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^{1}H NMR STUDY OF THE STRUCTURE OF α-LITHIO SULFOXIDES

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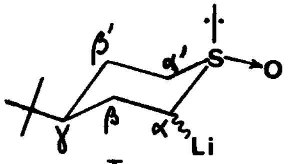
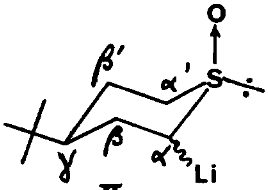
The origin of the stereoselectivity of electrophilic α substitutions of sulfoxides and the structure of the α-sulfinyl anion have been the subject of much discussion and controversy (I-5). The results have generally been interpreted by the hypothesis of a pyramidal α carbon, according to the ab initio calculations of S. WOLFE and coll. (6). However, no direct experimental evidence concerning the structure of these anions is available. For this reason, we have examined the structure of the α lithio sulfoxides I and II by ^{1}H NMR. These models have been selected since we have extensively studied the stereochemistry of deuteration and methylation of these compounds (3a) and of their α,α' dimethylated homologues (3b). The main advantage of these substrates compared with the benzylalkylsulfoxides studied by the groups of T. DURST (I), M. NISHIO (2) and J. F. BIELLMANN (4), is that they present no conformational ambiguity. Furthermore, in these compounds hybridisation of the metalated carbon is not perturbed by an aromatic ring.

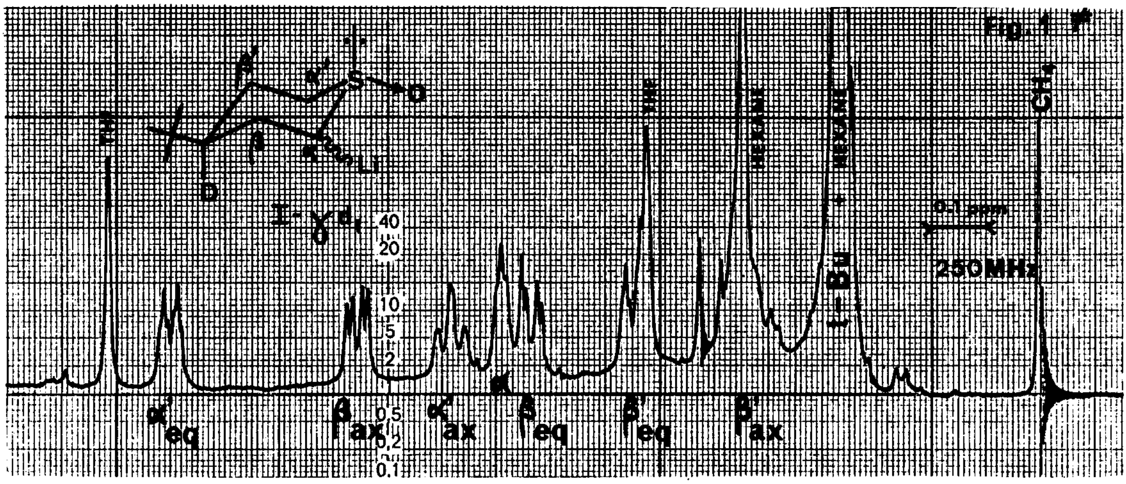


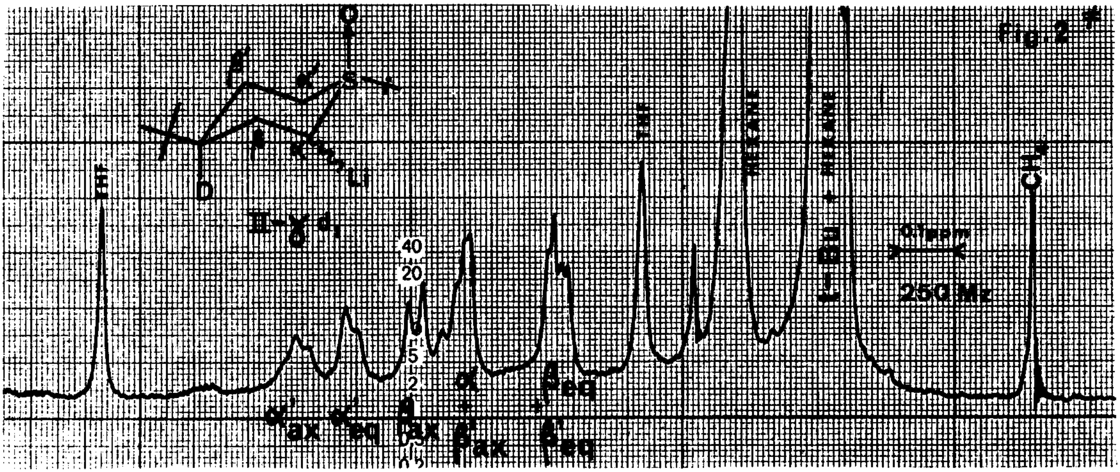
I



II

The lithio derivatives I and II have been generated in the NMR tube, using CH_3Li-THF-d_8(1, 1eq) at -78° under argon. They are stable enough for the spectra to be run at room temperature (Fig. I and 2). Integration and spin decoupling show the presence of a monolithio species. Assignments are based on examination of the coupling constants.





≠ These spectra were obtained on a CAMECA spectrometer (C.E.N. Grenoble. Laboratory of Pr. P. SERVOZ-GAVIN) with the assistance of MM. A. ROUSSEAU and H. REUTENAUER whom we wish to acknowledge sincerely.
After the spectra had been recorded, the lithio derivatives were always quenched with ICH_3 and the only reaction occurring was a quantitative methylation. (The lithio derivatives themselves start to decompose after 3-4 h at 30°). The analysis of the spectra of I and II, at IOO and 250 MHz, will be discussed in the full paper and the experimental procedure will be given.

