

ON THE NATURE AND GEOMETRY OF THE YLIDIC INTERMEDIATES IN THE METHYLATION OF SIX-MEMBERED RING  
SULFONIUM SALTS

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*<sup>13</sup>C N M R. data indicate that different types of intermediates are generated by deprotonation of sulfonium salts with lithium bases viz almost 'free' or 'tight ion-pair' ylids, with different geometries at the carbanionic carbon*

The methylation of six-membered ring sulfonium cations, 1-p-tolyllithium and cis and trans 1-thioniabicyclo[4.4.0]decane, is highly stereospecific<sup>1a,b</sup>.

The origin of this high stereoselectivity is still a matter for debate. To answer this question it is necessary to know the nature of the intermediate, whether it is a 'free' sulfonium ylid or a lithiosulfonium salt<sup>2</sup>, with a particular regard to the geometry of the carbanionic carbon<sup>1,2</sup>.

To obtain direct experimental evidence for the intermediate species, ylids 1, 2 and 3 were prepared in an N.M.R. tube by  $\alpha$ -proton abstraction from the PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> salts with LDA (1.2 equivalents with respect to the starting salt), in THF-d<sub>8</sub> at -78°C, and the <sup>13</sup>C spectra run at 50.3 MHz (Varian XL-200).

It is well known that  $\delta$  and <sup>1</sup>J<sub>CH</sub> give information about the geometry of the carbanionic centers with a reasonable degree of approximation<sup>3</sup> and that their dependency on the presence of lithium coordinating agents is related to the existence of C<sup>-</sup>,Li<sup>+</sup> ion-pairing phenomena<sup>4</sup>, which in turn may play a role in the stereochemistry of the electrophilic attack<sup>5</sup>.

The relevant N.M.R. parameters  $\delta$  (ppm, with respect to TMS) and <sup>1</sup>J<sub>CH</sub> (Hz) of the carbanionic carbon of ylids 1, 2 and 3 (0.15 molar solutions) are reported in the following table. The  $\delta$  and <sup>1</sup>J<sub>CH</sub> values of the corresponding carbon in the parent salts are given in parentheses.

The linewidth of all lines of ylid 1 at -78°C is 3-5 Hz. For  $\alpha$ -lithiosulfoxides in THF a large line broadening and the appearance of more than one line for the carbanionic carbon were observed at low temperature and ascribed to the existence of slowly exchanging aggregates<sup>3b</sup>. The sharp signals observed for 1 may be due either to the exchange among aggregates being fast even at temperatures as low as -78°C, which seems unlikely, or to the ylid existing as a monomer. Moreover the sharpness of the <sup>13</sup>C resonance indicates either the lack of <sup>13</sup>C, <sup>7</sup>Li coupling or that <sup>1</sup>J<sub>C,Li</sub> is very small. <sup>1</sup>J<sub>C,Li</sub> values of 40-45 Hz for several lithiocarbenoids<sup>6a</sup> and of 14.5 Hz for tetrameric methylolithium<sup>6b</sup> have been found experimentally, whereas theoretical calculations

indicate a value of over 200 Hz for monomeric  $\text{CH}_3\text{Li}^{6\text{c}}$ . Thus we take our experimental results as evidence for the lack of such coupling in 1. The large shielding, with respect to the parent salt, of the ylidic carbon of 1 (31.8 ppm) is related to the increment of negative charge on this center following deprotonation<sup>7a</sup>. According to current approximations<sup>8,3b</sup>, the large increase of the  $^1J_{\text{CH}}$  value for the ylidic carbon (27 Hz) can be ascribed, at least in part, to a larger % of s character of the C-H bond in the ylid with respect to the parent salt. The very large value of  $^1J_{\text{CH}}$  (175Hz) is typical of an  $\text{sp}^2$  hybridised carbon and indicates that the carbanionic carbon in 1 is nearly planar<sup>7b</sup>. No change of  $\delta$  and  $^1J_{\text{CH}}$  is observed upon addition of 2 equivalents of HMPA<sup>4,8</sup>, a strong solvating agent for  $\text{Li}^+$ . This result indicates that, in THF, a very weak interaction exists between the carbanionic carbon and the lithium cation. Hence,

