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REDUCTION OF ALDEHYDES AND KETONES WITH $Cp_2Zr(Cl)BH_4$

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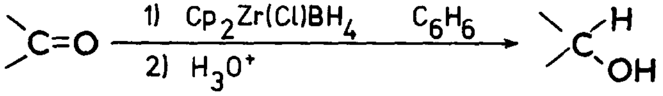
The use of covalent transition metal tetrahydroborate complexes[1] as stoichiometric reducing agents in organic chemistry has been proposed recently[2], however, the only reported example of such a reagent is $(Ph_3P)_2CuBH_4$ which converts acid chlorides to aldehydes in high yields under mild conditions.[2,3] The possibility that a lanthanide tetrahydroborate complex is instrumental in the reduction of α,β-unsaturated ketones to allylic alcohols has also been noted[4], but that case is not well defined. The present report deals with the reactions of bis(cyclopentadienyl) chlorotetrahydroborato zirconium(IV)[5], $Cp_2Zr(Cl)BH_4$, which promises to be the prototype for an entire series of stoichiometric reducing agents.

The zirconium tetrahydroborate complex, 1, is conveniently prepared by the addition of one equivalent of borane-methyl sulfide to a stirred suspension of $Cp_2Zr(H)Cl$[6] followed by precipitation and recrystallization to give a free-flowing white powder in 70-80% yield. As a reagent, 1 has been found to reduce aldehydes and ketones to alcohols in benzene solution at 25° (equation 1). The reactions are generally complete within a few minutes, and isolated yields are often high (Table 1).[7]



(1)

A comparison of $Cp_2Zr(Cl)BH_4$ with conventional boron and aluminum hydride reducing agents demonstrates the potential utility of 1. First, it is more selective than many hydridic reagents such as $LiAlH_4$ and its derivatives[8], borane[8], and the trialkylborohydrides.[9] Thus, carboxylic acids, esters, nitriles, and nitro compounds react very slowly with 1 allowing selective reduction of aldehyde and ketone carbonyl groups.[10] Second, since its reactivity is similar to sodium borohydride, $Cp_2Zr(Cl)BH_4$ may be used to carry out reductions of non-polar substrates which are insoluble in the alcoholic media generally used with $NaBH_4$. Finally, its use does not require an inert atmosphere as many simpler alane and borane derivatives do.

Unfortunately, certain aspects of the regio- and stereoselectivity of 1 are disappointing.[11] For example, α,β-unsaturated ketones are reduced in poor yield, giving both the saturated and unsaturated alcohols (Table 1). Also, little stereoselectivity is observed in the reduction of 4-*t*-butylcyclohexanone. Hopefully, these shortcomings can be remedied by derivatives of 1, and work toward this goal is in progress.

Table 1

Starting Material	Product	Yield[a]
nonanal	nonanol	90
4-chlorobenzaldehyde	4-chlorobenzyl alcohol	96
4-nitrobenzaldehyde	4-nitrobenzyl alcohol	100
cinnamaldehyde	cinnamyl alcohol	49[b]
acetophenone	1-phenylethanol	98
4-*t*-butylcyclohexanone	4-*t*-butylcyclohexanol	90[c]
2-cyclohexenone	2-cyclohexenol	18[d]
	cyclohexanol	18

a) Yields are for isolated, distilled products (reference 7). b) No reduction of the C=C bond was observed; 28% yield of polymer was obtained. c) A 2:1 mixture of the *trans* and *cis* compounds was obtained. d) 34% yield of polymer was obtained.

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REFERENCES AND NOTES

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5. This compound has been reported previously; however, no detail for either its preparation or characterization was presented. R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1978 (1964)
6. Cp$_2$Zr(H)Cl (Schwartz's reagent) is commercially available from the Ventron Corporation, Alfa Division. Its preparation has been described: D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974). Detailed procedures for the preparation of **1** and of other metal tetrahydroborate complexes via the metal hydride-borane route will be described in a forthcoming paper.
7. Isolated compounds had proton nmr spectra identical to authentic samples and were generally >97% pure by glc or tlc analysis. The preparation of 1-phenylethanol is representative: to a stirred solution of 166.2 mg of acetophenone in 2 mL of benzene was added, in one portion, 400.6 mg of **1**. After 13 min (the reaction was monitored by glc), 1 mL of 5% hydrochloric acid and 20 mL of saturated NaCl were added and the solution extracted with three 10-mL portions of ether. The ether extracts were dried over MgSO$_4$ and then filtered through a short column (2.5 x 9 cm) of 60-200 mesh silica. The silica was washed with 200 mL of chloroform and the combined organic portion evaporated to give an oil. Bulb-to-bulb distillation at reduced pressure gave 165.2 mg (98%) of 1-phenylethanol.
8. H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Inc., Reading, 1972, pp 45-144.
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10. Carboxylic acid chlorides are reduced slowly to alcohols (after hydrolysis) although the yields are poor.
11. A puzzling feature of these reactions is the formation of adducts of **1** with compounds which are not easily reduced. Thus, the concentration of a benzene solution of ethyl benzoate decreases with time upon addition of **1** (monitored by glc). However, after hydrolysis of the mixture with dilute acid, 90-95% of the starting ester is observed once again. The nature of these adducts is under investigation.

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