

Hydrometallation of Alkenes and Alkynes with Magnesium Hydride

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Summary Conditions and catalyst have been found that cause the hydrometallation of terminal olefins with MgH_2 in nearly quantitative yield.

SINCE the advent of hydroboration of olefins,¹ numerous attempts have been made to develop hydrometallation reactions with more readily available and less expensive main-group metal hydrides.²⁻⁴ Because magnesium metal is considerably less expensive than boron metal and its hydride (MgH_2) can be prepared from magnesium metal and hydrogen, there has been considerable interest in the hydrometallation of olefins with MgH_2 . Previous workers⁵ reported that MgH_2 reacts with ethylene in poor yield and

then only under rather severe conditions. We report here that MgH_2 adds readily to carbon-carbon multiple bonds in the presence of a titanium catalyst.

The reaction was studied by adding a catalytic amount of various transition metal compounds to a mixture of oct-1-ene and MgH_2 and following the appearance of octane (by g.l.c.) after hydrolysis. The amount of active magnesium alkyl produced was determined by quenching the reaction mixture with D_2O and analysing the product by mass spectroscopy. Although TiCl_3 and ZrCl_4 ⁶ have been shown to be excellent co-reactants in the hydrometallation of olefins with LiAlH_4 , these compounds were not effective in the reaction of MgH_2 with olefins. We evaluated the catalytic

TABLE. Reactions (at 60 °C unless otherwise noted) of alkenes and alkynes with MgH₂ in THF catalysed by Cp₂TiCl₂.^a

Substrate	Time/h	Quenching agent	Product (% Yield)
Oct-1-ene	1	H ₂ O	Octane (98)
		D ₂ O	[² H ₁]Octane (93)
Hex-1-ene	1	H ₂ O	Hexane (94)
		D ₂ O	[² H ₁]Hexane (89)
Styrene ^b (room temp.)	1	H ₂ O	Ethylbenzene (100)
		D ₂ O	CH ₂ CHDPh, CH ₂ DCH ₂ Ph (90, 10)
Methylenecyclohexane	48	H ₂ O	Methylcyclohexane (95)
		D ₂ O	[² H ₁]Methylcyclohexane (60)
<i>cis</i> -Hex-2-ene	68	H ₂ O	Hexane (66)
		D ₂ O	<i>trans</i> -Hex-2-ene (26)
<i>trans</i> -Hex-2-ene	92	H ₂ O	[² H ₁]Hexane (20)
		D ₂ O	Hexane (70)
3-Methyleneheptane	92	H ₂ O	<i>cis</i> -Hex-2-ene (2.5)
		D ₂ O	[² H ₁]Hexane (0)
Oct-1-yne (room temp.)	1	H ₂ O	3-Methylheptane (85)
		D ₂ O	[² H ₁]-3-Methylheptane (0)
Oct-4-yne (room temp.)	1	H ₂ O	Oct-1-ene (60)
		D ₂ O	Oct-1-yne (40)
Oct-4-yne (room temp.)	1	H ₂ O	[² H ₁]Oct-1-ene (50)
		D ₂ O	[² H ₁]Oct-1-yne (40)
		H ₂ O	<i>cis</i> -Oct-2-ene (100)
		D ₂ O	<i>cis</i> -[² H ₁]Oct-4-ene (65)

^a Ratio substrate: MgH₂:Cp₂TiCl₂ = 2.00:1.00:0.05. ^b Ref. 7.

ability of many transition metal compounds (many of which effected the reduction of oct-1-ene, but showed no evidence of the intermediate magnesium alkyl as determined by reaction of the product with D₂O), and determined that bis-(cyclopentadienyl)titaniumdichloride (Cp₂TiCl₂) produced the best results.

The Table displays the results of reactions involving a variety of alkenes and alkynes with MgH₂ in tetrahydrofuran (THF) using Cp₂TiCl₂ as a catalyst. The data show that this reaction appears to be most useful for monosubstituted olefins (*e.g.* oct-1-ene, hex-1-ene, styrene). In 1 h at room temperature or at 60 °C the reaction is quantitative in forming the reduction product and nearly quantitative in forming the intermediate organomagnesium compound. The cyclic *exo*-methylene compound (methylenecyclohexane) and the internal alkyne (oct-4-yne) react with moderate success while the results with internal olefins are not as good. In the case of the terminal alkyne (oct-1-yne) there is competition between MgH₂ addition and deprotonation. For aliphatic olefins the rate of reaction decreases with increasing substitution; the reaction of oct-1-ene is about 75 times faster than the reaction with *cis*-hex-2-ene and the trisubstituted olefin, 1-methylcyclohexene, shows virtually no reactivity at all. It is also notable that the amount of active magnesium alkyl, as determined from the deuterium incorporation experiments, increases as the reaction time decreases.

The hydrometallation reaction is influenced by both steric and electronic effects. When the reaction with oct-1-ene and MgH₂ is quenched with iodine the product is 1-iodooctane with >95% isomeric purity (as determined by g.l.c. and n.m.r.). On the other hand, when the reaction of styrene with MgH₂ is quenched with D₂O the deuteriated ethylbenzene produced is a 90:10 mixture of isomers in which the greater portion of the deuterium is located at the position α to the phenyl group implying that electronic effects are very important.

A typical experiment involves the preparation of 1 mmol of active magnesium hydride by the reaction of LiAlH₄ and diethylmagnesium in diethyl ether.^{6,7} The precipitated MgH₂ is then washed ($\times 3$) with diethyl ether and suspended in THF. In a separate vessel the substrate (2 mmol) is mixed with Cp₂TiCl₂ (0.05 mmol) in THF.† The catalyst-substrate solution is then added to the MgH₂ with rapid stirring. The reaction mixture turns black or blue-grey (the more reactive substrates yield a black homogeneous solution). This mixture is then heated in an oil bath if necessary. It should be noted that Cp₂TiCl₂ in the presence of reducing agents fixes nitrogen⁸ so that all manipulations must be carried out under argon.

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† In the reaction with styrene 0.10 mmol of Cp₂TiCl₂ was used in order to minimize polymerization.

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⁷ Magnesium hydride prepared from NaH and MgCl₂ in THF (E. C. Ashby and R. Schwartz, *Inorg. Chem.*, 1971, **10**, 355) showed similar results with oct-1-ene.

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