It indicates that adenosine chromophore remains unchanged, strongly suggesting that the photoadducts are not C_4-cycloaddition products but simple addition products in contrast to pyrimidine base adducts. Photobinding of DMC oc curs to adenosine through covalent bond formation between carbon-3 (for photoadduct I) and carbon-4 (for photoadduct II) of the pyrone ring of DMC and ribose carbon-5' of adenosine (Figure 7).

Acknowledgement. This investigation was supported by the Korea Science and Engineering Foundation Grant.

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Asymmetric Reduction of Prochiral Ketones with Potassium 9-O-isopinocampheyloxy-9-boratabicyclo[3,3,1]nonane+

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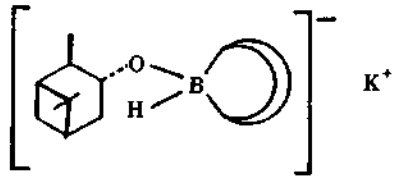
Received March 19, 1987

Asymmetric reduction of a series of aliphatic ketones and representative other classes of ketones with potassium 9-*O*-isopinocampheyloxy-9-boratabicyclo[3,3,1]nonane (K 9-*O*-Ipc-9-BBNH) was studied. All the ketones examined were reduced smoothly to the corresponding alcohols in THF at-78°C. Thus, the reduction of 2-butanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butanone, 2-octanone, and 4-phenyl-2-butanone provides 51% ee, 61% ee, 44% ee, 35% ee, and 33% ee of optical inductions, respectively. The reduction of other classes of ketones gave 52% ee for 2,2-dimethyl-cyclopentanone, 47% ee for acetophenone, 23% ee for 3-acetylpyridine, 50% ee for methyl benzoylformate, 4.8% ee for 2-chloroacetophenone, 30% ee for *trans*-4-phenyl-3-butene-2-one, and 2% ee for 4-phenyl-3-butyn-2-one. Thus, the reagent was found to be most useful in the asymmetric reduction of acyclic and cyclic aliphatic series of ketones.

One of the simplest and most useful methods for introduction of a chiral center in a molecule is the asymmetric reduction of prochiral ketones. Although this reaction has been studied extensively over the past several decades[2], it has only been the past few years that exceptional progress has been achieved[3]. Such the success has been accomplished particularly in alkyl aromatic ketones with chiral reducing agents, such as K-Glucoride[3b], diisopinocampheylchloroborane[3c], Binal-H[3d], borane-aminoalcohol[3e], Alpineborane[3f], modified lithium borohydride[3g], modified lithium aluminum hydride[3h]. For simple aliphatic ketones, however, success has been only limited[3e,3f,4]. Consequently, asymmetric reduction of such aliphatic ketones remains as a major challenge to organic chemists.

Recently, we have reported the preparation of new chiral dialkylmonoalkoxyborohydrides and their asymmetric reduction of acetophenone and 3-methyl-2-butanone[5]. During the study, we discovered an unexpected but highly in-



K 9-O-Ipc-9-BBNH, 1

Table 1. Asymmetric Reduction of Aliphatic Ketones with Potassium 9-O-Isopinocampheyloxy-9-boratabicyclo[3,3,1] nonane in THF at-78°C[a]

Ketone	Time, h	Alcohol Products Yield[b], %	% ee[c]	Abs. Config.[d]
2-Butanone	6	98	51	S
3-Methyl-2-butanone	6	98	61	S
3,3-Dimethyl-2-butanone	16	97	44	S
2-Octanone	10	98	35	S
4-Phenyl-2-butanone	10	96	33	S
2,2-Dimethylcyclopentanone	24	90	52[e]	R

[a][H⁻]:[Ketone] = 1.1:1.0, [Ketone] = 0.3 M. [b]GC yield [c]By capillary GC analysis of MTPA esters, unless otherwise indicated. [d]By comparing the elution order of diastereomers of MTPA esters to those of the corresponding authentic alcohols in capillary GC analyses unless otherwise indicated. [e]By capillary GC analysis of menthylcarbonate derivative.

teresting fact that potassium 9-*O*-isopinocampheyloxy-9-boratabicyclo[3,3,1] nonane (K 9-*O*-Ipc-9-BBNH, **1**) provides good optical induction (61% ee) for 3-methyl-2-butanone. The value is considerably better than with the corresponding trialkylborohydride, Li 9-Ipc-9-BBNH, 36% ee[6], and is almost as good as the 68% ee achieved with the improved reagent, NB-Enantride[4a]. Encouraged by the result, we investigated the asymmetric reduction of other aliphatic ketones. Consistently moderate optical yields (33% ee-61% ee) were obtained for a series of aliphatic ketones. The reduction of representative ketones of other classes was also studied with the reagent **1**.

