Synthesis of Dialuminium Substituted Cyclopentyl Derivatives *via* the Hydroalumination of Hex-1-en-5-yne

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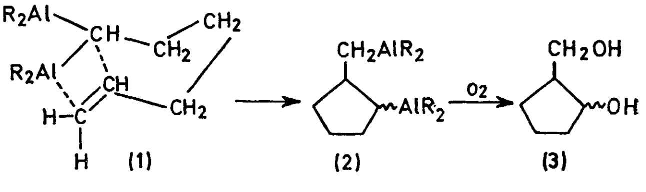
Summary The dihydroalumination of hex-1-en-5-yne in diethyl ether or triethylamine affords 2,α-bis-aluminomethylcyclopentane and 2,α-bis-alumino-3-methylcyclopentene derivatives, respectively.

ZIEGLER and his co-workers[1] have shown that the reactions of di-isobutylaluminium hydride with hexa-1,5-dienes afford nearly quantitative yields of α-aluminomethylcyclopentanes. Subsequent investigations revealed that the reaction was essentially limited to 1,5-dienes.[2,3]

The hydroalumination of alk-1-ynes can be controlled by choice of solvent; mono-, di-, or tri-hydroalumination products are obtained by carrying out the reaction in hydrocarbon,[4] ether or THF,[5] or trialkylamine[6] respectively. These observations coupled with the known low reactivity of R_2AlH toward double bonds† suggest that intramolecular cyclization reactions of organoalanes derived from hex-1-en-5-yne might lead to novel substituted cyclopentyl systems, and this has been confirmed.

Thus, hydroalumination of hex-1-en-5-yne with di-isobutylaluminium hydride (2 mol. equiv.) in diethyl ether (37°; 4 h) followed by hydrolysis of the reaction mixture gave methylcyclopentane (80%) and unchanged enyne (15%). The precursor for methylcyclopentane appears to be (**1**) (Scheme 1) resulting from dihydroalumination of the triple bond,[5] which then undergoes intramolecular Al–C bond addition to the double bond. The reaction mixture was treated with molecular oxygen and a mixture of *cis*- and *trans*-2-hydroxycyclopentylmethanol (**3**) was obtained,‡ establishing that the initial cyclization product is the 2,α-dialuminomethylcyclopentane (**2**).§



SCHEME 1

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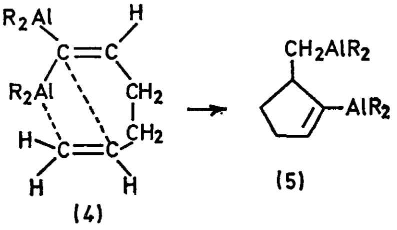
† Competition experiments have revealed that oct-1-yne is selectively hydroaluminated in the presence of hex-1-ene.

‡ Recently, evidence has been presented to show that oxidation of the Al–C bond with molecular oxygen may not proceed cleanly with retention of configuration (ref. 3). Hence, it is not known whether the observed *cis-trans* ratio reflects the actual stereochemistry of the 2,α-dialuminomethylcyclopentane.

§ It is noteworthy that dihydroalumination of hex-1-en-5-yne in hydrocarbon solvents at 50° for 2 h affords, after hydrolysis, a 40% yield of methylenecyclopentane.

In trialkylamine alkyl-1-ynes react with R_2AlH (1 mol. equiv.) to give the corresponding alkynylalanes and hydrogen.[7] In the presence of additional R_2AlH, 1,1,1-trialuminoalkanes are formed.[6] Reaction of R_2AlH (3 mol. equiv.) with hex-1-en-5-yne (1 mol. equiv.) in triethylamine (8 h, 50°) gave, after hydrolysis, 3-methylcyclopentene (59%) and hex-1-ene (17%). However, when the metallation was carried out at 25° using 1 mol. equiv. of R_2AlH per mol. equiv. of enyne, followed by the slow addition of R_2AlH (1·2 mol. equiv.) at 50°, 3-methylcyclopentene (79%) and hex-1-ene (1%) were obtained. Deuteriolysis gave dideuterio-3-methyl cyclopentene having one deuterium atom in the methyl group and the other at the double bond. Unfortunately, the spectral data did not permit the direct assignment of the position of the deuterium on the double bond. However, selective iodination[8] of the vinyl C-Al bond with one mol. equiv. of iodine at −65°, followed by hydrolysis, gave vinyl iodide which was converted with lithium dimethylcopper[9] into 2,3-dimethylcyclopentene. This sequence of interconversions establishes that the dialumino-species is 2,α-bis-(di-isobutylalumino)-3-methylcyclopentene.

The fact that the amount of hex-1-ene, the hydrolysis product derived from 1,1,1-trialuminohex-5-ene, decreased on changing the R_2AlH:enyne ration from 3:1 to 2:1 suggests that the precursor for the cyclic alane (5) is 1,1-dialuminohexa-1,5-diene (4) (Scheme 2). A direct synthesis of the 1,1-dialuminoalkene has so far eluded us.



SCHEME 2

The synthesis of cyclopentyl systems containing aluminium at various positions should be useful from a synthetic view point, especially since it is possible to convert the C–Al bond into a variety of other derivatives.

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