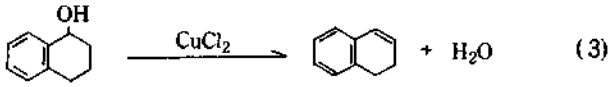
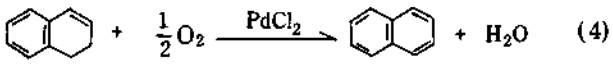
gests the following dehydration mechanism:



(3)

$CuCl_2$ or $PdCl_2$, etc., as a Lewis acid catalyst accelerates the dehydration of α-tetralol to 1,2-dihydronaphthalene(3) and the latter is then oxidatively dehydrogenated to naphthalene catalyzed by palladium(II) species(4):



(4)

Each of the reactions(3) and (4) was confirmed by the separate experiments as follows. α-Tetralol afforded 1,2-dihydronaphthalene and water when treated with $CuCl_2$, and 1,2-dihydronaphthalene was catalytically converted to naphthalene by $PdCl_2$ under oxygen atmosphere.

Conclusion

Cyclopentene was catalytically oxidized to cyclopentanone by palladium complex-dioxygen couple in tetralin solvent at ambient temperature. The oxidation proceeded by co-oxidation mechanism, in which tetralin was first oxidized to α-tetralyl hydroperoxide by radical chain reaction and the hydroperoxide as an oxygen donor converted then cyclopentene to cyclopentanone. As the secondary products, 2-cyclopenten-1-one, 2-cyclopenten-1-ol, α-tetralone and α-tetralol formed by the radical chain reaction, and furthermore, 1,2-dihydronaphthalene and naphthalene were produced by the α-tetralol dehydration followed by the oxidative dehydrogenation.

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Asymmetric Reduction of Prochiral α,β-Acetylenic Ketones With Potassium 9-O-(1,2: 5,6-Di-*O*-isopropylidene-α-*D*-glucofuranosyl)-9-boratabicylco[3, 3, 1] nonane†

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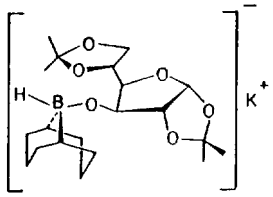
The asymmetric reduction of representative prochiral α,β-acetylenic ketones with a new chiral borohydride reducing agent, potassium 9-O-(1,2: 5,6-Di-O-isopropylidene-α-*D*-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane, **1**, in THF at −78°C was studied. Structurally different acetylenic ketones such as internal α,β-acetylenic ketones $RC{\equiv}CCOCH_3$ and terminal α,β-acetylenic ketones $HC{\equiv}CCOR$ were chosen. Thus, the reduction of internal α,β-acetylenic ketones yields the corresponding propargyl alcohols, such as 67% ee for 3-hexyn-2-one, 75% ee for 5-methyl-3-hexyn-2-one, 86% ee for 5,5-dimethyl-3-hexyn-2-one, 74% ee for 3-nonyn-2-one and 61% ee for 4-phenyl-3-butyn-2-one. Terminal α,β-acetylenic ketones, such as 3-butyn-2-one, 1-pentyn-3-one, 4-methyl-1-pentyn-3-one and 1-octyn-3-one, are reduced to the corresponding alcohols with 59% ee, 17% ee, 44% ee and 12% ee of optical induction respectively. With one exception (4-methyl-1-pentyn-3-one), all propargyl alcohols obtained are enriched in R-enantiomers.

Since the acetylenic unit provides a convenient handle for transforming into a variety of functionalities, optically active propargyl alcohols are very useful precursors and intermediates in chiral syntheses of biologically active substances.[1] One of the most convenient methods for the preparation of optically active propargyl alcohols is the asymmetric reduction of α,β-acetylenic ketones with chiral reducing agents.[2]

Recently we discovered a well-difined, new chiral borohydride reducing agent, potassium 9-O-(1,2: 5,6-Di-O-isopropylidene-α-D-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane (K9-O-DIPGF-9-BBNH, K-Glucoride,[3] **1**). This reagent provides highly effective asymmetric induction for a