TABLE

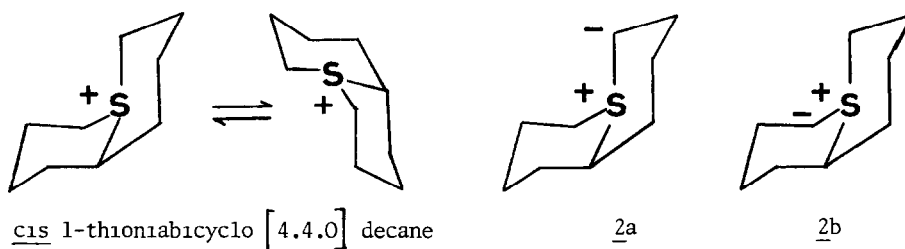
	<u>1</u>		<u>2</u>		<u>3</u>	<u>4</u>	
	THF	THF, HMPA <sup>(a)</sup>	THF	THF, HMPA <sup>(a)</sup>	THF	THF	THF, HMPA <sup>(a)</sup>
$\delta_{\text{C}^-}$	9.1 (40.9)	9.1	17.6 (29.7 or 34.2)	17.3	22+26 (39.4)	12.4 (25.1)	11.9
$^1J_{\text{C}^-\text{H}}$	175 (148)	175	153 (148)	180		150 (146)	162

(a) 2 equivalents with respect to LDA, \*90%  $^{13}\text{C}$  enriched

contrary to what has been recently proposed<sup>2</sup>, 1 is closer to a 'free' ylid than to a lithio-sulfonium salt. It could be argued, however, that in this substrate the lithium cation is preferentially associated with the aryl substituent on sulfur through lithium-arene  $\pi$  coordination<sup>9</sup>, but this is unlikely since no change of the  $^{13}\text{C}$  parameters of the aromatic portion of the spectrum is observed upon addition of HMPA.

Because of the rapid chair $\rightleftharpoons$ chair interconversion, five lines are observed in the  $^{13}\text{C}$  spectrum of the cis 1-thioniabicyclo[4.4.0]decane salt in THF at room temperature, the one belonging to C-2 and C-9 occurring at 31.8 ppm. At  $-78^\circ\text{C}$  nine resonances are present, as expected for this kind of compounds when the conformational interconversion is frozen<sup>10</sup>. The resonance at 31.8 ppm is now split into two resonances at 29.7 and 34.2 ppm ( $T_{\text{coalescence}} \approx 40^\circ\text{C}$  at 20 MHz). In principle, deprotonation with LDA can occur at C-2 or C-9, giving rise to ylids 2a and/or 2b. If, as seems reasonable, 2a and 2b do not interconvert at  $-78^\circ\text{C}$ , two distinct high field<sup>8</sup> resonances (doublets in the  $^1\text{H}$  coupled spectrum) for the ylidic carbons should be present. Instead,

