

## 보란-염화리튬에 의한 유기화합물의 환원반응

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(1977. 11. 12 접수)

## Effect of Lithium Chloride on the Borane Reduction of Organic Compound<sup>1</sup>

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(Received Nov. 12, 1977)

**요 약.**  $BH_3$ -THF 용액에 염화리튬을 가한 새로운 환원계의 환원특성에 대한 연구가 대표적인 작용기를 가진 유기화합물을 가지고 표준조건 ( $0^\circ$ , THF)에서 이루어졌다. 조사 연구된 화합물중 벤조페논, 4가지 에스테르 및 시클로헥센은  $BH_3$  환원과 별 차이를 보이지 않았으나, 2-헵탄온, 아세토페논, 염화벤조일, 프탈산부수물, 그리고 3가지 에폭시화물은 소량의 염화리튬에 의해 빠른 속도로 환원이 완결되었다. 특히, 에폭시화시클로헥센의 환원에 있어서는 소량의 염화리튬 존재하에서는 정량적으로 시클로헥산올을 생성하였으나 염화리튬의 양이 증가하면 2-클로로시클로헥산올이 시클로헥산올과 함께 생성됨을 알았다. 또한, 에폭시화시클로헥센과의 반응에 있어서 질산리튬은 염화리튬과는 달리 별로 효과가 없었다. 따라서 보란-염화리튬용액에 클로로수소화붕소리튬의 생성가능성을 논의하였다.

**ABSTRACT.** The effect of lithium chloride on the borane reduction of organic compounds was studied for three ketones, seven acid derivatives, three epoxides and cyclohexene in tetrahydrofuran at  $0^\circ$ . When compared with borane itself, borane-lithium chloride system enhanced the rates of reductions markedly of 2-heptanone, acetophenone, benzoyl chloride, phthalic anhydride, and three epoxides, whereas the reductions of benzophenone, four esters and cyclohexene showed little or no effect.  $BH_3$ -LiCl(1:0.1) reduced styrene oxide in 2 hr at  $0^\circ$  to give 94.2 % yield of alcohols, 1-to 2-phenylethanol ratio being 60.8 to 39.2. And in the reduction of cyclohexene oxide,  $BH_3$ -LiCl(1:0.1) gave a quantitative yield of cyclohexanol in 2 hr at  $0^\circ$ , however  $BH_3$ -LiCl(1:1) gave 58 % cyclohexanol and 42 % 2-chlorocyclohexanol. In the reduction of cyclohexene oxide, lithium nitrate showed no rate enhancement even when the salt was added in large excess. A formation of lithium chloroborohydride in the  $BH_3$ -LiCl system is suggested.

### INTRODUCTION

Recently we have carried out a systematic study of the approximate rates and stoichiome-

tries of the reaction of lithium borohydride with representative organic compounds<sup>2</sup>. In this study, we have noticed remarkable contrast in reducing ability between lithium borohydride and borane.

Thus, carboxylic acids are reduced rapidly with borane, but almost inert to lithium borohydride. On the other hand, borane reduces acyl halides very slowly, whereas lithium borohydride reduces it very rapidly. Amides and nitriles are inert to lithium borohydride, but moderately reduced with borane. On these tremendous contrasts, we attributed them mainly due to the "acidic" character of borane and the "basic" character of lithium borohydride.

And we have reported<sup>3</sup> that epoxides are rapidly reduced with borane in the presence of a catalytic amount of lithium or sodium borohydride, a "basic" reducing agent, in contrast to the slow reduction with borane, and also observed borohydride-catalyzed reaction of borane offer major advantages for the *anti*-Markovnikov opening of trisubstituted epoxides, *e.g.*, in the case of 1-methylcyclohexene oxide, the products ratio of *cis*-2-methylcyclohexanol to 1-methylcyclohexanol is 74:26. Such phenomena indicate that borohydride ion plays a major role on the borane reduction of epoxides as a catalyst, and we have suggested that in the presence of borohydride, the reaction proceeded through the initial coordination of borane to the oxygen of the epoxide, and the adduct was rapidly attacked by the borohydride, a stronger hydride donor than borane.