Results and Discussion

The reducing agent **1** was prepared by the reaction of the corresponding borinic ester with excess potassium hydride in THF at 25°C[5]. The borinate (9-*O*-Ipc-9-BBN) can be readily prepared by the reaction of 9-borabicyclo[3,3,1]nonane (9-BBN) and (1R,2R,3R,5S)-(-)-isopinocampheol in THF at 25°C[5]. Asymmetric reduction of prochiral ketones was carried out with 10% excess of the hydride **1** in THF at-78°C. At the completion of reduction, the reaction mixture was quenched by addition of anhydrous methanol at-78°C. Then the mixture was oxidized by alkaline hydrogen peroxide except in one case for 2-chloroacetophenone, and the product was worked up following the representative procedure (See experimental section). The optical purities of product alcohols were determined by capillary GC analyses of MTPA esters[7] or 1-menthylcarbonate derivatives[8]. In the case of *trans*-4-phenyl-3-buten-2-one and 2-chloroacetophenone, the optical purities were determined by measuring the rotation

Table 2. Asymmetric Reduction of Representative Functionalized Ketones with Potassium 9-O-Isopinocampheyloxy-9-boratabicyclo-[3,3,1]nonane in THF at-78°C[a]

Ketone	Time, h	Alcohol Products Yield[b], %	% ee[c]	Abs. Config.[d]
3-Methyl-2-butanone	6	98	61	S
2,2-Dimethylcyclopentanone	24	90	52[e]	R
acetophenone	24	98	47	S
3-Acetylpyridine	24	95	23	S
Methyl benzoylformate	10	88	50	S
2-Chloroacetophenone	16	78[f]	4.8[g]	R[g]
4-Phenyl-3-buten-2-one	16	96	30[h]	S[h]
4-Phenyl-3-butyn-2-one	10	96	2	S

[a-e]See the corresponding footnotes in Table I. [f]GC yield of styrene oxide. [g]By conversion to styrene oxide, observed value $[\alpha]_D^{20}$ 2.25 (*c* 1.49, benzene); Based on $[\alpha]_D^{18}$ 46.84 (*c* 1.08, benzene), R, ref. 14. [h]Observed value $[\alpha]_D^{23}$ -11.73 (*c* 4.15, $CHCl_3$); Based on calculated value $[\alpha]_D^{20}$ 39.6 (*c* 5.26, $CHCl_3$), R, ref. 13.

of the product alcohols (or epoxide for 2-chloroacetophenone) and comparing the values with the maximum reported rotations.

Asymmetric Reduction of Aliphatic Ketones. Following the general procedure, asymmetric reductions of a series of aliphatic ketones, such as 2-butanone, 3-mentyl-2-butanone, 3,3-dimethyl-2-butanone, 2-octanone, and 4-phenyl-2-butanone were carried out. The reactions were complete within 12 h (24 h for 3,3-dimethyl-2-butanone). The results are summarized in Table 1. Thus, the reduction provides consistently moderate optical yields, such as 51% ee for 2-butanone, 61% ee for 3-methyl-2-butanone, 44% ee for 3,3-dimethyl-2-butanone, 35% ee for 2-octanone, and 33% ee for 4-phenyl-2-butanone. The optical purities obtained, 51% ee for 2-butanone and 61% ee for 3-methyl-2-butanone are among the best values achieved with the most promising reagents for the class of aliphatic ketones, except the case of the most recently reported chiral 2,5-dimethylborolane, 80.3% ee for 2-butanone and 100% ee for 3-methyl-2-butanone.

Asymmetric Reduction of Other Classes of Ketones. In order to study the scope and limits of the reagent for asymmetric reduction of prochiral ketones, several representative ketones were selected from various classes of ketones. By carrying out asymmetric reduction of these representative ketones, the promising area of useful application can be readily recognized and developed further. The selected ketones are 3-methyl-2-butanone, 2,2-dimethylcyclopentanone, acetophenone, 3-acetylpyridine, methyl benzoylformate, 2-chloroacetophenone, 4-phenyl-3-buten-2-one and 4-phenyl-3-butyn-2-one. All the ketones examined were reduced smoothly to the corresponding alcohols in THF at -78°C. The results are summarized in Table 2. Thus, the reduction affords consistently moderate optical yields, such as 61% ee for 3-methyl-2-butanone, 52% ee for 2,2-dimethylcyclopentanone, 47% ee for acetophenone, 23% ee for acetylpyridine, 50% ee for methyl benzoylformate, and 30% ee for 4-phenyl-3-buten-2-one. Two exceptional cases are 4.8% ee for 2-chloroacetophenone, and 2% ee for 4-phenyl-3-

butyn-2-one. Although, optical purities obtained for acetophenone and methyl benzoylformate (47% and 50% ee respectively) are moderate, there are other reagents affording excellent results for alkyl aromatic ketones[3] and Alpine-Borane[3j] and K-Glucoride[3b,9] for α-keto esters. Consequently, the reagent **1** was found to be most useful in the asymmetric reduction of acyclic and cyclic aliphatic series of ketones.

