Salt Effects in the Reaction of 7,7-Dibromonorcarane with Methyl-lithium

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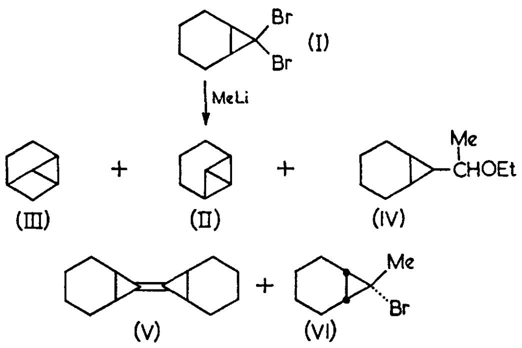
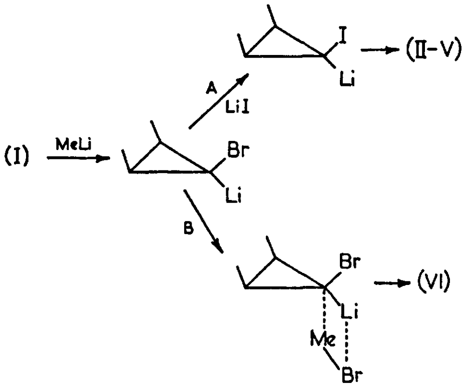
THE reaction of 7,7-dibromonorcarane (I) with methyl-lithium has been shown[1] to give (II), (III), (IV), and (V). The origin of these products is best rationalized on the basis of carbenoid behaviour of an intermediate 7-bromo-7-lithio-compound for which there is ample precedent in other systems.[2] We report here a profound salt effect on the carbenoid reactivity of this intermediate which should prove to be general. The methyl-lithium used for this reaction as originally reported[1] was prepared from lithium and methyl iodide and the solution therefore contained one mole-equivalent of lithium iodide. We have observed that the use of methyl-lithium derived from methyl chloride drastically changes the course of the reaction and gives 7-bromo-*trans*-7-methylnorcarane (VI) in yields as high as 55% (Table).[3-5] Unlike other products of the reaction, (VI) cannot be the result of a carbenoid insertion reaction as it is formed *stereospecifically* and its strain energy is greater than that





TABLE

Variation in product composition (%)

Conditions	(II) + (III)	(IV)	(V)	(VI)
−80° −0°, LiI present[1]	39	20	30	—
0°, Fwd. Addn.,* LiCl present	33	35	trace	32
−78°, Fwd. Addn., LiCl present	14	64	7	10
0°. Inv. Addn., LiCl present	27	17	trace	55

* "Fwd. addn.", addition of ethereal methyl-lithium to (I)

of the *cis*-methyl isomer. In either reaction the formation of the lithio-bromo-intermediate is accompanied by the formation of one mole-equivalent of methyl bromide. It appears that in the former case the carbenoid reactivity of the organometallic intermediate is substantially greater and its transformation into (VI) does not compete with the insertion reactions leading to (II), (III), (IV), and (V). This enhancement of carbenoid reactivity by iodide ion is best interpreted as a result of the known rapid halogen exchange reaction[2,7] of α-halogenoalkyl-lithiums to give, in this case, the 7-iodo-7-lithio-compound (Scheme A). The carbenoid reactivity of this substance would be expected to be greater than that of its bromo-analogue. The lithio-bromo-compound, on the other hand, appears to be sufficiently long-lived to react with methyl bromide in a stereospecific manner giving (VI) (Scheme B).

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[3] Methyl-lithium prepared from methyl chloride (Foote Mineral Co.) was also used in the study of 8,8-dibromobicyclo[5,1,0]octane; E. T. Marquis and P. D. Gardner, *Tetrahedron Letters*, 1966, 2793.

[4] Other examples of the incorporation of a methyl group in reactions of methyl-lithium with polyhalogeno-compounds have been observed. T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 4876; H. D. Hartzler, *ibid.*, p. 526.

[5] The n.m.r. spectrum of (VI) exhibits a very sharp singlet at τ 8·25. The stereochemistry of this substance was established in part on the basis of its easy reaction with aqueous silver nitrate (ref. 6).

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