

수소화붕소아연에 의한 선택환원. 수소화붕아연의  
대표적 유기화합물과의 반응

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Selective Reduction with Zinc Borohydride. Reaction of Zinc  
Borohydride with Selected Organic Compounds Containing  
Representative Functional Groups

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요 약. 수소화붕소아연의 선택환원성을 조사하기 위하여 대표적 유기화합물 54종을 택하여 수소화붕소 아연과 일정한 조건 (THF 용액, 실온, 수소화이온의 농도 : 0.5 M, 유기화합물의 농도 : 0.125 M) 하에서 반응시켜 대략의 반응속도와 정량관계를 알아보았다.

**ABSTRACT.** The addition of one mole of zinc chloride to 2.33 moles of sodium borohydride in tetrahydrofuran at room temperature gave a clear chloride-free supernatant solution of zinc borohydride after stirring three days and standing at room temperature. The approximate rates and stoichiometry of the reaction of zinc borohydride with 54 selected organic compounds were determined in order to test the utility of the reagent as a selective reducing agent. Aldehydes and ketones were reduced rapidly, aromatic ketones being somewhat slowly, and the double bond of cinnamaldehyde was not attacked. Acyl halides were reduced rapidly within one hour, but acid anhydrides were reduced at a moderate rate. Carboxylic acids, both aliphatic and aromatic, were slowly reduced to alcoholic stage. Esters were inert to this reagent but a cyclic ester,  $\gamma$ -butyrolactone, was slowly attacked. Primary amides were reduced slowly with partial evolution of hydrogen, whereas tertiary amides underwent neither reduction nor hydrogen evolution. Epoxides and nitriles were all inert, as well as nitro, azo, and azoxy compounds. Cyclohexanone oxime and phenyl isocyanate were reduced slowly but pyridine was inert. Disulfide, sulfoxide, sulfone and sulfonic acids were stable to this reagent.

INTRODUCTION

The discoveries of sodium borohydride and

lithium aluminumhydride in 1940's have lead an efficient route in the reduction of functionalized molecule, and they are commonly used in

organic laboratory nowadays<sup>1</sup>. In spite of their efficiency and convenience the two hydride reagents stand at the extreme ends, lithium aluminumhydride being capable of reducing nearly all of the functional groups, and sodium borohydride being relatively weak reducing agent only for aldehydes, ketones and acid chloride. Thus controlling the reducing power of such reagents has been one of main interest to organic chemists for many years. In fact advances in such field have been realized by changing solvents, cation, and the substituents in the complex ion and introducing acidic reagents such as alane, borane and their derivatives<sup>1, 2</sup>. Accordingly we undertook a exploratory study concerning the reducing characteristics of zinc borohydride.

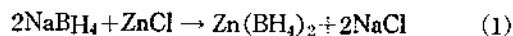
Zinc borohydride was first synthesized from zinc hydride and diborane<sup>3</sup>, and later Wiberg *et al.* reported another preparation from zinc chloride and lithium borohydride<sup>4</sup>. More recently Nöth *et al.* prepared pure form of this hydride by treating zinc methoxide with diborane in the presence of ethereal solvents<sup>5</sup>. But its first use in organic chemistry was carried out by Gensler *et al.* in the reduction of podophylotoxone<sup>6</sup>. Recently Corey group and Crabbe *et al.* also employed successfully zinc borohydride in the selective reduction of a 2-en-1-one, a prostaglandin intermediate, with an unspecified method of preparation of the reducing agent in their communications<sup>7</sup>.

Zinc Borohydride is soluble in more common ethereal solvent such as ether<sup>4-6</sup> and THF in which sodium borohydride is hardly soluble, whereas sodium borohydride can only be used either in alkaline stabilized hydroxylic solvent (water, metanol, and ethanol), or in diglyme [*bis*-(2-methoxyethyl) ether]. And another advantage of zinc borohydride is neutral and epimerization and/or isomerization, which would

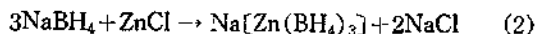
accompany with sodium borohydride reduction, do not occur<sup>6, 7</sup>.

