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# SELECTIVE REDUCTION OF RACEMIC 1,2-BUTYLENE OXIDE WITH (-)-DIISOPINOCAMPHEYLBORANE IN THE PRESENCE OF LITHIUM CHLORIDE

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Summary Two equivalents of 1,2-butylene oxide was reduced with one equivalent of (-)-diisopinocampheylborane lithium chloride (1 0.1) system at 0° and -20° to give optically active R-2-butanol, 22.0% e.e. and 22.6% e.e., respectively.

(-)-Diisopinocampheylborane($IPC_2BH$) in high optical purity is an ideal asymmetric hydroborating agent for cis-olefins[1], and it has also been applied for the asymmetric reduction of representative ketones[2].

In previous studies, we have reported that the presence of a small amount of lithium chloride showed the tremendous rate enhancement in the borane reduction of acyl chloride, acid anhydride, and epoxide[3]. And this lithium chloride effect was also observed in the reduction of 1,2-butylene oxide with alkylboranes, such as thexylborane, disiamylborane and diisopinocampheylborane[4].

Some time ago, it was shown that the reaction of borane with 1,2-butylene oxide is slow but the presence of a small amount of borohydride (basic hydride) accelerates the rate tremendously[5]. Therefore it was proposed that the $BH_3$($RBH_2$ or $R_2BH$)-LiCl system is in equilibrium with lithium chloroborohydrides (basic hydrides), as follows[3] (eq 1).

$$BH_3(RBH_2 \text{ or } R_2BH) + LiCl \rightleftharpoons LiBH_3Cl(LiRBH_2Cl \text{ or } LiR_2BHCl) \qquad (1)$$

And the facile reduction of 1,2-butylene oxide has been interpreted by the initial coordination of borane species on the epoxide oxygene and the rapid attack of the adduct by the basic hydrides.

Therefore it was of our interest to find out whether a chiral borane, (-)-$IPC_2BH$, can coordinate preferentially either on R- or S-1,2-butylene oxide. If (-)-$IPC_2BH$ coordinate exclusively on R-1,2-butylene oxide in the reaction with racemic 1,2-butylene oxide, we would get R-2-butanol and S-1,2-butylene oxide would remain unattacked. We tested this possibility by reacting two equivalents of racemic 1,2-butylene oxide with one equivalent of (-)-$IPC_2BH$ in the presence of 0.1 equivalent of LiCl. The reactions were carried out at $0^\circ$ and at $-20^\circ$ in THF. Judging from the disappearence of the (-)-$IPC_2BH$ precipitate in 0.5 hr, the reductions were almost complete in 0.5 hr. but both reductions were carried out for 3 hours.

Table 1. Selective Reduction of Racemic 1,2-Butylene Oxide with (-)-Diisopinocampheylborane[a]-Lithium Chloride(1 0.1) in Tetrahydrofuran

| Temp, $^\circ C$ | Product | Yield % | $[\alpha]_D^{25}$ deg(neat) | Enantiomeric[d] excess % | Config n |
|---|---|---|---|---|---|
| 0 | 2-Butanol[b] | 81 | -2.97 | 22.0 | R |
| 0 | 2-Butanol[c] | 79 | +2.57 | 19.0 | S |
| -20 | 2-Butanol[b] | 76 | -3.06 | 22.6 | R |
| -20 | 2-Butanol[c] | 77 | +3.00 | 22.2 | S |

a) Prepared with 92% optically pure (+)-α-pinen, $[\alpha]_D^{22}$ $+47.1^\circ$(neat) b) From the reduction of 1,2-butylene oxide with (-)-$IPC_2BH$-LiCl(1 0.1) c) From the reduction of distillate of the unreacted epoxide with lithium aluminum hydride d) Based on the known value of $[\alpha]_D^{25}$ -13.51(neat) for R-(-)-2-butanol[8]

As shown in Table 1, R-(-)-2-butanol was obtained in a yield of 81% with an enantiomeric excess of 22.0% at $0^\circ$. And the remaining one equivalent of 1,2-butylene oxide was treated with lithium aluminum hydride to give S-(+)-2-butanol in 79% yield with 19% e.e. The selective reduction was also carried out at $-20^\circ$ in the hope to increase the selectivity, but the results were almost same. Therefore by reacting with one equivalent of (-)-$IPC_2BH$, two equivalents of the epoxide gave approximately 0.6 R-alcohol and 0.4 S- alcohol, leaving 0.4 R-epoxide and 0.6 S- epoxide unattacked.