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

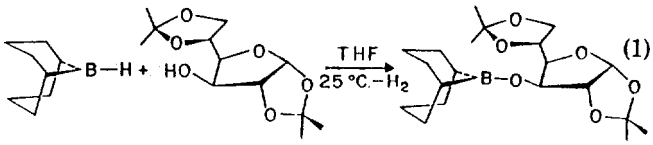


K9-0-DIPGF-9-BBNH, **1**

variety of prochiral carbonyl compounds, giving R-or S-enantiomers consistently by the nature of carbonyl groups.[4] It appears desirable to explore the applicability of this reagent for the asymmetric reduction of α,β-acetylenic ketones. We now report a convenient method for the preparation of optically active propargyl alcohols from the acetylenic ketones using **1**.

Results and Discussion

General. The chiral reducing agent **1** was prepared by the reaction of the corresponding borinic ester **3** with excess potassium hydride in THF at 25°C (eqs 1 and 2).[4a]



(1)

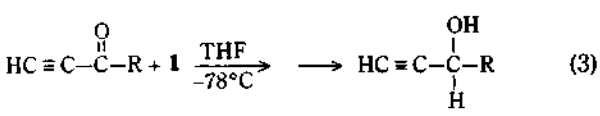
9-BBN DIPGF **2** 9-0-DIPGF-9-BBN, **3**

$$\mathbf{3} + \underset{\text{excess}}{\text{KH}} \xrightarrow[25°C,\ 2\ h]{\text{THF}} \mathbf{1} \qquad (2)$$

The asymmetric reduction was carried out in tetrahydrofuran (THF) at -78°C. In the experiments, the ketones were precooled to -78°C and added to the reagent **1** precooled to -78°C. At the end of completion of the reaction, the reaction mixture was quenched with anhydrous methanol at -78°C. The product alcohols were obtained by alkaline hydrogen peroxide oxidation.[5]

The optical purities of the obtained alcohols were determined by measuring the rotations of the alcohols obtained and comparing the values with the maximum reported rotations. The enantiomeric excess of these alcohols were also determined by capillary GC analysis of their MTPA esters.[6]

Asymmetric Reduction of α,β-Acetylenic Ketones. In the reduction of α,β-acetylenic ketones, it seems that asymmetric induction may depend on the steric inequality of the two moieties (R and R') attached to the carbonyl groups in R'C≡C-COR. Accordingly, we examined the effect of variations in the steric bulk of both moieties in a systematic manner. First, we selected methyl, ethyl, isopropyl and *n*-pentyl groups for the *R* groups in terminal α,β-acetylenic ketones, HC CCOR, **4**. The reduction was complete within 6 h in THF at -78°C. Thus, the reductions of 3-butyn-2-one (**4**, R = Me). 1-pentyn-3-one (**4**, R = Et) and 1-octyn-3-one (**4**, R = *n*-pentyl) were reduced to the corresponding alcohols with 59% ee, 17% ee and 12% ee respectively. All of the obtained alcohols were consistently enriched in *R*-enantiomers. Substitution by an isopropyl group (**4**, R = *i*-Pr), however, breaks this trend and produces the opposite S configuration with 44% ee. The results imply that *Si* side attack of the hydride **1** to the ketones is less favorable by increasing a size of *R* groups. Probably this is the reason why optical induction decreased dramatically by increasing a size of *R* in eq. 3.



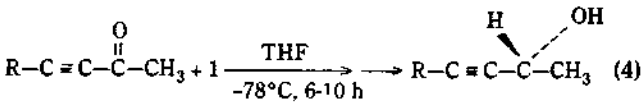
(3)

4 **5**

R = Me, Et, *i*-Pr, *n*-Pentyl

R = Me_3,	59% ee, *R*
= Et,	17% ee, *R*
= *i*-Pr,	44% ee, *S*
= *n*-Pentyl,	12% ee, *R*

