CYCLOPROPANE DERIVATIVES FROM THE LITHIUM ALUMINIUM HYDRIDE REDUCTION OF METHOXYALKYNOLS

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<u>Summary</u>: Lithium aluminium hydride reduction of methoxyalkynol(1) yields cyclopropane derivatives (2) and (3), both formed by loss of a methoxy group; a reaction scheme for their formation is presented.

In the course of a study of the effects of the reaction solvent on the lithium aluminium hydride reduction of alkynols, we examined the reactions of some methoxyalkynols. It was envisaged that the methoxy group might replace a solvent ether molecule in solvating the aluminium atom of a reacting alkynyloxyaluminium hydride, but be otherwise inert. However, we now report the involvement of the methoxy function in secondary reactions.

Lithium aluminium hydride reduction of $alkynol(1)^{1}$ in tetrahydrofuran at 65[°] for 3h. gave a crude product from which the cyclopropane derivative(2), dimer(3), and the (E)-alkenol(4)¹ were



isolated and identified through their spectroscopic data. The formation of compounds (2) and (3) each involves the loss of a methoxy group.

On reaction of alkynol(1) with lithium aluminium deuteride, under similar conditions to the above, the cyclopropane derivative(2) and the dimer(3) were found $({}^{1}H$ and ${}^{13}C$ n.m.r.) to be deuteriated at the positions shown, while the deuterium label was distributed between the C4 and C5 positions (see Table) of the (E)-alkenol(4). The extent and location of deuterium labelling



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Concentration (g l ⁻¹) of alkynol(1) in THF	(2)	Product (3)	Yields (4)	(6)	Attack by H (D leading to (4)) at C4:C5 Overall
20	7	30	51	-	46:5 ²	46:42 ³
2	6	8	67	8	47:20	47:42

TABLE Product yields of reactions of alkynol(1) with lithium aluminium hydride (deuteride) in tetrahydrofuran.

in compounds (2) and (3) are consistent with their formation via deuteride ion attack on the intermediate deuteroallene(6), followed by reactions of the delocalised carbanion(7). Internal

displacement of methoxide ion from carbanion(7) would yield the cyclopropane derivative(2), while the dimer(3) could be formed by intermolecular attack (see (8)) on a second deuteroallene(6), again with loss of methoxide ion.

In more dilute solution $(2g l^{-1} alkynol(1), still 1.1 molar equivalents LiAlH₄) the yield of dimer(3) was sharply reduced (Table) consistent with an intermolecular mechanism, and the unstable allene(6) was isolated. From the corresponding lithium aluminium deuteride reduction of alkynol(1), the compounds (2), (3) and (6) carried deuterium labels at the expected positions, while the higher yield of the monodeutero-(E)-alkenol(4) was a reflection of incomplete conversion of carbanion(5) into deuteroallene(6)$



prior to reaction quenching. Unfortunately allene(6) proved in our hands to be too unstable for a convincing conversion into compounds (2) and (3) by reaction with lithium aluminium hydride.

NOTES

- 1. Satisfactory elementary analysis data were obtained for new compounds.
- 2. These ratios were determined from a comparison of the peak intensities of the protonated alkene-carbons in the repetitive-pulse, Fourier-transform ¹³C n.m.r. spectra of monodeuteriated products(4), all obtained under near-identical conditions to minimise effects due to possible differences in carbon relaxation times.
- 3. These values are estimated to be ±3.

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