Conclusion

A new, easily prepared chiral dialkylmonoalkoxyborohydride, potassium 9-*O*-isopinocampheyloxy-9-boratabicyclo [3,3,1]nonane affords consistently moderate optical yields in the asymmetric reduction of a series of aliphatic ketones and representative functionalized ketones. The reagent reveals the most promising results in the asymmetric reduction of acyclic and cyclic aliphatic series of ketones, especially for 2-butanone and 3-methyl-2-butanone. Thus, the present study provides a useful method to obtain optically active aliphatic secondary alcohols via asymmetric reduction.

Experimental

The reaction flasks and glasswares were dried in an oven at 140°C overnight and assembled hot in a stream of nitrogen. The experimental techniques used in handling air-sensitive materials are described elsewhere[10]. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in *d* relative to BF_3:Et_2O. GC analyses were carried out with a Hewlett-Packard 5730 A equipped with a Hewlett-Packard 3390 A integrator/plotter using 10% Carbowax 20 M on Chromosorb W (100-200 mesh), 14 ft X 0.125 in. column. The enantiomeric excesses of the alcohols were determined by capillary GC analyses using a Hewlett-Packard 5890 gas chromatograph attached to a Hewlett-Packard 3390 A integrator/plotter and 15 m Supelcowax or 50 m methylsilicone capillary column. Optical rotations were measured on a Rudolph Polarimeter Autopol III.

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. 9-Borabicyclo [3,3,1]nonane (9-BBN), (-)-Isopinocampheol ($[\alpha]_D^{22}$ -34°C, *c* 20, EtOH), (-)-menthyl-chloroformate and all the carbonyl compounds except 2,2-dimethyl-cyclopentanone were purchased from Aldrich Chemical Co., and used without further purification. 2,2-Dimethylcyclopentanone was purchased from Wiley Organics. Potassium hydride was purchased from Aldrich Chemical Co. and used as oil-free form[5]. (R)-α-Methoxy-α-(trifluoromethyl)phenyl acetic acid (MTPA) was purchased from Aldrich Chemical Co., and was converted to the acid chloride[12] and distilled.

Asymmetric Reduction of Prochiral Ketones with 1. The reductions of the following compounds are representative.

2-Butanone. An oven-dried 50 m*l*, long necked round bottomed flask equipped with a side arm, a magnetic stirring bar and a stopcock adaptor was cooled to room temperature under nitrogen atmosphere. To the flask was added **1** in THF (5.5 mmol, 0.48 M, 11.5 m*l*) and cooled to-78°C. To this was added a THF solution of 2-butanone (5 mmol, 5 m*l*) precooled to-78°C via a double ended needle[10]. The reaction was carried out for 6 h at-78°C. Then, unreacted hydride was destroyed by the addition of 1 m*l* of anhydrous methanol at -78°C. The temperature was raised to 25°C, and solvent was evaporated under reduced pressure (14 mm Hg, at 25°C). The residue was dissolved in ethyl ether (15 m*l*) and oxidized with using 4 m*l* of 3 N NaOH and 2 m*l* of 30% hydrogen peroxide (6 h, 25°C). The aqueous layer was saturated with anhydrous potassium carbonate and extracted with ethyl ether (15 m*l* × 2). The combined ethereal extract was dried over anhydrous magnesium sulfate. GC analysis indicated the presence of 98% of 2-butanol in ether solution. The product alcohol was isolated by fractional distillation using a Widmer column, and derivatized to the MTPA esters[7]. Capillary GC analysis of the MTPA esters using 50 m Methylsilicone capillary column (95°, isothermal) revealed a composition of 75.5% S and 24.5% R (i.e. 51% ee). Following the same procedure, the reduction of 3-methyl-2-butanone and 3,3-dimethyl-2-butanone were carried out and the product alcohols were analyzed. The reduction products from 2-octanone, 2,2-dimethylcyclopentanone, 4-phenyl-2-butanone, acetophenone, and 4-phenyl-3-butyn-2-one were isolated by bulb-to-bulb distillation after evaporation of solvent without using the fractional column. Enantiomeric excesses of all the alcohols except 2,2-dimethylcyclopentanol were determined by capillary GC analyses of their MTPA esters. The optical purity of 2,2-dimethylcyclopentanol was determined by capillary GC analysis of its menthylcarbonate derivative[11]. The menthylcarbonates of racemic 2,2-dimethylcyclopentanol was well resolved to give two diastereomeric peaks of equal intensity by capillary GC analysis using 15 m Supelcowax capillary column[11]. The results are summarized in Table 1.

