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A SIMPLE PROCEDURE FOR SELECTIVE REDUCTION OF α,β-UNSATURATED CARBONYL COMPOUNDS USING Al-NiCl$_2$ SYSTEM

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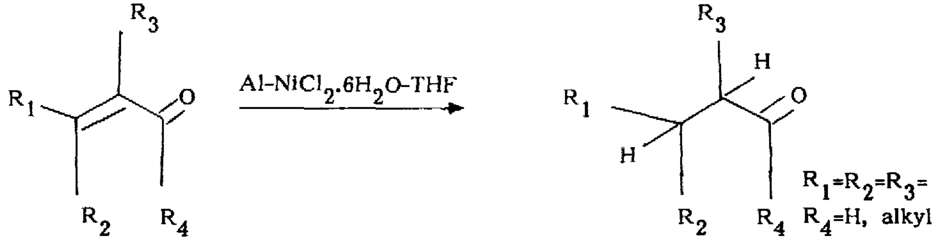
Summary - *A combination of aluminium and nickel chloride in THF has been shown to effect the selective reduction of the olefinic double bond of the α-enone system. Isolated double bonds and aliphatic carbonyls remain unaffected under these conditions. However, aromatic aldehydes and ketones are converted to the corresponding hydroxy compounds by this system in good yields.*

Chemoselective reduction of the double bond of the α,β-unsaturated carbonyl compound is an important transformation in organic chemistry and new methods to effect this transformation appear regularly in the literature. Reagents which are normally used for this conversion include CuI/LAH[1] homogenous metal hydride catalysts[2], Mg/MeOH[3], Li/EtNH$_2$[4], lithium di-isopropyl amide (LDA)[5] zinc-copper couple[6], LAH in the presence of lanthanide salts[7] etc. More recently Petrier et al. reported aqueous Zn-NiCl$_2$ system under ultrasonic sound to be an effective reagent for this transformation[8,9]. High cost of the reagents, poor selectivity or stringent reaction conditions are one or the other drawbacks of most of the reported procedures. We report herein a new and a simple general procedure for the reduction of α-enone system 1 to their saturated analogues 2 by treatment with aluminium powder and NiCl$_2$.6H$_2$O in THF (Scheme I).

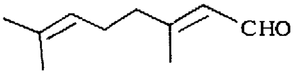
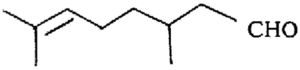
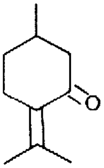
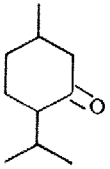
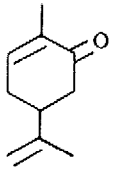
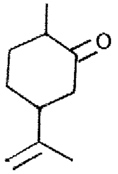
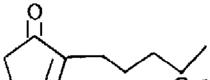
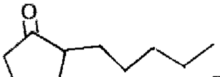
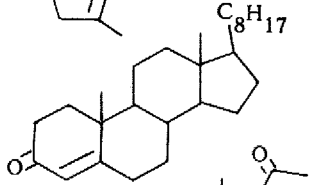
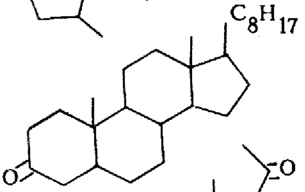
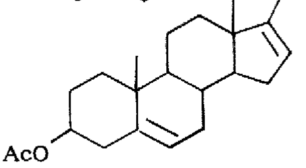
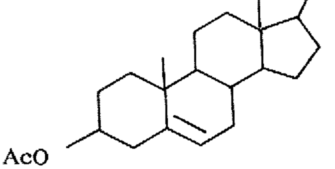
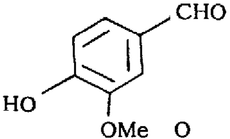
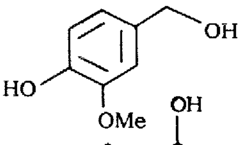
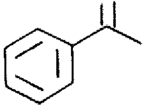
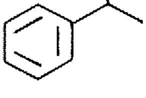


1   2

SCHEME - I

In this method the reaction time is short, yields of 2 are excellent and the work up procedure is very simple.

Table 1 : Reduction of α,β-unsaturated carbonyl compounds with Al-NiCl$_2$.6H$_2$O-THF system.

Sl. No.	Substrate	Reaction time (min)	Product[a]	Yield[b]
1		10		80
2		10		75
3		15		68
4		10	 [c]	84
5		5		92
6		5		95
7		5		85
8		10		95

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a, Products are characterized by IR, NMR and MS and by direct comparison with the authentic compounds.

b, Yield refers to the yields of the pure isolated products.

c, Both 5β-cholestanone and 5 α-cholestanone are formed in the ratio of 60 : 40.

To illustrate the potential of the present method a number of reactions of various *α-enone systems were examined and the corresponding reduced products were obtained in high* yields (Table 1).

It was observed that isolated double bonds,carbonyls and ester functions are not effected by this reagent.

The mechanism of the above reaction is still not clear; however it is known[10] that highly electropositive aluminium replaces nickel from nickel chloride in an aqueous solution in the form of Ni (O)[11] which have a strong tendency to lose electrons to go to its oxidation states. In our system also the possibility of formation of Ni (O) is not ignored and is being explored.

It is noteworthy that although aliphatic aldehydes and ketones are resistant to this system, aromatic aldehydes and ketones are smoothly reduced to the corresponding alcohols in good yields (entry 7 and 8 in Table 1). The most plausible reason for this selectivity could be the fact that the potential needed to transfer an electron to an aliphatic carbonyl group is much higher than that needed for corresponding aromatic aldehydes and ketones, and that the aromatic ring is not directly involved in this process.

General Procedure

To a stirred solution of the substrate (0.3 mmol) in THF[12] (10 ml) is added $NiCl_2.6H_2O$ (3 mmol) and aluminium powder (3 mmol). An exothermic reaction takes place immediately. Stirring of the reaction mixture is continued at r.t. while monitoring the reaction on TLC. After about 10 minutes, when TLC showed disappearance of the starting material the reaction mixture is diluted with THF (50 ml) and filtered. Evaporation of the filtrate gave the reduced products which are purified further by chromatography.

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References & Notes

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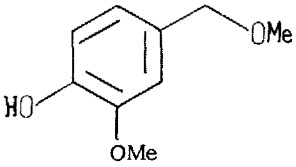
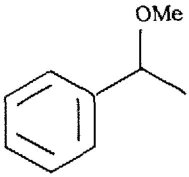
12. Substrates mentioned in entry 1 to entry 6 (Table 1) were successfully reduced to the desired products in good yields using methanol in place of THF. But in case of entry 7 and entry 8 when the reaction was carried out in MeOH, compounds A and B are formed along with the desired products in yields of 60% and 20% respectively.



A



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