chloride (34 g, 0.255 mol) and *p*-nitrobenzoyl chloride (34 g, 0.183 mol) were dissolved in 2 L of CH_2Cl_2 and added with mixing to the resin mixture through a funnel fitted with a glasswool plug.[28] The resulting orange mixture was then allowed to stand at room temperature for 40 h with occasional stirring. The resin was then collected in a large coarse porosity fritted-glass funnel and washed with dioxane/4 N aqueous HCl (3:1, 6 L), dioxane/water (3:1), DMF, MeOH (4 L each), swollen with CH_2Cl_2 (2 L), washed with MeOH (2 L), and dried under suction and then vacuum. Yield, 221 g of pale yellow nitrobenzophenone resin. The above keto resin was converted to the oxime in pyridine/ethanol (1:5, 1.8 L) containing hydroxylamine hydrochloride (200 g). The mixture was heated at gentle reflux for 22 h and then collected in a fritted-glass funnel. The resin was washed with MeOH (2 × 1.5 L) and dried under vacuum. Yield, 223 g of oxime resin. A small sample of this resin was coupled with *t*-Boc-glycine, and the substitution level was determined by picric acid titration to be 0.60 mmol/g.[23,29]

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Registry No. **2**, 5350-47-0; **3**, 120712-34-7; **4**, 120712-35-8; (*E*)-**5**, 120712-37-0; (*Z*)-**5**, 120712-36-9; (*E*)-**6**, 120712-39-2; (*Z*)-**6**, 120712-38-1; 4-$(NO_2)C_6H_4COCl$, 122-04-3; PhMe, 108-88-3; $H_2NCH_2CH_2NH_2$, 107-15-3; BOC-Gly-OH, 4530-20-5; BOC-Ala-OH, 15761-38-3; BOC-Leu-OH, 13139-15-6; BOC-Gln-OH, 13726-85-7; BOC-Asn-OH, 7536-55-2; BOC-Asn-Asn-Gln-Leu-Ala-Gly-OH, 120712-40-5; BOC-Asn-Asn-Gln-Leu-Ala-Gly-OPip, 120712-41-6; succinic anhydride, 108-30-5; PepSyn gel resin, 120788-21-8; styrene-divinylbenzene copolymer, 9003-70-7.

(28) We thank Dr. Jeffrey Kelley for using this protocol to prepare a batch of oxime resin and sharing his results. In earlier experiments we did not filter the solution of $AlCl_3$ and nitrobenzoyl chloride on addition to the polystyrene beads. If filtration is omitted, the product resin may contain a small amount of dark granular impurity which does not interfere with the use of the resin.

(29) This procedure can also be used to prepare an oxime resin from macroporous polystyrene (Aldrich). After coupling of *t*-Boc-glycine, the substitution level of this material was determined by amino acid analysis to be 0.6 mmol/g and by picric acid titration[23] to be 0.1 mmol/g. These preliminary results suggest that diffusion of reagents through macroporous polystyrene is poor and not well suited to peptide synthesis (see also ref 20). These results were obtained by Dr. Tomikazu Sasaki.

Asymmetric Reduction of Ketones with Crystalline Cyclodextrin Complexes of Amine–Boranes

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One of the easist methods for the preparation of optically active secondary alcohols is the asymmetric reduction of prochiral ketones. Among the asymmetric reducing agents for ketones, chirally modified borane derivatives or complexes have been widely studied owing to their selectivity, stability, and solubility in a variety of solvents, and high asymmetric inductions have been reported in individual cases.[1-8] Significant asymmetric inductions have been also achieved by the use of borohydrides in a chiral environment such as in the presence of optically active catalysts under phase-transfer conditions[9,10] and in the chiral domain of D-glucofuranose,[11] bovine serum albumin,[12] and chiral crown ethers.[13,14]

Cyclodextrins provide also a chiral binding site[15] capable of including guest molecules and are known to induce asymmetric reductions of prochiral ketones dissolved[16] or suspended[17] in an alkaline aqueous solution of sodium borohydride to give the corresponding alcohols in low enantiomeric excess up to 36%. However, no amine–borane complexes included in cyclodextrins have been investigated as asymmetric reducing agents. In connection with our interest in solid state reactions, the use of microcrystals of cyclodextrin complexes has been investigated as rigid chiral matrices controlled by the crystalline lattice for asymmetric reaction,[18] and those studies mentioned above

