

## 수소화붕소리튬, 보란 및 보란-염화리튬(1 : 0.1)에 의한 카르보닐화합물의 선택환원<sup>1</sup>

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## Selective Reduction of Carbonyl Compounds with Lithium Borohydride, Borane, and Borane-Lithium Chloride(1 : 0.1) in Tetrahydrofuran<sup>1</sup>

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요 약. 수소화붕소리튬, 보란 그리고 보란-염화리튬(1 : 0.1)의 카르보닐화합물 환원에 있어서의 선택성을 5쌍의 대표적인 카르보닐화합물 쌍(벤즈알데히드-아세트페논, 벤즈알데히드-2-헵탄온, 2-헵탄온-벤조페논, 아세트페논-벤조페논, 2-헵탄온-아세트페논)에 대해서 이들 수소화물의 제한된 양을 반응시켜 알아보았다. 이들 수소화물중 보란-염화리튬(1 : 0.1)이 제일 선택성이 좋았고, 수소화붕소 리튬과 보란도 2-헵탄온-아세트페논 쌍을 제외하고는 좋은 선택성을 보였다.

**ABSTRACT.** In order to find out the selective reducing characteristics of lithium borohydride, borane, and borane-lithium chloride (1 : 0.1) in the reduction of carbonyl compounds, five representative equimolar mixtures of carbonyl compounds were chosen; benzaldehyde-acetophenone, benzaldehyde-2-heptanone, 2-heptanone-benzophenone, acetophenone-benzophenone, and 2-heptanone-acetophenone, and reacted with limited amount of lithium borohydride, borane or borane-lithium chloride (1 : 0.1) in tetrahydrofuran (THF) at 0°. Borane-lithium chloride (1 : 0.1) showed the excellent selectivity, however, lithium borohydride and borane also exhibited good selectivity except for the 2-heptanone-acetophenone.

### INTRODUCTION

Since the introduction of sodium borohydride and lithium aluminum hydride in 1940's, selective reductions of organic functional groups have been successfully investigated with these hydrides and their modified derivatives including

boranes and alanes. Among them, one of the most challenging subject would be the selective reduction of one carbonyl group in the presence of another carbonyl group. Several hydrides<sup>2-9</sup> have been reported to have a good selectivity between different carbonyl compounds. For example, in the competitive reduction between

benzaldehyde and acetophenone, 100 : 8 selectivity with sodium triacetoxyborohydride<sup>3</sup>, 100 : 9 with sodium borohydride in the presence of thiol<sup>8</sup>, and 94 : 2 with 9-borabicyclo[3, 3, 1]-nonane (9-BBN)-pyridine<sup>9</sup> have been reported.

Recently we have studied<sup>10</sup> the effect of lithium chloride on the borane reduction, and observed the tremendous rate enhancement in borane reduction of acyl chloride, acid anhydride, and epoxides by the addition of a small amount of lithium chloride. And we found that 2-heptanone was reduced much more rapidly with borane-lithium chloride (1 : 0.1) than with borane itself, whereas benzophenone was reduced in nearly equal rate with the both reagents. This selective rate enhancement by the presence of lithium chloride should offer major advantage over borane reduction of carbonyl compounds.

However, in the course of our literature survey, we were amazed by the fact that the selectivity of borane or lithium borohydride in the reduction of carbonyl compounds has never been studied, even though it was almost two decades ago<sup>11, 12</sup> that a factor of 400 in rate constants of benzaldehyde and acetophenone was realized in the reduction with sodium borohydride in isopropyl alcohol. Therefore, we have decided to study in detail the selective reduction of carbonyl groups with lithium borohydride, borane, and borane-lithium chloride (1 : 0.1).

## RESULT AND DISCUSSION

### Procedure for the Competitive Experiment.

The procedure adopted in this competitive experiments was to add 20 ml THF solution of 10 mmoles of aldehyde (or ketone) and 10 mmoles of ketone (or another ketone) to the 20 ml THF solution of 2.5 mmoles of  $\text{LiBH}_4$  (10 mmoles in hydride) at 0°, that is, the ratio of

hydride to compound is 1 : 1. Thus, the reaction mixture was 0.0625 *M* in  $\text{LiBH}_4$  (*i. e.*, 0.25 *M* in hydride) and 0.25 *M* in each compound. At the end of appropriate reaction periods, 4 ml of aliquot was removed from the reaction mixture and hydrolyzed with water. To this hydrolyzed aliquot, an internal standard was added, worked up, and analyzed by glpc. When the hydride to compound ratio was changed, the concentration of compound was kept constant (0.25 *M*) and the concentration of hydride was changed. In the case of reduction with borane or borane-lithium chloride, 5.0 mmoles of borane (15 mmoles of hydride), instead of 2.5 mmoles of  $\text{LiBH}_4$ , was used, that is, the ratio of hydride to compound is 1.5 : 1.