According to the paper by Aftandilian and his coworkers<sup>4</sup>, lithium thiocyanoborohydride and potassium fluoroborohydride were produced in the yields of 56 % and 100 %, respectively, in the reaction of borane with lithium thiocyanate and potassium fluoride in monoglyme solution. These monosubstituted borohydrides are expected to show the "basic" character, similar to lithium borohydride. These results suggest that the mere addition of an appropriate salt to the borane solution would change the reducing characteristics of borane solution. Therefore,

we have decided to examine the reducing characteristics of borane solution in the presence of lithium chloride, a salt which dissolves easily in THF.

## RESULTS AND DISCUSSION

**Procedure for Rate and Stoichiometry Studies.** Fourteen representative organic compounds were chosen and tested for the effect of lithium chloride on the borane reduction. The procedure adopted was to add 5.0 mmoles of the compound to 6.66 mmoles of  $\text{BH}_3$  and 0.66 mmole of lithium chloride in sufficient THF to give 20 ml of solution at 0°. The rate of the reduction was determined by checking the residual hydride after appropriate time intervals. The reactions were also carried out in the presence of equimolar amount of lithium chloride, and in the absence of lithium chloride. In the following four tables, the corresponding rate with lithium borohydride are cited from our previous study for discussion<sup>2</sup>.

**Ketones.** 2-Heptanone, acetophenone and benzophenone were studied and the results are summarized in Table 1.

As shown in Table 1, lithium chloride showed little effect on benzophenone reduction. However, the reductions of 2-heptanone and acetophenone were accelerated by the addition of lithium chloride. Since these ketones were reduced rapidly with lithium borohydride under the same condition, it may suggest the partial formation of a basic reducing agent, however the result with benzophenone should require an additional explanation.

However, it is interesting to note that lithium chloride affect the rate of ketone reduction differently according to the structure of the ketones. This suggest that the  $\text{BH}_3\text{-LiCl}$  system might be more effective than the  $\text{BH}_3$  system for the selective reduction of 2-heptanone *vs.* benzophenone, and acetophenone *vs.* benzo-

phenone. We are currently studying the selective reduction of carbonyl groups with  $\text{BH}_3\text{-LiCl}$  (1:0.1) system. This will be reported shortly.

**Carboxylic Acid and Its Derivatives.** Benzoic acid, benzoyl chloride and phthalic anhydride were studied and the results are summarized in

Table 1. Reaction of borane-lithium chloride and other metal hydrides with representative ketones in tetrahydrofuran at 0°.

Compound <sup>a</sup>	Temp. (°C)	Time, (hr)	$\text{BH}_3\text{-LiCl}^b$		$\text{BH}_3$	$\text{LiBH}_4^d$
			1 : 0.1	1 : 1		
2-Heptanone	0	0.25	1.02 <sup>c</sup>	1.00 <sup>e</sup>	0.68 <sup>f</sup>	
		0.5	1.02	1.00	0.82	1.00 <sup>g</sup>
		1.0	1.02	1.00	0.94	
		2.0			1.01	1.00
Acetophenone	0	0.25	1.01	1.00	0.73	
		0.5	1.01	1.00	0.81	1.00
		1.0			0.86	
		3.0			0.95	1.00
Benzophenone	0	0.5	0.34	0.36	0.31	0.99
		1.0	0.49	0.49	0.45	
		6.0	0.92	1.01	0.89	0.99
		9.0	1.02	1.01	1.00	

a) 5.0 mmoles of compound to 20.0 mmoles of hydride ; b)  $\text{BH}_3$  to  $\text{LiCl}$  in the mole ratio of 1 : 0.1 and 1 : 1 ; c) mmoles of hydride uptake per mmole of compound ; d) see ref. (2), data therein.

Table 2. Reaction of borane-lithium chloride and other metal hydrides with representative carboxylic acid and its derivatives in tetrahydrofuran at 0°.

