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Reaction of Lithium Gallium Hydride with Selected Organic Compounds Containing Representative Functional Groups

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Received June 1, 1994

The approximate rates and stoichiometry of the reaction of excess lithium gallium hydride with selected organic compounds containing representative functional groups were examined under the standard conditions (diethyl ether, 0 ℃) in order to compare its reducing characteristics with lithium aluminum hydride and lithium borohydride previously reported, and enlarge the scope of its applicability as a reducing agent. Alcohols, phenol, and amines evolve hydrogen rapidly and quantitatively. However lithium gallium hydride reacts with only one active hydrogen of primary amine. Aldehydes and ketones of diverse structure are rapidly reduced to the corresponding alcohols. Conjugated aldehyde and ketone such as cinnamaldehyde and methyl vinyl ketone are rapidly reduced to the corresponding saturated alcohols. *p*-Benzoquinone is mainly reduces to hydroquinone. Caproic acid and benzoic acid liberate hydrogen rapidly and quantitatively, but reduction proceeds slowly. The acid chlorides and esters tested are all rapidly reduced to the corresponding alcohols. Alkyl halides and epoxides are reduced rapidly with an uptake of 1 equiv of hydride. Styrene oxide is reduced to give 1-phenylethanol quantitatively. Primary amides are reduced slowly. Benzonitrile consumes 2.0 equiv of hydride rapidly, whereas capronitrile is reduced slowly. Nitro compounds consumed 2.9 equiv of hydride, of which 1.9 equiv is for reduction, whereas azobenzene, and azoxybenzene are inert toward this reagent. Cyclohexanone oxime is reduced consuming 2.0 equiv of hydride for reduction at a moderate rate. Pyridine is inert toward this reagent. Disulfides and sulfoxides are reduced slowly, whereas sulfide, sulfone, and sulfonate are inert under these reaction conditions. Sulfonic acid evolves 1 equiv of hydrogen instantly, but reduction is not proceeded.

Introduction

The discovery of lithium aluminum hydride[1] and lithium borohydride[2] brought about a revolutionary change in the procedures utilized for the reduction of functional groups in organic chemistry. Of these two reagents, lithium borohydride[3] is relatively mild reducing agent which is practically specific for the carbonyl group in aldehydes, ketones, and esters, whereas lithium aluminum hydride[4] is an exceedingly powerful reagent which attacks almost all reducible groups.

Therefore, lithium di- and trialkoxyaluminum hydride,[5] lithium trialkylaluminum hydride,[6] lithium trichloroaluminum hydride,[7] lithium bis- and tris(dialkylamino)aluminum hydride,[8] lithium mono- and trialkylborohydride,[9] and lithium cyanoborohydride[10] were studied in order to control the reducing abilities of lithium aluminum hydride and lithium borohydride. But, the previous studies were restricted to aluminohydride and borohydride species.

In 1973, Raman and infrared data of various metal hydride salts with monovalent cation were reported by Shirk and Shriver.[11] They showed that the stretching frequencies of metal hydrides were $AlH_4^- = 1757$ cm^{-1}, $GaH_4^- = 1807$ cm^{-1}, and $BH_4^- = 2294$ cm^{-1}, and the calculated associated force constants of metal-hydrogen were $AlH_4^- = 1.84$ mdyn/Å, $GaH_4^- = 1.94$ mdyn/Å and $BH_4^- = 3.07$ mdyn/Å. From these results, we thought that if the bonded alkali metal is same, the reducing power of metal hydride would be $AlH_4^- > GaH_4^- > BH_4^-$. Indeed it was reported that lithium aluminum hydride had much stronger reducing power than that of lithium borohydride. But the reducing abilities of gallium hydride species were not studied. So we decided to carry out the systematic study for the reduction of organic compounds containing representative functional groups with lithium gallium hydride.

Results and Discussion

Lithium gallium hydride was prepared by the reaction of gallium chloride with lithium hydride in diethyl ether as reported by Shrik and Shriver.[12] The general procedure for reduction was to add 1 mmol of the organic compound to

Table 1. Reaction of Lithium Gallium Hydride with Representative Alcohols, Phenol, Thiols, and Amines in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Hexanol	0.5	1.01	1.01	0.00
	1.0	1.01	1.01	0.00
Benzyl alcohol	0.5	1.00	0.98	0.02
	1.0	1.00	0.98	0.02
3-Hexanol	0.5	1.04	1.02	0.02
	1.0	1.04	1.02	0.02
3-Ethyl-3-pentanol	0.5	1.03	1.04	0.01
	1.0	1.03	1.03	0.00
Phenol	0.5	1.05	1.05	0.00
	1.0	1.05	1.05	0.00
Hexanethiol[d]	0.5	1.03	1.02	0.01
	1.0	1.02	1.01	0.00
Benzenethiol[d]	0.5	1.07	1.06	0.01
	1.0	1.07	1.06	0.01
Hexylamine	0.5	0.60	0.61	0.01
	1.0	0.75	0.76	0.01
	3.0	0.85	0.85	0.00
	6.0	0.95	0.95	0.00
	12.0	1.06	1.06	0.00
Diethylamine	0.5	0.62	0.63	0.01
	1.0	0.79	0.80	0.01
	3.0	0.89	0.91	0.02
	6.0	0.98	0.98	0.00
	12.0	0.98	0.98	0.00

[a] 1 mmol compound to 1 mmol of $LiGaH_4$ (4 mmol of hydride) in 8 mL of solution (0.125 M in compound and 0.5 M in hydride). [b] Mmol per mmol of compound. [c] Hydrogen evolved from blank minus the hydrogen evolved on hydrolysis of the reaction mixture after the indicated reaction period. [d] White gel-like precipitate formed immediately.

