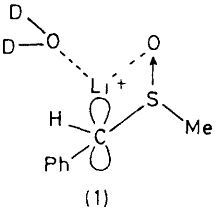
High Control of the Stereochemistry of the Reactions of Carbanions α to Sulphoxides *via* an Aluminium 'Ate' Complex

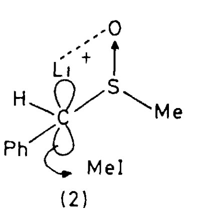
By YOSHINORI YAMAMOTO* and KAZUHIRO MARUYAMA
(*Department of Chemistry, Faculty of Science, Kyoto University, Kyoto* 606, *Japan*)

Summary The deuteriation of α-lithio benzyl methyl sulphoxide in the presence of Et_3Al occurs with inversion, while that in the absence of the additive occurs with retention, the corresponding aluminium ate' complex (**3**) is presumably involved as an intermediate

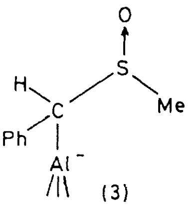
THE stereoselectivity of the reactions of α-lithio sulphoxides with electrophiles is known to depend upon the nature of the electrophile [1] For example, protonation of the lithio derivative of benzyl methyl sulphoxide occurs with retention [structure (**1**)] while methylation with MeI proceeds *via* configurational inversion at carbon [structure (**2**)] The stereochemistry of these processes can be markedly affected by the addition of macrocyclic polyethers[1e] or Li salts [1f] Unfortunately, however, complete stereochemical control is not possible with these methods, attack by protons occurs, predominantly but not exclusively, from the reverse side We report a new method in which 'reversed' stereoselectivity may be realized, in protonolysis *via* the corresponding aluminium ate complex (Scheme)



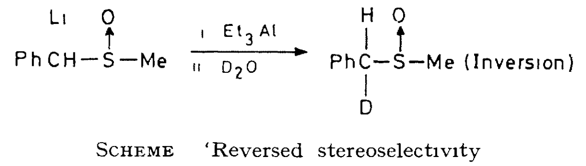
(1)



(2)



(3)



$$PhCH(Li)-\overset{O}{\overset{\uparrow}{S}}-Me \xrightarrow[\text{ii } D_2O]{\text{i } Et_3Al} PhC(H)(D)-\overset{O}{\overset{\uparrow}{S}}-Me \text{ (Inversion)}$$

SCHEME 'Reversed stereoselectivity

It has been proposed that the stereochemistry is controlled by cation–carbanion interactions and by the ability of Li^+ to form a chelate with oxygen [1h,i] Displacement of Li^+ would proceed with predominant retention of configuration when the electrophile can act as a chelating reagent (**1**), and with inversion when it cannot act in this way (**2**) This suggests that the corresponding ate complex (**3**) may be formed *via* inversion since Lewis acids such as R_3B and R_3Al cannot form a chelate with Li^+, and the protonolysis of (**3**) may proceed with retention in the same manner as most electrophilic substitutions Therefore, it was expected that protonolysis in the presence of Lewis acids would exhibit stereoselectivity in the opposite sense The results are summarized in the Table

TABLE 'Reversed stereoselectivity in the deuteriation of α-lithio benzyl methyl sulphoxide[a]

Lewis acid	Electrophile	Gegen-cation[b]	Diastereoisomer ratio,[c] % Retention (*RR/SS*)	Inversion (*RS/SR*)
None[d]	D_2O	Li	94	6
None[d]	D_2O	K	57	43
$B(OMe)_3$	D_2O	Li	43	57
Et_3B	D_2O	Li	57	43
Et_3Al	D_2O	Li	13	87
Et_3Al	D_2O	K	5	95
None[d]	MeI	Li	5	95
Et_3Al	MeI	Li	5	95

[a] Racemic benzyl methyl sulphoxide was treated with Bu^nLi in tetrahydrofuran (THF) at −70 °C The appropriate Lewis acid was subsequently added After the mixture had been stirred for a while an excess of the electrophile was added at −70 °C Et_3Al was destroyed by the slow addition of water and Et_3B by oxidation with H_2O_2–NaOH Yields of the deuteriation or methylation were generally high [b] The potassium salts were prepared by the addition of Bu^tOK to a THF solution of the corresponding lithium salt M Stahle J Hartmann and M Schlosser, *Helv Chim Acta*, 1977, **60**, 1730 [c] Determined by ^1H n m r spectroscopy [1a] [d] The normal reaction with an electrophile

Among the Lewis acids examined, Et_3Al gives the best result; deuterium attacks almost completely from the reverse side. The longer C–Al bond may exert less steric hindrance, and its greater ionic nature may facilitate electrophilic substitution. The stereochemistry of the methylation is not affected by the presence of Et_3Al, supporting the hypothesis that the ate complex formation proceeds *via* inversion and the substitution *via* retention. Irrespective of the precise mechanism, this work clearly indicates that stereochemical control of the reactions of certain carbanions may be realized through ate complexes.[2]

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[1] (a) K. Nishihata and M. Nishio, *J. Chem. Soc., Perkin Trans* 2, 1972, 1730; (b) *Tetrahedron Lett.*, 1972, 4839; (c) R. Viau and T. Durst, *J. Am. Chem. Soc.*, 1973, **95**, 1730; (d) M. B. D'Amore and J. I. Brauman, *J. Chem. Soc., Chem. Commun.*, 1973, 398; (e) J. F. Biellmann and J. J. Vicens, *Tetrahedron Lett.*, 1974, 2915; (f) T. Durst and M. Molin, *ibid.*, 1975, 63; (g) K. Nishihata and M. Nishio, *ibid.*, 1976, 1695; (h) J. F. Biellmann and J. J. Vicens, *ibid.*, 1978, 467; (i) G. Chassaing, R. Lett, and A. Marquet, *ibid.*, 1978, 471; (j) V. Cere, S. Pollicino, E. Sandri, and A. Fava, *ibid.*, 1978, 5239.

[2] Regiochemical control of the reactions of allylic carbanions may also be accomplished *via* ate complex formation: Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1979, 158; *J. Org. Chem.*, 1980, **45**, 195.