**Benzaldehyde vs. Acetophenone.** On the competitive reaction between benzaldehyde and acetophenone, the results with  $\text{LiBH}_4$ ,  $\text{BH}_3$ , and  $\text{BH}_3\text{-LiCl}$  (1 : 0.1) in varying hydride concentration are listed in Table 1.

As shown in Table 1, lithium borohydride, with one equivalent of hydride to compound, showed an excellent selectivity with only a trace of attack on acetophenone within 15 minutes at 0°, whereas with one and half equivalent of hydride, the excess hydride easily attacked acetophenone. In the case of borane, with one and half equivalent of hydride, it attacked acetophenone to the extent of 8 % within 30 minutes. However, the  $\text{BH}_3\text{-LiCl}$  (1 : 0.1) system, with one and half equivalent of hydride, reduced only benzaldehyde cleanly to benzyl alcohol without attacking acetophenone within 30 minutes. With one equivalent of hydride, benzaldehyde was reduced very slowly showing only 60 % in 6 hours, presumably forming a less reactive dialkoxy borane.

In comparison with other metal hydrides,  $\text{BH}_3\text{-LiCl}$  (1 : 0.1) and  $\text{LiBH}_4$  are superior to all of the earlier reagents in its ability to dis-

Table 1. Competitive reduction between benzaldehyde and acetophenone with lithium borohydride, borane, and borane-lithium chloride (1:0.1) in tetrahydrofuran.

Reagent	H <sup>-</sup> /Cpd	Temp. (°C)	Time (hr)	Products (Mole %) <sup>a</sup>			
				Benzaldehyde	Benzyl alcohol	Acetophenone	1-Phenylethanol
LiBH <sub>4</sub>	1:1 <sup>b</sup>	0	0.25	2.0	97.5	>99.0	trace
			0.5	2.0	98.0	>98.5	trace
	1.5:1 <sup>c</sup>	0	0.25	0.0	100.0	53.5	46.0
			0.5	0.0	100.0	49.5	50.0
BH <sub>3</sub>	1.5:1	0	0.25	6.5	93.5	92.5	7.5
			0.5	6.0	94.0	92.0	8.0
			1.0	6.0	94.0	92.0	7.5
BH <sub>3</sub> -LiCl (1:0.1)	1:1	0	0.25	50.5	49.5		
			0.5	46.5	53.0		
			1.0	43.5	56.5	100.0	0.0
			3.0	41.0	58.5		
			6.0	39.5	60.5	100.0	0.0
	1.5:1	0	0.25	trace	100.0	100.0	0.0
			0.5	0.0	100.0	100.0	trace

<sup>a</sup> Determined by glpc from the response ratios using authentic samples and an internal standard.<sup>b,c</sup> Hydride to compound in the ratio of 1:1 and 1.5:1, respectively.

inguish effectively between benzaldehyde and acetophenone: *i.e.*, 100:8 with sodium triacetoxymethylborohydride<sup>3</sup>, 97:3 (74% conversion) with lithium di-*n*-butyl-9-BBN "ate" complex<sup>6</sup>, 100:9 with sodium borohydride in the presence of thiol<sup>8</sup>, and 94:2 with 9-BBN-pyridine<sup>9</sup>.

**Benzaldehyde vs. 2-Heptanone.** The selective reduction of benzaldehyde in the presence of 2-heptanone, which is more reactive than acetophenone, was also carried out, and the results are summarized in Table 2.

Table 2 shows that lithium borohydride and borane can not distinguish effectively between these two reactive carbonyl compounds, showing 11% and 6.5% attacks on 2-heptanone respectively, both in 30 minutes. On the other hand, BH<sub>3</sub>-LiCl (1:0.1), with one and a half equivalents of hydride, reduced benzaldehyde selectively within 30 minutes at 0° in the ratio of 100:2.5. However, when the reaction temperature was lowered to -20°, only benzaldehyde

was reduced cleanly without any sign of attack on 2-heptanone in one hour.