## RESULTS and DISCUSSION

**The Reagent.** Gensler prepared zinc borohydride solution by stirring zinc chloride with 16.6% excess over stoichiometric amount of sodium borohydride in ether during appropriate time and letting the solution settle down. Clear chloride-free solution of zinc borohydride was obtained.



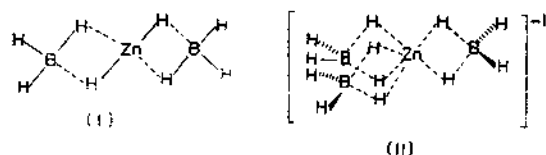
However Nöth *et al.* reported that the reaction does not exactly follow the equation (1) but part of the reaction proceeds as equation (2)<sup>5</sup>



In this study we followed the Gensler's procedure<sup>6</sup>, however we changed the solvent from ether to tetrahydrofuran because it was difficult to measure the residual hydride gasometrically due to the high vapor pressure of ether. In agreement with the reports mentioned above we could get chloride-free solution of the hydride and found the excess NaBH<sub>4</sub> (16.6%) was remaining in solution in spite of low solubility of sodium borohydride in THF (0.1g/100g of THF). Thus we obtained ca. 1.4 M (in H<sup>-</sup>) solution when 140mmoles of NaBH<sub>4</sub> and 60 mmoles of ZnCl<sub>2</sub> were mixed in 400ml of THF. Therefore the reagent in this study is believed to contain 2/3 of Zn(BH<sub>4</sub>)<sub>2</sub> and 1/3 of Na[Zn(BH<sub>4</sub>)<sub>3</sub>], being 0.1 M in Zn(BH<sub>4</sub>)<sub>2</sub> and 0.05M in Na[Zn(BH<sub>4</sub>)<sub>3</sub>], respectively.

The infrared spectrum of this hydride solution exhibited similar absorption characteristics to those that have been reported for Zn(BH<sub>4</sub>)<sub>2</sub> and Na[Zn(BH<sub>4</sub>)<sub>3</sub>] by previous workers<sup>5, 8</sup> (see experimental section) Hence it seems reasonable, at this moment, that the hydride solution

mainly consists of  $Zn(BH_4)_2$  (I) with minor contribution of  $Na [Zn(BH_4)_3]$  (II)



No further effort to use pure zinc borohydride was tried in this study because Gensler's solution was thought to be sufficiently useful as envisioned from our preliminary test and the results of previous workers<sup>6,7</sup>.

**Procedure for Approximate Rate and Stoichiometry Studies.** The procedure was to add 5 mmoles of an organic compound of interest in THF to 2.5 mmoles of zinc borohydride (calculated as  $Zn(BH_4)_2$ , 20 mmoles of  $H^-$ ) in THF to give 40 ml of the solution. Thus the concentrations of hydride and the compound are 0.5 M and 0.125 M, respectively, being the ratio of hydride to compound 4:1. If the compound would be expected to consume more than 3 equiv of hydride, the concentration of the compound was maintained constant but the hydride concentration was increased to 0.75 M, giving a hydride to compound ratio of 6:1. An aliquots was removed at appropriate intervals and analyzed gasometrically for the residual hydride. (In cases of active hydrogen compounds hydrolysis of the residual hydride was carried out after all of the expected volume of hydrogen evolved). The numerical values appeared in tables are expressed in terms of the number of hydride utilized for the reaction per mole of compound.

**Alcohols, Phenols, Amines and Thiols.** The all active hydrogen compound examined liberated hydrogen quantitatively except *n*-hexylamine which liberated only 0.4 mole of hydrogen per mole of compound even after 96 hr. It is

interesting to note that the rate of hydrogen evolution for the compounds increases in the order of the acidity of these active hydrogens<sup>9</sup>: amine < *tert*-alcohol < secondary alcohol < primary alcohol < phenol and thiol

In the reactions of alcohols and thiols, no additional hydride consumption was observed in our reaction condition, suggesting that hydrogenolysis of C—O or C—S bond does not occur with zinc borohydride. However it has been reported that benzylic alcohols capable of carbonium ion formation are prone to deoxygenated with sodium borohydride in the presence of Lewis acid such as boron trifluoride<sup>10</sup>. The results are summarized in *Table 1*.