On the other hand, we again examined the steric effect of *R* groups for the optical induction in the internal α,β-acetylenic ketones, $RC{\equiv}CCOCH_3$ **6** For the *R* groups, we selected ethyl, isopropyl, *tert*-butyl, *n*-pentyl and phenyl groups. All of the acetylenic ketones studied were reduced readily to the corresponding proparghl alcohols within 10 h in THF at -78°C. We expected that increase in the steric bulk of the *R* groups in **6** should increase the steric inequality of the two groups attached to the carbonyl functionality, causing enhancement of optical induction. Indeed, the expectation has been proven to be a fact. Thus, 3-hexyn-2-one (**6**, R = Et), 5-methyl-3-hexyn-2-one (6, R = *i*-Pr), 5,5-dimethyl-3-hexyn-2-one (**6**, R = *tert*-Bu) and 3-nonyn-2-one (**6**, R = *n*-pentyl) are reduced to the corresponding alcohols with 67% ee, 75% ee, 86% ee and 74% ee, respectively, showing an increase of optical induction by increasing the steric bulk of the *R* groups (eq 4). Substitution by the phenyl group is less effective for asymmetric induction than those by alkyl groups, providing 61% ee for 4-phenyl-3-butyn-2-one (6, R = Ph).



(4)

6 **7**

R = Et, *i*-Pr, *tert*-Bu, *n*-Pentyl, Ph

R=Et,	67% ee, *R*
= *i*-Pr,	74% ee, *R*
= *tert*-Bu,	86% ee, *R*
= *n*-Pentyl,	75% ee, *R*
= Ph	61% ee, *R*

Again, all alcohols obtained are consistently enriched in the *R*-enantiomers. The results are summarized in Table I. In the results, 86% ee for 5,5-dimethyl-3-hexyn-2-one (**6**, R = *tert*-Bu) is one of the highest values reported. For this particular substrate, Alpineborane, one of the most promising reducing agents for reduction of acetylenic ketones, gave 73% ee.[7]

Conclusions

The present study provides a convenient method for the preparation of propargyl alcohols, such as $RC{\equiv}CCHOHCH_3$, with high optical purities by the reduction of the corresponding α,β-acetylenic ketones with reagent **1**. For such ketones, the optical induction was enhanced sighificantly by increasing a size of *R* groups. In contrast, the asymmetric induction for terminal α,β-acetylenic ketones, HC≡CCOR, decrease by increasing a size of *R* groups. The present study

Table 1. Asymmetric Reduction of α,β-Acetylenic Ketones With K-Glucoride in THF at −78°C[a]

ketone	time h	yield[b] %	optically active alcohols $[\alpha]_D^{22}$ obsd. deg.	ee[d] %	abs. config.
3-butyn-2-one	6	(96)[c]	31.20 (*c* 2.23, dioxane)	59(61)[e]	*R*[f]
1-pentyn-3-one	6	(96)	1.13 (*c* 2, dioxane)	17	*R*[g]
4-methyl-1-pentyn-3-one	6	78	−7.82 (*c* 2, dioxane)	44(49)[h]	*S*[h]
1-octyn-3-one	6	81	2.71 (*c* 1.7, ethyl ether)	12	*R*[g]
3-hexyn-2-one	6	80	28.2 (*c* 2, dioxane)	67	*R*[g]
5-methyl-3-hexyn-2-one	6	85	28.49 (*c* 2, dioxane)	75	*R*[g]
5,5-dimethyl-3-hexyn-2-one	8	87	31.19 (*c* 2, dioxane)	86	*R*[g]
3-nonyn-2-one	6	80	22.27 (*c* 2, dioxane)	74	*R*[g]
4-phenyl-3-butyn-2-one	10	(95)	23.13 (*c*4.69,ethanol)	61(74)[i]	*R*[g]

[a][H⁻]:[ketone] = 1.1:1.0, [ketone] = 0.3 M [b]Isolated yields, unless otherwise indicated. [c]The data in parentheses indicates GC yield. [d]Determined by capillary GC analysis of the MTPA ester derivatives. [e]Based on calculated $[\alpha]_{Dmax}^{25}$ 52 (*c* 2,3, dioxane): Vigneron, J-P.; Bloy, V. *Tetrahedron Lett.* 2683 (1979). [f]Based on [S]-(-)-configuration: Weidmann, R.; Schoofs, A.; Horeau, A. *Bull. Soc. Chem. Fr.* 645 (1976). [g]Absolute configuration is unknown, but probably *R*, based on the order of elution of the MTPA derivatives in capillary GC analysis and (+) sign of rotation measured. [h]Based on calculated $[\alpha]_D^{23}$ 15.97 (*c* 0.11, dioxane), ref. 2d. [i]Based on calculated $[\alpha]_D^{25}$ 31.26 (*c* 5.15, ethanol): Brown, H. C.; Pai, G. G. *J. Org. Chem.* **50**, 1384 (1985).

affords another valuable application of the new reagent **1**, *K*-Glucoride, which should find major applications in organic synthesis.