Several reducing agents have been reported for the selective reduction of an aliphatic or aromatic aldehyde in the presence of an aliphatic ketone, however none of those reagents can distinguish more effectively than the BH<sub>3</sub>-LiCl system: 92:5 between nonaldehyde and 2-undecanone with tetrabutylammonium cyanoborohydride<sup>2</sup>, 95:5 (57% conversion) between *n*-heptanal and 2-heptanone with lithium di-*n*-butyl-9-BBN "ate" complex<sup>6</sup>, 89:8 between hexanal and 2-heptanone with 9-BBN<sup>5</sup>, 94.5:2.5 between octanal and 3-pentanone with 9-BBN-pyridine<sup>9</sup>, and 93:1.5 between benzaldehyde and cyclohexanone with 9-BBN-pyridine<sup>9</sup>.

**2-Heptanone vs. Benzophenone.** On the selective experiment between two different ketones, 2-heptanone *vs.* benzophenone, the results are summarized in Table 3.

As shown in Table 3, 2-heptanone is so

Table 2. Competitive reduction between benzaldehyde and 2-heptanone with lithium borohydride, borane, and borane-lithium chloride (1 : 0.1) in tetrahydrofuran.

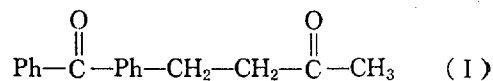
Reagent	H <sup>-</sup> /Cpd	Temp. (°C)	Time (hr)	Products (Mole%) <sup>a</sup>			
				Benzaldehyde	Benzyl alcohol	2-Heptanone	2-Heptanol
LiBH <sub>4</sub>	1 : 1	0	0.25	12.5	87.0	90.0	10.0
			0.5	11.5	88.5	88.5	11.0
			1.0	11.5	88.5	89.0	11.0
BH <sub>3</sub>	1 : 1	0	0.25	35.5	64.0	>99.5	trace
			0.5	34.5	65.0		
			1.0	34.0	66.0	>99.5	trace
			3.0	33.0	66.5		
			6.0	33.0	67.0	100.0	trace
	1.5 : 1	0	0.25	2.5	97.0	93.5	6.5
			0.5	2.5	97.5	93.5	6.5
			1.0	2.0	97.5	93.0	7.0
BH <sub>3</sub> -LiCl (1 : 0.1)	1 : 1	0	0.25	33.5	66.5		
			0.5	33.0	66.5		
			1.0	33.0	67.0	100.0	0.0
			3.0	31.0	68.5		
			6.0	31.0	68.5	100.0	0.0
	1.5 : 1	0	0.25	0.0	99.5	97.5	2.5
			0.5	0.0	100.0	97.5	2.5
			1.0	0.0	99.5	97.5	2.5
			0.25	3.5	96.5		
			0.5	1.0	98.5	100.0	0.0
			1.0	0.0	>99.5	100.0	0.0
		-20					

<sup>a</sup> See corresponding footnote in Table 1.

reactive than benzophenone that, lithium borohydride and borane showed excellent selectivities with only little attacks on benzophenone, however excess lithium borohydride easily attacked benzophenone. In the case of the BH<sub>3</sub>-LiCl (1 : 0.1) system, with one and a half or two equivalents of hydride, it reduced 2-heptanone cleanly with only a trace of attack on benzophenone, and the reduction rate of 2-heptanone with the BH<sub>3</sub>-LiCl (1 : 0.1) system was faster than that with borane itself.

Yamamoto *et al.* have reported<sup>6</sup> that lithium di-*n*-butyl-9-BBN "ate" complex reduced the carbonyl group selectively in the presence of diaryl group in a diketone (I) which contains

both dialkyl and diaryl carbonyl groups.



The selective reduction of the diketone and the competitive reduction of 2-heptanone *vs.* benzophenone might be quite different, however, our results suggest that the selective reduction of the diketone should not be difficult with these simpler reagents; LiBH<sub>4</sub>, BH<sub>3</sub> or BH<sub>3</sub>-LiCl (1 : 0.1).

**Acetophenone *vs.* Benzophenone.** The competitive experiment on the aryl-alkyl ketone and diaryl ketone, such as acetophenone *vs.* benzophenone, was also carried out, and the

Table 3. Competitive reduction between 2-heptanone and benzophenone with lithium borohydride, borane, and borane-lithium chloride (1:0.1) in tetrahydrofuran.