**Aldehydes and Ketones.** All the aldehydes and ketones studied consumed one mole of hydride for reduction to the corresponding alcohols. As with other hydrides<sup>14,2</sup> aromatic ketones were reduced much slowly. Again there was little evidence of hydrogenolysis even for the case of benzophenone. It is noteworthy that double bond in cinnamaldehyde was not reduced with this hydride, which is a marked contrast to sodium borohydride<sup>11</sup>. Encouraged by this result we treated cinnamaldehyde with this reagent to afford nearly quantitative yield of cinnamyl alcohol with a trace of hydrocinnamyl alcohol as revealed by glpc analysis<sup>16a</sup> (*Table 2*).

**Quinones.** As was pointed out earlier<sup>12</sup> the reduction of a quinone to hydroquinone is expected to consume 2 equiv. of hydride, one for reduction and one for hydrogen evolution. On the other hand reduction to the 1,4-dihydro-2,5-cyclohexadiene stage should consume 2 equiv of hydride without hydrogen evolution. Therefore it is believed that the reduction of *p*-benzoquinone with this hydride should go largely to hydroquinone with a minor contamination by 1,4-dihydroxy-2,5-cyclohexadiene.

On the other hand, anthraquinone is believed

Table 1. Reaction of zinc borohydride with representative "active hydrogen" compounds in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1-Hexanol	0.5	0.00		
	1.0	0.08		
	3.0	0.50		
	6.0	0.90		
	24.0	1.01	1.02	0.01
Benzyl alcohol	0.5	0.06		
	1.0	0.14		
	3.0	0.30		
	6.0	0.44		
	24.0	1.01	1.04	0.03
3-Hexanol	0.5	0.23		
	1.0	0.25		
	3.0	0.33		
	6.0	0.42		
	24.0	0.71		
	48.0	0.90		
	72.0	1.00	1.00	0.00
96.0	1.00	1.00	0.00	
3-Ethyl-3-pentanol	0.5	0.02		
	1.0	0.04		
	3.0	0.07		
	6.0	0.11		
	24.0	0.35		
	48.0	0.69		
	96.0	1.03	1.03	0.00
Phenol	0.5	0.99		
	1.0	1.05	1.03	0.00
	3.0	1.05	1.05	0.00
n-Hexylamine	0.5	0.04		
	1.0	0.06		
	3.0	0.09		
	6.0	0.11		
	24.0	0.21		
	48.0	0.37		
96.0	0.40	0.40	0.00	
1-Hexanethiol	0.5	1.00	1.02	0.02
	1.0	1.00	1.02	0.02
	3.0	1.00	1.02	0.02
Benzenethiol	0.5	1.00	1.02	0.02
	1.0	1.00	1.02	0.02
	3.0	1.00	1.02	0.02

a. 5 mmoles of compounds was added to 2.5mmoles of zinc borohydride (20 mmoles of hydride) in 40 ml of solution, 0.125M in compound and 0.5M in hydride.

b. Millimoles/millimole of compound.

Table 2. Reaction of zinc borohydride with representative aldehydes and ketones in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Caproaldehyde	0.5	0.05	1.01	0.96
	1.0	0.05	1.05	1.00
	3.0	0.05	1.05	1.00
	6.0	0.05	1.05	1.00
Benzaldehyde	0.5	0.05	1.05	1.00
	1.0	0.05	1.09	1.04
	3.0	0.05	1.05	1.00
	6.0	0.05	1.05	1.00
2-Heptanone	0.5	0.05	0.81	0.76
	1.0	0.05	1.05	1.00
	3.0	0.05	1.05	1.00
	6.0	0.05	1.05	1.00
Norcamphor	0.5	0.04	0.95	0.91
	1.0	0.04	0.99	0.95
	3.0	0.04	1.10	1.06
	24.0	0.04	1.10	1.06
Acetophenone	0.5	0.05	0.28	0.23
	3.0	0.05	0.84	0.79
	6.0	0.05	1.00	0.95
	24.0	0.05	1.08	1.03
	48.0	0.05	1.08	1.03
Benzonphenone	1.0	0.00	0.33	0.33
	2.0	0.00	0.49	0.49
	6.0	0.00	0.65	0.65
	12.0	0.00	0.81	0.81
	24.0	0.00	1.01	1.01
Cinnamaldehyde	48.0	0.00	1.02	1.02
	0.5	0.00	1.00	1.00
	1.0	0.00	1.04	1.04
	3.0	0.00	1.04	1.04
	3.0	0.00	1.04	1.04

