Reduction of Organic Compounds with Rare Earth Intermetallic Compounds containing Absorbed Hydrogen

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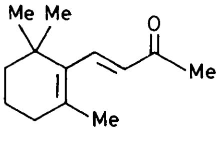
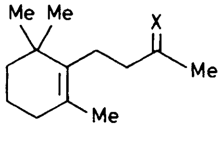
Various organic compounds are reduced in excellent yields with $LaNi_5H_6$ under nitrogen at atmospheric pressure.

Rare earth intermetallic compounds (alloys) such as $LaNi_5$, $PrCo_5$, and $SmCo_5$ absorb large quantities of hydrogen rapidly and reversibly under mild conditions of temperature and pressure, and they are used as convenient hydrogen storage substances.[1] The physicochemistry of these alloys has been extensively studied,[1,2] especially with regard to their use in energy storage, while less attention has been paid to their use in chemical reactions, except for the reduction of small molecules such as nitrogen, carbon monoxide, ethylene, and butadiene.[3] We have been interested in the properties of these intermetallic compounds, particularly in their use for reduction of organic functional groups. This communication reports a new and synthetically useful method for hydrogenation using rare earth metal alloys containing absorbed hydrogen.

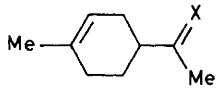
We used the $LaNi_5$ alloy which is a representative rare earth intermetallic compound and is readily available at moderate cost. The alloy was activated by the standard procedure,[4] and allowed to absorb hydrogen at room temperature. The intermetallic hydride ($LaNi_5H_6$) obtained was cooled to −78 °C and a solution of the organic compound in THF–MeOH (2 : 3) was added. The mixture was warmed slowly to room temperature with stirring under nitrogen at atmospheric pressure. The reduction usually proceeded at 0 °C through to room temperature, whereupon hydrogen gas evolved slowly. After completion of the reaction, the alloy was recovered by filtration† and the organic product was isolated in the usual manner. Using similar procedures, the reductions of a variety of organic compounds were examined. Typical results are listed in Table 1.



(1)



(2)a; X = O
b; X = H,OH



(3)a; X = CH_2
b; X = Me,H

Alkynes, mono-, and di-substituted alkenes were reduced to the corresponding saturated hydrocarbons in excellent yields. Several aldehydes including thiophene-3-carbaldehyde and *p*-chlorobenzaldehyde were smoothly converted into the primary alcohols, while the reductions of ketones required prolonged reaction times. For α,β-unsaturated carbonyl compounds, hydrogenation of the conjugated double bond was very fast, but subsequent reduction of the carbonyl group proceeded only slowly. Thus, selective reduction could be achieved by control of the reaction time, as is exemplified by the reductions of 1,3-diphenylprop-2-en-1-one, β-ionone, and citral. Our method is also effective for the reduction of nitro compounds and imines, especially as the $LaNi_5$ alloy is not poisoned by the liberated amines.

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† The alloy can be used repeatedly.

Table 1. The reductions of organic compounds over $LaNi_5H_6$.[a]

Compound	Conditions	Product	Yield (%)[b]
$PhC{\equiv}CPh$	0 °C (6 h), r.t.[c] (9 h)	$Ph[CH_2]_2Ph$	96
$n\text{-}C_{10}H_{21}CH{=}CH_2$	0 °C (6 h), r.t. (15 h)	$n\text{-}C_{12}H_{26}$	86
$p\text{-}ClC_6H_4CHO$	0 °C (6 h), r.t. (8 h)	$p\text{-}ClC_6H_4CH_2OH$	95
Thiophene-3-carbaldehyde	0 °C (6 h), r.t. (14 h)	3-Thiophenemethanol	96
$n\text{-}C_{11}H_{23}CHO$	0 °C (4 h), r.t. (14 h)	$n\text{-}C_{11}H_{23}CH_2OH$	98
$n\text{-}C_6H_{13}COMe$	0 °C (4 h), r.t. (37 h)	$n\text{-}C_6H_{13}C(H)(OH)Me$	91
PhCOCOPh	0 °C (6 h), r.t. (11 h)	PhC(H)OHCOPh	96
$PhCH{=}CHCO_2Et$	0 °C (2 h), r.t. (15 h)	$Ph[CH_2]_2CO_2Et$	93
$PhC{\equiv}CCO_2H$	0 °C (2 h), r.t. (15 h)	$Ph[CH_2]_2CO_2H$	99
$PhCH{=}CHCOPh$	0 °C (6 h), r.t. (2 h)	$Ph[CH_2]_2COPh$	93
$PhCH{=}CHCOPh$	0 °C (4 h), r.t. (43 h)	$Ph[CH_2]_2C(H)(OH)Ph$	99
(1)	0 °C (6 h), r.t. (6 h)	**(2a)**	89
(1)	0 °C (4 h), r.t. (33 h)	**(2b)**	95
$Me_2C{=}CH[CH_2]_2\text{-}C(Me){=}CHCHO$	0 °C (3 h)	$Me_2C{=}CH[CH_2]_2\text{-}CH(Me)CH_2CHO$	89
$Me_2C{=}CH[CH_2]_2\text{-}C(Me){=}CHCHO$	0 °C (6 h), r.t. (12 h)	$Me_2C{=}CH[CH_2]_2\text{-}CH(Me)[CH_2]_2OH$	95
(3a)	0 °C (6 h), r.t. (11 h)	**(3b)**	88
$p\text{-}O_2NC_6H_4CO_2Et$	0 °C (6 h), r.t. (13 h)	$p\text{-}H_2NC_6H_4CO_2Et$	97
$PhCH{=}NC_6H_{11}$	0 °C (6 h), r.t. (13 h)	$PhCH_2NHC_6H_{11}$	97

[a] All reactions were carried out on a 1 mmol scale using 3 g of $LaNi_5$. The alloy was used repeatedly. [b] Isolated yield. [c] r.t. = Room temperature.

However, attempted reductions of sulphoxides, sulphones, and oximes were unsuccessful, and in each case the starting compounds were recovered. Hydrogenolyses of peptides protected with the benzyloxycarbonyl group, dithioacetals, and acid chlorides were also unsuccessful. These results indicate that the alloy hydride exhibits quite different reactivities in comparison with conventional catalytic hydrogenation agents, *e.g.* Raney nickel, and palladium and rhodium metal.

The present method, employing a rare earth intermetallic compound, has the following characteristics. (1) The alloy used is not poisoned by compounds containing an amino group, halogen atom, or thiophene ring. (2) The alloy can be used repeatedly without decrease in activity. (3) The reduction can be carried out under mild conditions, and selective reduction can also be achieved. This method, then, has potential applicability in organic syntheses.

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