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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS, IX. A MOST UNUSUAL REACTION : ELECTROPHILIC ATTACK ON SULPHUR IN α-THIOCARBANIONS

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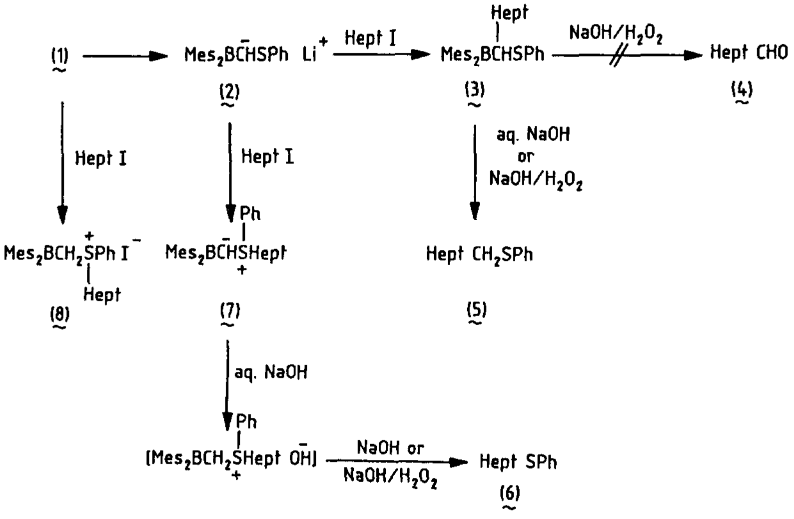
Summary: Predominant alkylation of a boron-stabilised carbanion containing an α-phenylthio group is unprecedentedly on sulphur rather than carbon. Even in lithium phenylthiomethane a similar effect can be observed, its importance being solvent dependant.

In the course of studies on the properties of boron-stabilised carbanions[1] we produced highly purified dimesitylboryl(phenylthio)methane (1) as shown in equation (1).

$$PhS.SO_2Ph + Mes_2BCH_2Li \longrightarrow \underset{(1)}{Mes_2BCH_2SPh} + LiSO_2Ph \qquad (1)$$

Using either mesityl lithium or lithium dicyclohexylamide it was possible to quantitatively convert (1) into its anion (2) (Scheme 1), which was then reacted with heptyl



Scheme 1

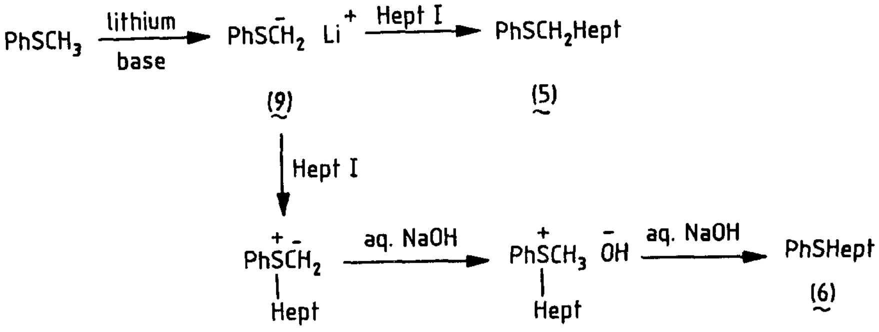
iodide in tetrahydrofuran (THF) in a reaction designed to give (3). However, alkaline hydrogen peroxide oxidation of the product gave no octanal (4) and a trace only of the hydrolysis product (5). Instead a 91% yield of heptyl phenyl sulphide (6) resulted. A similar result was obtained using simple alkaline hydrolysis, which became our standard procedure. In parallel experiments the addition of one equivalent of TMEDA, or two of cyclohexylamine had little effect, though one equivalent of HMPA did slightly raise the amount of attack on carbon.

Direct heptylation of (1) proceeded by slow attack on sulphur to give 27% of (8) in 3h, this being considerably slower than the attack on carbanion (2).