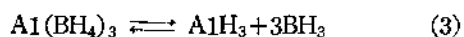
<sup>a, b</sup> See corresponding footnotes in Table 1.

to be reduced to 9,10-dihydroxyanthracene.<sup>12</sup> The results are summarized in Table 3.

#### Carboxylic Acids and Their Derivatives.

Carboxylic acid evolved 1 equivalent of hydrogen instantaneously and reduced slowly to the alcoholic stage, consuming 2 hydrides in 96 hr. This kind of reduction with zinc borohydride seems remarkable, since carboxylic acids are hardly attacked by alkali metal borohydride even in forcing condition<sup>1</sup>. The slow reduction of

carboxylic acids by aluminum borohydride has been explained by slow dissociation of the hydride into alane and borane<sup>12</sup>, and the presence



of borane, which can reduce carboxylic acids with extreme ease,<sup>13</sup> was verified by the fact that olefins can be hydroborated by the hydride<sup>12,14</sup>. However there was no sign of such dissociation with zinc borohydride, since no hy-

Table 3. Reaction of zinc borohydride with representative quinones in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, ho	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
p-Benzoquinone <sup>c</sup>	1.0	0.89	1.80	0.91
	3.0	0.89	2.01	1.12
	6.0	0.89	2.02	1.13
Anthraquinone <sup>d</sup>	0.5 <sup>e</sup>	0.13	0.38	0.25
	1.0 <sup>f</sup>	0.21	0.53	0.32
	3.0 <sup>f</sup>	0.59	1.36	0.77
	6.0 <sup>h</sup>	0.77	1.67	0.90
	24.0 <sup>h</sup>	0.74	2.02	1.08
	48.0 <sup>h</sup>	0.99	2.07	1.08

<sup>a, b</sup> See corresponding footnotes in Table 1.

<sup>c</sup> solution became turbid (Gelatinous white precipitate).

<sup>d</sup> compounds were added as solids, reverse addition. The color of the precipitate changes from light yellow to intense yellow, <sup>e</sup> yellow green<sup>f</sup>, green<sup>g</sup>, finally to dark green<sup>h</sup>.

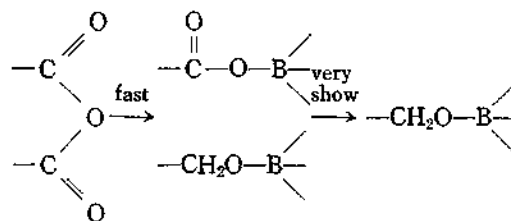
<sup>h</sup> Hydrolysis of the reaction mixture resulted in homogeneous purple solution.

dride uptake could be seen in the reaction with isopropenyl acetate (*vide infra*). But acidic proton of the carboxylic acid generates borane. Thus in a reaction of a equimolar mixture of benzoic acid and 1-hexene with zinc borohydride for 48 hr, followed by the established oxidation, a 84% yield of 1-hexanol has been realized, as revealed by glpc. Consequently the borane generated by the acidic proton should be responsible for the slow reduction. Although it has been reported that diborane deteriorates slowly at room temperature<sup>2c</sup> careful glpc analysis of the reaction mixture of caproic acid and this hydride showed 60.3% yield of 1-hexanol after 96 hr. Now it is believed that the hydride uptake shown in the Table 4 constitutes mainly the hydride used for reduction with a minor contribution of hydride loss during the reaction.

Acid chlorides were reduced readily, even more rapidly than some of ketones. On the other hand, acid anhydrides consumed two hydrides in exceedingly faster rates and thereafter reductions were proceeded very slowly, showing 3.62 (acetic anhydride), 3.96 (succinic anhydride), 3.46 (phthalic anhydride) equiv. of hy-

dride uptake in 48 hr out of 4 equivalents of hydride expected for complete reduction to diol.

