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CARBENE AND CARBENOID CHEMISTRY. II. THE REACTIONS OF METHYLENE BROMIDE AND BROMOFORM WITH METHYLLITHIUM AND CYCLOHEXENE (1)

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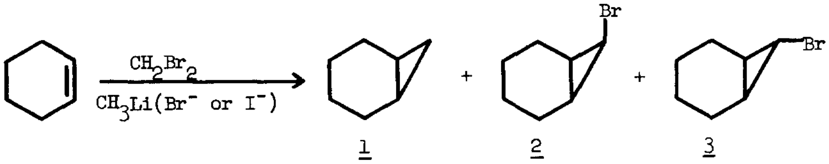
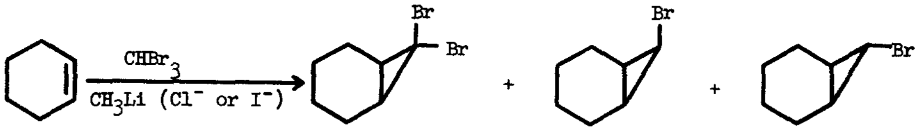
Bromocarbene (or bromocarbenoid) has been postulated as an intermediate in the reaction of methylene bromide and potassium t-butoxide (2) and in the reaction of bromoform with metallic lithium (3). Recently Closs and Coyle reported the preparation of free bromocarbene from thermolysis and photolysis of bromodiazomethane (4). The reaction of methyllithium and methylene bromide, however, evidently does not give bromocarbenoid but rather bromomethyllithium (carbenoid) by metal-halogen exchange (5); in the presence of cyclohexene, norcarane was obtained (6). Earlier we reported an analogous reaction in which phenylcyclopropane was obtained as the only isolable cyclopropyl derivative from styrene, methylene bromide, and methyllithium prepared from methyl iodide (1). We would like to report some preliminary results on the generation of carbenoid, bromocarbenoid, and dibromocarbenoid from methylene bromide and bromoform with methyllithium. The effect of iodide ion on these reactions was also investigated.

The reaction of cyclohexene with methylene bromide and ethereal methyllithium prepared from methyl bromide gave a 5% yield (based on methyllithium) of norcarane derivatives which consisted of norcarane, 1, (75-93%), cis-, 2, (4-14%), and trans-7-bromonorcarane, 3, (3-11%).



The reaction of cyclohexene with methylene bromide and methyllithium prepared from methyl iodide gave a similar yield and distribution of the norcaranes, 1-3. However the main product of this reaction was methylene iodide (7). Thus, the presence of iodide ion has little or no effect on the cyclopropyl products in contrast to the pronounced effect of iodide ion in the analogous reactions of methylene chloride (8). Another difference between the methylene bromide and methylene chloride reactions is the formation of methylene iodide in the former reaction with methyllithium prepared from methyl iodide, while in the latter reaction, methylene iodide was formed only if externally added lithium iodide was present (8).

The reaction of cyclohexene with bromoform and methyllithium prepared from methyl chloride or iodide gave an 8% yield of norcarane products consisting of 7,7-dibromonorcarane, 4, (88%), and the monobromo derivatives, 2 (7%) and 3 (5%).