Compound <sup>a</sup>	Temp. (°C)	Time, (hr)	$\text{BH}_3\text{-LiCl}^b$		$\text{BH}_3$	$\text{LiBH}_4^d$
			1 : 0.1	1 : 1		
Benzoic acid	0	1.0	0.74 <sup>e</sup> (1.00) <sup>f</sup>	0.61(1.00) <sup>e</sup>	1.18(1.00) <sup>e</sup>	0.01(1.03) <sup>f</sup>
		3.0	1.32	1.12	1.71	0.01
		6.0	1.66	1.46	1.98	0.08
Benzoyl chloride	0	1.0	1.32	1.82	0.05	2.01
		2.0	1.50	2.01	0.09	
		3.0	1.67	2.01	0.12	2.01
		7.0	1.99			
Phthalic anhydride <sup>f</sup>	0	1.0	2.51	2.49	0.08	1.36
		3.0	2.80	2.78	0.14	1.54
		6.0	3.03	3.00	0.29	1.66
		12.0	3.41	3.39	0.45	1.80
		24.0	4.02	4.01	0.64	1.96
	rt	0.5	3.62 <sup>g</sup>	3.57 <sup>g</sup>		
		1.0	4.04 <sup>g</sup>	4.02 <sup>g</sup>	0.53	2.10
	2.0	4.02 <sup>g</sup>	4.05 <sup>g</sup>	1.02	2.23	

a)~d) See corresponding footnotes in Table 1 ; e) mmoles of hydrogen evolved per mmole of compound ; f) hydride to compound in the ratio of 6 : 1, and immediately white gelatinous precipitate was observed ; g) result from the total hydrolysis after the indicated periods.

**Table 2.**

As shown in *Table 2*, benzoic acid was reduced more slowly in the presence of lithium chloride, showing 83 % reduction with  $\text{BH}_3\text{-LiCl}$  (1:0.1) and 73 % reduction with  $\text{BH}_3\text{-LiCl}$  (1:1) both in 6 hours when 100 % reduction was realized with  $\text{BH}_3$ . On the other hand, benzoyl chloride was reduced rapidly with  $\text{BH}_3\text{-LiCl}$  (1:0.1) in 7 hours, and with  $\text{BH}_3\text{-LiCl}$  (1:1) in 2 hours both at  $0^\circ$ . This is a big contrast to the inertness of benzoyl chloride to borane<sup>5</sup>. Phthalic anhydride showed similar pattern like benzoyl chloride with  $\text{BH}_3\text{-LiCl}$  system. This anhydride was reduced completely in 24 hours at  $0^\circ$  when it was reduced only 16 % with borane and 50 % with lithium borohydride. At room temperature, the reduction was completed in 1 hour, but the reduction with borane or lithium borohydride was similar with the results at  $0^\circ$ .

These results strongly suggest the formation of a basic borohydride, since acyl chloride and acid anhydride are susceptible to the attack of a basic borohydride, and relatively inert to borane.

The very sluggish reduction of benzoic acid, and the rapid half reduction of phthalic anhydride with lithium borohydride suggest that benzoic acid salt is not reactive with borohydride. Therefore the somewhat slower rate realized with  $\text{BH}_3\text{-LiCl}$  (1:1) and the slower rate with  $\text{BH}_3\text{-LiCl}$  (1:2) could be interpreted on the basis of a partial formation of benzoic acid salt in these reactions.

**Esters.** Four esters, namely ethyl caproate, ethyl benzoate,  $\gamma$ -butyrolactone and isopropenyl acetate were tested, and the results are summarized in *Table 3*. Cyclohexene was tested for comparison with isopropenyl acetate.

As shown in *Table 3*, esters were generally reduced somewhat slowly with  $\text{BH}_3\text{-LiCl}$  system

than  $\text{BH}_3$ , but the effect was not so significant. Since cyclohexene was hydroborated rapidly with this system, the reduction of isopropenyl acetate is believed to have proceeded through hydroboration, elimination, rehydroboration and reduction as with  $\text{BH}_3$ .

Since lithium borohydride reacted only sluggishly with these esters, the partial formation of a basic borohydride may not affect the rate of ester reduction.

**Epoxides.** 1,2-Butylene oxide, styrene oxide and cyclohexene oxide were examined, and the results are summarized in *Table 4*.

