Asymmetric Reduction of Aromatic Ketones with Reagents Prepared from $NaBH_4$ and $ZnCl_2$ in the Presence of 1,2 : 5,6-Di-*O*-isopropylidene-α-D-glucofuranose

Akira HIRAO,* Masaki OHWA, Shinichi ITSUNO, Hidenori MOCHIZUKI, Seiichi NAKAHARA, and Noboru YAMAZAKI

Department of Polymer Science, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

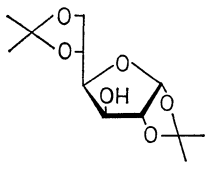
(Received August 29, 1980)

Asymmetric reduction of prochiral aromatic ketones using a freshly prepared complex derived from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) gives an excess of the corresponding (*S*)-alcohols in substantial optical yields (28—68%). The effects of the $NaBH_4/ZnCl_2/$**1** ratio, temperature, solvent, structure of various monosaccharide derivatives, and the metal cation of the reagent on the optical yields were examined.

Asymmetric reduction of carbonyl compounds has recently been achieved by use of metal hydrides modified by chiral compounds such as chiral diols,[1] amines,[2] and α-pinene.[3,4] The hydrides would be of use for the synthesis of enantiomerically pure molecules of biological interest.

However, only a few reports have been made on the application of sodium borohydride($NaBH_4$) to the same type of asymmetric reduction, the reagent being found to be less effective with ketones,[5-8] though $NaBH_4$ is a mild and highly selective reducing agent.

It was found that aromatic ketones are asymmetrically reduced by $NaBH_4$ in the presence of monosaccharide derivatives, attempts for selectivity not being quite successful.[9] Stereoselectivities have been greatly enhanced by addition of Lewis acids. We reported on a test of modified reagents derived from $NaBH_4$ and Lewis acids such as zinc chloride and aluminium chloride in the presence of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) for the asymmetric reduction of aromatic ketones.[10]



1

The results show that reaction of $NaBH_4$ with zinc chloride ($ZnCl_2$) affords a reagent, presumably a zinc borohydride or the related borohydride species, which give higher stereoselectivities than those achieved with $NaBH_4$ alone.

This paper describes a detailed study of asymmetric reduction of prochiral ketones with the reagents prepared from $NaBH_4$ and $ZnCl_2$ in the presence of **1** to establish the optimum conditions for maximum stereoselectivity. The species responsible for the maximum asymmetric induction (68%) has been discussed.

Results and Discussion

Asymmetric Reduction of Ketones with the Reagents Derived from $NaBH_4$ and $ZnCl_2$ in the Presence of ***1****.* Addition of 0.5 molar equiv of $ZnCl_2$ to the suspended $NaBH_4$ in tetrahydrofuran (THF) gave rise to quantitative precipitation of NaCl (1 mol) and the formation of soluble borohydride species in the solution. Subsequent addition of 2 equiv of monosaccharide **1** (R*OH) caused evolution of 2.0 mol of hydrogen, 2.0 equiv of hydride remaining in the reducing agents in the solution. No further hydrogen uptake took place after 24 h. The reaction of $NaBH_4$ with $ZnCl_2$ and subsequent addition of **1** seems to proceed according to the equation:

$$NaBH_4 + 1/2\,ZnCl_2 \rightleftarrows 1/2\,Zn(BH_4)_2 + NaCl\downarrow \quad (1)$$

$$1/2\,Zn(BH_4)_2 + 2\,R^*OH \longrightarrow 1/2\,Zn(BH_2(OR^*)_2)_2 + 2H_2\uparrow \quad (2)$$

Asymmetric reduction of propiophenone was carried out with suspension of $NaBH_4$ in THF to which $ZnCl_2$ in varying amounts and a fixed quantity (2 equiv to $NaBH_4$) of **1** had been added. The results are summarized in Table 1. We see that the stereoselectivity increases to a maximum and then decreases with addition of $ZnCl_2$. The reagent formed by adding 1/3 mol of $ZnCl_2$ per mole of $NaBH_4$ gives optimum induction; maximum selectivity as high as 68% was obtained. It was found that all the 1-phenyl-1-propanols produced with the reagents derived from $NaBH_4$ and $ZnCl_2$ have the (*S*)-configuration, while

