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## An Autorecycling System for the Specific 1,4-Reduction of $\alpha$ , $\beta$ -Unsaturated Carbonyl Compounds by 1,5-Dihydro-5-deazaflavin

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

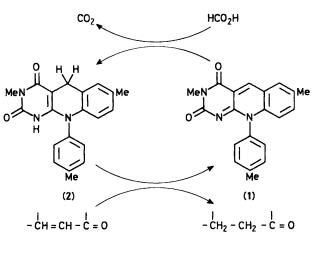
 $\alpha$ , $\beta$ -Unsaturated carbonyl compounds undergo attack by hydride ion in either a 1,2- or a 1,4-fashion. It is known that lithium aluminium hydride favours the 1,2-reduction of

**Table 1.** Reduction of  $\alpha,\beta$ -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

 $\alpha,\beta$ -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.<sup>1</sup> However,  $\alpha,\beta$ -unsaturated carbonyl compounds are generally inert towards hydride ion from NADH models such as Hantzsch ester or 1-alkyl-1,4-dihydronicotinamides.<sup>†</sup>

<sup>†</sup> 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.



Scheme 1

We now report the first example of an autorecycling system for the specific reduction of the carbon-carbon double bond of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds by a 1,5-dihydro-5deazaflavin, which can be regarded as an NADH model. The reaction occurs on heating the  $\alpha$ , $\beta$ -unsaturated carbonyl compound with a small amount of 5-deazaflavin catalyst in formic acid. 3,7-Dimethyl-10-*p*-tolyl-5-deazaflavin (1)<sup>2</sup> was selected as the catalyst, because this exhibited the strongest reducing ability in the reduction of benzaldehyde to benzyl alcohol.<sup>3</sup> In a typical procedure, (1) (6.6  $\mu$ mol) was added to a solution of the  $\alpha$ , $\beta$ -unsaturated carbonyl compound (1.89 mmol) in 98% formic acid (3 ml) and the mixture was stirred at 120 °C (oil bath) for 25 h. The reaction mixture was analysed by g.c. and the product was identified as the corresponding saturated carbonyl compound (see Table 1). No allylic alcohol or saturated alcohol was detected. Under these conditions, (1) was initially hydrogenated by formic acid to form 1,5-dihydro-3,7-dimethyl-10-*p*-tolyl-5-deazaflavin (2), which acted as the turnover catalyst for the specific 1,4-reduction (Scheme 1).

This reaction offers a useful autorecycling system for the specific 1,4-reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds to the saturated carbonyl compounds. This 1,4-reduction occurs stoicheiometrically using equimolar amounts of substrate and preformed (2) in formic acid under milder conditions.

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