The results of reaction of (2) with benzyl iodide were similar, with sulphur attack to give benzyl phenyl sulphide predominating over attack on carbon to give phenethyl phenyl sulphide by 5:2. We therefore assume predominant attack on sulphur is general for attack by primary iodides on carbanion (2).

It appears that, in a reaction that to our knowledge has no precedent, carbanion (2) must be predominantly alkylated to give ylid (7) rather than (3). The rate of reaction at sulphur is enhanced in (2) as compared with (1) in a fashion reminiscent of the α-effect.[2] It should be noted that (2) undergoes normal boron-Wittig reactions[3] with aldehydes and ketones to give vinyl sulphides*, which reactions <u>do</u> involve electrophilic attack on the negatively charged methine group of (2).

In view of these results we studied the well known[4] thioanisole anion (9) to see whether conditions could be defined in which this intrinsically simple carbanion underwent attack on sulphur as well as carbon (Scheme 2).



Scheme 2

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* These reactions will be reported separately.

The results of our experiments, all carried out in parallel under exactly comparable conditions, are shown in the Table. We take the ratio of (5) to (6) as a minimum index of attack on carbon vs attack on sulphur.

Table

Heptylation of lithium phenylthiomethane (9)

Base	Solvent	Yield(%)[a]	6 : 5
BuLi[b]	THF	97	<0.1 : 97
	Glyme	97	1 : 96
	Ether	4	1 : 12
PhLi[b,c]	THF	90	1 : 72
	Glyme	80	1 : 3
	Ether	8	2 : 1
None	THF	0.4	-
	Glyme	0.4	-
	Ether	1.2	-

a) Yield of sulphides after alkaline hydrolysis of the product.

b) 18h period used for anion formation.

c) Mesityl lithium in THF gave 80% yield in the ratio 1:85.

In THF with butyl lithium as base, the yield is good and there is almost no attack on sulphur.[4] In glyme ca 1% of product results from sulphur attack. In ether, due to inefficient carbanion formation the yield is low, but ca 8% of it is due to attack on sulphur. With phenyl lithium the results are more striking. In glyme there is a good overall yield of sulphides of which 25% results from attack on sulphur. In ether the yield is low (only ca 10% anion formation) but 66% is due to attack on sulphur!

Benzylation of the anion (9) formed in THF using phenyl lithium as base gives product in 80% yield with the ratio of attack on carbon to attack on sulphur being 5:1.

In the heptylation study of (9) we assign the consistent differences between the use of butyl lithium and phenyl lithium to the differences in the solvent used to market these bases. The former is a solution in hexane, the latter comes either in benzene-ether (70:30) or cyclohexane-ether (70:30). In parallel experiments in glyme in the presence of the same overall proportions of ether, but slightly different amounts of hexane/cyclohexane, butyl lithium gave (5):(6) in the ratio of 1:17 (66%) and phenyl lithium in the ratio 1:6 (73%). These ratios are very much closer than those (Table) without added ether.

Two important points emerge. (i) The ratio of products is solvent dependant. (ii) The reactions of anion (**9**) are considerably faster than the parent thioanisole. Thus in glyme, (**9**) gives 20% of product derived from sulphur attack and thioanisole in the same conditions gives only 0.4%. In the case of thioanisole derived (**9**) the solvent dependency may be a function of the state of aggregation of the carbanion. However, the fact that carbanion (**2**) undergoes overwhelming and relatively solvent insensitive heptylation on sulphur points to an intrinsic factor that may be a combination of the steric effect of the large dimesitylboron group together with a smearing out of the negative charge through the boron over an aromatic ligand as well as the sulphur atom.

Calculations on charge distribution in these carbanions are in hand. In any case, we believe that this is the first time that there has been definition of electrophilic attack on a hetero-atom α to a carbanion rather than on the carbon of the carbanion.

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