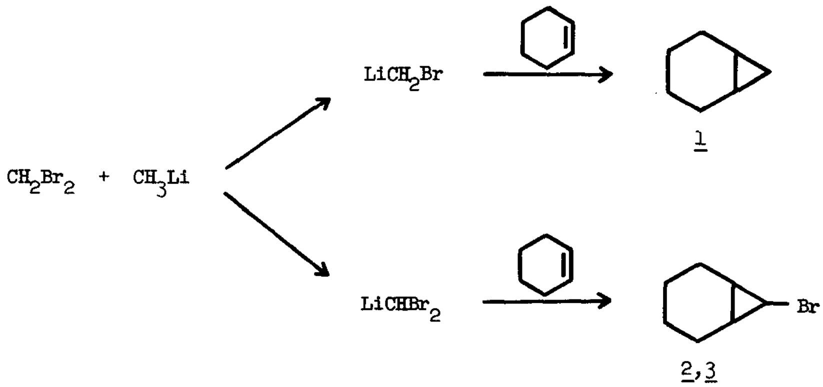


4 2 3

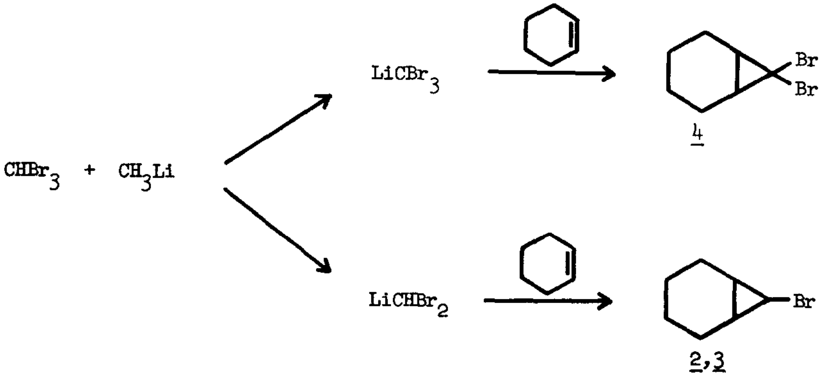
All of the norcarane derivatives obtained were isolated by preparative gas chromatography and identified by comparison of their infrared and n.m.r. spectra with those reported in the literature for the respective compounds (9).

The reactions shown in Scheme 1 are consistent with the cyclopropyl products observed from methylene bromide with halogen-metal exchange being the predominant path (10).

The predominant formation of the dibromo compound, 4, from bromoform indicates that the principal reaction in this case is metalation, Scheme 2 (12). The increased acidity of the proton in bromoform accounts for the greater tendency of this compound to undergo metalation, as compared to methylene bromide.



Scheme 1



Scheme 2

The low yields of the cyclopropyl products observed in the above reactions are probably due to side reactions of the highly reactive mono-, di-, and tribromomethyllithiums and possibly other reactions between the polybromomethanes and methyllithium, such as alkylation. We have not examined these side reactions in the present study except for the formation of methylene iodide. We did observe a number of components which had shorter gas chromatographic retention times than the norcaranes, 1-4. These components were also formed in control experiments in the absence of cyclohexene. In an earlier paper we reported the formation of methane, ethylene, methyl bromide, and ethyl bromide from the reaction of methylene bromide and methyllithium under similar reaction conditions (ether solution, 5-15°) (1).

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7. In separate control experiments, methylene iodide was shown to result from the reaction of methylene bromide, methyllithium prepared from methyl chloride, and lithium iodide, but not from the reaction of methylene bromide and lithium iodide in the absence of methyllithium.
8. W. L. Dilling and F. Y. Edamura, unpublished results.
9. (a) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, J. Org. Chem., 31, 295 (1966); (b) R. T. LaLonde and M. A. Tobias, J. Am. Chem. Soc., 85, 3771 (1963); (c) D. Seyferth, H. Yamazaki, and D. L. Alleston, J. Org. Chem., 28, 703 (1963); (d) W. v. E. Doering and A. K. Hoffmann, J. Am. Chem. Soc., 76, 6162 (1954).
10. No deuterium incorporation (<2%) was observed in the norcarane, 1, obtained when the reaction of cyclohexene, methylene bromide, and methyllithium prepared from methyl bromide was carried out with deuterium oxide work-up. The recovered methylene bromide also showed no trace of deuterium incorporation (<1%). Therefore the alternate route to 1 via halogen-metal exchange on 2 or 3 with subsequent hydrolysis is not likely (11).
11. Cf. (a) H. M. Walborsky, Record Chem. Progr. 23, 75 (1962); (b) H. M. Walborsky, F. J. Impastato, and A. E. Young, J. Am. Chem. Soc., 86, 3283 (1964).
12. The monobromo compounds, 2 and 3, could arise via halogen-metal exchange of 4 followed by hydrolysis (13). The reaction of carbon tetrabromide with n-butyllithium and cyclohexene gave 4 in 11% yield probably by halogen-metal exchange and elimination of lithium bromide (6).
13. Cf. (a) W. R. Moore and H. R. Ward, J. Org. Chem., 25, 2073 (1960); Chem. Ind. (London), 594 (1961); (b) E. T. Marquis and P. D. Gardner, Tetrahedron Letters, 2793 (1966).