

*Journal of Organometallic Chemistry*, 111 (1976) C17—C20  
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### Preliminary communication

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## STRUCTURE OF SULFUR-STABILIZED CARBANIONS. A $^{13}\text{C}$ NMR STUDY OF SOME $\alpha$ -LITHIO-SULFOXIDES AND SULFONES

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(Received February 15th, 1976)

### Summary

$^{13}\text{C}$  chemical shifts and  $^1J(^{13}\text{C}-\text{H})$  coupling constants provide information on the structures of some  $\alpha$ -lithio-sulfoxides and sulfones.

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Carbanions  $\alpha$  to sulfur are important intermediates in organic synthesis and have interesting stereochemical properties [1], but their structure is still a matter of controversy [1a, 1b, 2]\*\*. We have studied the lithium salts of sulfur-stabilized carbanions by  $^{13}\text{C}$  NMR spectroscopy, this technique having been successful in the study of compounds raising related questions, such as arylmethylolithium [3] or phosphorous ylids [4]. We report below our mutual results for some simple representative sulfoxides and sulfones.

### Results

The main features of the spectra are shown in Table 1 along with some literature data included for comparison.

#### $^1J(^{13}\text{C}-\text{H})$ coupling constant of the metalated carbon

$^1J(^{13}\text{C}-\text{H})$  coupling constants, which are highly sensitive to the hybridization state and to the electron density on the carbon atom, have been widely used for investigating the structure of carbanionic species. For every lithio derivative we have studied, this coupling constant is always higher than in the starting compound. This is due to a change in the hybridization state, since a charge increase

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\*\*We recently reported an  $^1\text{H}$  NMR study of the  $\alpha$ -lithio derivatives of the two 4-t-butylthiacyclohexane oxides [2]. The determination of  $\alpha,\beta$  vicinal coupling constants in these cyclic anachomeric molecules was expected to solve the problem of the pyramidal or planar configuration of the metalated  $\alpha$ -carbon. The observed  $^3J$  values did not allow a definite conclusion, but showed that the possibility of a planar structure had to be considered for  $\alpha$ -lithio sulfoxides.

TABLE 1

CHEMICAL SHIFTS AND  $^1J(^{13}\text{C}-\text{H})$  OF THE METALATED CARBON IN ORGANOLITHIUM COMPOUNDS AND THE SHIFT AND COUPLING CONSTANT DIFFERENCES ( $\Delta\delta, \Delta J$ ) WITH THE PARENT STARTING COMPOUND<sup>a</sup>

	$\delta(\text{C-Li})^b$	$\Delta\delta^c$	$^1J(^{13}\text{CHLi})$	$\Delta^1J$	$\delta(\text{C(1)})^b$	$\Delta\delta(\text{C(1)})^c$	$\delta(\text{C(4)})^b$	$\Delta\delta(\text{C(4)})^c$
I PhCHLiSOCH <sub>3</sub>	67.4	+6.7	160	+20	148.7	+16.7	113.2	-15.0
II PhCHLiSO <sub>2</sub> CH <sub>3</sub>	59.8	-1.9	163	+23	144.8	+13.9	114.9	-14.4
III PhCHLiSO- <i>t</i> -Bu	55.8	+2.2	161	+23	150.3	+23.1	111.7	-16.4
IV PhCHLiSO <sub>2</sub> - <i>t</i> -Bu	51.1	-2.1	160	+21	145.9	+19.1	114.7	-17.3
V <i>t</i> -BuSOCH <sub>2</sub> Li	19.5	-12.9	147.5	+10	—	—	—	—
VI <i>t</i> -BuSO <sub>2</sub> CH <sub>2</sub> Li	21.1	-13.5	142	+4	—	—	—	—
VII CH <sub>2</sub> Li [3b] <sup>e</sup>	-16.3	-13.0	98	-27	—	—	—	—
VIII PhCH <sub>2</sub> Li [3a,d] <sup>e</sup>	30.7	+9.4	132	+7	116.4	+22.5	104.2	-21.6
IX Ph <sub>2</sub> CHLi [3a,d] <sup>e</sup>	76.8	+34.4	141	+15	147.3	+5.4	107.3	-19.1
X (CH <sub>2</sub> ) <sub>3</sub> P=CH <sub>2</sub> <sup>d,e</sup>	-2.3	-21.2	149	+20	—	—	—	—