Table 1. Effect of the ratio of $[ZnCl_2]/[NaBH_4]$ on optical yield in the presence of **1** in THF at 30 °C

Ratio $[ZnCl_2]/[NaBH_4]$	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
0	100	−8.32°	18	*R*
0.2	100	−16.74°	36	*S*
0.25	100	−18.42°	39	*S*
0.26	100	−20.25°	42	*S*
0.28	100	−25.96°	55	*S*
0.30	100	−26.05°	55	*S*
0.33	100	−32.12°	68	*S*
0.4	98	−27.65°	59	*S*
0.5	100	−21.77°	46	*S*
1.0	100	−4.71°	10	*S*
1.1	100	−3.39°	7	*S*

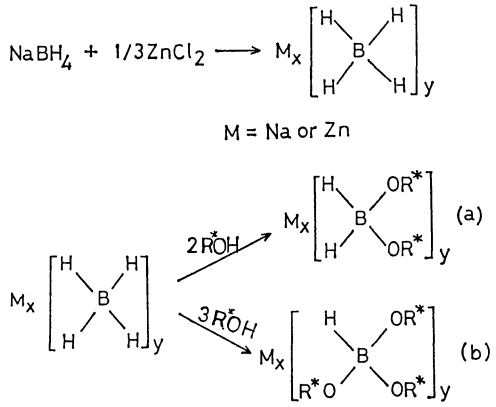
a) Based on $[\alpha]_D^{20}$ +47.03° reported by H. Kwart and D. P. Hoster, *J. Org. Chem.*, **32**, 1867 (1967).

Table 2. Effect of the ratio of [1]/[$NaBH_4$+1/3 $ZnCl_2$] on optical yield in the asymmetric reduction of propiophenone in THF at 30 °C

Ratio	Produced alcohol			
[1]/[$NaBH_4$+1/3 $ZnCl_2$]	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
0.5	100	−11.21°	24	*S*
1.0	100	−19.33°	41	*S*
2.0	100	−32.12°	68	*S*
3.0	80	−8.95°	19	*S*
4.0	0	—	—	—

the reduction with $NaBH_4$ alone gives the same alcohol of the (*R*)-configuration in 18% of an optical yield.

The effect of the amount of **1** to the $NaBH_4$–1/3 $ZnCl_2$ reagent on optical yield was examined (Table 2). Optical yield increased with the increase in the ratio of **1** to the reagent based on $NaBH_4$. The maximum selectivity could be obtained at a *ca.* 2 molar ratio. A marked fall in selectivity took place by addition of 3 molar equiv of **1**. This is curious since the resulting monohydride (**b**) would be in a more steric and chiral environment than the corresponding dihydride (**a**):



Further addition of **1** (4 equiv) might remove all hydrides on the reagent giving tetrasubstituted alkoxyborate complex which can not react further. Addition of 4 equiv of **1** evolved 4.0 mol of hydrogen, giving rise to incomplete reduction of propiophenone. The stoichiometric quantities of $NaBH_4$, $ZnCl_2$, and **1** were found to be optimum at 1,/1/3,/ and 2.0, respectively.

We next examined the dependency of selectivity on chemical yield with the complex from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 2 equiv of **1** and found that selectivity is constant until less than one equiv of propiophenone to the reagent was used (Table 3). However, a significant decrease in the optical yield was observed when 1.5 equiv of ketone was used. This suggests that of two available hydrides on the complex (**a**) as described above, the first hydride would be more effective for the asymmetric induction.

Optical yields vary with solvent, THF being the best in stereoselectivity (Table 4).

Table 3. The effect of [propiophenone]/[$NaBH_4$+1/3$ZnCl_2$] on optical yield in the asymmetric reduction of propiophenone in THF at 30 °C

Ratio	Produced alcohol			
[propiophenone]/[$NaBH_4$+1/3 $ZnCl_2$]	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
0.3	100	−29.63°	63	*S*
0.5	100	−29.16°	62	*S*
0.8	100	−32.12°	68	*S*
1.0	100	−32.08°	68	*S*
1.5	100	−13.54°	29	*S*

Table 4. Solvent effct on optical yield in the asymmetric reduction of propiophenone with a reagent prepared from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 2 equiv of **1** at 30 °C