at  $-78^{\circ}\text{C}$  the spectrum of 2 consists of nine lines, with only one high field doublet at 17.6ppm. Thus, only one ylid, 2a or 2b is present.  $^{13}\text{C}$  N.M.R. data do not allow a safe choice between the two structures to be made. The linewidth of all resonances at  $-78^{\circ}\text{C}$  is 3-8 Hz. In this respect, the same considerations made for ylid 1 on the state of aggregation and the  $^1\text{J}_{\text{C,Li}}$  coupling hold also for ylid 2. The shielding of the ylidic carbon of 2 with respect to the parent salt (12.1 or 16.6 ppm) is large but smaller than that observed for ylid 1. The  $^1\text{J}_{\text{CH}}$  value of 153 Hz indicates that the ylidic carbon, though flattened with respect to the parent salt, is still pyramidal<sup>7b</sup>. This interpretation is supported by the very large increase of  $^1\text{J}_{\text{CH}}$  (27Hz) following addition of HMPA. It is noticeable that the final value of 180 Hz is very close to that of the ylidic carbon of 1. These findings are in agreement with the presence of a 'tight ion-pair' interaction between the carbanionic carbon and the lithium cation. Consequently, in THF, 2, can neither be considered a 'free' ylid nor a lithiosulfonium salt. When the lithium cation is removed by the coordinating agent, the ylidic carbon becomes planar. Thus, lithium induced pyramidalisation, as already observed for phosphonium ylids<sup>11a,b</sup> and 7-phenylbornyl carbanion<sup>11c</sup>, can also be assumed for 2.



Only six of the expected nine resonances are recognizable in the  $^{13}\text{C}$  spectrum of 3, the others, including the ylidic carbon, being hidden by the high field multiplet of the solvent. To prove unequivocally that the observed signals are in fact due to the expected ylid, 3 was converted into 2 by pyramidal inversion at the sulfur atom<sup>1b</sup>. The decrease of the signals due to 3 and the concomitant appearance of those belonging to 2 was followed by  $^{13}\text{C}$  N.M.R. at  $-20^{\circ}\text{C}$ . Unfortunately, due to the features of the  $^{13}\text{C}$  spectrum in THF, no  $^1\text{J}_{\text{CH}}$  value could be measured. We can only speculate that the close values of the shielding of the ylidic carbon of both systems with respect to the parent salts are an indication of similar 'anion'-'cation' interactions.

The present experimental results show that different types of intermediates are formed by deprotonation of sulfonium salts with lithium bases almost 'free' or 'tight ion-pair' ylids, with a planar and a pyramidal geometry at the carbanionic center, respectively. The existence of different types of  $\text{C}^{\ominus},\text{Li}^{\oplus}$  interactions (or bonds) in closely related sulfur  $\alpha$ -substituted organolithium compounds is well documented<sup>12</sup>. Also, it is well known that in solution phosphonium ylids are pyramidal or planar at the ylidic carbon, depending on the presence of the lithium cation<sup>11a,b</sup>. The results reported here and in reference 8 show that, in this respect, sulfonium and phosphonium ylids are quite similar. Comparison between compounds 2 and 4 (see table) indicates that in sulfonium ylids this behaviour is independent of the presence of steric constraints, which in principle should oppose planarisation of the ylidic carbon. Calculations<sup>13</sup> on the model compounds  $\text{CH}_2\text{SH}_2^{\oplus}$  and  $\text{CH}_2\text{PH}_3^{\oplus}$

indicate that in the gas phase a planar configuration of the carbanionic center is preferred in the most stable conformation. Accordingly, in all sulfonium ylids, the ylidic carbon is strongly flattened when the lithium cation is coordinated by HMPA. It has to be remarked, however, that in some cases, i.e. compound 1 here and compound 8 of reference 8, the carbanionic carbon is largely flattened even in the presence of the lithium cation, contrary to phosphonium ylids. Clearly, in these cases, the ion-pairing between  $C^-$  and  $Li^+$  and the concomitant pyramidalisation of the ylidic carbon are precluded by steric and/or stereoelectronic effects<sup>13b</sup>.

As to the origin of the stereoselectivity of the methylation reaction<sup>1</sup>, it appears that for 1, which has a planar ylidic carbon, this is due to the attack of  $CH_3I$  at the least hindered face of the molecule, i.e. trans to the aryl group, leading to the thermodynamically favoured product. For 2 and presumably for 3, where the ylidic carbon is pyramidal, the attack of the electrophile occurs most probably with retention of configuration<sup>4,14</sup>.

**Aknowledgments** We are grateful to G. Chaissaing and A. Marquet, University of Paris VI, for many helpful discussions

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(Received in UK 26 October 1981)