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INTRAMOLECULAR CYCLIZATIONS OF ORGANOMETALLIC COMPOUNDS

V 6,6-BIS(DIETHYLALUMINUM)-1-HEXENES TO SUBSTITUTED CYCLOPENTANES.[1]

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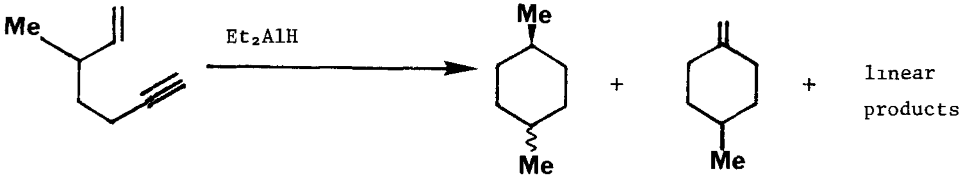
SUMMARY 3-Substituted-hex-1-en-5-ynes were cyclized by treatment with diethylaluminum hydride, in hydrocarbon/ether solvent, trans-2-substituted-methylcyclopentane is produced, while in the absence of ether, the product is 2-substituted-methylenecyclopentane Yields are 69% to 76%

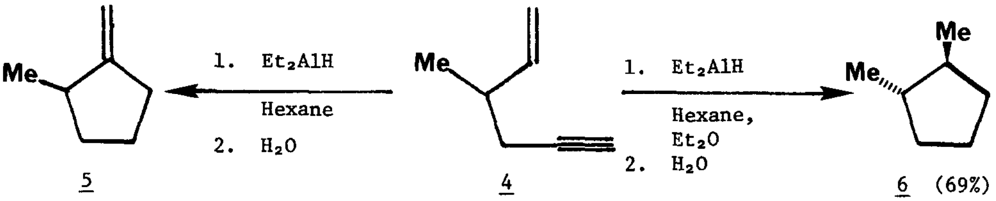
Intramolecular cyclizations of organoaluminum compounds have been the subject of reports by members of our group[3] and by others[4] Chum and Wilson[3] used catalytic amounts of diisobutylaluminum hydride to prepare methylenecycloalkanes from dienes and methylenebicycloalkanes from trienes Zweifel and coworkers[4a] and Rienäcker and Schwengers[4b] cyclized enynes to substituted cycloalkanes using two equivalents of dialkylaluminum hydride In the latter case, 3-methylhept-1-en-6-yne gave the mixture of products indicated in equation 1 The research presented here complements this previous work, and, since the cyclization occurs in good yield and with stereoselectivity, it emerges as a synthetically useful technique



Eq. 1

1 2 (cis & trans) 3

Triple bonds are doubly hydroaluminated in the presence of double bonds when such systems are treated with two equivalents of dialkylaluminum hydride.[4] Linear polyenynes could therefore serve as polycyclic precursors in which the locoselectivity of the hydroalumination is unequivocal This feature makes enynes valuable model systems. The first such system to be discussed presently is 4, from crotyl magnesium chloride/1,3-dichloropropene coupling followed by dehydrohalogenation ($NaNH_2$, NH_3)[5] Compound 4 can be cyclized using two equivalents of diethylaluminum hydride In the absence of ether, olefin 5 is the product, while trans-1,2-dimethylcyclopentane (6) results when the cyclization is performed in the presence of as little as two equivalents of ether [7] (equation 2) In the absence of electron donation by the ether, the product of the initial cyclization readily dehydroaluminates to a monoaluminum species which quenches to 5