Solvent	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
THF	100	−32.12°	68	*S*
Diethyl ether	100	−22.48°	48	*S*
Benzene	100	−14.48°	31	*S*

Table 5. Temperature effect on optical yield in the asymmetric reduction of propiophenone in THF

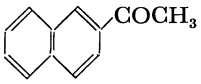
Temperature °C	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
50	99	−23.50°	50	*S*
30	100	−32.12°	68	*S*
0	93	−29.30°	62	*S*
−30	0	—	—	—

The temperature effect on asymmetric reduction of propiophenone appeared not to be critical in the range 0—50 °C (Table 5). Rise in temperature from 0 °C to 50 °C caused decrease in optical yield to some extent. No reduction took place at −30 °C even after 108 h.

The complex from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 2 equiv of **1**, reduced a variety of aromatic ketones in excellent chemical yields with substantial enantiomeric excesses (⩾50%) except for the case of isopropyl phenyl ketone. The same complex also reduced an alkyl ketone such as isobutyl methyl ketone with moderate selectivity. The six ketones were reduced with $NaBH_4$ in the presence of **1** (Table 6). It is apparent from a comparison of the results that the complex system is superior to the original system with use of $NaBH_4$ and **1**. In each case with the complex the (*S*)-configuration of the alcohols produced was opposite that of the alcohols obtained by $NaBH_4$ alone in which (*R*) isomer predominates.

In order to determine the structural effect of various

Table 6. Asymmetric reduction of various ketones with the complex prepared from $NaBH_4$, 1/3 $ZnCl_2$, and 2 equiv of **1** in THF at 30 °C

Ketones	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
$C_6H_5COCH_3$	100	−26.25°	50[a] (3)[b]	*S* (*R*)[b]
$C_6H_5COC_2H_5$	100	−32.12°	68[c] (18)	*S* (*R*)
$C_6H_5COC_3H_7$	100	−25.29°	58[d] (14)	*S* (*R*)
$C_6H_5COC_3H_7$-*i*	98	−13.36°	28[e] (9)	*S* (*R*)
	100	−28.49°	68[f] (20)	*S* (*R*)
$CH_3COC_4H_9$-*i*	99	+7.60°	37[g] (3)	*S* (*R*)

a) Based on $[\alpha]_D$ +52.5° (CH_2Cl_2) reported by U. Nagai and T. Shishido, *Tetrahedron*, **21**, 1701 (1965). b) Values in parentheses obtained by asymmetric reduction with $NaBH_4$ plus **1** in THF. c) Based on $[\alpha]_D^{20}$ +47.03° (Acetone) reported by H. Kwart and D. P. Hoster, *J. Org. Chem.*, **32**, 1867 (1967). d) Based on $[\alpha]_D$ +43.6° (C_6H_6) reported by S. Yamaguchi and H. S. Mosher, *J. Org. Chem.*, **38**, 1870 (1973). e) Based on $[\alpha]_D$ +47.7° (Diethyl ether) reported by P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **70**, 355 (1926). f) Based on $[\alpha]_D$ −41.9° (Ethanol) reported by T. A. Collyer and J. Kenyon, *J. Chem. Soc.*, **1940**, 676. g) Based on $[\alpha]_D$ +20.54 (neat) reported by J. Kenyon and H. E. Strauss, *J. Chem. Soc.*, **1949**, 2153.

Table 7. Asymmetric reduction of propiophenone with a reagent from $NaBH_4$ and 1/3 equiv of $ZnCl_2$ in THF 30 °C in the presence of various monosaccharide derivatives (values in parentheses were obtained in the asymmetric reduction with $NaBH_4$ plus **1**, **2**, **3**, **4**, **5**, or **6** in THF

