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THE EFFECT OF TRIETHYLBORANE IN THE REDUCTION OF EPOXIDES WITH LITHIUM BOROHYDRIDE

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Abstract —— The presence of triethylborane dramatically accelerated the reduction of epoxides with lithium borohydride. Thus the all three epoxides tested, namely, 1,2-butylene oxide, cyclohexene oxide and styrene oxide were reduced rapidly in 1 h at room temperature in the presence of 25 mole % of triethylborane whereas more than 24 h was required for these reductions with lithium borohydride itself.

Epoxides are reduced quite slowly either with borane or with borohydride[1,2]. However, addition of a catalytic amount of sodium borohydride dramatically increased the rate of the reaction with borane[3]. Such phenomena were interpreted as the reaction proceeded through the initial coordination of borane, a Lewis acid, to the oxygen of epoxide and the adduct was rapidly attacked by the borohydride, a basic hydride[3]. This interpretation suggests that the reduction of epoxide with lithium borohydride should be accelerated by the presence of a Lewis acid.

We tested this possibility for the representative epoxides, such as 1,2-butylene oxide, cyclohexene oxide and styrene oxide, choosing triethylborane as a representative Lewis acid[4]. As shown in Table I, the presence of triethylborane dramatically accelerated the reduction of these epoxides. However, 25 mole % of triethylborane was necessary for the rapid reduction in contrast to the borohydride catalyzed borane reduction[3]. Thus in the presence of 25 mole % of triethylborane, the three epoxides were rapidly reduced with lithium borohydride in 1 h whereas the reduction with lithium borohydride itself required 48 h at room temperature for the three epoxides to be reduced completely.

In the case of styrene oxide, the changes in product distribution were also examined as the amount of triethylborane was increased from 0% to 100% and the results are

Table I. Reduction of Representative Epoxides with Lithium Borohydride in the Presence of *Triethylborane in Tetrahydrofuran* at 25° [a]

Epoxides	Mole % Et$_3$B	Reduction [b,c]					
		0.5 h	1.0 h	3.0 h	6.0 h	24.0 h	48.0 h
1,2-Butylene oxide	none		0.10	0.24	0.51	0.89	1.02(100)
	5	0.50	0.64	0.89	1.00		
	10	0.62	0.76	1.00			
	25	0.99	1.01	1.01(97.8)			
Cyclohexene oxide	none		0.18	0.22	0.36	0.70	1.01[d]
	5	0.18	0.30	0.69	0.82	1.02	
	10	0.56	0.69	0.83	0.92	1.02	
	25	1.01	1.01	1.01			
Styrene oxide	none		0.15	0.20	0.30	0.68	1.00(97.3)[e]
	5	0.11	0.19	0.46	0.71	1.01	
	10	0.49	0.67	0.81	0.91	1.01	
	25	0.91	0.96	1.00	1.00(97.1)[f]		
	50	(98.9)[g]					
	100	(98.3)[h]					

[a] The reaction mixtures were both 0.25 M for epoxides and lithium borohydride. [b] *Hydride used for reduction*(mmoles/mmol of epoxides). [c] The figures in parentheses indicate the percent yields of the corresponding alcohols determined by glpc analysis. [d] At 36 h. The ratios of 1-phenylethanol to 2-phenylethanol were, [e] 99:1 [f] 87:13 [g] 81:19 [h] 77:23.

shown in Table I. The formation of substantial amount of 2-phenylethanol (23%) in the presence of equimolar triethylborane, *in contrast to the very small amounts* realized with LiBH$_4$ and with LiEt$_3$BH[6], also suggests the prior coordination of triethylborane to styrene oxide, since the coordination should increase positive charge more on the benzylic position than on the primary position of styrene oxide, increasing the yield of 2-phenylethanol. Previously we observed 38.4% yield of 2-phenylethanol in the reduction of styrene oxide with LiBH$_4$ in the presence of equimolar BH$_3$(more stronger Lewis acid than Et$_3$B)[7].

The relatively slow reduction in the presence of 5 and 10 mole % of triethylborane *in comparison with the reduction in the presence of* 25 or 100 mole % triethylborane (Fig. 1), may be attributed to the reaction of triethylborane[5] with lithium alkoxy-