Reagent	H <sup>-</sup> /Cpd	Temp. (°C)	Time (hr)	Product (mole %) <sup>a</sup>			
				2-Heptanone	2-Heptanol	Benzophenone	Benzhydrol
LiBH <sub>4</sub>	1:1	0	0.25	17.0	83.0	100.0	0.0
			0.5	6.5	93.5	>99.5	trace
			1.0	trace	>99.5	98.5	1.5
	2:1	0	0.25	0.0	99.5	82.5	17.5
			0.5	0.0	100.0	74.5	25.5
BH <sub>3</sub>	1.5:1	0	0.25	37.5	62.0		
			0.5	29.0	71.0		
			1.0	22.0	78.0	100.0	0.0
			3.0	14.0	86.5	>99.5	trace
			6.0	5.0	95.0	99.0	1.0
			12.0	2.5	98.0	97.5	2.5
	2:1	0	0.25	19.0	80.5	100.0	0.0
			0.5	9.5	90.5	100.0	0.0
			1.0	5.0	94.5	98.0	2.0
			3.0	3.0	97.0	96.5	3.5
			6.0	trace	>99.5	95.5	4.5
BH <sub>3</sub> -LiCl (1:0.1)	1:1	0	0.25	38.5	61.0	100.0	0.0
			0.5	38.0	61.5		
			1.0	37.0	63.0		
			3.0	32.0	66.5		
			6.0	30.0	69.5	100.0	0.0
			12.0	29.5	70.5		
	1.5:1	0	24.0	29.0	71.0	100.0	0.0
			0.25	23.0	77.0		
			0.5	11.5	88.0		
			1.0	2.5	97.5	100.0	0.0
			3.0	trace	>99.5	>99.5	trace
			6.0	0.0	100.0	>99.5	trace
	2:1	0	0.25	10.0	90.0		
			0.5	3.5	96.5	100.0	0.0
			1.0	0.0	100.0	>99.5	trace

<sup>a</sup> See corresponding footnote in Table 1.

results are summarized in Table 4.

As shown in Table 4, lithium borohydride fails to distinguish between these two ketones even with one equivalent of hydride, showing very easy attack on benzophenone. In the case of borane, the reduction proceeded very slowly with one and a half equivalents of hydride, showing 72 % reduction in 12 hours at 0°.

With two equivalents of hydride, it showed a good selectivity in the ratio of 94.5:5 in 12 hours at 0°. On the other hand, the BH<sub>3</sub>-LiCl (1:0.1) system, with one and a half equivalents of hydride, showed an excellent selectivity in 12 hours at 0°. And even with two equivalents of hydride, the BH<sub>3</sub>-LiCl (1:0.1) system reduced only acetophenone cleanly to 1-phenyl-

Table 4. Competitive reduction acetophenone and benzyophenone with lithium borohydride, borane, and borane-lithium chloride (1 : 0.1) in tetrahydrofuran.

Reagent	H <sup>-</sup> /Cpd	Temp. (°C)	Time (hr)	Products (Mole%)*			
				Acetophenone	1-Phenylethanol	Benzophenone	Benzhydrol
LiBH <sub>4</sub>	1 : 1	0	0.25	55.5	44.0	86.5	13.5
			0.5	48.0	52.0	82.5	17.5
			1.0	41.5	58.0	78.0	22.0
			3.0	36.0	63.0	73.0	27.0
			6.0	32.5	67.0	68.0	32.0
BH <sub>3</sub>	1.5 : 1	0	0.25	56.0	44.0		
			0.5	45.5	54.0	100.0	0.0
			1.0	40.0	59.5	>99.5	trace
			3.0	37.0	63.0	>99.5	trace
			6.0	33.5	66.5	>99.5	trace
			12.0	28.0	72.0	99.5	0.5
	2 : 1	0	0.25	37.0	62.5		
			0.5	26.0	74.0	100.0	0.0
			1.0	21.0	79.0	>99.5	trace
			3.0	14.5	85.0	98.5	1.5
			6.0	10.5	89.5	96.5	3.5
			12.0	5.5	94.5	95.0	5.0
BH <sub>3</sub> -LiCl (1 : 0.1)	1.5 : 1	0	0.25	37.0	62.5		
			0.5	30.5	69.5		
			1.0	22.0	78.0		
			3.0	13.5	86.0		
			6.0	6.5	93.0	100.0	0.0
			12.0	trace	>99.5	>99.5	trace
	2 : 1	0	0.25	24.0	75.5		
			0.5	17.0	83.0		
			1.0	7.0	92.5	100.0	0.0
			3.0	2.5	97.5		
			6.0	0.0	100.0	100.0	0.0

\* See corresponding footnote in Table 1.

ethanol without any sign of attack on benzophenone within 6 hours.

