The Mechanism of the "Salt Effect" in Carbenoid Reactions

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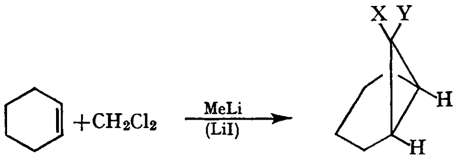
A RECENT Communication[1] concerning the mechanism of the "salt effect"[2] in carbenoid reactions prompts us to report some of our observations on the reaction of cyclohexene with methylene chloride–methyl-lithium, a known source of chlorocarbenoid.[3]

Dilling and Edamura[1] have investigated the change in the products of the reaction of cyclohexene with chlorocarbenoid depending upon which inorganic halide is present in the methyl-lithium. They have suggested that a mechanism similar to that suggested earlier by Closs and Coyle[2] for the reactions of carbenoids is most likely operative. We have repeated the Dilling and Edamura experiment with methyl-lithium from methyl iodide and, on the basis of the isolation of two new compounds and their subsequent reactions, suggest that a very different interpretation of the results must be considered.

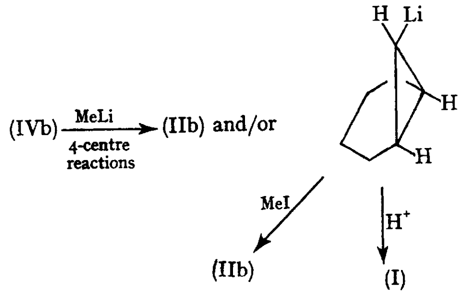
A 1·1 M-solution of methyl-lithium in ether was added over 1·5 hr. to a mixture of methylene chloride and cyclohexene at room temperature (the reagents being present in the mole ratio 1 : 2 : 4 respectively) and the yields of products, based upon methyl-lithium and the mechanism outlined in the text, were: norcarane (I), 0·9%; *cis*- and *trans*-7-methylnorcarane (IIa, b), 5·6%, 3·2%; *cis*- and *trans*-7-chloronorcarane (IIIa, b), 1·7%, 0·8%; *cis*- and *trans*-7-iodonorcarane (IVa, b), 4·6%, 2·9%; products were characterized by n.m.r. and mass spectra. The iodo-compounds, although not found by Dilling and Edamura,[1] were expected by us on the basis of the similar compounds obtained in the reaction of styrene with methylene chloride–methyl-lithium. (We shall be describing these results shortly elsewhere).



(I) X=Y=H (IIa) X=Me, Y=H (IIb) X=H, Y=Me
(IIIa) X=Cl, Y=H (IIIb) X=H, Y=Cl (IVa) X=I, Y=H
(IVb) X=H, Y=I

The following observations enable one to explain the origin of the unexpected products, (I), (IIa, b), and (IVa, b). Treatment of either of the chloro-compounds (IIIa, b) with anhydrous lithium iodide in ether does not yield the iodo-compounds (IVa, b); the iodo-compounds, therefore, must be primary products of the reaction, presumably from the addition of iodocarbenoid to cyclohexene. The methyl compounds (IIa, b) and norcarane (I) are, however, most likely *not* primary reaction products since treatment of *cis*-7-iodonorcarane (IVa) with methyl-lithium under the reaction conditions produces *cis*-7-methylnorcarane (IIa) (25%) and norcarane (I) (21%), while similar treatment of the *trans*-iodo-compound (IVb) yields the *trans*-methyl compound (IIb) (31%) and norcarane (I) (40%). It is clear that the iodo-compounds are precursors of both the methyl compounds and norcarane, although it is not certain that this is the exclusive route by which these products are obtained in the reaction of cyclohexene with methylene chloride–methyl-lithium. Finally, both of the chloro-compounds (IIIa, b) are inert to the action of methyl-lithium and, hence, are not precursors of either the methyl compounds or norcarane.

The stereospecific transformation of the iodo-compounds into the methyl compounds of retained configuration can most simply be explained by either a one-step or a two-step Wurtz reaction (illustrated for the *trans*-iodo-compound), while norcarane is undoubtedly produced by metal–halogen exchange followed by protonation. Consistent with the greater steric demands expected for the conversion of the *cis*-iodo-compound (IVa) into both (I) and (IIa) is the fact that, under identical conditions, 54% of the *cis*-iodo-compound (IVa) is recovered from the reaction with methyl-lithium in contrast to 29% recovery of the *trans*-iodo-compound (IVb).



From the above results, we suggest that the following scheme adequately explains the products formed in the reaction.

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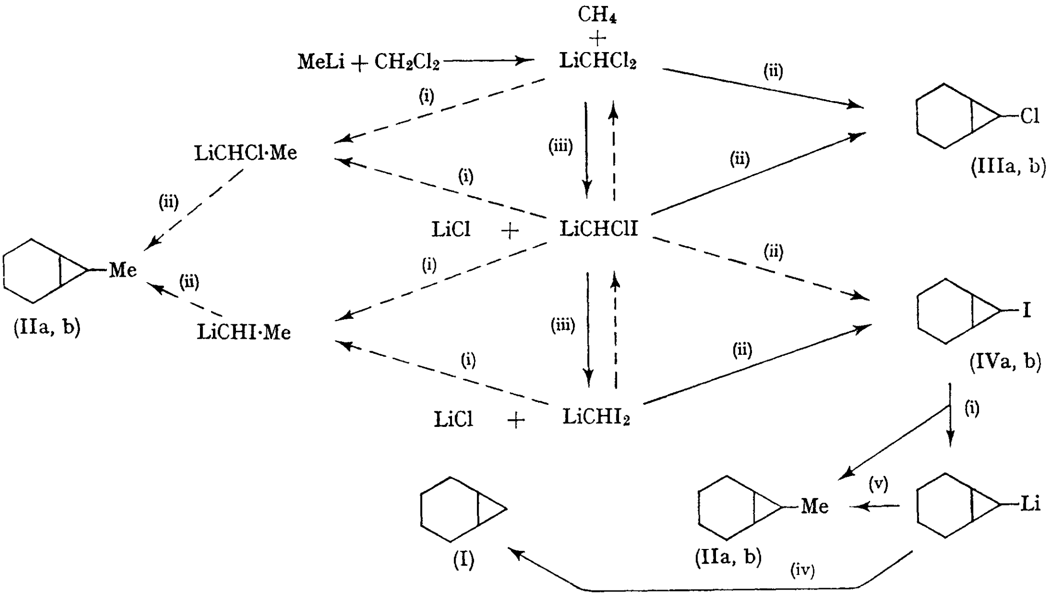

[*The broken arrows indicate reactions which may occur, but for which we have found no evidence.*] *Reagents*: (*i*) *MeLi*; (*ii*) *Cyclohexene*; (*iii*) *LiI*; (*iv*) *H*$^+$; (*v*) *MeI*.

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[1] W. L. Dilling and F. Y. Edamura, *Chem. Comm.*, 1967, 183.

[2] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 4876; G. L. Closs and J. J. Coyle, *J. Org. Chem.*, 1966, **31**, 2759; E. T. Marquis and P. D. Gardner, *Chem. Comm.*, 1966, 726; C. W. Jefford, E. H. Yen, and R. Medary, *Tetrahedron Letters*, 1966, 6317.

[3] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1960, **82**, 5723; G. L. Closs and G. M. Schwartz, *ibid.*, p. 5729.