In order to facilitate the analysis, we have synthesized (I-γd_1) and (II-γd_1) in which the separation of the $\{\alpha\beta\}$ and $\{\alpha'\beta'\}$ systems greatly simplifies the spectra. We have also prepared (I-β, $\beta' d_4$) and (II-β, $\beta' d_4$) to check independently some assignments resulting from selective spin-decoupling.

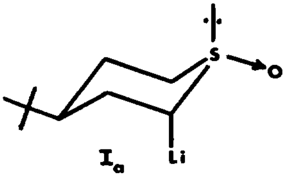
For (I-γd_1), only one large coupling (I3.9 Hz) is observed for the $\{\alpha\ \beta\}$ moiety, which is necessarily the geminal coupling between the two β protons. $^3J_{H_\alpha\ H_{\beta ax}}$ and $^3J_{H_\alpha H_{\beta eq}}$ are 5.4 and 4.5 Hz respectively.

For (II-γd_1), Hβax also shows only one large coupling constant which is again necessarily the geminal coupling with Hβeq. $^3J_{H\alpha H\beta ax}$ and $^3J_{H\alpha H\beta eq}$ are certainly smaller than 5 Hz.

Spectra were obtained at temperatures ranging from -40° to +50°. We observed neither important variations in the chemical shifts, nor modifications of the multiplet structures as the temperature was decreased, but only a continuous broadening of the peaks (compared with the sharp signal of CH_4 taken as an internal reference). Such a broadening was also observed when the polarity of the solvent was increased (pure THF or mixtures of THF with cyclohexane, benzène, toluene or pyridine).

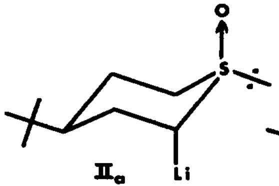
The results may be explained by postulating either a pyramidal or a planar metalated carbon :

If the carbon is pyramidal, the values of the αβ couplings≠ and the absence of a significant temperature effect÷ are consistent either with structures Ia and IIa, or with the equilibria Ia⇄ Ie, IIa⇄ IIe, highly shifted towards Ia and IIa.

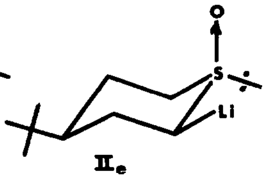


I_a

I_e

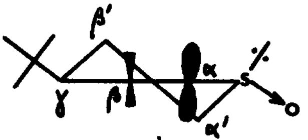


II_a

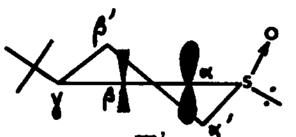


II_e

If the carbon is planar, the values are compatible with the "half-chair" conformations I' and II' where Hα approximately bissects the angle between the β protons.



I'



II'

The αβ couplings exclude the "chair" conformations with a planar Cα where H α and Hβeq are nearly eclipsed, since this should give a large ^3J value very different from ^3J between Hα and Hβax where the dihedral angle is approximately 120°.

Some of the data are difficult to explain with the hypothesis of a pyramidal carbon :

- the α protons on the lithiated carbon are less shielded, with respect to H α of the starting sulfoxides, than in simple alkyl lithium compounds°° .

≠ Ie and IIe should show a $^3J_{\alpha_{ax}\beta_{ax}}$ of about 15 Hz (7).

÷ The broadening of the lines and the small variations may be due to a solvation equilibrium (intimate ion pairs ⇄ solvent separated ion pairs) and to equilibria between polymeric aggregates (8).

°° δ/TMS (ppm) :

lithiosulfoxides (THF,30°) : H α(I) = 1,90 ; H α(II) = 1,99 ; Ph $SO\underline{CH_2}Li$ = 1,95

starting sulfoxides ($CDCl_3$,30°) : I { Hαeq = 3,36 ; Hαax = 2,53 } II { Hαeq = 3,0 ; Hαax = 2,3 } Ph $SO\underline{CH_3}$ = 2,64

C_3H_7-$\underline{CH_2}Li$ (THF,-70°) = -1,1

R-$\underline{CH_3}$ (CCl_4) ~ 0,9 (11)

Menthyl Li : >$\underline{CH}Li$ =-1,0 (Et_2O) (10)

Methylcyclohexane : >$\underline{CH_2}$ = 1,54 (CCl_4) (11)

- the H_β appear at similar fields in I an II while they are very different in the original sulfoxides, due to the "syn-axial effect" (3a). This may reflect an important ring deformation.

- $^2J_{\alpha' ax \alpha' eq}$ is the same for I and II (12.4-12.5 Hz) whereas for an axial sulfoxide it is always 14.5-15 Hz (9).

We consider that these data are not sufficient to completely exclude the possibility of pyramidal structures Ia and IIa and hope that a ^{13}C NMR study will allow a definite conclusion. We only note here that the possibility of a planar metalated α carbon must be strongly considered (this should also be true, a fortiori, for benzylalkylsulfoxides).

It is possible, according to this hypothesis, to propose consistent interpretations of our results, e.g. methylation always trans to the S → 0 bond (3). On the other hand, it is difficult to explain our results with the hypothesis of a pyramidal carbon e.g. the predominant occurence of species Ia and IIa. Indeed, methylation of II -exclusively axially- would reflect the stereochemistry of the stable lithio derivative whereas the opposite would hold for the equatorial derivative : equatorial methylation occurs very selectively whereas the lithio species Ie is, if present, the minor species. We shall discuss these problems in a forthcoming paper.

We also wish to point out that these results concerning α - lithio sulfoxides may not be valid for other organometallic derivatives and, a fortiori, are not necessarily useful in the discussions of the stereochemistry of H/D exchanges in protic media.

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