This suggests the following scheme.



This scheme is supported by our experimental observation that white ppt was observed immediately on reaction with succinic anhydride, but none with acetic anhydride, because the cyclic anhydride is expected to form a polymeric intermediate according to the above scheme.

**Esters and Lactones.** All the esters examined were inert to this reagent, On the other hand  $\gamma$ -butyrolactone was reduced slowly in  $\sim 48$  hr., whereas phthalide showed no sign of reduction. This interness to the ester function seems to be valuable, since ester functions are prone to be damaged, either hydrolyzed or transesterified in the reaction with sodium borohydride in the hydroxylic solvent.<sup>15</sup> Indeed we were able to

Table 4. Reaction of zinc borohydride with representative carboxylic acids and acyl derivatives in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr.	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Caproic acid	0.5	1.07	1.28	0.21
	3.0	1.07		
	6.0	1.07	1.44	0.37
	24.0	1.07	1.93	0.86
	48.0	1.07	2.14	1.07
	72.0	1.19	2.89	1.70
	96.0	1.19	3.27	2.08
Benzoic acid	0.5	1.02	1.08	0.06
	24.0	1.03	1.76	0.73
	48.0	1.03	2.14	1.11
	72.0	1.03	2.57	1.54
	96.0	1.03	2.96	1.93
Acetic anhydride <sup>c</sup>	1.0	0.12	2.26	2.14
	3.0	0.12	2.52	2.40
	6.0	0.12	2.91	2.79
	24.0	0.12	3.67	3.55
	48.0	0.12	3.74	3.62
	72.0	0.12	3.81	3.84
Succinic anhydride <sup>c,d</sup>	1.0	0.11	2.78	2.67
	3.0	0.12	3.38	3.26
	6.0	0.12	3.43	3.31
	24.0	0.12	3.52	3.40
	48.0	0.15	4.11	3.96
	72.0	0.15	4.18	4.03
Phthalic anhydride <sup>c,e</sup>	1.0	0.05	2.34	2.29
	3.0	0.05	2.56	2.51
	6.0	0.05	2.84	2.79
	24.0	0.05	3.37	3.32
	48.0	0.05	3.51	3.46
	72.0	0.05	3.67	3.62
Caproyl chloride	96.0	0.05	3.93	3.83
	0.5	0.11	2.08	1.98
	1.0	0.11	2.16	2.05
	3.0	0.11	2.16	2.05
Benzoyl chloride	1.0	0.04	1.96	1.92
	3.0	0.04	2.05	2.01
	6.0	0.04	2.05	2.01
	24.0	0.04	2.05	2.01

<sup>a,b</sup> See corresponding footnotes in Table 1.

<sup>c</sup> Hydride/Compd=6/1

<sup>d</sup> Gelatinous white precipitate

<sup>e</sup> Slight turbid solution

Table 5. Reaction of zinc borohydride with representative esters and lactones in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr.	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Ethyl caproate	0.5	0.05	0.05	0.00
	1.0	0.05	0.05	0.00
	6.0	0.05	0.05	0.00
	24.0	0.07	0.07	0.00
Ethyl benzoate	0.5	0.00	0.00	0.00
	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00
Phenyl acetate	24.0	0.00	0.06	0.06
	0.5	0.08	0.08	0.00
	3.0	0.08	0.08	0.00
	6.0	0.08	0.08	0.00
$\gamma$ -Butyrolactone	0.5	0.06	0.12	0.06
	3.0	0.06	0.12	0.06
	6.0	0.06	0.53	0.47
	24.0	0.06	0.78	0.72
Phthalide	48.0	0.11	2.04	1.93
	0.5	0.03	0.03	0.00
	1.0	0.03	0.03	0.00
	3.0	0.03	0.03	0.00
Isopropenyl acetate	6.0	0.03	0.03	0.00
	24.0	0.03	0.03	0.00
	0.5	0.05	0.14	0.09
	1.0	0.05	0.14	0.09
	3.0	0.05	0.14	0.09
	6.0	0.05	0.14	0.09

<sup>a, b</sup> See corresponding footnotes in Table 1.

