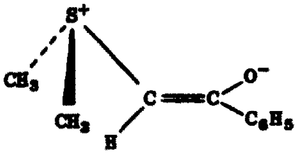
Ia

sulfur atom, which is, therefore, tetrahedral, possesses vacant d-orbitals which may overlap the adjacent filled p-orbitals (see Ib).

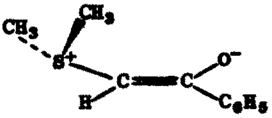


Ib

The cis alignment of the positive phosphorus and the negative oxygen atoms on a central C——C double bond (4) in P-ylids suggests the S-ylid may also prefer such geometry (Ic or Id). The nondirectional character of the 3d orbitals allows the orientation of the methyl groups so that they become equivalent.



Ic

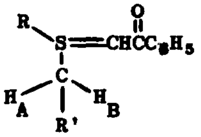


Id

The substitution of one hydrogen of the methyl groups of I introduces nonequivalence into the methylenic hydrogen atoms (H_A and H_B in II). The pattern of this nonequivalence is given in TABLE 1. The coupling constant for the nonequivalent hydrogens (J_{AB}) is 12 cps (1,5). The coupling constant for adjacent protons (J_{AX}) is 7 cps as expected. The chemical shift difference (ν_A - ν_B) is quite large (6) and variable with the structure.

TABLE 1

N.M.R. Spectra of Sulfonium Ylids ($CDCl_3$)



Example	R	R'	$\nu_A - \nu_B$ (cps)	J_{AB} (cps)	J_{AX} (cps)[c]
1.	CH_3[a]	H[a]	0	0	0
2.	C_2H_5	CH_3	56	12	7
3.	n-C_3H_7	C_2H_5	65	12	7
4.	C_6H_5[b]	H[a]	0	0	0
5.	CH_3[a]	C_2H_5	57	12	7
6.	CH_3[a]	C_6H_5	32	12	0

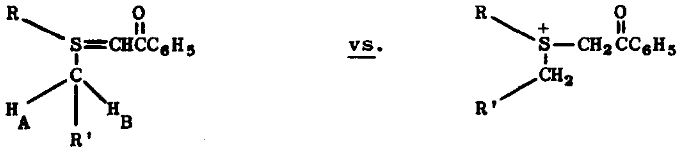
a) The methyl group appears as a singlet. b) H. Nozaki, K. Kondo and M. Takaku, Tetrahedron Letters 251 (1965).
c) J_{AX} = J_{BX} = coupling constants due to adjacent protons.

The nonequivalence is a consequence of the asymmetry or long-lived dissymmetry evident when molecule is observed along the methylenic carbon-sulfur bond (CH_AH_B-S in II). This is apparent since in cases where one methyl group is present (Examples 4,5 and 6, TABLE 1) it appears as a singlet while the same pattern of nonequivalence is observed in the other group attached to sulfur (Examples 5 and 6, TABLE 1).

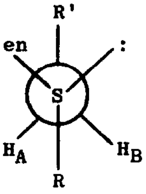
The nonequivalence is likely due to the enolate system $(\overset{\ominus}{C}H{=}\overset{O}{C}C_6H_5)$ in II because the corresponding salts do not exhibit such differences. The observed differences in the ylids is a shift of one proton to much higher field compared to the protons in the salt, consistent with greatly increased shielding of one proton (H_A) of the ylid (see TABLE 2).

TABLE 2

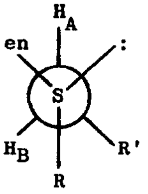
Comparison of Methylene Protons
in Salts and Ylids ($CDCl_3$)
(τ values given for center of multiplets)



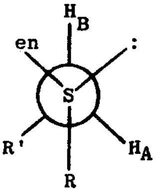
R	R'	Ylid		Salt(RCH_2S^+)
		H_A	H_B	
C_2H_5	CH_3	7.27	6.33	6.18
n-C_3H_7	C_2H_5	7.32	6.23	6.15
CH_3	C_2H_5	7.25	6.35	6.20
CH_3	C_6H_5	5.66	5.15	5.12



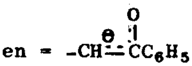
IIa



IIb



IIc



en = $-\overset{\ominus}{C}H\text{=}\overset{O}{C}C_6H_5$

The observed variations in the chemical shift differences between H_A and H_B can be explained assuming that $\tau(H_A) \gg \tau(H_B)$ in conformer IIa and $\tau(H_A) = \tau(H_B)$ in conformer IIb, i.e., the difference is primarily due to the increased shielding of H_A in IIa. Since IIc possesses maximum steric interactions the percent contribution of this conformer to the total chemical shift of H_A and H_B may be small. The differences in the chemical shifts ($\nu_A - \nu_B$) may result from the effect of the steric interactions upon the weighting of conformers IIa and IIb.

The chemical shift difference is markedly affected by solvent whereas the coupling constants are unchanged (see TABLE 3).

TABLE 3

Chemical Shift Difference of Methylene Protons of $(CH_3CH_2)_2S\text{-}CHCOC_6H_5$ as a Function of Solvent

Solvent	$\nu_A - \nu_B$ (cps)[a]	Solvent[b] dielectric constant
Carbon tetrachloride	71	2.24
Benzene	90	2.28
Diethyl ether	70	4.33
Chloroform	60	5.05
Chlorobenzene	79	5.94
Pyridine	59	12.5
Acetone	50	21.4
Nitrobenzene	56	36.1
N,N-Dimethylformamide	39	36.7
Acetonitrile	37	38.8
Dimethylsulfoxide	33	48.9

a) J_{AB} is 12 cps and J_{AX} is 7 cps in all cases. b) "Handbook of Chemistry and Physics", 44th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

The nonequivalence of the geminal protons decreases generally with increasing solvent polarity. The variance of the chemical shift indicates that solvent plays an important role in determining the magnitude of the nonequivalence. This qualitatively agrees with the observations of Roberts et. al. (7) that dielectric constant is inversely related to the degree of magnetic nonequivalence.

The compounds were prepared by the procedure previously described. Compounds 2, 3 and 5 are slightly unstable oils characterized by NMR and IR spectra and as the hydrobromide salts. Compounds 1, 4 and 6 are solids, characterized by spectra and correct microanalyses.

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