Although the reduction of epoxides with borane or lithium borohydride is quite slow, addition of 10 mole% of lithium chloride to borane showed a dramatic effect on the rate of the reduction. Thus, all the epoxides tested were reduced rapidly with  $\text{BH}_3\text{-LiCl}$  (1:0.1) within 2 hours. In the case of styrene oxide, it was reduced in 2 hours at  $0^\circ$  to the corresponding alcohols in yield of 94.2 % (60.8 % of 1-phenylethanol and 39.2 % of 2-phenylethanol) as revealed by glpc. In our previous study, we have observed that the reaction of styrene oxide with borane proceeded with unexpected large hydride uptake and gave only 28 % of 2-phenylethanol<sup>5</sup>, however, in the presence of lithium borohydride, the reaction proceeded smoothly to give 99.3 % of alcohols, 1-to 2-phenylethanol ratio being 61.6 to 38.4<sup>6</sup>.

However, when reacted with  $\text{BH}_3\text{-LiCl}$  (1:1) or  $\text{BH}_3\text{-LiCl}$  (1:2), the hydride uptake reaches rapidly to certain points and remain constant for all the three epoxides tested. Thus, one mmole of 1,2-butylene oxide consumed 0.7 mmole of hydride in 2 hr with  $\text{BH}_3\text{-LiCl}$  (1:1) and 0.52 mmole of hydride in 0.5 hr with  $\text{BH}_3\text{-LiCl}$  (1:2), and no further hydride uptakes are apparent on both cases.

In the reduction of cyclohexene oxide,  $\text{BH}_3\text{-}$

Table 3. Reaction of borane-lithium chloride and other metal hydrides with representative esters in tetrahydrofuran at 0°.

Compound <sup>a</sup>	Temp. (°C)	Time (hr)	BH <sub>3</sub> -LiCl <sup>b</sup>		BH <sub>3</sub>	LiBH <sub>4</sub> <sup>d</sup>
			1 : 0.1	1 : 1		
Ethyl caproate	0	1.0	0.91 <sup>c</sup>	0.79	0.99	0.20
		3.0	1.42	1.29	1.46	0.22
		6.0	1.72	1.54	1.74	0.26
Ethylbenzoate	0	1.0	0.11	0.11	0.09	0.05
		2.0	0.11	0.12	0.10	
		3.0	0.12	0.14	0.11	0.08
γ-Butyrolactone	0	6.0	0.14	0.18	0.20	0.09
		1.0	0.60	0.26	0.19	0.25
		3.0	1.17	1.21	1.69	0.55
Isopropenyl acetate	0	6.0	1.67	1.77	1.97	0.88
		0.5	2.96	3.20		
		1.0	3.14	3.40	3.16	0.39
Cyclohexene <sup>e</sup>	0	3.0	3.52	3.57	3.60	0.65
		6.0	3.80	3.97		1.15
		12.0	4.01		3.80	1.73
Cyclohexene <sup>e</sup>	0	0.5	0.98	0.99	1.01	
		1.0	0.98	0.99	1.00	

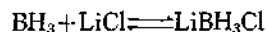
a)~d) See corresponding footnotes in Table 1; e) tested for comparison with isopropenyl acetate.

LiCl (1:0.1) gave a quantitative yield of cyclohexanol in 2 hours at 0° in marked contrast to the BH<sub>3</sub> reduction which show only 11% reduction. However, as the concentration of lithium chloride increases, the hydride uptake rapidly reaches to 0.56 with BH<sub>3</sub>-LiCl (1:1) and 0.41 with BH<sub>3</sub>-LiCl (1:2), and remain constant. The glpc analysis revealed that 58% cyclohexanol and 42% 2-chlorocyclohexanol were obtained with BH<sub>3</sub>-LiCl (1:1) in 3 hours at 0°. We did not examine the reaction products of 1,2-butylene oxide and styrene oxide with BH<sub>3</sub>-LiCl (1:1) or BH<sub>3</sub>-LiCl (1:2), however, we believe the corresponding chlorohydrins should have been produced together with the normal reduction products.

The reduction of cyclohexene oxide with borane was also carried out in the presence of lithium nitrate. As shown in Table 4, the rates were slightly increased in the presence of

lithium nitrate when compared with the reaction with borane itself. Therefore the effect of lithium ion and/or salt effect are not significant in these reactions.