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Table I. Asymmetric Reduction of Ketones with Crystalline Cyclodextrin Complexes of Amine–Boranes[a]

no.	ketone	reducing agent[b] amine	reducing agent[b] cyclodextrin	yield,[c] %	$[\alpha]^{25}_D$, deg	solvent[d]	ee, %	config
1	$C_6H_5COCF_3$	C_6H_5N	α-CD	50	+0.6	C_6H_6	4[e]	S
2	$C_6H_5COCF_3$	C_6H_5N	β-CD	96	+1.9	C_6H_6	13[e]	S
3	$C_6H_5COCF_3$	C_6H_5N	γ-CD	93	−1.2	C_6H_6	8[e]	R
4	$C_6H_5COCF_3$	$(CH_3)_3N$	β-CD	27	−0.3	C_6H_6	2[e]	R
5	$C_6H_5COCH_2Cl$	C_6H_5N	β-CD	70[f]	+17.2	C_6H_{12}	36[g]	S
6	$C_6H_5COCH_2Cl$	$(CH_3)_3N$	β-CD	50[f]	−0.9	C_6H_{12}	2[g]	R
7	$C_6H_5COCH_2Br$	C_6H_5N	β-CD	67[f]	−7.8	$CHCl_3$	20[h]	R
8	$C_6H_5COCH_3$	C_6H_5N	β-CD	8[i]	−47.7	CH_2Cl_2	91[j]	S
9	$C_6H_5C_2H_4COCH_3$	C_6H_5N	β-CD	26[i]	−17.2	C_6H_6	89[k]	R
10	$C_2H_5COCH_3$	C_6H_5N	β-CD	22	−6.4	neat	47[l]	S
11	$C_6H_5COCO_2CH_3$	C_6H_5N	β-CD	63	−12.7	$CHCl_3$	7[m]	R

[a] The ketones were reacted with the crystalline cyclodextrin complex of amine–borane dispersed in water at 0 °C for 20 h. [b] The amine and cyclodextrin are indicated in the amine–borane complex included in the cyclodextrin. α-, β-, and γ-CD mean α-, β-, and γ-cyclodextrins: pyridine–borane·α-CD is 0.5:1.0 complex; pyridine–borane·β-CD, pyridine–borane·γ-CD and trimethylamine–borane·β-CD are 1:1 complexes. [c] Isolated yield. [d] c = 0.5–2.0: C_6H_6 = benzene, C_6H_{12} = cyclohexane. [e] Based on the reported maximum rotation value of $[\alpha]_D$ = +14.76° (benzene) for the *S* enantiomer.[19] [f] Reacted in carbon tetrachloride for 3 days. [g] Based on the reported maximum rotation value of $[\alpha]^{25}_D$ = −48.1° (*c* 1.73, cyclohexane) for the *R* enantiomer.[21] [h] Based on the reported maximum rotation value of $[\alpha]^{25}_D$ = −39° (*c* 8.00, chloroform) for the *R* enantiomer.[21] [i] Reacted in water for 21 days. [j] Based on the reported maximum rotation value of $[\alpha]^{23}_D$ = −52.5° (*c* 2.27, methylene chloride) for the *S* enantiomer.[22] [k] Based on the reported maximum rotation value of $[\alpha]_D$ = +19.4° (benzene) for the *S* enantiomer.[23] [l] Based on the reported maximum rotation value of $[\alpha]_D$ = −13.5° (neat) for the *S* enantiomer.[24] [m] Based on the reported maximum rotation value of $[\alpha]^{25}_D$ = −174.2° (*c* 0.58, chloroform) for the *R* enantiomer.[25]

prompt us to report our investigation of the contribution of cyclodextrin to this reduction. In this paper, we report a novel asymmetric reduction of prochiral ketones utilizing crystalline cyclodextrin inclusion complexes of achiral amine–boranes, which act effectively in the enantioselective reduction of aliphatic and aromatic ketones.

The results summarized in Table I have been obtained under identical standard conditions (see the Experimental Section) and were reproducible within 10%. Thus, significant improvements on these inductions were obtained by reducing the ketones with the preformed β-cyclodextrin complex of pyridine–borane suspended in water or carbon tetrachloride, compared with the reduction of ketones included in β-cyclodextrin by using sodium borohydride aqueous alkaline solution.[17] Reduction of 1-phenylethanone and 4-phenyl-2-butanone yielded (*S*)-1-phenylethanol and (*R*)-4-phenyl-2-butanol in 91 and 89% ee, respectively (no. 8 and 9), whereas the same substrates included in β-cyclodextrin and treated with an aqueous sodium borohydride solution are converted to the corresponding (*S*)-alcohols in 3.5 and 15.9% optical yields.[17]