Monosaccharid derivative	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
1	100	−32.12°	68(18)	*S* (*R*)
2	97	−4.23°	9(25)	*S* (*R*)
3	100	+4.71°	10(13)	*R* (*S*)
4	94	−11.90°	25(7)	*S* (*S*)
5	100	+5.22°	11(6)	*R* (*S*)
6	100	−7.52°	16(0)	*S* (—)

monosaccharide derivatives on the reaction, we have examined the asymmetric reduction of propiophenone with the complexes prepared from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 2 equiv of **2**, **3**, **4**, **5**, or 2/3 equiv of **6** (2 equiv for OH moiety) in THF at 30 °C. The reactions resulted in complete reduction in all cases. The enantiomeric excess from each reduction is given in Table 7. Selectivity was generally low as compared with that obtained by the complex from **1**. The order of asymmetric induction by the complexes from **1** to **6** is not the same as that by $NaBH_4$. An increase in the stereoselectivity of $NaBH_4$ by adding 1/3 equiv of $ZnCl_2$ occurred with **1**, but it is not as

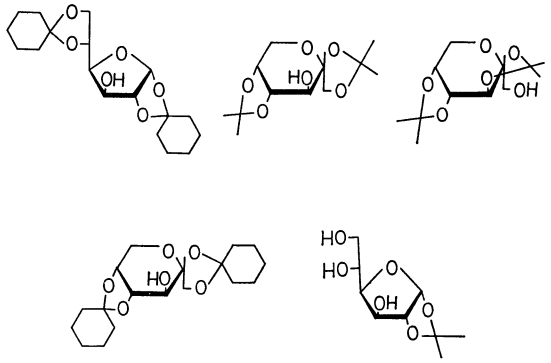


Table 8. Asymmetric reduction of propiophenone with reagents from various metal borohydrides and 1/3 equiv of $ZnCl_2$ in the presence of **1** in THF at 30 °C (values in parentheses were obtained by the asymmetric reduction with $LiBH_4$, $NaBH_4$, KBH_4, $RbBH_4$, or $CsBH_4$ plus **1** in THF at 30 °C)

Reagents	Produced alcohol			
	Chemical yield/%	$[\alpha]_D^{20}$	Optical yield/%	Configuration
$LiBH_4$+1/3 $ZnCl_2$	100	0	0(0)	—(—)
$NaBH_4$+1/3 ZnCl	100	−32.12°	68(18)	*S* (*R*)
KBH_4+1/3 $ZnCl_2$	100	−17.12°	36(5)	*S* (*R*)
$RbBH_4$+1/3 $ZnCl_2$	100	−25.02°	53(—)[a]	*S* (—)
$CsBH_4$+1/3 $ZnCl_2$	70	−20.69°	44(—)[a]	*S* (—)

a) Chemical yields in both cases were less than 10% Optical rotations could not be measured.

pronounced as with other monosaccharides, **2**—**6**.

Four additional modified reagents were prepared from lithium, potassium, rubidium, or caesium borohydrides and 1/3 equiv of $ZnCl_2$ and were applied to the asymmetric reduction of propiophenone with subsequent addition of 2 equiv of **1** in THF at 30 °C. The results are summarized in Table 8. We see that the reagents from sodium, potassium, rubidium, and caesium borohydrides and 1/3 equiv of $ZnCl_2$ have emerged as more effective asymmetric reducing agents than the corresponding metal borohydrides and propiophenone can be reduced with these reagents in good chemical and optical yields, giving product mixtures in which the (*S*)-alcohol configuration predominates. Neither $LiBH_4$–1/3 $ZnCl_2$ nor $LiBH_4$ showed asymmetric induction, although the reducing yields were quantitative, the order of the influence of the metal cation on selectivity being $Na > Rb > Cs \simeq K \gg Li$. The cause of the effect is not clear so far.

The rates of reduction by these reagents were much greater than those by the corresponding metal borohydrides except for the case when the metal was lithium: chemical yields: 100% with $NaBH_4$–1/3 $ZnCl_2$ *vs.* 20% with $NaBH_4$ for 2 h; 100% with KBH_4–1/3 $ZnCl_2$ *vs.* 25% with KBH_4 for 24 h; 100% with $RbBH_4$–1/3 $ZnCl_2$ *vs.* 10% with $RbBH_4$ for 72 h; 70% with $CsBH_4$–1/3 $ZnCl_2$ *vs.* 5% with $CsBH_4$ for 72 h. This can be, at least, attributed to the great increase in solubility of the metal borohydrides caused by the

addition of $ZnCl_2$. The order of reduction rate by the reagent, $LiBH_4$–1/3 $ZnCl_2$ > $NaBH_4$–1/3 $ZnCl_2$ > KBH_4–1/3 $ZnCl_2$ > $RbBH_4$–1/3 $ZnCl_2$ > $CsBH_4$–1/3 $ZnCl_2$, is in line with the order of the reducing strength of the metal borohydrides, $LiBH_4$ > $NaBH_4$ > KBH_4 > $RbBH_4$ > $CsBH_4$.[11]

