Carbene and Carbenoid Chemistry: the Effect of Iodide Ion on Some Chlorocarbenoid Reactions[1]

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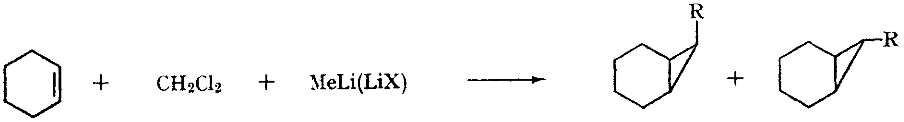
THE reaction of methylene chloride with an alkyl-lithium in the presence of an olefin usually gives a chlorocyclopropane,[2] presumably *via* an intermediate carbenoid species.[3] Recently several reports have appeared describing anomalies which result when this reaction is carried out with methyl-lithium prepared from methyl iodide.[4,5]

We have examined the reactions of cyclohexene with methylene chloride and methyl-lithium prepared from various methyl halides.



(I) R = Cl (II)
(III) R = Me (IV)
(V) R = Br (VI)
(VII) R = H

The results are given in the Table.

TABLE

Yields of norcarane derivatives and methylene iodide from cyclohexene, methylene chloride, and methyl-lithium[a]

Source of MeLi	(I) *cis*-Cl	(II) *trans*-Cl	(III) *cis*-Me	(IV) *trans*-Me	(V) *cis*-Br	(VI) *trans*-Br	(VII) *cis*-H	CH_2I_2
MeCl + Li ..	28	13	1	1	—	—	—	—
MeBr + Li ..	26	12	3	2	1[b]	1	—	—
MeI + Li ..	3	1	19	12	—	—	1	—[c]
MeCl + Li .. (LiI added)[d]	3	1	11	4	—	—	1	15[e]

[a] Reactions carried out by adding 1·0—1·7 M-ethereal methyl-lithium to an excess of cyclohexene and methylene chloride at 5—15°. Yields of norcarane derivatives based on methyl-lithium assuming the reaction sequence shown in the Scheme; yield of methylene iodide based on lithium iodide.

[b] The formation of bromocyclopropanes in a similar reaction has been reported. (C. W. Jefford and R. Medary, *Tetrahedron Letters*, 1966, 2069, 2792.)

[c] Less than 0·5%.

[d] One mole of lithium iodide per mole of methyl-lithium.

[e] In separate control experiments, methylene iodide in 10% yield was obtained from the reaction of methylene chloride, methyl-lithium prepared from methyl chloride, and lithium iodide. However no trace (<0·5%) of methylene iodide was obtained from the reaction of methylene chloride and lithium iodide in the absence of methyl-lithium, or from the reaction of methylene chloride and methyl-lithium prepared from methyl iodide (<0·1%).

The reaction of methylene chloride and methyl-lithium prepared from methyl iodide, in the presence of 2,3-dimethylbut-2-ene, gave 3-chloro-1,1,2,2-tetramethylcyclopropane (VIII) (6%), and pentamethylcyclopropane (IX) (8%).* A small amount of chloroiodomethane was detected, but no trace of 1,1,2,2-tetramethylcyclopropane or methylene iodide was evident.

All of the products observed in the above

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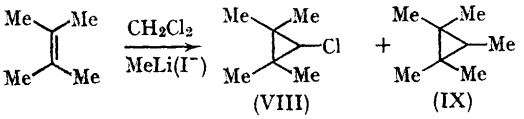
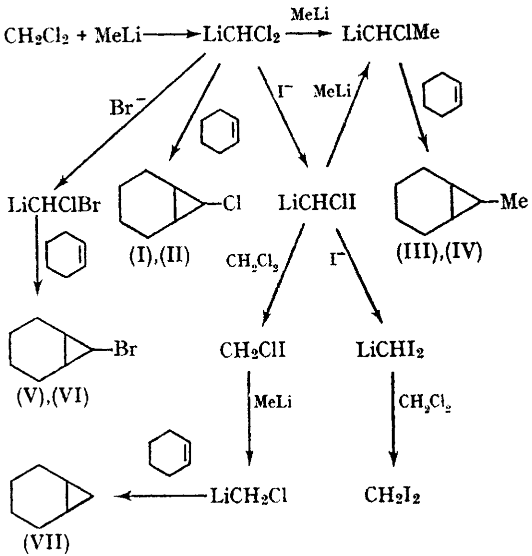
* The chloro-compound (VIII) in 67% yield was the only product reported when n-butyl-lithium prepared from the chloride was used (ref. 2).



reactions were isolated by preparative gas chromatography and characterized by their n.m.r., infrared, and mass spectra. Satisfactory combustion or high-resolution mass spectral analyses were obtained for all new compounds.

The above results show that iodide ion (either from methyl iodide plus lithium or from externally added salt) is indeed responsible for the altered course of the carbenoid addition reactions, but that the two different sources of iodide ion do not lead to identical reactions. A possible sequence of reactions to explain the above products is shown in the Scheme.[6]

A detailed discussion of these reactions will be presented later.



SCHEME

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[1] Carbene and carbenoid chemistry. Part II, W. L. Dilling and F. Y. Edamura, *Tetrahedron Letters*, in the press.

[2] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1960, **82**, 5723; W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964, p. 188.

[3] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, 1965, **87**, 4270, and references cited therein.

[4] W. L. Dilling, *J. Org. Chem.*, 1964, **29**, 960; see also R. A. Moss, *J. Org. Chem.*, 1965, **30**, 3261; T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 4876.

[5] Several other related reactions in which the products depended on the presence of iodide ion in the methyl-lithium have been reported; E. T. Marquis and P. D. Gardner, *Chem. Comm.*, 1966, 726; G. L. Closs and J. J. Coyle, *J. Org. Chem.*, 1966, **31**, 2759; U. Schöllkopf and J. Paust, *Angew. Chem. Internat. Edn.*, 1963, **2**, 397; *Chem. Ber.*, 1965, **98**, 2221.

[6] Köbrich and co-workers (G. Köbrich, K. Flory, and W. Drischel, *Angew. Chem. Internat. Edn.*, 1964, **3**, 513; G. Köbrich and H. R. Merkle, *Chem. Ber.*, 1966, **99**, 1782) have demonstrated the existence of dichloromethyl-lithium at low temperatures. The reaction of alkyl-lithiums with chlorocarbenoid has been postulated previously (W. Kirmse and B.-G. v. Bülow, *Chem. Ber.*, 1963, **96**, 3316; G. L. Closs, *J. Amer. Chem. Soc.*, 1962, **84**, 809).