In the enantioselective reduction of 2,2,2-trifluoro-1-phenylethanone, the β-cyclodextrin complex of pyridine–borane was the most efficient among the three cyclodextrin complexes (no. 1–3) and much more effective than the trimethylamine–borane complex (no. 4 and 6). The crystalline complex of pyridine–borane included in β-cyclodextrin was also found to be a much more efficient chiral reducing agent for 2-chloro-1-phenylethanone than the trimethylamine–borane complex (no. 5 and 6). Interestingly, reduction of the same substrates by using pyridine– or trimethylamine–borane complexes included in β-cyclodextrin gave the alcohols with the opposite configuration; the pyridine complex produced (*S*)-alcohols (no. 2 and 5), whereas the trimethylamine complex gave the opposite (*R*)-alcohol isomers (no. 4 and 6). These results clearly show that β-cyclodextrin forms complexes with pyridine– and trimethylamine–boranes such that the addition of hydride anion from these two reagents occurs to different enantiofaces of the carbonyl group of the ketone to yield alcohols of opposite chiralities.

The hydride anion from an amine–borane complex is well known to be a strong nucleophile which attacks the atom with the lowest electron density in a ketone molecule, and the electron-withdrawing substituent on the α-carbon atom of the carbonyl compound provides a rate increase of reduction.[19] In fact, Table I shows that electron-withdrawing substituents, R, such as halomethyl (no. 1–7) and ester (no. 11) groups of the ketones $RCOC_6H_5$, increase the rate, but decrease the asymmetric induction. The present study, however, cannot explain why the enantioselectivity decreases. A detailed study on this problem is now in progress and will be reported elsewhere. Although the present method offers a quite simple way to obtain chiral alcohol of high opticaly purity, optimization of substrates and conditions may lead to substantial improvements.

Experimental Section

Crystalline Cyclodextrin Complexes of Amine–Boranes. An equimolar amount of a borane complex of various amines, such as pyridine, trimethylamine, dimethylamine, and *tert*-butylamine, was added to an aqueous solution of α-, β-, γ-cyclodextrins and dissolved with mixing at 25 °C. The solution was then cooled at 0 °C for 3 days. White precipitates were obtained in 80–90% yields in the case of trimethylamine–borane with β-cyclodextrin, and of pyridine–borane with the three kinds of cyclodextrins, respectively. The X-ray diffraction patterns of these powdered samples showed that they were highly crystalline and not physical mixtures of the amine–borane and the cyclodextrin. The stoichiometry of the complexes was determined by ^1H NMR spectra of the precipitates in dimethyl-d_6 sulfoxide. The molar ratios of pyridine–borane to α-, β-, and γ-cyclodextrins were found to be 0.5, 1.0, and 1.0, respectively. The same stoichiometry of 1:1 was observed for the complex of trimethylamine–borane with β-cyclodextrin. Moreover, these samples had characteristic infrared absorption bands at 2360–2370 cm^{-1}, which can be assigned to the stretching modes of B–H bond of the amine–borane. No such cyclodextrin complexes were obtained with the borane complexes of dimethylamine and *tert*-butylamine, and with sodium borohydride under the same conditions. The microcrystalline samples of the cyclodextrin inclusion complexes were collected by filtration and used without drying in vacuo; the order of their crystallinity was found to decrease upon dehydration.[20]

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Asymmetric Reduction. The general procedure for the reduction of ketones with the cyclodextrin inclusion complexes of the amine–boranes was as follows. About 1.5 g wet weight or 1 mmol of the cyclodextrin complex was suspended and stirred in 2 mL of water containing 1 mmol of a ketone at 0 °C for the specified time. All the reaction mixtures were heterogeneous under such condition even for 3 weeks. The reduction of some water-insoluble ketones such as 2-chloro- and 2-bromo-1-phenylethanones did not proceed in water, but in carbon tetrachloride in the presence of the crystalline β-cyclodextrin complexes of pyridine– and trimethylamine–boranes. After the reaction, 0.1 M aqueous HCl solution was added to hydrolyze the unreacted amine–boranes, and then water was added to dissolve the complexes. The aqueous solution was extracted with diethyl ether. The combined ether extracts were washed with an aqueous sodium chloride solution, dried, and evaporated in vacuo. The residue (90–95% recovery) was purified by column chromatography on silica gel (Wakogel C-300) using dichloromethane as a eluent. The isolated products were identified by comparison of their NMR and IR spectra with those of authentic samples, and the optical rotations were measured at 25 °C in a suitable solvent. The absolute configuration and the enantiomeric excess were determined from the known values of optical rotation given in the literature.