Table 6. Reaction of zinc borohydride with representative epoxides in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr.	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1,2-Butylene oxide	1.0	0.04	0.04	0.00
	3.0	0.04	0.04	0.00
	24.0	0.04	0.04	0.00
Styrene oxide	1.0	0.02	0.02	0.00
	6.0	0.02	0.02	0.00
	12.0	0.02	0.02	0.00
	24.0	0.02	0.02	0.00
Cyclohexene oxide	0.5	0.04	0.04	0.00
	1.0	0.04	0.04	0.00
	3.0	0.04	0.04	0.00
	24.0	0.04	0.04	0.00

<sup>a, b</sup> See corresponding footnotes in Table 1.



reduce ethyl 6-ketoheptanoate to the corresponding hydroxy ester with this hydride in 83.0% yield (isolated)<sup>16b</sup>.

The results are summarized in *Table 5*.

**Epoxydes.** All the three epoxydes tested were inert to this reagent. Sodium borohydride has been known to reduce epoxydes slowly<sup>17,18</sup>. Borane is also capable to reduce epoxydes through the epoxyde-borane adduct<sup>19</sup>. Therefore it seems to us that zinc borohydride is much weaker than sodium borohydride (in hydroxylic solvents) as a hydride donor and has much less ability to form adduct as with borane as expected. Thus zinc borohydride has a potentiality for the selective reduction of epoxy ketones to epoxy alcohol. We proved this possibility by reducing isophorone oxide to yield *trans*-isophorol oxide in 89.5% of isolated yield<sup>16b</sup>. The results are summarized in *Table 6*.

**Amides and Nitrile** Primary amides evolved hydrogen steadily, but such gas evolution stopped when nearly 0.5 mole of hydrogen evolution was realized. The reduction proceeded to the extent of 65% after 48 hr for caproamide but on aromatic amide, benzamide, showed only 45% for the same period of reaction. However, tertiary amides, which have been reported to be more reactive toward the hydride reagents than primary ones<sup>2</sup>, were not affected at all. This difference with other hydrides can not fully understood at this moment. Possibly borane generated via the reaction of the borohydride with acidic hydrogen would be responsible for it. Finally, nitriles did neither evolve hydrogen, nor undergo reduction. This suggests a selective reduction of carbonyl group in the presence of nitrile functional group. The results are summarized in *Table 7*.

**Nitro Compounds and Their Derivatives.** Aliphatic and aromatic nitro compounds, azobenzene, and azoxybenzene proved quite inert to zinc borohydride in any reasonable time at stan-

dard condition. This is similar to sodium borohydride<sup>1</sup>. The results are summarized in *Table 8*.

**Other Nitrogen Compounds.** Cyclohexanone oxime liberated 1 mole of hydrogen rapidly and reduced very slowly, showing only 1.75 hydrides uptake in 48 hr out of of 2 hydrides expected for the reduction to amine stage. The acidic hydrogen reacts first, followed by slow addition of hydride to the carbon-nitrogen double bond. This is a interesting contrast to the fact that the hydrogen evolution competes with the reduction of the oxime with boranes<sup>2</sup>. Phenyl isocyanate consumed two hydrides in 24hr, presumably leading to *N*-hydroxymethylaniline as with borane derivatives and alane<sup>12</sup>. Pyridine was stable to this hydride but pyridine *N*-oxide took up nearly 2 equiv of hydrides in 24 hr, presumably being attacked on the aromatic ring. The results are summarized in *Table 9*.

**Sulfur Compounds.** All the sulfur compounds examined did not exhibit any appreciable reduction. Both the sulfonic acids studied liberated the theoretical amount of hydrogen instantly but were not reduced. These results are similar to those realized with lithium tri-*t*-butoxyaluminumhydride<sup>20</sup>. Cyclohexyl tosylate appeared to undergo very slow uptake of hydride. The results are summarized in *Table 10*.