<sup>a</sup>The  $\alpha$  lithio derivatives are prepared in a 4/1 mixture THF/C<sub>6</sub>D<sub>6</sub> (c 0.8 mol/l) by the previously described technique [2]. The spectra were run at 20 MHz on a Varian CF1 20 spectrometer using THF (C<sub>6</sub> 68.1 ppm/TMS C $\beta$  26 ppm/TMS) as an internal standard. After the spectra had been recorded, the lithio derivatives were quenched with ICH<sub>3</sub> and the only reaction to occur was quantitative methylation. <sup>b</sup>In ppm from TMS, <sup>c</sup> $\Delta\delta$ : > 0 = downfield shift; < 0 = upfield shift. <sup>d</sup> $\Delta\delta$  and  $\Delta^1J$  with respect to the CH<sub>2</sub> of the same molecule. <sup>e</sup>Solvent: THF.

induces a decrease of  $J(^{13}\text{C}-\text{H})$ . In  $\text{CH}_3\text{Li}$ , which can be considered as a model for a pyramidal lithiated carbon\*,  $^1J(^{13}\text{C}-\text{H})$  is 27 Hz smaller than in  $\text{CH}_4$ , in spite of the large degree of covalent character of the C—Li bond [3].

In the benzylic derivatives (I—IV) values of  $^1J$  are almost the same for sulfoxides and sulfones and are very high, consistent with a nearly planar configuration: the  $\Delta^1J$  value is greater than in IX, for which a primarily  $sp^2$  hybridization of the benzylic carbon is assumed [3], and is the same as that observed in X, for which the planar configuration of the methylenic carbon has been established\*\* [4]. But X is a neutral, salt-free species, and it has been shown [4c] that in the presence of lithium salts, coordination with  $\text{Li}^+$  decreases the coupling constant. Hence, a very loose C...Li bond must be assumed in I, II, III and IV. Speculation on the nature of this bond on the basis of these data is risky, but participation of the  $\pi$  cloud of the phenyl ring, as it was found in arylmethylolithiums and fluorenyllithium [9] must be considered. In these four lithio derivatives, an important delocalization of the charge in the aromatic ring is shown by the strong shielding of the *para* carbon of the phenyl group\*\*\*.

In the dialkyl compounds V and VI, the  $\Delta^1J$  values are smaller but still too high for an  $sp^3$  carbon. A hybridization state intermediate between  $sp^2$  and  $sp^3$  as proposed for benzyllithium VIII [3], is the most probable. It is difficult to decide whether the decreased  $sp^2$  character is due to the intrinsic nature of the carbanionic species or to a more covalent C—Li bond or to both. In contrast with the previous examples, a significant difference between the sulfoxide V and the sulfone VI is observed. It may be tentatively explained by a stronger S→O...Li chelation and thus a looser C...Li interaction in the sulfoxide.

### $^{13}\text{C}$ chemical shifts

In the dialkyl compounds V and VI, the metalated carbon is shielded by about 13 ppm with respect to the starting compound. This shielding, as high as in  $\text{CH}_3\text{Li}$  (VII), is consistent with a high electron density on this carbon. In the benzylic derivatives, this carbon is either slightly shielded in the sulfones II and IV, or slightly deshielded in the sulfoxides I and III, whereas it is strongly deshielded in compound VIII. But as  $^{13}\text{C}$  chemical shifts have a complex origin, a thorough interpretation of these values requires other data, thus the ylidic carbon of X is also shielded in spite of its assumed  $sp^2$  hybridization.

On the basis of theoretical work [1b] it has generally been assumed in the last ten years that lithium salts of carbanions  $\alpha$  to sulfoxides are pyramidal even in a benzylic position [1]. The experimental results we report here do not support this assumption.

Further work is in progress to obtain more information on the relation between the structure of sulfoxides and sulfones and the properties of their lithio derivatives. Influences of solvent, cation and external salt, are also being studied. Other classes of carbanions are under investigation.

\*For ethyllithium [5] and cyclohexyllithium [6], the metalated carbon has been shown to be pyramidal in the crystal.

\*\*This carbon is planar, as shown by the X-ray structure of  $\text{Ph}_3\text{P}=\text{CH}_2$  [7], for which  $^1J(^{13}\text{C}-\text{H})$  is about the same as in  $(\text{CH}_3)_3\text{P}=\text{CH}_2$  [4c]. On the other hand, an ylidic structure with a tetrahedral methylenic carbon was recently postulated for  $(\text{CH}_3)_3\text{As}=\text{CH}_2$  on the basis of  $J(^{13}\text{C}-\text{H})$  values of 133.8 and 130.9 Hz for  $\text{CH}_3$  and  $\text{CH}_2$ , respectively [8].

\*\*\*The *ortho* and *meta* carbons are not yet identified. The *para* carbon has been assigned by its relative  $T_1$ .

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