










to the corresponding hydride reagent, 9-*O*-(1,2:5,6-di-*O*-cyclohexylidene- β -D-glucofuranosyl)-9-boratabicyclo [3.3.1] nonane **6** by treatment with excess potassium hydride (25°C, 6 h) in essentially quantitative yield: ^{11}B NMR δ -1.3 (br.s); IR $\nu_{\text{B-H}}$ 2012 cm^{-1} . This reagent was analyzed for stoichiometric ratio of K:B:H = 1:1:1.

Asymmetric reductions for 9 selected representative classes of ketones⁵ with **6** were carried out in THF at -78°C. The results are compared with them by K glucoride and summarized in Table 1. Generally, the rates of reduction for the selected ketones examined with this reagent were somewhat slower than those by K glucoride under the same reaction condition. Thus the reduction of unhindered aliphatic ketone, 3-methyl-2-butanone, proceeded to completion within 12 h to give 58% ee. The optical induction is noteworthy as compared with 36% ee by K glucoride.^{3a,5,8} For relatively hindered aliphatic ketone, 2,2-dimethylcyclopentanone, high optical yield (80% ee) was obtained, although the reduction was very sluggish, requiring 4 days for 90% reduction. This reagent provided the best result in the reduction of α -keto ester, methyl benzofornate to give α -hydroxy ester, methyl mandelate of 92% ee as well as K glucoride.^{3a,c,5} The asymmetric reduction for other ketones examined appeared essentially same optical inductions as those given by K glucoride, giving 77% ee for acetophenone, 55% ee for 3-acetylpyridine, 78% ee for 2-chloroacetophenone, 60% ee for *trans*-4-phenyl-3-buten-2-one, and 62% ee for 4-phenyl-3-buten-2-one. Absolute configurations for the product alcohols are exactly same as those given by K glucoride.^{3a} The reduction of 2-cyclohexenone, unfortunately, gave 1,4-addition product mainly. The results indicated that steric difference at C-1, C-2 and C-5, C-6 in **3** and **4** provided almost no effects in asymmetric induction for such ketones

Table 1. Asymmetric reduction of representative ketones with **6** in THF at -78°C^a

ketone	4			K glucoride ^b		
	time	yield(%) ^b	%ee ^c	config.	%ee	config.
	12 h	98	58	R	36	R
	4 d	90	80 ^d	R	84	R
	30 h	97	77	R	78	R
	30 h	96	55	R	70	R
	24 h	80 ^e	78 ^e	S	77	S
	16 h	85	92	S	92	S
	24 h	93	60	R	60	R
	16 h	d	-	-	-	-
	16 h	95	62	R	61	R

^a[H⁻]:[cpd] = 1.1:1.0, [ketone] = 0.3M. ^bBy GC analysis. ^cGC yield of styrene oxide. ^dMainly 1,4 reduction. ^eDetermined by capillary GC analysis of MTPA ester. ^fDetermined by capillary GC analysis of (-)-menthyl carbonate. ^g $[\alpha]_D^{25}$ -37.28 (*c* 1.05, benzene) as styrene oxide. Based on calculated $[\alpha]_D^{25}$ + 46.84 (*c* 1.08, benzene); G. Berti, F. Bottari, P. L. Ferrorini, and B. J. Maccia. *J. Org. Chem.* **30**, 4091 (1965). ^hData taken from ref. 3a and 5.

examined except 3-methyl-2-butanone. The following procedure is representative. The flask was charged with 5.5 mmol of **6** in THF (0.5M, 11 ml) and cooled to -78°C via a double ended needle. After 16 h, the unreacted hydride was destroyed by addition of methanol at -78°C. The solvent was pumped off under reduced pressure, followed by hydrogen peroxide oxidation. (pH 7 buffer solution in ethyl ether, 0°C, 3 h). The aqueous layer was extracted with ethyl ether. The ethereal extracts were concentrated in vacuo and the product, methyl mandelate, was obtained by bulb-to bulb distillation. (GC yield: 85%). Optical purity was measured by capillary GC analysis of

MTPA ester⁶ of the product: 92% ee enriched S configuration.

ACKNOWLEDGEMENT

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4. (a) R. C. Hockett, R. L. Miller and A. Scattergood, *J. Am. Chem. Soc.*, **71**, 3072 (1949); $[\alpha]_D^{31} - 2.20$ (c 2.27, EtOH); (b) Present work: $[\alpha]_D^{20} - 2.84$ (c 2.43, EtOH).
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8. The asymmetric reductions for the other aliphatic ketones are under investigation.