**2-Heptanone vs. Acetophenone.** Last of all, the competitive reduction between 2-heptanone and acetophenone was also carried out, and the results are summarized in Table 5.

Lithium borohydride, as shown in Table 5, fails to distinguish between these two reactive ketones. And borane also can not distinguish effectively, showing 24 % attack on acetophenone

in 24 hours at 0°. In the case of the BH<sub>3</sub>-LiCl system, with one and a half equivalents of hydride, it reduced 2-heptanone selectively in the selectivity of 81 : 18.5 in 6 hours at 0°. The reduction was repeated at -20° in order to find out any improvement, however, only the reduction was slowed down, and the selectivity was not improved.

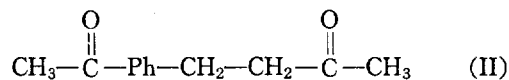
Yamamoto *et al.* have reported<sup>6</sup> that lithium di-*n*-butyl-9-BBN "ate" complex can distinguish

Table 5. Competitive reduction between 2-heptanone and acetophenone with lithium borohydride, borane, and borane-lithium chloride (1:0.1) in tetrahydrofuran.

Reagent	H <sup>-</sup> /Cpd	Temp. (°C)	Time (hr)	Products (Mole %) <sup>a</sup>			
				2-Heptanone	2-Heptanol	Acetophenone	1-Phenylethanol
LiBH <sub>4</sub>	1:1	0	0.25	45.0	54.5	69.0	30.5
			0.5	41.5	58.5	64.0	35.0
			1.0	37.5	62.5	61.5	38.0
	1.5:1	0	0.25	15.5	84.5	33.5	66.0
			0.5	15.5	84.5	33.5	66.0
BH <sub>3</sub>	1.5:1	0	0.25	58.0	42.0	89.0	11.0
			0.5	48.0	52.0	85.5	14.0
			1.0	41.0	58.5	82.0	17.5
			3.0	34.5	65.0	81.0	19.0
			6.0	31.0	69.0	80.0	20.0
			12.0	28.0	72.0	78.5	21.0
			24.0	24.0	75.5	76.0	24.0
BH <sub>3</sub> -LiCl (1:0.1)	1.5:1	0	0.25	33.5	66.5	83.0	17.0
			0.5	28.5	71.0	82.0	17.5
			1.0	26.5	73.5	82.0	17.5
			3.0	21.5	78.5	81.5	18.0
			6.0	18.5	81.0	81.5	18.5
	1.5:1	-20	0.25	51.5	48.5	91.0	9.0
			0.5	46.5	53.0	89.5	10.0
			1.0	40.5	59.5	89.0	11.0
			3.0	36.0	64.0	86.5	13.0
			6.0	33.5	66.0	86.0	14.0

<sup>a</sup> See corresponding footnote in Table 1.

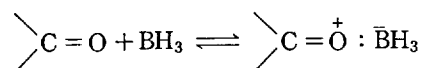
between dialkyl group and aryl-alkyl carbonyl group on the diketone (II), in the selectivity of 83:17. This is a similar selectivity realized with the BH<sub>3</sub>-LiCl (1:0.1) system.



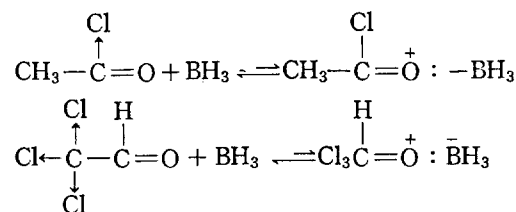
Thus we have shown that the borane-lithium chloride (1:0.1) system exhibited much better selectivity than either borane or lithium borohydride which also showed good selectivity in many cases.

Originally it was suggested that the initial stage of the reaction of borane with the carbonyl group involves an acid-base interaction with

borane adding to the oxygen atom<sup>14</sup>.



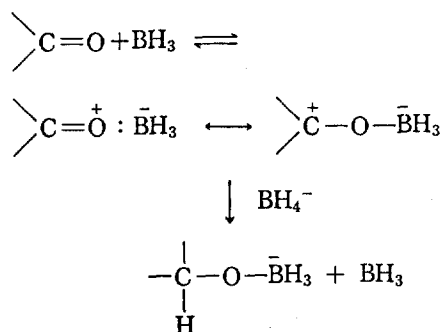
The inertness of acetyl chloride and of chloral toward borane was therefore attributed to the decreased basic properties of the oxygen atom of the carbonyl group<sup>15</sup>.



