Solvent Effect on Hydride Reduction

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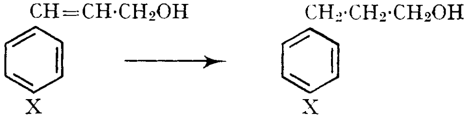
BECAUSE lithium aluminium hydride reacts very rapidly with typical functional groups, solvent effects on the rate of reduction have not been studied. We have been able to measure the rates of reduction of the olefinic bond, as a function of solvent, in cinnamyl alcohol and the less reactive *p*-methyl and *p*-methoxy-derivatives.

The results in the Table demonstrate that tetrahydrofuran is more effective than ether as a solvent medium by a factor of 7·5, that 1,2-dimethoxyethane is better than tetrahydrofuran by a factor of 4—6† and better than ether by a factor ranging from 13 to 47.† It has been recognized[1] that the cation solvating ability for organolithium compounds increases along the series: ether, tetrahydrofuran, and 1,2-dimethoxyethane. It is apparent that similar solvating effects are operative in hydride reductions, so that lithium aluminium hydride becomes a substantially stronger reducing agent in the better cation solvating media.

Solvent effects on double-bond reduction in cinnamyl alcohols[a]



Substrate		Solvent	60% Reduction time, min.[b]
X=H	0°	Ether	140
		Tetrahydrofuran	18·5
		1,2-Dimethoxyethane	3
X=Me	0°	Tetrahydrofuran	64·5
		1,2-Dimethoxyethane	15
X=OMe	25·0°	Ether	170
		1,2-Dimethoxyethane	13

[a] A 1 : 1 molar ratio of alcohol to lithium aluminium hydride, at constant alcohol concentration, was employed.

[b] In ether and tetrahydrofuran the time interval for the reduction of the first half of the substrate is recorded, because the rates in these solvents do not follow a first order rate law. In dimethoxyethane more than 60% of the reaction conforms to a first-order rate expression, and half-lives for the reduction are recorded.

This work was supported by funds from the National Science Foundation Institutional Grant and by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(*Received, June* 19*th*, 1968; *Com.* 804.)

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† These factors are dependent on the structure of the alcohol, since the reduction in ether and 1,2-dimethoxyethane is characterized by a reaction constant of different magnitude (unpublished results from these laboratories).

[1] *e.g.* G. Köbrich, H. R. Merkle, and H. Trapp, *Tetrahedron Letters*, 1965, 969.