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INTRAMOLECULAR CYCLIZATIONS OF ORGANOMETALLIC COMPOUNDS.
III. THE CATALYTIC CYCLIZATIONS OF POLYENES USING DIISOBUTYLALUMINUM HYDRIDE.

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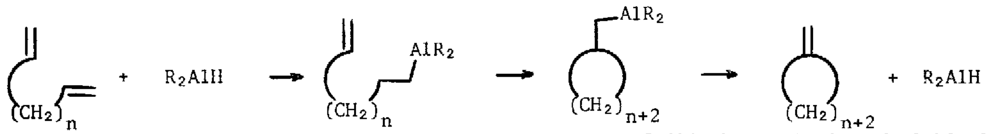
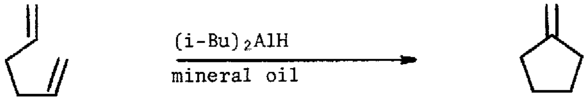
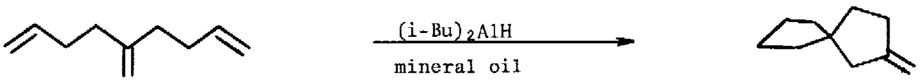
It has been known for some time that insertion of a carbon-carbon double bond into an aluminum-carbon σ bond can occur in an intramolecular fashion producing a cyclic structure.[1] Such reactions have been employed in the construction of 5- and 6-membered rings.[2] Since the insertion of a carbon-carbon double bond into an aluminum-hydrogen bond readily takes place in a reversible manner, it seemed possible that cyclization could be accomplished using a catalytic amount of dialkylaluminum hydride.[3]



Treatment of 1,5-hexadiene with a catalytic amount of diisobutylaluminum hydride in mineral oil resulted in the generation of methylenecyclopentane in good yield. Similarly methylenecyclohexane was produced from 1,6-heptadiene and bicyclo [3.2.1] oct-2-ene from 4-vinylcyclohexene. Presumably all of these simple cyclizations proceed through the same type of mechanism: insertion of a terminal double bond into the aluminum-hydrogen bond followed by insertion of the remaining double bond in the molecule into the aluminum-carbon bond and loss of a β-hydrogen to form the product and regenerate the catalyst.



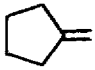
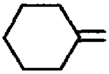
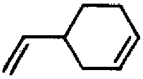
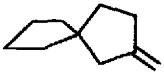
Spiral substances can also be generated by this reaction as exemplified in the cyclization of 5-methylene-1,8-nonadiene. In this case two double bonds undergo the intramolecular insertion reaction.



The experimental results are provided in Table I. The reactions were conducted under nitrogen in a sealed tube. The mineral oil was heated to 90° under reduced pressure before being used as the solvent. After being immersed in a constant temperature oil bath, the tube was removed and opened. All volatile components were vacuum transferred and collected in a cold trap.

Table I

Yields of Cyclization Products

Polyene	Amount of Polyene Used (mmol)	Amount of (i-Bu)$_2$AlH Used (mmol)	Reaction Temp °C	Reaction Time (hr)	Product Isolated	Yield[a] %
	6.1	0.61	115	56		81[b]
	5.2	0.52	105	48		56[b]
	4.7	0.50	210	48		61[c]
	3.7	0.37	110	48		78[d]

[a] All yields were determined by gas chromatographic analysis using a linear hydrocarbon as an internal standard without detector response factor correction. Hexene (solvent for diisobutylaluminum hydride) was the only other substance isolated with indicated product.

[b] 5% TCEP column. [c] 5% OV-17 column. [d] 3% OV-101 column.

Acknowledgments

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