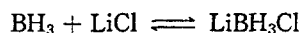
On the other hand, sodium borohydride, a

basic borohydride, reduce both acetyl chloride and chloral much more rapidly than simple aldehydes and ketones showing preferential attack on the more electron-deficient center<sup>15</sup>.

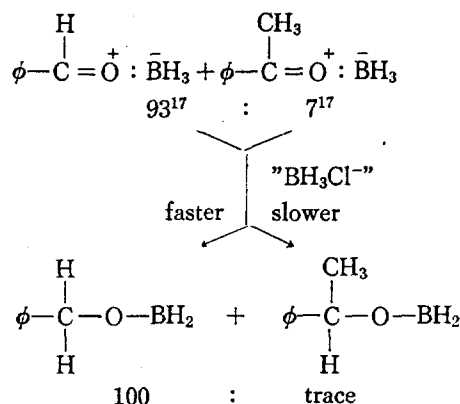
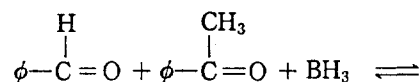
Later study showed that the rate of ketone reduction with borane in the presence of lithium borohydride is first order in ketone, borane, and borohydride.<sup>16</sup> These results suggest that the reduction proceeds initial coordination of borane to the carbonyl oxygen and the following hydride attack by the basic borohydride on the electron deficient carbon of the adduct.



Since the borane-lithium chloride (1 : 0.1) system is believed to contain lithium chloroborohydride, a basic borohydride, according to the following equilibrium,<sup>10</sup> the rate of reduction of carbonyl compound would be



expected to be first order in borane, chloroborohydride, and carbonyl compound. Therefore the much better selectivity exhibited by the borane-lithium chloride system may be explained as a combined result of two selectivities, namely the selectivity of borane coordination to the carbonyl oxygen and the selective hydride attack by chloroborohydride on the borane adduct. A possible scheme is illustrated with the competitive reduction of benzaldehyde and acetophenone with the borane-lithium chloride (1 : 0.1) system.



## CONCLUSION

We have demonstrated that the borane-lithium chloride (1 : 0.1) system exhibits remarkable selectivity between structurally different carbonyl compounds.

The particular ability to the selective reduction by the addition of a small amount of lithium chloride to the borane solution should be applied to organic synthesis, and should also give an information for the mechanism of borane reduction.

## EXPERIMENTAL

**General.** The substrates used for the reductions were all commercially available, and were purified just before use. Tetrahydrofuran was dried over excess lithium aluminum hydride and distilled under nitrogen. Thoroughly dried-out lithium chloride (reagent grade, J. T. Baker Chemical Co.) was used without further purification. Hypodermic syringes were used at all times to transfer materials. All reactions were carried out under the dry nitrogen.

Borane and lithium borohydride solution in THF were prepared and stored according to our previously published papers.<sup>10,13</sup>

Glc analyses were carried out on Varian Model 3,700 and F&M Model 720 gas chromatographs equipped with 6- or 9-ft  $\frac{1}{4}$  inch col-



umn (20% Carbowax 20 M on Chromosob W or 10 % Carbowax 20 M on Chromosob G).

**Competitive Reduction Procedure.** The following competitive reduction on acetophenone and benzophenone is representative for determining the relative reactivities between two carbonyl groups. Into an oven-dried hot flask, equipped with a rubber stopple and a stirring bar, was introduced 0.0280 g (0.66 mmole) of pre-dried lithium chloride. After connecting to a condenser, the flask was cooled to 0° under dry nitrogen. And then there were added 6.6 ml of 1.0 M BH<sub>3</sub> solution (6.6 mmoles in BH<sub>3</sub>, 20 mmoles in hydride) and 13.4 ml of THF with stirring. To this a pre-cooled mixture of acetophenone (1.2014g, 10 mmoles) and benzophenone (1.8221 g, 10 mmoles) in 20 ml THF was added. At the end of appropriate time intervals, each 4.0 ml aliquot of the reaction mixture was hydrolyzed with 3 ml of water, and 1 ml of 1.0 M 1-heptanol in THF was added as an internal standard. After separating the water layer with anhydrous K<sub>2</sub>CO<sub>3</sub>, the organic layer was dried over anhydrous MgSO<sub>4</sub> and subjected to glpc analysis using Varian Model 3,700 gas chromatograph. The product ratios in each time interval are summarized in Table 4.

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17. This ratio, 93:7, was taken from the product ratio of reduction of benzaldehyde and acetophenone with borane in Table 1.

