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LETTER

MgH_2 as a Reducing Agent in the Presence of Transition Metal Halides
III. Reduction of Ketones and Aldehydes

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In previous papers [1] we have shown that MgH_2 prepared according to Bogdanovic *et al.* [2] as an insoluble pyrophoric and finely subdivided material, hydrodehalogenates alkyl, aryl and vinyl halides in the presence of catalytic amounts of transition metal halides. We have now found that MgH_2 when similarly activated reduces the carbonyl functionality of ketones and aldehydes.

Experimental

The reactions were run under dinitrogen as follows. MgH_2 (3 mmol) suspended in THF (*c.* 1 mmol ml^{-1}) was siphoned over MX_n (MgH_2/MX_n 10:1 mol) in a Schlenk tube sealed with a rubber septum. The organic substrate (*c.* 1 mmol) was then added. The reaction mixture was magnetically stirred at the required temperature. When $FeCl_3$ was used as the promoter, the reaction mixture was prepared at −78 °C and slowly warmed up to room temperature as an exothermic reaction ensues on mixing $FeCl_3$ and MgH_2. The reaction was then quenched with dilute hydrochloric acid and the organic layer was extracted with ether. A suitable internal standard was added prior to GLC analysis.

TABLE 1. Reduction of ketones and aldehydes by MgH_2/MX_n[a]

Substrate	MX_n	Reaction temperature (°C)	Reaction time (h)	Substrate consumed (%)	Reduction product (%)[b]
Cyclohexanone		25	20	25	19
		67	8	80	15
	$TiCl_3 3THF$	25	20	91	18
	VCl_3	25	20	24	19
	$CrCl_3$	25	20	60	23
	$MnCl_2$	25	20	59	16
	$FeCl_3$	25	20	98	98
	$CoCl_2$	25	20	73	74
	$NiCl_2$	25	20	18	18
Cycloheptanone		67	6	28	13
	$FeCl_3$	67	3	86	75
Cyclooctanone		67	20	20	13
	$FeCl_3$	67	20	88	80
2-Octanone		67	20	79	24
	$FeCl_3$	67	20	100	85
Acetophenone		67	6	89	16
	$FeCl_3$	67	2	80	62
Cyclohexanecarboxyaldehyde		25	20	30	25
	$FeCl_3$	25	20	98	62
	$CoCl_2$	25	20	100	87
Benzaldehyde		25	20	33	22
	$FeCl_3$	25	20	79	68
	$CoCl_2$	25	20	100	90

[a]Substrate: $MgH_2:MX_n$ = 1:3:0.3. [b]Yields determined by GLC in the presence of a suitable internal standard.

Discussion

An extensive study has been carried out on cyclohexanone as the substrate (Table 1). A mixture of cyclohexanone, MgH_2 and metal halide promoter in the molar ratio 1:3:0.3 was stirred in THF at room temperature.

Among the first row transition metal halides the best conversions to cyclohexanol were obtained with $FeCl_3$ and $CoCl_2$, the former being more active than the latter. In all the other cases, while no appreciable activation with respect to MgH_2 alone was observed, variable quantities of the aldol condensation products were formed.

The reduction was then extended to a number of ketones. In each case good conversions to secondary alcohols were found in boiling THF in the presence of $FeCl_3$ as the promoter.

The MgH_2/MX_n system was also tested in the reduction of the carbonyl functionality of aldehydes. Cyclohexanecarboxyaldehyde and benzaldehyde, which were chosen as probe substrates, were extensively reduced to the corresponding alcohols in the presence of either $CoCl_2$ or $FeCl_3$. In this case $CoCl_2$ was somewhat more active than $FeCl_3$. The formation of the aldol condensation product is also drastically reduced in the presence of $CoCl_2$.

Conversely, the MgH_2/MX_n system is much less active in the reduction of esters. Thus reduction of ethyl benzoate in the presence of either $FeCl_3$ or $CoCl_2$ produced benzyl alcohol in low yields (15–36%).

Conclusion

In conclusion our results show that MgH_2, largely available according to the preparation method found by Bogdanovic *et al.* [2], may be used to reduce the carbonyl functionality of aldehydes and ketones in the presence of a suitable metal halide as the promoter. Thus MgH_2 behaves similarly to LiH and NaH which have also been activated by transition metal halides [3, 4].

References

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