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CYCLOPROPANES FROM OLEFINS AND LITHIUM CARBENOIDS

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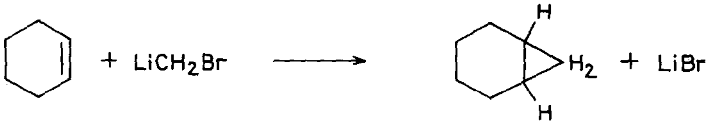
Metal carbenoids are more appropriate reagents for the conversion of alkenes to cyclopropanes than the unselective free CH_2 with its tendency for CH-insertion (1). Halomethyllithium has not been used extensively for this purpose. This reagent, generated from dibromomethane and methyllithium in ether, converts cyclohexene to only 4% norcarane (2-4) and styrene into 1.3% phenylcyclopropane. Chloromethyllithium in tetrahydrofuran is not capable of "cyclopropanation" (6).

After reacting butyllithium with dibromomethane and cyclohexene in a 1:2:2 ratio in hexane at 0°, the analysis by vpc using a capillary column showed 13% norcarane (1) and 1% ethylene; homologous alkyl bromides were the main product (7). The isolation of 1 by preparative vpc confirmed its identity

$$C_4H_9Li + H_2CBr_2 \longrightarrow LiCH_2Br + C_4H_9Br$$



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Analogously, iodomethyl- and chloromethyllithium were obtained from diiodomethane and bromochloromethane, respectively, by halogen-metal interconversion with butyllithium. The increase of the norwarane yield in going from iodomethyl- to chloromethyllithium is noteworthy (Table I).

Table I. Reactions of 11 mmol n-Butyllithium (free of LiHal) with 20 mmol Dihalomethane and 20 mmol Cyclohexene in 20 ccm Hexane at 0°; Product Yield Based on Lithium Carbenoid.

CH_2Hal_2	Carbenoid	% Norcarane	% Alkyl halides
CH_2I_2	$LiCH_2I$	0.4	70
CH_2Br_2	$LiCH_2Br$	13	70
CH_2BrCl	$LiCH_2Cl$	27	64

The yield of **1** increased to 33% when cyclohexene was reacted with $LiCH_2Cl$ *in situ* at -50°. Under these conditions other alkenes also were converted to cyclopropanes (Table II) which were isolated, characterized spectroscopically and identified with specimens prepared from alkenes by the Simmons-Smith reagent (8). 1-Octene and $LiCH_2Cl$ gave hexylcyclopropane, free of isomers, while methylene iodide + Zn/Cu in ether furnished products which are derived from double bond-isomerized octenes to the extent of 1/3.

Table II. Reactions of 22 mmol Butyllithium with 40 mmol Bromochloromethane and 40 mmol Alkene in 35 ccm Pentane at -50°.

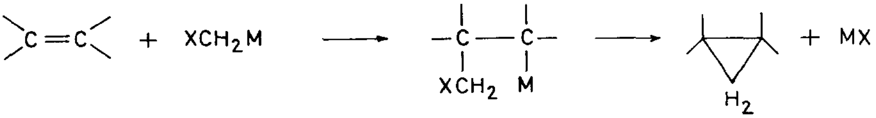
Alkene	%	Cyclopropane
Cyclohexene	33	Norcarane
1-Octene	37	Hexyl-
Styrene	39	Phenyl
α-Methylstyrene	39	1-Methyl-1-phenyl-

The *in situ*-reactions of $LiCH_2Cl$ with *cis*- and *trans*-stilbenes yielded *cis*- and *trans*-1.2-diphenylcyclopropane stereospecifically within an analytical limit of 0.5%. The competition of styrene and cyclohexene for chloromethyllithium or bromomethyllithium, respectively, resulted in different relative rate constants (Table III). Thus, it leaves no doubt that the reacting carbenoid species still contains the halogen atom.

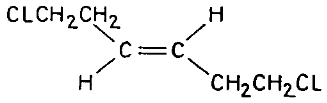
Table III. Competition of Styrene and Cyclohexene for $LiCH_2Hal$ Generated in situ in Pentane at -50°.

Molar ratio Styrene : Cyclohexene	k(Styrene) / k(Cyclohexene) for	
	$CH_2BrCl + C_4H_9Li$	$CH_2Br_2 + C_4H_9Li$
0.44	3.7	5.6
0.70	4.0	5.3
0.89	3.6	5.5
2.1	3.6	5.3

Hoberg (9) has discussed a two-step mechanism for the "methylenation" by metal carbenoids. This mechanism was disproved by the *in situ*-reaction of



chloromethyllithium in hexane at -35° with the chloroalkenes **2** and **3**; pure homogeneous cyclopropanes were obtained, while the primary metalorganic addition should lead to isomeric mixtures. The same models **2** and **3** have been applied earlier to refute the Hoberg mechanism for the carbenoids from zinc chloride + diazomethane (10) and cuprous chloride + diazomethane (11).



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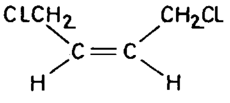

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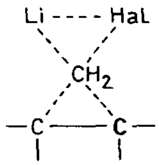

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All available data - including the small substituent influence on the acceptor activity of the olefinic double bond (12) - point *per exclusionem* to the "butterfly structure" **4** as the transition state for the one-step methylenation. This picture has already been proposed for zinc carbenoids (8).

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