## CONCLUSION

The reducing properties of zinc borohydride have now been characterized. In the reduction of polyfunctional molecule, one can proceed with reasonable confidence that certain groups will not be attacked by zinc borohydride in the course of reducing the functional groups. We believe this systematic study will serve not only for the selective reduction but also for the mechanistic studies of these reductions.

## EXPERIMENTAL

**Materials.** The standard list of organic com-

Table 7. Reaction of zinc borohydride with representative amides and nitriles in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr.	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Caproamide	0.5	0.11	0.38	0.27
	1.0	0.21	0.60	0.39
	3.0	0.45	0.98	0.53
	6.0	0.51	1.21	0.70
	24.0	0.54	1.73	1.19
	48.0	0.54	1.89	1.35
	72.0	0.54	2.26	1.73
Benzamide	0.5	0.34	0.45	0.11
	1.0	0.40	0.67	0.27
	3.0	0.43	0.98	0.55
	6.0	0.44	1.06	0.62
	24.0	0.44	1.13	0.69
	48.0	0.44	1.36	0.92
	72.0	0.44	2.04	1.60
<i>N, N</i> -Dimethyl caproamide	0.5	0.05	0.05	0.00
	1.0	0.05	0.05	0.00
	3.0	0.05	0.05	0.00
	6.0	0.05	0.05	0.00
	24.0	0.05	0.05	0.00
<i>N, N</i> -Dimethyl benzamide	0.5	0.06	0.07	0.01
	1.0	0.06	0.07	0.01
	3.0	0.06	0.07	0.01
	6.0	0.06	0.07	0.01
Capronitrile	1.0	0.03	0.03	0.00
	6.0	0.03	0.03	0.00
	24.0	0.03	0.03	0.00
	48.0	0.03	0.03	0.00
Benzonitrile	0.5	0.05	0.05	0.00
	1.0	0.05	0.05	0.00
	3.0	0.05	0.05	0.00
	24.0	0.05	0.05	0.00

<sup>a, b</sup> See corresponding footnotes in Table 1.

pounds examined is essentially the same as those previously utilized<sup>2, 12, 17</sup>. All of the compounds used were of high purity, purified by distillation, recrystallization or sublimation. The sodium borohydride was 95% pure and used without further purification. Tetrahydrofuran was distilled from lithium aluminumhydride. All experiments were carried out in a dry nitrogen atmosphere. Hypodermic syringes were used to

transfer the solution.

**Preparation of Zinc Borohydride Solution<sup>21</sup>.** Sodium borohydride (5.58 g 95%, 0.14mole, 16.6% excess) of sodium borohydride and 300 ml of tetrahydrofuran were introduced in a 500 ml oven-dried flask, fitted with rubber cap on the side arm, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler. To this slurry solution 100ml of THF solution of

zinc chloride (8.1774 g, 0.06 mole) was added slowly with stirring by means of a hypodermic syringe. The solution was stirred for 3 days, and then allowed to stand at room temperature

Table 8. Reaction of zinc borohydride with nitro compounds and their derivatives in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1-Nitropropane	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
	48.0	0.00	0.00	0.00
Nitrobenzene	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
	48.0	0.00	0.00	0.00
Azobenzene	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
	48.0	0.00	0.00	0.00
Azoxybenzene	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
	48.0	0.00	0.00	0.00

<sup>a, b</sup> See corresponding footnotes in Table 1.

Table 9. Reaction of zinc borohydride with nitrogen compounds in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride use for reduction <sup>b</sup>
Cyclohexanone oxime	0.5	0.78	1.60	0.82
	1.0	0.93	1.92	0.99
	3.0	0.93	2.14	1.21
	6.0	0.93	2.37	1.44
	24.0	0.93	2.60	1.67
	48.0	0.93	2.68	1.75
	72.0	0.93	2.83	1.90
Phenyl isocyanate	0.5	0.01	0.96	0.95
	1.0	0.01	0.96	0.95
	3.0	0.01	1.45	1.44
	24.0	0.01	2.00	1.99
Pyridine	0.5	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.00	0.00

Pyridine <i>N</i> -oxide <sup>c</sup>	0.5	0.23	0.23	0.00
	1.0	0.23	0.28	0.05
	3.0	0.23	0.56	0.33
	6.0	0.23	0.72	0.49
	24.0	0.23	1.98	1.75

<sup>a, b</sup> See corresponding footnotes in Table 1.