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Effect of Phase-Transfer Catalysis on the Selectivity of Hydrogen Peroxide Oxidation of Aniline

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Several methods for the oxidation of aniline are reported in the literature. Classical stoichiometric oxidants as MnO_2[1] are used in order to obtain azobenzene.[1] Aqueous peracids oxidize ortho-substituted anilines to nitrobenzene[2] and nonsubstituted anilines to azo- and azoxybenzene[3] while anhydric peracids oxidize even unsubstituted aniline to nitrobenzene.[4] Catalytic systems as t-BuO_2H–Mo(VI), V(V),[5] or t-BuO_2H–Ti(IV)[6] are applied to produce nitrobenzene or azoxybenzene, respectively, in a selective manner. These oxidants are expensive and produce serious environmental problems.

Diluted hydrogen peroxide being cheap and nonpolluting can be an answer to these problems. Indeed an H_2O_2–WO_4^{-2} oxidation of aniline to mixtures of nitroso- and azoxybenzene[7] and the oxidation of *p*-chloroaniline to dichloroazobenzene in the presence of H_2O_2–boric acid[8] were reported.

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We made an interesting observation that while H_2O_2 oxidizes aniline selectively to azoxybenzene and the addition of either $RuCl_3$ or quaternary ammonium chlorides do not affect the selectivity at all, a ternary system of H_2O_2–$RuCl_3$ quaternary ammonium chloride (R_4NCl) or a binary system H_2O_2–quaternary ammonium bromide (R_4NBr) produce mixtures of nitro and azobenzene. Nitrobenzene becomes the main product when a H_2O_2–$RuCl_3$–quaternary ammonium bromide system is employed. Scheme I presents these alternatives.

Scheme I

$$2PhNH_2 + 3H_2O_2 \xrightarrow[\text{or no catalyst}]{RuCl_3 \text{ or } R_4NCl} PhN(O)=NPh + 5H_2O \quad (1)$$

$$3PhNH_2 + 6H_2O_2 \xrightarrow[\text{or } R_4NBr]{RuCl_3 + R_4NCl} PhN(O)=NPh + PhNO_2 + 9H_2O \quad (2)$$

$$PhNH_2 + 3H_2O_2 \xrightarrow{RuCl_3 + R_4NBr} PhNO_2 + 4H_2O \quad (3)$$

We have investigated the nature of this reaction and studied the effect of various parameters such as amount of hydrogen peroxide and amount and structure of the phase-transfer and metal catalysts on the selectivity of the process.

Results and Discussion

Oxidations were carried out at 90 °C with 30% H_2O_2 (640 mmol), which was added to the following mixture: aniline (54 mmol), PT catalyst (3 mmol), $RuCl_3 \cdot 3H_2O$ (0.077 mmol), and 10 mL of 1,2-dichloroethane as solvent.

In the absence of both PT and metal catalysts, the main product is azoxybenzene (90% yield). When quaternary ammonium chloride (e.g. didecyldimethylammonium chloride, DDACl) or ruthenium chloride were separately added to the system, no significant changes were observed. Note that $RuCl_3$ is totaly extracted by aniline into the organic phase.

The combination of both DDACl and $RuCl_3$ produces an interesting and surprising change in products distribution: in addition to azoxybenzene 35% nitrobenzene was found in the reaction mixture. The nitrobenzene is evidently produced via a parallel pathway since when azoxybenzene was exposed to the same conditions no reaction occurred.

A possible interpretation of this phenomenon is that once extracted into the organic phase by either DDACl or aniline, $RuCl_3$ and H_2O_2 form together a more active oxidant specie[9] capable of oxidizing aniline to nitrobenzene. Based on our observation that indicated significant difference in catalytic activity between ammonium salts possessing similar lipophilicity but different symetry (see later), we tend to believe that the PT catalyst not only has a role in the extraction process but also participates in the formation of the active oxidation complex. A similar result is obtained in the presence of DDABr alone, suggesting the existence of an alternative pathway for the oxidation of aniline to nitrobenzene in which the oxidant species seems to be bromide anion. In fact, when the quaternary ammonium bromide is replaced by NaBr (9 mmol), the same amount of nitrobenzene is obtained. A higher amount of nitrobenzene (60% yield) is produced when a combination of the two systems (DDABr and $RuCl_3$) is employed. Analyzing this system, we found a strong de-

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