3-Acetylpyridine. The reduction was carried out following the same procedure as described above. After 24 h, the mixture was quenched by addition of anhydrous HCL in ethyl ether (10 mmol) precooled to-78°C. Then the temperature was raised to 25°C and solvent evaporated under reduced pressure (14 mm Hg, 25°C). The residue was dissolved in chloroform (15 m*l*), treated with 4 mL of 3 N HCL for 1 h at 25°C, and finally made alkaline with 6 N NaOH. The aqueous layer was saturated with anhydrous potassium carbonate and then extracted with chloroform (15 m*l* × 2). The combined organic layer was dried over anhydrous magnesium sulfate. GC analysis revealed the formation of 98% product alcohol. After evaporation of solvent, the product was isolated by bulb-to-bulb distillation. The distilled mixture was directly derivatized with MTPA acid chloride and the MTPA ester was analyzed by capillary GC using 15 m Supelcowax capillary column (200°C, isothermal), providing a composition of 61.7% S and 38.3% R (i.e. 23.4% ee).

Methyl benzoylformate. Following the procedure described in the previous experiment, 5 mmol of the methyl benzoylformate was treated with 5.5 mmol of **1** in THF at-78°C. After 10 h, unreacted hydride was destroyed by addition of anhydrous methanol (1 m*l*). The mixture was warmed to room temperature and solvent evaporated under reduced pressure (14 mm Hg, 25°C). The residue was dissolved in ethyl ether (15 m*l*). To this was added pH 7 buffer solution (2 m*l*) at 0°C and the mixture was oxidized with 30% Hydrogen peroxide 92 m*l*) for 3 h at 0°C. The aqueous layer was saturated with sodium chloride, and extracted with ethyl ether (15 m*l* × 2). The combined ethereal solution was dried over anhydrous magnesium sulfate. GC analysis showed the presence of 88% methylmandelate. The distillate (bulb-to-bulb) was directly derivatized with MTPA acid chloride. Capillary GC analysis of the MTPA ester using 15 m Supel-

cowax capillary column (200°C, isothermal) indicated a composition of 75% S and 25% R (i.e. 50% ee).

trans-4-Phenyl-3-buten-2-one. The reaction was carried out with the exactly the same procedure described for 2-butanone. The distillate (bulb-to-bulb) was further purified by column chromatography (silica gel 60-200 mesh) using cyclohexane-ethyl acetate (8:2) as eluent. The fraction containing pure *trans*-4-phenyl-3-buten-2-ol was concentrated and the optical rotation of the alcohol was measured: $[\alpha]_D^{23}$ −11.73 (*c* 4.15, $CHCl_3$). 30% ee, S, based on calculated $[\alpha]_D^{20}$ 39.6, R, (*c*, 5.26, $CHCl_3$)[13]. Both the MTPA esters and menthylcarbonate derivatives of *trans*-4-phenyl-3-buten-2-ol are not resolved by capillary GC analysis using both 15 m Supelcowax column and 50 m Methylsilicone capillary columns.

2-Chloroacetophenone. The ketone (10 mmol) was treated with **1** (11 mmol) as described in the previous experiments. After 16 h, the reaction mixture was quenched by addition of anhydrous HCL in ethyl ether (20 mmol) precooled to-78°C. Then temperature was brought to 25°C, and solvent evaporated under reduced pressure (14 mm Hg, 25°C). The residue was dissolved in 25 m*l* of ethyl ether-n-pentane (1:1). To this was added 2 N HCL (7 m*l*) and the mixture was stirred for 0.5 h at 25°C. Then, organic layer was separated and cooled to 0°C. To this was added 3 N NaOH (8 m*l*) and the mixture was stirred for 2 h at 0°C. Aqueous layer was extracted with ethyl ether (25 m*l* × 2). The combined organic layer was dried over anhydrous magnesium sulfate. GC analysis revealed the formation of 78% styrene oxide. The distillate (bulb-to-bulb) was further purified by column chromatography (silica gel 60-200 mesh) using cyclohexane-ethyl acetate (9:1) as eluent. The fraction containing pure styrene oxide was collected, concentrated and distilled: $[\alpha]_D^{20}$ 2.25 (*c* 1.49. benzene), 4.8% ee, R, based on calcuated $[\alpha]_D^{18}$ 46.84 (*c* 1.08, benzene)[14].

Acknowledgement. We thank Professor Herbert C. Brown, Wetherill Research Professor of Chemistry, Purdue University for providing laboratory facilities and valuable discussion.

References and Notes

+ Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.
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