

An Autorecycling System for the Specific 1,4-Reduction of α,β -Unsaturated Carbonyl Compounds by 1,5-Dihydro-5-deazaflavin

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A useful autorecycling system for the specific 1,4-reduction of α,β -unsaturated carbonyl compounds to the corresponding saturated carbonyl compounds using a 10-aryl-5-deazaflavin and formic acid is reported.

α,β -Unsaturated carbonyl compounds undergo attack by hydride ion in either a 1,2- or a 1,4-fashion. It is known that lithium aluminium hydride favours the 1,2-reduction of

α,β -unsaturated carbonyl compounds to give the corresponding allylic alcohols and sodium tetrahydroborate usually gives a mixture of 1,2- and 1,4-reduction products. Even modified complex hydride reagents lack the general specificity for 1,4-reduction to the saturated carbonyl compounds.¹ However, α,β -unsaturated carbonyl compounds are generally inert towards hydride ion from NADH models such as Hantzsch ester or 1-alkyl-1,4-dihydronicotinamides.[†]

Table 1. Reduction of α,β -unsaturated carbonyl compounds to saturated carbonyl compounds by 1,5-dihydro-3,7-dimethyl-10-*p*-tolyl-5-deazaflavin in formic acid at 120 °C for 25 h.

Substrate	Product	Yield/%
Cyclopent-2-en-1-one	Cyclopentanone	51
Cyclohex-2-en-1-one	Cyclohexanone	81
Crotonaldehyde	Butyraldehyde	66
Cinnamaldehyde	3-Phenylpropionaldehyde	100

[†] As a special case, the carbon-carbon double bond of 2-cinnamoylpyridine, which contains a basic nitrogen function and carbonyl group that is ideally suited for bidentate chelation with a metal ion, was reduced by NADH models in the presence of Mg^{2+} and Zn^{2+} ; R. A. Gase and U. K. Pandit, *J. Chem. Soc., Chem. Commun.*, 1977, 480.



- 1 D. H. R. Barton and W. D. Ollis, 'Comprehensive Organic Chemistry,' Pergamon, Oxford, 1979, vol. 1, p. 1078; vol. 3, p. 764.
- 2 This compound was synthesised from 3-methyl-6-*p*-toluidino-uracil and 3-methylbenzaldehyde according to the known procedure; F. Yoneda, K. Tsukuda, K. Shinozuka, F. Hirayama, K. Uekama, and A. Koshiro, *Chem. Pharm. Bull.*, 1980, **28**, 3049.
- 3 F. Yoneda, K. Kuroda, and M. Kamishimoto, *J. Chem. Soc., Chem. Commun.*, 1981, 1160.