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NOTE

수소화붕소 아연에 의한 α, β-불포화 알데히드와 케톤의 환원반응

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Zinc Borohydride Reduction of α, β-Unsaturated Aldehydes and Ketones

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Sir: The selective reduction of carbonyl group in α, β-unsaturated aldehydes and ketones by metal hydrides has offered considerable difficulty[1]. In many instances, 1, 2-addition competes with 1, 4-addition, resulting the mixture of allylic alcohol, and saturated alcohol and/or carbonyl compound.

Recently we have studied the reducing characteristics of zinc borohydride systematically and found that cinnamaldehyde, an α, β-unsaturated

Table 1. Rate and stoichiometry of reduction of α, β-unsaturated carbonyl compounds with zinc borohydride[a] in THF at room temperature.

Compound[b]	Hydride used for reduction[c]				
	0.5 hr	1.0 hr	3.0 hr	6.0 hr	12.0 hr
Acrolein[d]	1.02	1.02	1.03	1.04	
Crotonaldehyde	0.61	0.78	0.96	1.02	1.03
Cinnamaldehyde	0.54	0.69	0.85	1.03	1.05
Methyl vinyl ketone	0.89	0.97	1.11	1.15	1.16
2-Cyclohexenone	0.53	0.76	0.96	1.01	1.00
3-Methyl-2-cyclohexenone	0.33	0.53	0.72	0.96	1.03[e]

[a] Zinc borohydride was prepared by mixing 140 mmoles of $NaBH_4$ with 60 mmoles of $ZnCl_2$ in THF for 3 days at room temperature

[b] 5 mmoles of compound was added to 2.5 mmoles of zinc borohydride (20 mmoles of hydride) in 40 ml of THF solution (0.5 *M* in hydride and 0.12 *M* in compound)

[c] Number of moles of hydride used per mole of compound

[d] Ice-bath at initial period of addition of hydride (20min)

[e] After 24.0 hr, 1.03 moles of hydride was utilized per mole of 3-methyl-2-cyclohexenone.

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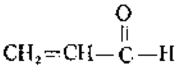
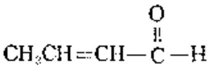
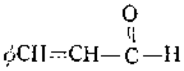
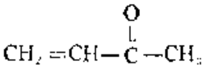
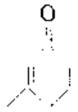
*Department of Chemistry, Chonnam National University, Kwangjoo, Korea aldehyde, consumed only one mole of hydride per mole of the compound, suggesting the clean reduction to cinnamyl alcohol[2]. Some years ago Corey *et al.*, also applied zinc borohydride successfully for the reduction of an 2-en-1-one, a prostaglandin intermediate, to the corresponding allylic alcohol[3].

Encouraged with these results, we have decided to investigate the reduction of α, β-unsaturated carbonyl compounds with this hydride more in detail. Three aldehydes; acrolein, crotonaldehyde, and cinnamaldehyde, and three ketones; methyl vinyl ketone, 2-cyclohexenone, and 3-methyl-2-cyclohexenone were reduced with zinc borohydride at standard condition (THF, room temperature, 0.5 *M* in hydride and 0.125 *M* in compound).

First, we have studied approximate rates and stoichiometries of the reactions under the standard condition. As shown in *Table* 1, all the compounds tested consumed only one mole of hydride per mole of compound as expected. Next, in order to examine the products, these compounds were reduced on a preparative scale. Thus 100 mmoles of each compound was added to 150 mmoles of hydride, total reaction mixture being 200 m*l*; 0.75 *M* in hydride and 0.5 *M* in compound. All the reductions were completed in 6 hours at room temperature as revealed by the hydride consumption. After waiting 2 more hours excess hydride was destroyed by adding small amount of water. The water layer was saturated with potassium carbonate and THF layer was seperated. The THF layer was dried over anhydrous magnesium sulfate and subjected to rotary evaporator. The residue was distilled. The yields of the distilled products and the compositions of alcohols are shown in *Table* 2, and compared with the results of sodium borohydride reduction reported by Johnson and Rickborn[1c].

Table 2. Reduction products of α, β-unsaturated carbonyl compounds with zinc borohydride[a] in THF at room temperature.

Compound[b]	Total yield[c] (%)	Unsaturated alcohol[d]	Saturated alcohol[d]
 $CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H$	68.2	100[e] (85)[f]	0 (15)
 $CH_3CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H$	87.5	100 (92)	0 (8)
 $\phi CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H$	96.2	100	trace
 $CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$	84	91 (57)	9 (43)
	84	96 (59)	4 (41)
	97.6	97.4 (70)	2.6 (30)

[a] See corresponding footnote in *Table* 1

[b] The concentration of hydride and compound were 0.75 *M* and 0.5 *M*, respectively

[c] Isolated yield.

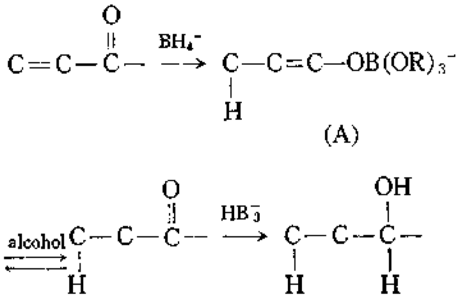
[d] Determined by glpc using Carbowax 20 *M* and Silicone oil columns.

[e] Normalized %.

[f] Results obtained with $NaBH_4$ in 50 % aq. EtOH: M. R. Johnson and B. Rickborn, *J. Org. Chem.*, 35, 1041 (1970).

The results show that zinc borohydride is excellent for the reduction of α, β-unsaturated aldehydes to the corresponding allylic alcohols. However the reduction of α, β-unsaturated ketones gave some amount of the saturated alcohols in all three cases. The amount decreases as the substitution at 4 position increases. In general, zinc borohydride (THF) is much superior to sodium borohydride (50% aqueous ethanol) in selectivity.

Johnson and Rickborn proposed a scheme for the formation of saturated alcohol as fallows[1c].



$$\mathrm{C{=}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}} \xrightarrow{\mathrm{BH_4^-}} \mathrm{\underset{\underset{\displaystyle H}{|}}{C}{-}C{=}C{-}OB(OR)_3^-}$$

(A)

$$\xrightleftharpoons{\text{alcohol}} \mathrm{\underset{\underset{\displaystyle H}{|}}{C}{-}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}} \xrightarrow{\mathrm{HB_3^-}} \mathrm{\underset{\underset{\displaystyle H}{|}}{C}{-}C{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}}$$

(B)

However the enolate (A), resulted from the hydride attack at 4 position, is unlikely to isomerize to saturated ketone (B) in zinc borohydride reduction since there is no proton source available in zinc borohydride solution in THF. We are going to investigate this more in detail.

SUMMARY

Reduction of α, β-unsaturated aldehydes and ketones with zinc borohydride proceeds selectively to the corresponding allylic alcohols in good yield, as revealed by gas chromatography.

ACKNOWLEDGEMENT

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3. E. J. Corey *et al.*, *J. Amer. Chem. Soc.*, **93**, 1491(1971) and references therein.