Examination of the Reaction Species from $NaBH_4$ and $ZnCl_2$ in the Presence of **1**. The complex prepared from $NaBH_4$ and 1/3 equiv of $ZnCl_2$ with further addition of 2 equiv of **1** reduced propiophenone with the highest optical yield (68%). The complex responsible for the asymmetric induction was examined.

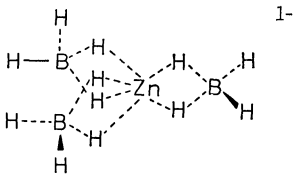
$ZnCl_2$ (7 mmol) in THF was added to a suspension of 21 mmol of $NaBH_4$ in THF at 30 °C. A solid was always present during the course of reaction. The resulting slurry was stirred at 30 °C for 3 h and then filtered. A very small amount of the starting zinc compound but no active hydride species was present in the solid product. From the result of analysis this seems to be sodium chloride, yield of which is nearly quantitative based on initial sodium amount. The filtrate contained *ca.* 100% of the initial amounts of zinc and the active hydrides. The analysis gave a Na:Zn: hydride (B-H): Cl of 1.0:1.0:12.3:0, indicating a physical mixture of $NaBH_4$ and $Zn(BH_4)_2$ at 1:1 molar ratio or a double hydride complex of $NaZn(BH_4)_3$. The reaction may be represented as follows.

$$NaBH_4 + 1/3\ ZnCl_2 \longrightarrow 1/3\ NaBH_4 + 1/3\ Zn(BH_4)_2 + 2/3\ NaCl\downarrow \quad (1)$$

$$NaBH_4 + 1/3\ ZnCl_2 \longrightarrow 1/3\ NaZn(BH_4)_3 + 2/3\ NaCl\downarrow \quad (2)$$

If the reaction of $NaBH_4$ and $ZnCl_2$ gives a physical mixture of $NaBH_4$ and $Zn(BH_4)_2$ (Eq. 1), the reaction might afford precipitates of $NaBH_4$ and NaCl, leaving $Zn(BH_4)_2$ in solution, since $NaBH_4$ is sparingly soluble in THF[12] and $Zn(BH_4)_2$ is soluble in THF. However, the reaction actually gave only a "soluble borohydride species" and a precipitate of sodium chloride. Thus, the product is not a physical mixture of the two simple borohydrides, but may be a soluble double borohydride complex, $NaZn(BH_4)_3$ (Eq. 2).

The double borohydride complex, first prepared by Nöth and his coworkers in 1971,[13] has been characterized by the ^{11}B-NMR, IR-spectra, and elemental analysis. The BH_4 groups in the reagent are bonded *via* double hydrogen bridges to the central Zn atom. The structure is as follows.



1-

Further addition of 2 equiv of **1** evolved 2.2 moles of hydrogen, 1.8 equiv of hydrogen remaining in the complex. The reaction of the reagent with **1** seems to take place as follows.

$$NaBH_4 + 1/3\ ZnCl_2 \longrightarrow 1/3\ NaZn(BH_4)_3 + 2/3\ NaCl\downarrow$$

$$\downarrow 2\ R^*OH$$

$$1/3\ NaZn(BH_2(OR^*)_2)_3 + 2\ H_2\uparrow \quad (3)$$

The complex formed was soluble in THF and reduction with it was homogeneous, in contrast to $NaBH_4$ as reducing agent which was sparingly soluble in THF and gave reduction which was heterogeneous, at least in part.

Additional evidence for a homogeneous reduction was given when a suspension prepared from $NaBH_4$, 1/3 equiv of $ZnCl_2$, and 2 equiv of **1** was filtered under N_2 atomsphere. Addition of propiophenone to this clear filtrate resulted in the same asymmetric reduction obtained with the originally prepared complex.

