The Origin of Methylcyclopropanes in the Alkene–Methylene Chloride–Methyl-lithium Reaction

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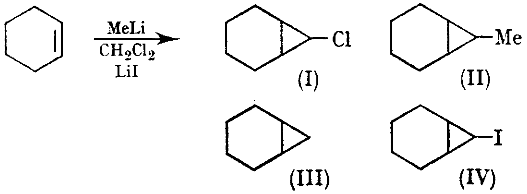
THE reaction of cyclohexene with methylene chloride and methyl-lithium (from methyl iodide) has been shown by Dilling and Edamura[1] to give *cis*- and *trans*-(I), *cis*- and *trans*-(II), and traces of (III). It was suggested that the methylnorcaranes (II) are formed directly from cyclohexene by reaction with an intermediate organometallic of the type $CH_3{\cdot}CHXLi$.[2,3] A similar study by Magid and Welch[4] revealed that *cis*- and *trans*-(IV) are also among the major reaction products. From the observation that (IV) reacts stereospecifically with methyl-lithium to give (II) and (III), it was suggested that (II) and (III) are most likely not primary reaction products but are derived from (IV). An extensive study of this reaction in our laboratories has provided data in general agreement with those of Magid and Welch but which differ in one very important respect. The reaction of (IV) with methyl-lithium was observed to give (II) and (III) as reported.[4] However, its reaction with methyl-lithium under conditions employed in the reaction of cyclohexene (25—30°, 0·5 hr., methylene chloride present†) proceeded only to the extent of 3% and gave no compound (II). The 97% of unreacted (IV) was recovered and the 3% which reacted went exclusively to (III). It is thus clear that the reaction of methyl-lithium with methylene chloride is much faster than that with (IV) and that none of the (II) produced from cyclohexene is formed *via* the iodo-compounds (IV). *The methylnorcaranes are primary reaction products as originally proposed.*[1] Support for the carbenoid mechanism was obtained from the reaction of 1,1-di-iodoethane‡ and methyl-lithium with cyclohexene. Although the conversion of cyclohexene was very low, the only products boiling higher than cyclohexene were (II) (*cis*:*trans* = 58:42). Significantly, the *cis*:*trans* ratio of (II) produced in the cyclohexene–methylene chloride–methyl-lithium reaction at essentially the same temperature was 60:40.



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† Professor Magid has kindly informed us (private communication) that methylene chloride was not present in their experiments with (IV).

‡ 1,1-Dichloroethane has been shown (ref. 3) to react with dipotassium cyclo-octatetraenide to give an intermediate having carbenoid properties.

[1] W. L. Dilling and F. Y. Edamura, *Chem. Comm.*, 1967, 183.
[2] G. L. Closs and J. J. Coyle, *J. Org. Chem.*, 1966, **31**, 2759, and references cited therein.
[3] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 4876.
[4] R. M. Magid and J. G. Welch, *Chem. Comm.*, 1967, 518.