Experimental

General Procedure. All glassware was dried at 140°C overnight, assembled hot and cooled to room temperature in a stream of nitrogen. All reactions involving air-sensitive materials were carried out under a static pressure of nitrogen. The liquids were transferred with dry syringes or double-ended needles. ^{11}B NMR spectra were recorded on a Varian FT-80 spectrometer and all ^{11}B chemical shifts were reported in δ (ppm) relative to $BF_3.OEt_2$. ^1H NMR spectra were scanned on a Varian T-60A spectrometer with Me_4Si as an internal standard and all of the chemical shifts were reported in δ (ppm) relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer equipped with a Perkin-Elmer 3600 IR data station. Gas chromatographic analyses were carried out with a Hewlett-Packard 5730A instrument attached with a Hewlett-Packard 3390A integrator/plotter using 6 ft × 0.125 in column of 10% Carbowax 20M on Chromosorb W and an internal standard. Capillary gas chromatographic analyses were carried out with a Hewlett-Packard 5890 chromatograph attached with a Hewlett-Packard 3390A integrator/plotter using 15m Supelcowax or 50m methyl silicone 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-Borabicycl [3.3.1]nonane (9-BBN), potassium hydride, 1,2:5,6-di-0-isopropylidene-α-D-glucofuranose (DIPGF), 3-butyn-2-one, 4-phenyl-3-butyn-2-one and [*R*]-(+)-MTPA were purchased from Aldrich Chemical Company. The MTPA was converted to the acid chloride[8] and distilled. 3-Hexyn-2-one was purchased from Farchan Research Laboratory. 1-Pentyn-3-one, 4-methyl-1-pentyn-3-one, 1-octyn-3-one, 5-methyl-3-hexyn-2-one, 5,5-dimethyl-3-hexyn-2-one and 3-nonyn-2-one were prepared by Jones oxidation of the corresponding alcohols.[9]

Preparation of 9-0-(1,2: 5,6-Di-0-isopropylidene-α-D-glucofuranosyl)-9-boratabicyclo [3.3.1]nonane (K9-0-DIPGF-9-BBNH, 1). To a slurry of 9-BBN (32.3 g, 265 mmol) suspended in THF (200 m*l*) was added the solution (330 m*l*) of DIPGF, **2** (69 g, 265 mmol) in THF dropwise *via* a double-ended needle with vigorous stirring. After evolution of hydrogen ceased (~1h), the mixture was stirred for an additional 2 h to insure completion. Evaporation (25°C, 14 torr) of the solvent followed by distillation under vacuum gave highly viscous 9-0-DIPGF-9-BBN, **3** (89 g, 88% yield): bp 198-201°C/0.5 torr, ^{11}B NMR δ 56.30(s); MS, M⁺ 380. An oil suspension of potassium hydride transferred to a flask was allowed to settle and most of the oil decanted with a double-ended needle. Then the potassium hydride was washed with *n*-pentane (3 × 100 m*l*). After evaporation (25°C, 14 torr) of *n*-pentane, THF was added to the oil-free potassium hydride. To this suspension of oil-free potassium hydride (12 g, 300 mmol) in THF (150 m*l*) was added a THF solution (250 m*l*) of **3** (76 g, 200 mmol) slowly *via* a double-ended needle with vigorous stirring. The reaction became slightly exothermic after a 10-30 min induction period. The reaction was monitored both by hydrolysis of centrifuged aliquots and by ^{11}B NMR. It was complete within 2 h, producing the addition compound, K9-0-DIPGF-9-BBNH, **1** (0.48 M, 96% yield): ^{11}B NMR δ 1.33 (br, s): IR ν_{B-H} 2038 cm^{-1}. The hydride and potassium were determined as H_2 and KOH following hydrolysis; boron was estimated by GC analysis of 1,5-cyclooctanediol following oxidation by alkaline hydrogen peroxide: $[H^-] = 0.48$ M; $[K^+] = 0.48$ M; [B] = 0.50 M. Therefore, a stoichiometry of K:B:H of 1:1:1 was established. The hydride solution of **1** in THF can be stored over excess potassium hydride under positive nitrogen pressure at 25°C for at least 6 months without any disproportionation or loss of hydride activity.