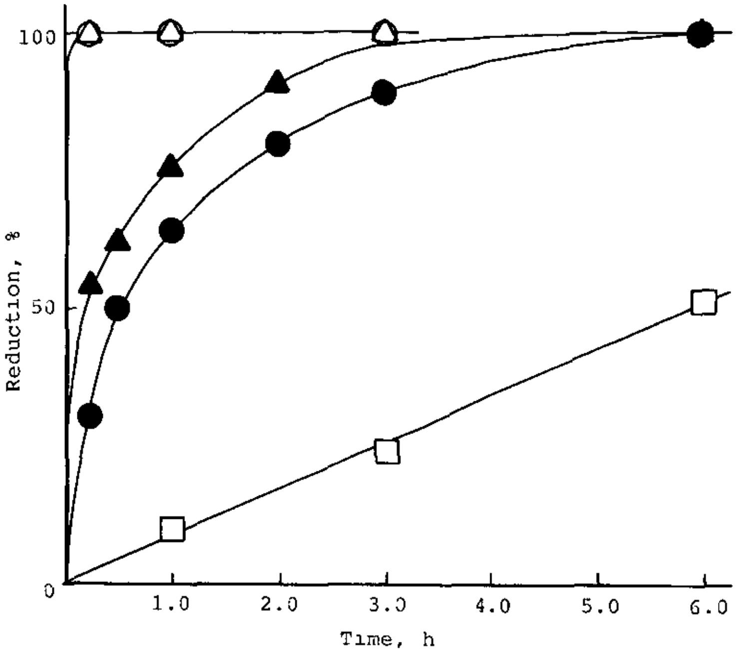

Fig.1 The Reduction of 1,2-Butylene Oxide with Lithium Borohydride in the Presence of Various Mole % of Triethylborane in Tetrahydrofuran at 25°, $[LiBH_4]$=[Butylene oxide]= 0.25 M. $LiBH_4/BEt_3$;1/1(○), 1/0.25(△), 1/0.10(▲), 1/0.05(●), 1/0.00(□).

borohydrides, which would have been produced during the reduction, as shown below.

$$LiBH_n(OR)_{4-n} + Et_3B \rightleftharpoons LiEt_3BOR + BH_n(OR)_{3-n} \qquad n=3,2,1 \text{ or } 0 \tag{1}$$

The reduction of styrene oxide with lithium borohydride in the presence of 25 mole % triethylborane is described as a representative. A 100-ml oven-dried flask, equipped with a side arm fitted with a rubber septum, a magnetic stirring bar, and a reflux condenser connected to a gas burette, was cooled down to room temperature under a stream of nitrogen. The flask was immersed into a water bath (ca. 25°C). Then THF (6 ml) was introduced into reaction flask followed by lithium borohydride solution in THF (8 mmol, 8 ml), triethylborane solution in THF (2 mmol, 2 ml) and naphthalene solution in THF (8 mmol, 8 ml) to serve as an internal standard for glpc analysis. Finally, styrene oxide solution in THF (8 mmol, 8 ml) was added slowly to the reaction mixture with stirring at room temperature (ca 25°C). After the appropriate periods, each 4 ml aliquot of the reaction mixture was withdrawn by a hypodermic syringe and hydrolyzed with 2 N sulfuric acid-THF mixture. The amount of residual hydride was measured gasometrically and the number of mmol of hydride consumed per mmol of styrene oxide were estimated to be 0.91(0.5 h), 0.96(1.0 h) and 1.00(3.0 h) respectively. At 6.0 h, the reaction mixture was hydrolyzed, separated the THF layer with K_2CO_3, and dried with anhydrous $MgSO_4$. Glpc analysis using 10% carbowax 20 M on chromosorb WHP, 10 ft, 0.125 inch, revealed the formation of phenylethanols in the yield of 97.1%, the normalized percentages of 1- and 2-phenylethanol being 87% and 13%, respectively. The results are summarized in Table I.

Since the lithium borohydride is a relatively mild reducing agent at room temperature[2], the rapid reduction in the presence of triethylborane suggests the possibility of the selective reduction of epoxide in the presence of carboxylic acid, ester, halogen, and other functional groups. These selective reductions are now under investigation.

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REFERENCES AND NOTES

1. H. C. Brown, P. Heim and N. M. Yoon, J. Am. Chem. Soc., 1970, 92, 1637.
2. a/ N. M. Yoon and J. S. Cha, J. Korean Chem. Soc., 1977, 21, 108.
   b/ K. I. Choi, M. S. Thesis, Sogang Univ. Seoul, Korea, 1982.
3. The catalytic amount of borohydride remarkably enhanced the rate of borane reduction of epoxides; H. C. Brown and N. M. Yoon, J. AM. Chem. Soc., 1968, 90, 2686.
4. A small amount of BH_3 does not accelerate the reduction of epoxide with $LiBH_4$, presumably due to the formation of LiB_2H_7, a basic hydride,
   $BH_3 + LiBH_4 \longrightarrow LiB_2H_7$
5. The existance of "ate" complex, $LiEt_3BOR$, was suggested in the reaction of $LiEt_3BH$ and ROH; H. C. Brown, S. C. Kim and S. Krishnamurthy, J. Org. Chem.,1980, 45, 1.
6. When $LiEt_3BH$ was utilized in the reduction of styrene oxide, the ratio of 1-phenylethanol to 2-phenylethanol was 97:3 ; Reference 5.
7. When styrene oxide was reduced with BH_3-$LiBH_4$(1:1), the ratio of 1-phenylethanol to 2-phenylethanol was 61.6:38.4 ; H. C. Brown and N. M. Yoon, unpublished results.

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