$$\begin{array}{lll} \text{R-Oxide} & 1.0 & \\ \text{S-Oxide} & 1.0 & \end{array} \xrightarrow[0^\circ \text{ or } -20^\circ]{IPC_2BH\ 1.0} \begin{array}{lll} \text{R-Alc.} & 0.6 & + \text{ R-Oxide } 0.4 \\ \text{S-Alc.} & 0.4 & + \text{ S-Oxide } 0.6 \end{array}$$

Thus R-1,2-butylene oxide was attacked preferentially over S-1,2-butylene oxide in 3 2 ratio. Since the hydride attack of the adduct by basic borohydride is presumably a rapid step, this 3 2 selectivity is believed to be due to the selectivity in the coordination of chiral $IPC_2BH$ on the R-, and S-1,2-butylene oxide. We are going to study this kind of selective reductions of racemic epoxides more in detail.

The following procedure for the selective reduction of 1,2-butylene oxide at $0^\circ$ is representative. All operations were carried out under anhydrous nitrogen atomsphere[7]. An oven dried 250-ml flask with septum inlet, charged with 0.424 g of pre-dried lithium chloride (10 mmol), was assembled with a reflux condenser connected to a mercury bubbler. The apparatus was flamed out with a Bunsen burner while flushing the system with dry nitrogen. After cooling to $0^\circ$ in an ice-bath under a positive nitrogen pressure, the flask was charged with 80 ml of 1.25 M $BH_3$-THF solution (100 mmol) using hypodermic syringe, and 31.3 g (230 mmol, 15% excess) of (+)-α-pinene (Aldrich, $[\alpha]_D^{22}$ +47.1, 92% e.e.), which was freshly distilled over lithium aluminum hydride, was added dropwise with constant srirring. After stirring for about 3 hours at $0^\circ$, the flask was stored at $0^\circ$ for 3 days[1]. After 3 days, the flask was immersed in an ice-water bath, and 20 ml of 10.00 M THF solution of 1,2-butylene oxide (200 mmoles) was added as rapidly as possible with vigorous stirring. The precipitate of hydride reagent was disappeared after 0.5 hr. The reaction mixture was stirred for an additional 3 hours in an ice-water bath and then allowed to warm to room temperature. Excess α-pinene and unreacted epoxide were collected by the distillation under a slow stream of nitrogen. Any remaining volatile material was removed by evaporation in vacuo, and to this residual oil was added 200 ml of ether. The mixture was hydrolyzed with water, followed by oxidation with alkaline hydrogen peroxide in the usual manner[7], maintaining the temperature below $40^\circ$. The mixture was saturated with potassium carbonate and the ether layer separated and then dried over anhydrous magnesium sulfate. The residue after removal of ether was fractionally distilled through an efficient microcolumn, and provided 6g of 2-butanol (81% yield, 95% gc purity), bp $97.5^\circ$ (763 mm). It was further purified through 10% SE 30 M column, $n_D^{20}$ 1.3970. (lit[7]., $n_D^{20}$ 1.3970) The optical rotation of 2-butanol product was measured by an auto-digital polarimeter $[\alpha]_D^{25}$ -2.97 (neat), 22.0% e.e. in R[8].

The collected portion of 1,2-butylene oxide was reduced to 2-butanol with excess lithium aluminum hydride at 0°, and then the mixture was treated with 20 ml of 1.25 M $BH_3$-THF solution to hydroborate excess α-pinene (The seperation of 2-butanol from isopinocampheol is easier then from α-pinene.). The solvent was removed by aspirator under a slow stream of nitrogen, and to this residue was added ether and water. The mixture was oxidized with alkaline hydrogen peroxide. The ether layer was separated, dried, and 2-butanol was purified as described above. There was obtained 5.8g of 2-butanol (79% yield), bp 98° (761 mm), $n_D^{21}$ 1.3969, $[\alpha]_D^{22}$ +2.57 (neat), 19.0% e.e. in S[8].

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