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ELECTROPHILIC ASSISTANCE AND STEREOSELECTIVITY OF THE REACTIONS OF CARBANION α TO SULFOXIDE

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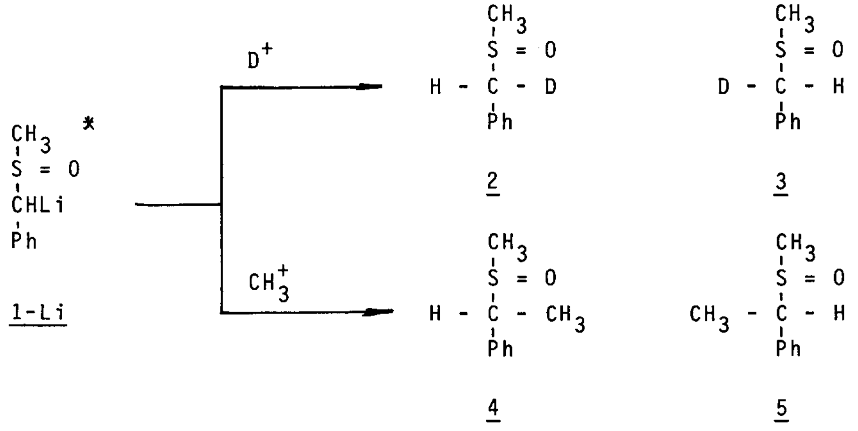
Previously we have shown that ion pairs presenting an internal chelation are to some extent responsible for the high stereoselectivity of the electrophilic reactions given by α lithiated benzyl methyl sulfoxide (1) We proposed that the reaction with methyl iodide occurs with inversion whereas there is retention with deuterium oxide (1). The deuteriolysis in the presence of lithium salts has been found to be less stereoselective. This has been attributed to a shift of the ion pair equilibrium by the common ion effect (2).

We now present evidence for the role of lithium cation on the stereochemical course of these reactions. For this purpose electrophiles (D^+ and CH_3^+) were added at -78° in THF to the carbanion(s) derived from benzyl methyl sulfoxide, except for runs 3 and 4 which were performed at 0°. The results are summarised in Table I (3).



* *racemate was used in this work*

TABLE I

Run	E^+	Diastereoisomer ratio R_D = $\underline{2}/\underline{3}$
1	D_2O or CH_3OD or CH_3COOD	1/15
2	EtOD	1/5
3	tBuOD	1/3
4	$CF_3COO^-NEt_3D^+$	1/2
5	D^+ sponge (4)	1/1
6	$LiBPh_4$ (excess) + D_2O	1/4
7	$MgCl_2$ $(D_2O)_6$	1/3
		R_{CH_3} = $\underline{4}/\underline{5}$
8	CH_3I * or $(CH_3O)_2SO_2$	19/1
9	CH_3I at 0°	5/1
10	$(CH_3O)_3PO$ at 0°	1/1.5

* *also in presence of $LiBPh_4$ (excess)*

Deuteriolysis

The stereoselectivity decreases in the order : $D_2O \sim CH_3OD \sim CH_3COOD > EtOD > LiBPh_4 + D_2O > tBuOD \sim MgCl_2(D_2O)_6 > CF_3COO^-NEt_3D^+ > D^+$ sponge (4). The values of the association constant between lithium cation and alcohols in acetonitrile at 35° follows a similar trend (5). With deuteron donor unable to associate with lithium cation (runs 4 and 5), the stereoselectivity is almost lost. In the presence of $LiBPh_4$ (run 6) or of $MgCl_2$ $(D_2O)_6$ (run 7), the stereoselectivity is low due to catalysis by cations other than that of the ion pair. Thus stereoselectivity is related to the chelation ability of the proton donor.

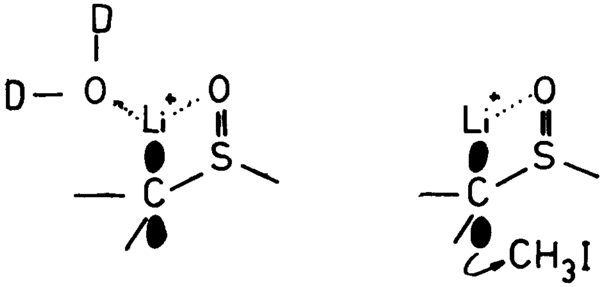
Recently the stereochemistry of the reaction of the carbanion derived from methyl benzyl sulfoxide with CO_2 and acetone has been shown to occur with the same stereochemistry as the reaction with D_2O (6). It is reasonable also to assume an electrophilic assistance for these reactions.

Methylation

If a methylating agent interacts with lithium cation prior to methylation, the reaction would occur with retention. A species like HMPT interacts strongly with the cation and the related methylating agent : trimethyl phosphate could be the desired reagent. Indeed the runs 9 and 10 show that stereoselectivity is reversed on going from methyl iodide to trimethylphosphate.

Catalysis by the cation has been found in reactions such as the protonation of an aromatic radical anion with water (7) and the fluoradenyl carbanion initiated cleavage of ethylene oxide (8).

From our results, we propose for the reaction with deuterium oxide and with methyl iodide, the following scheme :



As this carbanion α to a sulfoxide and to a phenyl group has certainly some degree of sp^2 character, we propose the following generalisation : an sp^2 carbanion <u>engaged in an ion pair</u> tends to react with retention with chelating reagent and with inversion with non chelating reagent. On the other hand an sp^3 carbanion would react with retention with all reagents. An example of the sp^3 carbanion may be the anion derived from dithiane which reacts always with the same stereochemistry (9). However the absolute configuration of the lithium species has in most of the cases not been demonstrated with required certainty.

Acknowledgement

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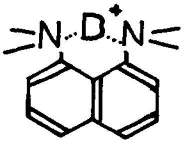
(4)  CF_3COO^- R.D. ALDER, P.S. BOWMANN, W.R.S. STEELE and D.R. WINTERMAN, *Chem. Comm.*, 723 (1968).

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