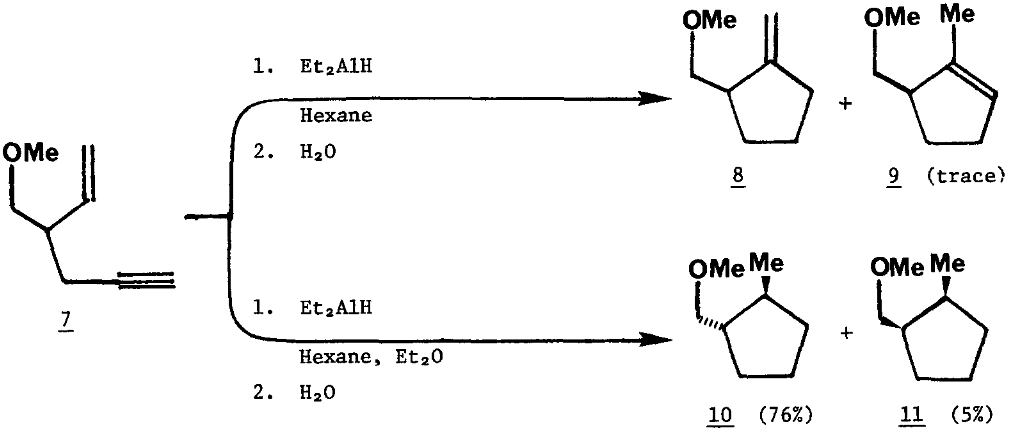


Eq. 2

The production of 6 is noteworthy in that it contrasts with the cyclization of homologue 1 The latter reaction is nonstereoselective and gives products having a substitution pattern different than that of compound 6

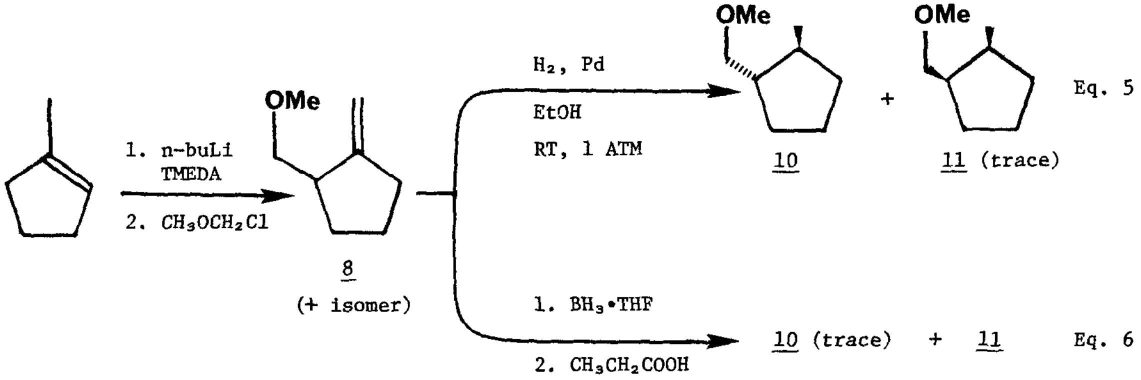
An appropriately placed heteroatom can influence the course of the cyclizations of alkenyllithiums.[8] Based on this precedent and reports by Zakharkin and Savina[9] that inter- and intramolecular complexation is involved in the addition of trialkylaluminums to alkenyl ethers, we sought to find evidence of similar interaction in the cyclizations of heteroatom-containing alkenylaluminum compounds.

The methoxymethyl analogue of 4 was prepared by the methylation of the appropriate alcohol, obtained by the method of Courtois, *et al*[10], and isolated by preparative scale GLC Enyne methyl ether 7 was cyclized using two equivalents of diethylaluminum hydride, produced were exclusively cyclic products as shown in equations 3 and 4 As before, a dehydroalumination product, 2-methoxymethylmethylenecyclopentane (8), is the main product in the absence of added ether. In the presence of added ether, saturated products result as before, in this case, mainly *trans*-2-methoxymethyl-1-methylcyclopentane (10)[11]. The structures of 8, 10, and 11 were assigned on the basis of the results of reactions 5 and 6, on the next page. The palladium catalyzed reduction of 2-substituted methylenecyclopentanes reportedly gives predominantly *trans* products[12] The result of the hydroboration/protonolysis reaction can be explained on the basis of approach of the borane-tetrahydrofuran complex to the least hindered face of the double bond