These results clearly suggest that the BH<sub>3</sub>-LiCl system should contain a basic borohydride, presumably lithium chloroborohydride although it is not clear to what extent the following equilibrium exist toward lithium chloroborohydride.



### CONCLUSION

The reducing characteristics of the borane-lithium chloride solution in tetrahydrofuran showed remarkable contrast to that of borane itself, and this could be rationalized in terms of the formation of a basic borohydride, presumably lithium chloroborohydride.

Table 4. Reaction of borane-lithium chloride and other metal hydrides with representative epoxides in tetrahydrofuran at 0°.

Compound <sup>a</sup>	Temp. (°C)	Time (hr)	BH <sub>3</sub> -LiCl <sup>b</sup>			BH <sub>3</sub>	LiBH <sub>4</sub> <sup>d</sup>	BH <sub>3</sub> -LiBH <sub>4</sub> (1 : 0.1)
			1 : 0.1	1 : 1	1 : 2			
1,2-Butylene oxide	0	0.5	0.68 <sup>e</sup>	0.65	0.52	0.04	0.08	1.01
		1.0	0.94	0.68	0.52	0.08	0.17	1.01
		2.0	1.02	0.70	0.52	0.13		1.02
		3.0	1.02	0.70	0.52	0.17	0.27	
Styrene oxide	0	0.5	0.57	0.48	0.47	0.18	0.12	0.97
		1.0	0.84	0.54	0.51	0.34	0.13	1.01
		2.0	1.00 <sup>f</sup>	0.59	0.53	0.60		1.02
		3.0	1.01	0.59	0.54	0.78	0.18	
Cyclohexene oxide	0	0.5	0.78	0.56	0.41	0.05	0.09	0.99
		1.0	0.92	0.56	0.44	0.08	0.11	1.00
		2.0	0.99	0.56	0.47	0.11		0.99
		3.0	0.99 <sup>g</sup>	0.56 <sup>h</sup>	0.48	0.13	0.17	
Cyclohexene oxide <sup>c</sup> (Lithium nitrate)	0	0.5	0.06	0.07	0.06	0.05		
		1.0	0.10	0.12	0.13	0.08		
		3.0	0.15	0.18	0.19	0.11		
		6.0	0.18	0.22	0.23	0.13		

a)~d) See corresponding footnotes in Table 1; e) tested for determining of the salt effect, and the mole ratios of lithium nitrate added were the same as the case of lithium chloride; f) total 94.2% yield of alcohols (1-phenylethanol; 60.8%, 2-phenylethanol; 39.2%); g) quantitative yield of cyclohexanol and a trace of 2-chlorocyclohexanol; h) 58.1% yield of cyclohexanol and 41.9% yield of 2-chlorocyclohexanol.

The selective rate enhancement by the addition of lithium chloride, we believe, should not only increase application of borane to organic reductions but also serve for the reaction mechanism of the borane reductions.

### EXPERIMENTAL PARTS

**General.** All of the compounds used were commercial products of the highest purity available and were further purified just before use if necessary.

Thoroughly dried out sodium borohydride (98% purity, Ventron) and lithium chloride (reagent grade, J. T. Baker Chemical Co.), and dimethyl sulfate (99+% purity, gold label, Aldrich Chemical Company, Inc.), were used without further purification. Tetrahydrofuran, distilled freshly over slight excess lithium alu-

minum hydride, was stored under nitrogen atmosphere with a connection to the mercury bubbler.

Hypodermic syringes were used at all times to transfer materials. All glassware was dried thoroughly in a drying oven at 125° for more than 3 hours, assembled quickly, and then cooled under a stream of dry nitrogen. Thus, all reaction were carried out under the anhydrous nitrogen condition.

F and M Model 720 gas chromatograph equipped with a 6 ft and  $\frac{1}{4}$  inch column (5% Carbowax 20 M on Chromosob G), and Yanaco Model G8 gas chromatograph with a 4 ft and  $\frac{1}{8}$  inch column (10% di-*n*-decyl phthalate on Chromosob W), were used for glpc analysis. And product was also identified by Mass spectrometry with Hitachi RMU-7 M Mass-spec-

trometer.