Apart from the asymmetric induction, a comparison of the reagent from $NaBH_4$ and 1/3 equiv of $ZnCl_2$ with conventional hydridic reducing agents such as $NaBH_4$ demonstrates the potential utility of the reagent in organic reactions. (1) The reagent has a selectivity for functional groups similar to that of $NaBH_4$ but acts as a THF soluble analogue (*ca.* 4.5 g/100 mL at 25 °C) of $NaBH_4$ allowing selective reduction of carbonyl compounds in THF. Aldehydes and ketones are reduced in THF with much higher rates than those with $NaBH_4$ in the same solvent. For example, propiophenone was reduced to the corresponding alcohol quantitatively over a 2 h reaction period with the reagent in THF at 30 °C, whereas less than 20% of the alcohol was obtained with $NaBH_4$ under the same conditions. (2) The reagent can be easily modified in a stepwise fashion by various alcohols, *i.e.* even highly hindered alcohols such as **1**. No similar modification has been proposed for sodium borohydride. The highly hindered reagents thus formed indicate the possibility of developing a superior reducing agent with a high stereochemical selectivity.

Experimental

All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran, diethyl ether, and benzene were heated under reflux over sodium metal and distilled from lithium aluminium hydride in a nitrogen atmosphere. Acetophenone, propiophenone, phenyl propyl ketone, and isopropyl phenyl ketone were dried and distilled over calcium hydride. Methyl 2-naphthyl ketone was purified by recrystallization. Sodium borohydride was purified by recrystallization from 2,5,8-trioxanonane. Zinc chloride was purified by sublimation and dried at 100 °C. The monosaccharide derivatives, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **1**, 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose **2**, 1,2:4,5-di-*O*-isopropylidene-D-fructopyranose **3**, 2,3:4,5-di-*O*-isopropylidene-D-fructopyranose **4**, 1,2:4,5-di-*O*-cyclohexylidene-β-D-fructopyranose **5**, and 1,2-*O*-isopropylidene-D-glucofranose **6** were prepared according to the methods reported.[14–17] All the substances were stored under a nitrogen atmosphere prior to use. GLPC analyses were performed on a Shimadzu GC-6A instrument using a Silicone SE-30 prepared column. NMR spectra were measured on a Hitachi R-22, 90 MHz spectrometer. Optical rotations were taken on a Zeiss visual polarimeter with reading to ±0.02° using a 1 dm cell. IR spectra were measured with a JASCO IR-G instrument for nujol mulls. Na analysis by flame photometry was performed on a Hitachi 170-30 instrument. Hydrogen evolution was measured by Brown's method.[18] Zinc was determined by EDTA titration, halogens (chlorine) by Volhard procedure.

General Procedure for Asymmetric Reduction of Propiophenone with $NaBH_4$–$ZnCl_2$ Reagent in the Presence of **1** *in THF.* All experiments were carried out under a nitrogen atmosphere, transfer being made with a syringe through rubber septums. A typical experiment is as follows. THF suspension of $ZnCl_2$ (3 mmol) was added to a THF suspension of $NaBH_4$ (9 mmol) at 30 °C. After stirring for 3 h at 30 °C, THF solution of **1** (18 mmol) was added. On addition of **1**, hydrogen gas evolved slowly. After stirring at 30 °C for 24 h, hydrogen gas evolution was completed, propiopheone (7.2 mmol) then being added dropwise. The resulting mixture was decomposed by addition of 2 mol/l hydrochloric acid. The hydrolyzed mixture was filtered, the organic solvents being removed by evaporation under reduced pressure. The resulting aqueous layer was stirred for 1 h in order to decompose **1** completely. The aqueous mixture was extracted with three 10 mL portions of diethyl ether and the extract washed with saturated NaCl solution (2×10 mL). The etheral layer was dried over $MgSO_4$, and concentrated to give a crude product which was analyzed by GLPC. This was further purified by distillation under reduced pressure. The optical rotation was measured for this purified sample. Absolute configuration and optical yield were calculated from known values.

A number of other asymmetric reductions using different reagents such as ketones and sugar derivatives were performed under conditions similar to those described above.