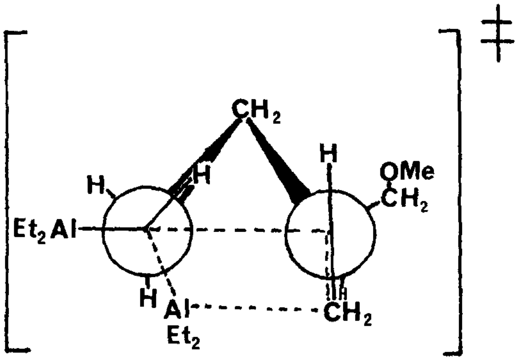


Eq. 3

Eq. 4



The production of the trans ring juncture in 10 might be explained using steric arguements, as in cyclization transition state 12, which contains no internal complexation An alternative explanation, depicted in 13, involves complexation of one aluminum with the alkoxyl group and of the other with the double bond[13]. Only in cases in which steric effects must compete with complexation (e.g , 3-t-butyl-3-methoxymethyl-hex-1-en-5-yne) could the explanations be tested.



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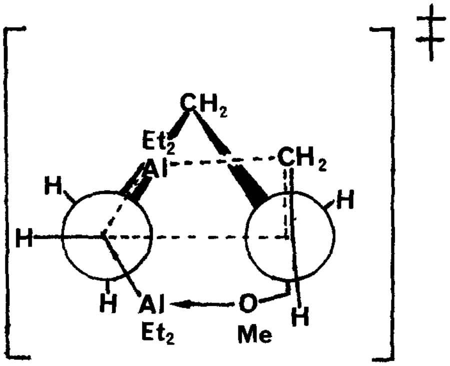

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In spite of some uncertainty about the cause of the stereoselectivity in the alkoxyl case, the synthetic value of the technique is intact. This method offers a means to stereoselect trans-2-substituted 1-methylcyclopentanes in good yield via an organoaluminum cyclization in the presence of ether.

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Notes and References

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6. Compound **6** possesses an NMR spectrum identical to that of a commercial sample of *trans*-1,2-dimethylcyclopentane The spectrum of **6** is readily distinguishable from that of authentic *cis*-1,2-dimethylcyclopentane

7 An experimental procedure for the cyclization is as follows The reaction is done under inert atmosphere. To a solution, maintained at 0°C, of the enyne (1 to 5 mmole) and solvents (hexane and/or diethyl ether, dried and with total volume of 1 to 4 mL) is added diethylaluminum hydride (1 3 M in hexane, 2 0 equivalents) After 30 minutes at 0°, the contents of the flask are taken to reflux and held there overnight Reactions are quenched by cooling to -22°C (tetrachloroethylene slush) and addition of saturated ammonium chloride solution Aluminum salts are separated by centrifuging and decanting, and the organic layer is vacuum transferred A hydrocarbon internal standard is added and yields are calculated and products isolated by GLC (SE-30 or carbowax)

8 Reference 1, above

9 a L. Zakharkin and L Savina, *Bull Acad. Sci. USSR, Engl. Transl.*, 1959, 420
  b L Zakharkin and L Savina, *ibid.*, 1960, 970.

10 G. Courtois, B Mauze, and L Miginiac, *J Organometal Chem.*, 1974, **72**, 309

11 2-Methoxymethyl-1-methylcyclopentane has been prepared by M Gadzhiev, *et al.* (*Zh Org Kh , Engl Transl ,* 1974, **10**, 1381), but apparently not with stereoselection

12 S. Mitsui, *et al* , *Tetrahedron*, 1972, **28**, 4751

13 T. Dolzine and J Oliver, *J Amer Chem Soc* , 1974, **96**, 1737

14 Acceptable elemental analyses were obtained for compounds **4** and **7**

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