**Preparation of THF Solution of Borane Reagent.** Into a 500 ml hot round-bottom flask provided with a inlet port and magnetic stirring bar, there was introduced pre-dried hot sodium borohydride (11.534 g, 293.4 mmoles), and the flask was cooled to room temperature while flushing with dry nitrogen, and 267.6 ml of moisture-free distilled THF was introduced with stirring. Then, about 5% excess over the stoichiometric amount of dimethyl sulfate (32.4 ml, 322.74 mmoles) was added dropwise with a syringe over a period of 1 hour with vigorous stirring. After 8 hours, the standard reagent solution was cooled to 0° under the slight stream of dry nitrogen, allowed to stand to settle down the precipitate, and stored in an ice box under positive nitrogen pressure. The hydride concentration was estimated by hydrolyzing aliquots from the clear supernatant with a 2N sulfuric acid-THF mixture and measuring the hydrogen evolution. Thus, the solution was found to be about 3.1 M in hydride, 1.03 M in borane.

The THF solution of borane reagent in the presence of lithium chloride was stable over the period of reaction. Thus, THF was not affected from the attack of chloride ion for more than 24 hours at 0°.

**Procedure.** The reaction of cyclohexene oxide is described to represent the procedure generally used in determining the rates and product analysis. Into an oven-dried hot 100ml flask, fitted with a rubber stopple and a stirring bar, was introduced 0.028 g of pre-dried lithium chloride (0.66 mmole) in the case of ten to one equivalent of  $BH_3$  and LiCl. After connecting to a condenser, the flask was cooled to 0° in an ice bath under a stream of dry nitrogen. And then there were added 6.5 ml of  $BH_3$ -THF solution (20 mmoles of hydride) and 8.5 ml of THF with stirring. To this 5.0 ml of 1.0 M pre-cooled

cyclohexene oxide solution in THF (0.4907 g, 5.0 mmoles) was added dropwise with a syringe. This makes the reaction mixture 0.33 M in  $BH_3$  (*i. e.*, 1.0 M in hydride), 0.033 M in LiCl, and 0.25 M in the compound. After the appropriate periods, each 4.0 ml aliquot of the reaction mixture was hydrolyzed with 2N sulfuric acid-THF mixture. And the residual hydride content was measured gasometrically. The residual hydride was 3.22 mmoles at 0.5 hr, 3.08 mmoles at 1 hr, 3.01 mmoles at 2 hr, and 3.01 mmoles at 3 hr all for the 4 ml reaction mixture. Since the 4 ml of reaction mixture originally contained 4 mmoles of hydride and 1 mmole of compound, 0.78 mmole of hydride was consumed per mmole of compound at 0.5 hr, 0.92 mmole at 1 hr, 0.99 mmole at 2 hr, and 0.99 mmole at 3 hr.

For analyzing the product, the reduction was continued for 3 hours without measuring of the residual hydride content. At the end of 3 hr, excess hydride was destroyed carefully with 4 ml of water and *n*-heptanol was added as an internal standard. After separating the water layer with anhydrous  $K_2CO_3$ , the THF layer was dried over anhydrous  $MgSO_4$  and subjected to glpc analysis, indicating the presence of approximate 100% cyclohexanol and trace of 2-chlorocyclohexanol.

In the case of mole ratio of 1:1, the procedure is exactly same as above except that the amount of lithium chloride was increased to 6.6 mmoles (equimolar to  $BH_3$ ) from 0.66 mmole. The separated reaction mixture in THF was analyzed by glpc using di-*n*-decylphthalate column, which showed 58.1% of cyclohexanol and 41.9% of 2-chlorocyclohexanol. 2-Chlorocyclohexanol was identified by glpc analysis with the authentic sample, prepared from cyclohexene<sup>7</sup>, and further confirmed by the mass spectrum:  $p(134)/p+2(136)$  is 3/1.

**ACKNOWLEDGEMENT**

We would like to thank Chong Kun Dang Corporation for the financial assistance.

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