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CARBON-13 NMR SPECTROSCOPY OF SULFONIUM YLIDES

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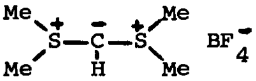
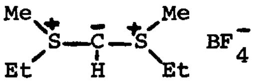
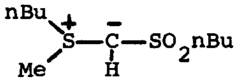
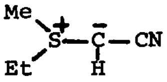
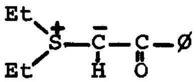
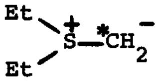
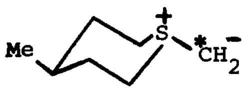
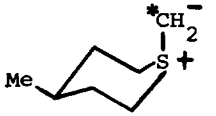
C-13 NMR data for a series of stabilized and unstabilized ylides indicate flattening at the ylidic carbon with respect to the parent salts. For unstabilized ylides association between the carbanionic center and the lithium cation cannot be neglected.

Sulfonium ylides are the intermediates in the H/D base-catalysed exchange[1] and in the methylation[2] of sulfonium salts, both reactions being often highly stereoselective. The results of the exchange reaction have been explained on the basis of a pyramidal ylidic carbon and this interpretation is supported by *ab initio* calculations[1b]. The results of the methylation reaction may be accounted for either by a planar or by a pyramidal ylidic carbon[2]. Direct experimental evidence on the structure of sulfonium ylides appears to be a necessary step to elucidate the factors determining the stereoselectivity of these reactions, in analogy with what has been done for other sulfur compounds[3]. To our knowledge only a few proton[4] and carbon-13[5] NMR data on stabilized sulfonium ylides (i.e. bearing electron-withdrawing groups attached to the ylidic carbon) have been reported. On the contrary an abundance of data exists on phosphonium ylides, for which experimental[6,7] and theoretical[7] evidence indicates a pyramidal and a planar geometry at phosphorus and carbon respectively.

We present here the C-13 parameters (δ, $^1J_{CH}$) of the carbanionic carbon for a series of stabilized (1-5) and unstabilized (6-8) sulfonium ylides, which indicate that the ylidic carbon is more flattened (if not planar) than in the corresponding salts. Compounds 1-5 are either known compounds or were prepared according to established procedures[8]. Compounds 6-8 were obtained directly in the NMR tube at -70°C by treatment of the salts in THF-d_8 with $LiCHCl_2$(1.2 eq.)[9]. After recording the spectra the starting salts were regenerated by quenching with CH_3OH; decomposition was less than 20%. Spectra were recorded on a Varian FT-80 spectrometer at probe temperature (25±2°C) for 1-5 and at -70°C for 6-8. J's are in Hz and δ's are in ppm with respect to CD_3CN or THF-d_8. The accuracy is

± 1 Hz for J and ± 0.2 ppm for δ .

TABLE

Compound	n°	Solvent	δ	Δ δ	J	Δ J
	1	CD_3CN	20.1	- 30.6	190	+ 32
			(51.3)[a]		(158)[a]	
	2	CD_3CN	15.0	- 32.7	196	+ 36
			(47.7)		(160)	
	3	CD_3CN	35.6	- 22.3	177	+ 22
			(57.9)		(155)	
	4	CD_3CN	4.3	- 23.8	189	+ 33
			(28.1)		(156)	
	5	CD_3CN	47.7	- 3	177	+ 31
			(50.7)		(146)	
	6	THF-d_8	- 2.6	- 22.4	158	+ 12
			(19.8)		(146)	
		[b]THF-d_8/HMPA	- 3.9	- 23.7	164	+ 18
	7	THF-d_8	6.3	- 18.0	153	+ 7
			(24.3)		(146)	
		[b]THF-d_8/HMPA	5.2	- 19.1	159	+ 13
	8	THF-d_8	- 4.5	- 20.9	158	+ 12
			(16.4)		(146)	
		[b]THF-d_8/HMPA	- 5.3	- 21.7	159	+ 13

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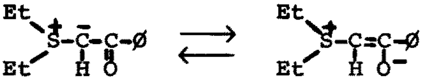
* 90% Carbon-13 enriched

a) values in parentheses are those of the parent salts

b) 3 equivalents with respect to the added lithium base (~8% v/v)

Deprotonation of the sulfonium salts leads to a large shielding of the involved carbon in all but one case (5) and to a large increment in the one-bond carbon-hydrogen coupling constant. The same trend is observed for phosphonium ylides, for which, however, both effects are generally smaller[6,7]. The large shielding effects ($\Delta\delta = \delta_{ylide} - \delta_{salt}$) observed for 1-8 can be safely related to the increment of the negative charge on the ylidic carbon[10a]. The small $\Delta\delta$ value (-3 ppm) observed for compound 5 is in agreement with this interpretation, since it is generally admitted that phenacylic ylides exist largely in the enol form (b), with the negative charge on the oxygen atom[4].



5a 5b

The negative charge on the ylidic carbon should lead to a decrease of $^1J_{CH}$[10b], contrary to what is observed. According to current approximations, the magnitude of $^1J_{CH}$ depends also on the mean excitation energy of the molecule and on the s character of the C-H bond[10b]. Although the relative importance of the factors affecting the coupling constant is difficult to evaluate, it is reasonable to ascribe, at least in part, the significant increase of the $^1J_{CH}$ values of compounds 1-8 to a larger % of s character of the C-H bond, resulting in flattening at the carbanionic carbon. The same explanation has been proposed for phosphonium ylides[6,7] and α-metallated sulfur derivatives[3b]. It is to be noted that the ΔJ values for compounds 6-8 are similar to those reported for α-lithiosulfoxides[3b]. Whatever the explanation may be, this finding is interesting insofar as a close parallelism also exists in the stereochemistry of methylation of cyclic sulfoxides and sulfonium salts[2b]. The different values of ΔJ's reported in the Table could be explained by different degrees of flattening at the ylidic carbon in the various substrates. Although we favour this interpretation for compound 3, for compounds 6-8 the possibility of association of the carbanionic center with the lithium cation, which in phosphonium ylides leads to a smaller $^1J_{CH}$ (i.e. $Ø_3PCH_2$= 153 Hz, $Ø_3PCH_2Li$ = 133 Hz)[7a], can't be neglected. This hypothesis is supported by the sizeable enhancement of $^1J_{CH}$, following the addition of HMPA (Li^+ solvating agent), for compounds 6 and 7. The data for 7 and 8, different J's in THF and the same J in THF/HMPA, suggest that steric factors play a role in these anion-cation interactions. Since these interactions may be important in the stereoselectivity of the reactions with electrophiles[11], work is in progress in this direction, as well as on the general aspects of the geometry of sulfonium ylides.

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