Reaction of $NaBH_4$ with $ZnCl_2$. THF suspension of $ZnCl_2$ (10 mmol) was added to a suspension of $NaBH_4$ (30 mmol) at 30 °C. The resulting slurry was stirred at 30 °C for 3 h. The solid was separated by filtration under a nitrogen atmosphere and dried at room temperature *in vacuo*. The filtrate contained 33% and 100% of initial sodium and zinc concentrations, respectively. The solid product was found to be sodium chloride by analysis. The filtrate showed Na:Zn:hydridic hydrogen in the ratio 1:1.00:12.3, analyzed by flame photometry, EDTA titration, and hydrogen evolution measurement, but no chloride.

References

1) a) R. Noyori, I. Tomino, and Y. Tanimoto, *J. Am. Chem. Soc.*, **101**, 3129 (1979); b) R. Noyori, I. Tomino, and M. Nishizawa, *ibid.*, **101**, 5843 (1979).

2) a) Mukaiyama, M. Asami, J. Hanna, and S. Kobayashi, *Chem. Lett.*, **1977**, 783; b) T. Mukaiyama, K. Soai, T. Sato, H. Shimizu, and K. Suzuki, *J. Am. Chem. Soc.*, **101**, 1455 (1979); c) J. P. Vigneron and V. Bloy, *Tetrahedron Lett.*, **1979**, 2683; d) N. Cohen, R. J. Lopresti, C. Neukom, and G. Saucy, *J. Org. Chem.*, **45**, 582 (1980).

3) M. M. Midland, S. Greer, A. Tramontano, and S. A. Zderic, *J. Am. Chem. Soc.*, **101**, 2352 (1979); b) M. M. Midland, D. C. McDowell, R. L. Hatch, and A. Tramontano, *ibid.*, **102**, 867 (1980).

4) S. Krishnamurthy, F. Vogel, and H. C. Brown, *J. Org. Chem.*, **42**, 2534 (1977).

5) J. P. Masse and E. R. Parayre, *J. Chem. Soc., Chem. Commun.*, **1976**, 371.

6) S. Colonna and R. Fornasier, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 371.

7) T. Sugimoto, Y. Matsumura, S. Tanimoto, and M. Okano, *J. Chem. Soc., Chem. Commun.*, **1978**, 926.

8) Y. Shida, N. Ando, Y. Yamamoto, J. Oda, and Y. Inoue, *Agric. Biol. Chem.*, **43**, 1979 (1797).

9) A. Hirao, H. Mochizuki, S. Nakahama, and N. Yamazaki, *J. Org. Chem.*, **44**, 1720 (1979).

10) A. Hirao, S. Nakahama, H. Mochizuki, S. Itsuno, M. Ohwa, and N. Yamazaki, *J. Chem. Soc., Chem. Commun.*, **1979**, 807.

In the communication, we used $[\alpha]_{D\ max}^{20}$ +34.8° (in diethyl ether) as maximum rotation of 1-phenyl-1-propanol which was quoted in *J. Chem. Soc., Perkin Trans. 1*, **1978**, 371. However, the value was found to be erroneous, the true value being $[\alpha]_{D\ max}$ $52\pm1°$ (in diethyl ether). Revision of the data for 1-phenyl-1-propanol is being made. During this study, the optical rotations of 1-phenyl-1-propanol were measured in acetone and the optical yields calculated by the observed and known maximum rotations reported by H. Kwart and D. P. Hoster, *J. Org. Chem.*, **32**, 1867 (1967). The optical yields thus obtained were found to agree reasonably with those obtained in neat, ethanol, and chloroform.

11) A. J. Porker, *Quarterly Reviews*, **9**, 196 (1955).

12) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979).

13) H. Nöth, E. Wiberg, and L. P. Winter, *Z. Anorg. Allg. Chem.*, **386**, 73 (1971).

14) R. L. Whistler and M. L. Wolfrom, "Method in Carbohydrate Chemistry," Academic Press Inc., New York and London (1963), Vol. 2, p. 320.

15) R. C. Hockett, R. E. Miller, and A. Scattergood, *J. Am. Chem. Soc.*, **71**, 3072 (1949).

16) R. F. Brady, Jr., *Carbohydr. Res.*, **15**, 35 (1970).

17) K. James, A. R. Tatchell, and P. K. Ray, *J. Chem. Soc., C*, **1967**, 2681.

18) "Organic Syntheses *via* Boranes," ed by H. C. Brown, John Wiley and Sons, New York (1975), p. 214.