<sup>c</sup> Solution became turbid.

Table 10. Reaction of zinc borohydride with representative sulfur derivatives in tetrahydrofuran at room temperature.

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Di- <i>n</i> -butyl disulfide	0.5	0.03	0.04	0.01
	1.0	0.03	0.04	0.01
	3.0	0.03	0.04	0.01
	6.0	0.03	0.04	0.01
Methyl <i>p</i> -tolyl sulfide	0.5	0.00	0.00	0.00
	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
Dimethyl sulfoxide	0.5	0.03	0.03	0.00
	1.0	0.03	0.03	0.00
	3.0	0.03	0.03	0.00
	6.0	0.03	0.03	0.00
Diphenyl sulfone	0.5	0.00	0.00	0.00
	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
Methanesulfonic <sup>c</sup> acid	0.5	1.08	1.10	0.02
	1.0	1.08	1.08	0.10
	3.0	1.08	1.15	0.07
	6.0	1.08	1.10	0.02
<i>p</i> -Toluenesulfonic acid monohydrate	0.5	3.13	3.13	0.00
	1.0	3.13	1.15	0.02
	3.0	3.13	3.16	0.03
Cyclohexyl tosylate	0.5	0.06	0.12	0.06
	1.0	0.06	0.16	0.10
	6.0	0.12	0.23	0.11
	24.0	0.13	0.24	0.11

<sup>a, b</sup> See corresponding footnotes in Table 1.

<sup>c</sup> Solution became turbid.

to permit the sodium chloride precipitate to settle down. Clear chloride-free supernatant solution was visualized after 2~3 hr, and an aliquot was removed by a syringe and analyzed for hydride gasometrically.

The slight excess (16.6%) of sodium boro-

hydride greatly facilitates the quantitative precipitation of chloride as sodium chloride. The hydride concentration of the solution obtained was 1.37*M*, which is larger by 14% than calculated value, 1.2*M* based on zinc chloride added. This means that excess amount of sodium

borohydride was dissolved in this hydride solution as  $\text{Na}[\text{Zn}(\text{BH}_4)_3]$  whereas sodium borohydride alone hardly dissolve in tetrahydrofuran.

The ir spectrum of this solution exhibited bands at 2430 (*v. s.*), 2380(*s*), 2340(*m*), 2290 (*w*), 2220(*w*), 2190(*w*), 2090(*s*), 2430(*v. s.*), 1930(*w*), 1105(*s*) [lit.<sup>5,8</sup> for  $\text{Zn}(\text{BH}_4)_2$  in THF. 2440, 2390, 2220, 2090, 1120, for  $\text{Na}[\text{Zn}(\text{BH}_4)_3]$  in ether, 2425, 2370, 2330, 2310, 2195, 2090, 2020.]

The solution was stored under positive nitrogen pressure without filtering out the precipitate and did not show any measurable change of the concentration over 30 days(see discussion).

**Procedure.** The zinc borohydride solution [15.3 ml of 0.16 M(40 mmoles hydride)] and 4.7 ml of tetrahydrofuran were placed into a pre-dried 100 ml flask fitted with rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connector to a gas buret. To this solution 10 ml of 0.5 M of a compound of interest was injected slowly with stirring. Now the reaction mixture is 0.5 M in hydride and 0.125 M in the compound of interest. If the compound would be expected to consume more than 3 hydrides with this reagent, the ratio of hydride to compound was increased as shown in tables. At different time interval as indicated in tables, the hydrogen gas collected on the gas buret, was measured and a 4.0 ml aliquot of the reaction mixture was removed and injected into a 4 N  $\text{H}_2\text{SO}_4$ -THF mixture to hydrolyze residual hydride. And then the difference of hydrogen evolution between a blank (in which 10 ml of tetrahydrofuran was substituted for the 10 ml of the solution of the compound) and the reaction mixture was calculated in terms of the numbers of mmole of hydride used per mmole of the compound.

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