# Solvent Effects in the Reactions of Alkynols with Lithium Aluminium Hydride

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*Summary* From a comparison of the reactions of alkynols (**1a**) and (**1b**) with lithium aluminium deuteride, a specific solvent role in alkynol reductions is identified and is in keeping with the observed marked solvent-dependence of product ratios

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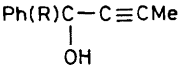
In the lithium aluminium hydride (LAH) reduction of 1,1-diphenylbut-2-yn-1-ol to give the allene, 1,1-diphenylbuta-1,2-diene, and the (*Z*)- and (*E*)-1,1-diphenylbut-2-en-1-ols, the yields of products and the site of initial hydride (or deuteride) attack on the acetylenic system were markedly solvent-dependent [1] We now report the results of a comparative study of the LAH reductions of 2,2-dimethyl-3-phenylhex-4-yn-3-ol (**1a**) and its 1-methoxy-derivative (**1b**), which illuminate further the nature of the solvent dependence

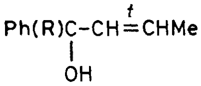


$\mathrm{Ph(R)}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}C{\equiv}CMe}$

(1) a; R = $Bu^t$
b; R = $-CMe_2CH_2OMe$

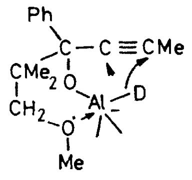
$\mathrm{Ph(R)C{=}C{=}CHMe}$

(2)



$\mathrm{Ph(R)}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}CH}\overset{t}{=}\mathrm{CHMe}$

(3)



(4)

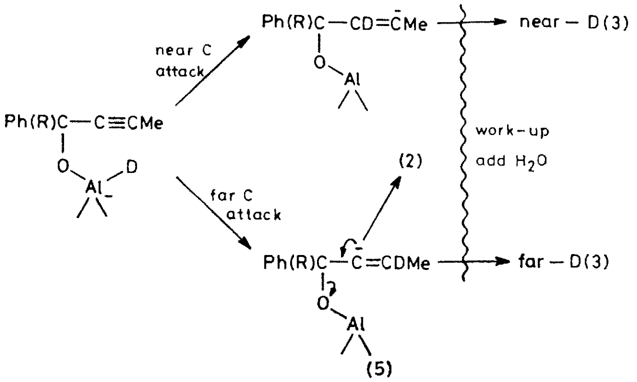
The data in the Table pertain to reactions of the alkynols (**1**) with lithium aluminium deuteride in a range of ether solvents, the reactions being quenched by the addition of water For the alkynol (**1a**) the relative yields of products (**2a**) and (**3a**) vary appreciably with the solvent used and, in the case of tetrahydrofuran (THF), with the reaction

Table Product yields of reactions of alkynols(1) with lithium aluminium deuteride

| Alkynol | Solvent, temp (°C), time (h) | Yield (%) |  | Attack by $D^-$ at near : far carbon |  |
|---|---|---|---|---|---|
|  |  | Allene (**2**) | (*E*)-Alkenol (**3**) | Leading to (**3**) | Overall |
| (**1a**) | $Et_2O$, 35, 89 | 84 | Trace | — | *ca* 0:84 |
|  | THF, 35, 89 | 30 | 60 | 60 0[a] | 60:30[b] |
|  | THF, 65, 2 5 | 66 | 18 | 18:0 | 18:66 |
|  | 2,5-$Me_2$-THF, 65, 2·5 | 92 | 2 | 2:0 | 2:92 |
| (**1b**) | $Et_2O$, 35, 16 | 69 | 27 | 24:3 | 24·72 |
|  | THF, 35, 16 | 29 | 70 | 30:40 | 30·69 |
|  | THF, 65, 2 5 | 57 | 42 | 25:17 | 25:74 |
|  | 2,5-$Me_2$-THF, 35, 16 | 54 | 44 | 26:18 | 26:72 |
|  | 2,5-$Me_2$-THF, 65, 2·5 | 67 | 30 | 23:7 | 23:74 |
|  | 2,5-$Me_2$-THF, 91, 0 5 | 75 | 25 | 25:0 | 25:75 |

[a] These ratios were determined from a comparison of the peak intensities of the protonated alkene-carbons in the repetitive-pulse, Fourier-transform $^{13}C$ n m r spectra of monodeuteriated products (**3**), all obtained under near-identical conditions to minimise effects to possible differences in carbon relaxation times [b] These values are estimated to be ±2

temperature. Further, the relative yields of products formed by deuteride attack at the near : far acetylenic carbon atoms (see the Scheme) also vary.



SCHEME.

In contrast, for the reactions of alkynol (**1b**), while the relative yields of allene (**2b**) and alkenol (**3b**) are solvent- and temperature-dependent, the relative yields of products derived from near- and far-carbon deuteride attack are *independent* of both solvent and reaction temperature.

These results are interpreted in terms of internal solvation of aluminium by the methoxy-substituent in the reacting alkoxyaluminium deuteride (**4**); in the absence of an internal ether, an external and potentially variable ether solvent molecule solvates the aluminium. Given the consistent involvement of the methoxy-function as in (**4**), a constant near : far carbon attack is reasonable and, within the limit imposed by a near : far attack ratio of 1 : 3, the yield of allene (**2b**) is but a reflection of the extent to which the intermediate carbanion (**5**) (Scheme) is converted into allene (**2b**) prior to reaction quenching.

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[1] M. P. Hartshorn, R. S. Thompson, and J. Vaughan, *Aust. J. Chem.*, 1977, **30**, 865.