Asymmetric Reduction of α,β-Acetylenic Ketones. The following procedure for the asymmetric reduction of 5,5-dimethyl-3-butyn-2-one with **1** is representative. An oven-dried, 50 m*l*, long-necked, round-bottom flask equipped with a septum-capped sidearm, magnetic stirring bar and a stopcock adaptor was cooled to room temerature under a stream of nitrogen. The flask was charged with the hydride **1**

solution in THF (11 mmol, 0.48 M, 22.9 m*l*) and cooled to −78°C. To this was added THF solution of 5,5-dimethyl-3-butyn-2-one (10 mmol, 1.0 M, 10 m*l*) precooled to −78°C *via* a double-ended needle.[5] The reaction mixture was miantained for 8 h at −78°C. Then unreacted hydride was destroyed by addition of 2 mL of anhydrous methanol at −78°C. The mixture was warmed to room temperature and the volatiles pumped off under reduced pressure (14 mmHg, 25°C). The residue was dissolved by ethyl ether (25 m*l*) and oxidized with 8 m*l* of 3 *N* NaOH and 4 mL of 30% hydrogen peroxide for 10 h at 25°C. The aqueous layer was saturated with anhydrous potassium carbonate and extracted with ethyl ether (2×25 m*l*). The combined ethereal solvent was dried over anhydrous potassium carbonate and evaporated under reduced pressure (14 mmHg, 25°C). The product alcohol was isolated by distillation. Yield: 1.1 g(87%), bp 71-73°C/19 mmHg [lit.[10] bp 71°/18 mmHg]; n^{20} D 1.4344 [lit.[10] n^{20}D 1.4360]. IR (neat) cm^{-1} 3340, 2970, 2222. ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 9H), 1.4 (d, 3H, J=6.4Hz), 2.5 (s, 1H), 4.5 (m, 1H). The alcohol product was further purified by preparative GC (20% Carbowax 20M, 6 ft×0.5 in, 100°C, isothermal) and the rotation was measured: $[\alpha]_D^{22}$ 31.19 (c 2, dioxane). Since both the maxiumum reported optical rotation and absolute configuration of the alcohol is unknown, the optical purity was determined by capillary GC analysis (50 M methyl silicone capillary column, 160°C, isothermal) of the MTPA esters.[6] The analysis indicated 86% ee. Its absolute configuration is assumed to be *R* based on the order of elution of the MTPA esters in capillary GC analysis and (+) sign of optical rotation measures. The results are summarized in Table I.

Preparation of MTPA Esters. The [*R*]-(+)-α-methoxy-α-trifluoromethylphenyl acetic acid (MTPA) was converted to the acid chloride[8] and distilled. The propargyl alcohols (0.1 mmol), carbon tetrachloride (0.3 m*l*) and pyridin (0.3 m*l*) were mixed together in a vial fitted with a rubber septum. The MTPA acid chloride (26μl) was then injected into the vial and the mixture stirred for 3 h at 25°C. It was then diluted with ethyl ether (3 m*l*) and washed with 1 *N* HCl (2×2 m*l*) and brine (2 m*l*). The ether solution of the MTPA ester was dried over anhydrous magnesium sulfate. This ether solution was analyzed by capillary GC using 15 *M* Supelcowax or 50 *M* methyl silicone capillary columns.

Acknowledgement. The authors are indebted to Professor herbert C. Brown, Purdue University, for providing laboratory facilities, financial support, advice and encouragement during this study. Financial support from the United States Army Research Office (ARO DAAG29-85-K-0062) is gratefully acknowledged. B.T. Cho also expresses his thanks to the Korea Science and Engineering Foundation for financial support.

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