Table 2. Reaction of Lithium Gallium Hydride with Representative Aldehydes and Ketones in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Caproaldehyde	0.5	0.01	0.99	0.98
	1.0	0.01	1.02	1.01
Benzaldehyde	0.5	0.02	1.01	0.99
	1.0	0.02	1.02	1.00
2-Heptanone	0.5	0.00	0.77	0.77
	1.0	0.00	1.01	1.01
	3.0	0.00	1.02	1.02
Norcamphor	0.5	0.04	0.64	0.60
	1.0	0.04	0.80	0.76
	3.0	0.04	1.02	0.98
	6.0	0.04	1.02	0.98
Acetophenone	0.5	0.07	1.06	0.99
	1.0	0.07	1.09	1.02
Benzophenone	0.5	0.02	1.03	1.01
	1.0	0.02	1.03	1.01
Cinnamaldehyde	1.0	0.00	2.01	2.01
	3.0	0.00	2.03	2.03
Methyl vinyl ketone	0.5	0.04	1.70	1.66
	1.0	0.04	1.89	1.85
	3.0	0.04	2.06	2.02
	6.0	0.04	2.06	2.02
Cyclohexanone	0.5	0.00	1.01	1.01
	1.0	0.00	1.01	1.01

[a-c] See corresponding footnotes in table 1.

1 mmol of lithium gallium hydride in diethyl ether to give 8 mL of solution at 0 ℃. The hydrogen evolved on adding the compound to the reagent was noted. After the desired reaction time, the solution was hydrolyzed and the hydrogen evolved was noted. The hydride utilized for reduction by the compound was calculated from hydrogen evolution. In this way, it was possible to arrive at a value for the number of hydrides utilized by the compound to evolve hydrogen and the number of hydrides utilized for the reduction.

In some cases the hydride-to-compound ratio of 4 : 1 was inadequate to achieve complete reduction. In such cases the hydride concentration was maintained constant, but the concentration of compound was reduced to give a higher ratio.

Alcohols, Phenol, Thiols, and Amines. All of the alcohols, phenol, and thiols examined liberated hydrogen instantly and quantitatively. Whereas, hexylamine required 12 h for the liberation of 1 equiv of hydrogen, and no more hydrogen evolution was realized for 24 h. The result indicates lithium gallium hydride reacts with only one active hydrogen in primary amine. Lithium aluminum hydride[4] evolves 2 equiv of hydrogen rapidly in 30 min and lithium borohydride[3] reacts very slowly. And the reaction of secondary and tertiary alcohols with lithium borohydride[3] fails to liberate the theoretical quantity of hydrogen.

In the reaction of alcohols and thiols, no additional hydride consumption was observed in our reaction condition, indicating that hydrogenolysis of C-O or C-S bond did not occur with this reagent under the standardized condition. The results are summarized in Table 1.

Aldehydes and Ketones. All of the saturated aldehydes and ketones examined took up 1 equiv of hydride rapidly for reduction without evolution of any significant quantity of hydrogen. Consequently, in these cases the reduction goes cleanly to the alcohol stage. However, cinnamaldehyde and methyl vinyl ketone consumed two hydrides rapidly for reduction in 30 min, indicating a rapid involvement of the double bond.

In the case of lithium aluminum hydride,[4] α,β-unsaturated carbonyl compound takes up 2 equiv of hydride for reduction, but lithium borohydride[3] is reported to take up 1 equiv of hydride for reduction. The results are summarized in Table 2.

Quinones. *p*-Benzoquinone consumed 2.64 equiv of hydride per mol of compound, of which 2.0 equiv was utilized for the reduction and remaining 0.6 equiv for hydrogen evolution. This corresponds to the formation of 40% of 1,4-dihydroxycyclohexadiene and 60% of hydroquinone. Anthraqui-

Table 3. Reaction of Lithium Gallium Hydride with Representative Quinones in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
p-Benzoquinone[d]	0.5	0.57	2.61	2.04
	1.0	0.60	2.64	2.04
Anthraquinone[d]	0.5	0.22	1.92	1.70
	1.0	0.32	2.03	1.71
	3.0	0.32	2.03	1.71

[a-c] See corresponding footnotes in table 1. [d] The compound was added as solid, reverse addition (solution of reagent added to suspension of the quinone), immediate dark green precipitate.

none also consumed *ca.* 2 equiv of hydride rapidly and 0.3 equiv for hydrogen evolution. These data indicate that the reaction proceeds to give 70% of 9,10-dihydroxy-9,10-anthracenediol and 30% of 9,10-dihydroxyanthracene. The results are summarized in Table 3.

Carboxylic Acids and Derivatives. Caproic acid and benzoic acid evolved instantly 1 equiv of hydrogen with formation of white precipitate, but reduction proceeded slowly. In the case of AlH_3[13] and DIBAH,[14] no precipitate is formed during the course of reaction with carboxylic acid and the reductions are much faster than those with lithium gallium hydride. Whereas, lithium aluminum hydride[4] shows the somewhat slow reduction with a slight precipitate. The slow reaction with lithium gallium hydride seems due to the precipitation of carboxylic acid salts formed by the reaction of active hydrogen of carboxylic acid and such heterogeneous condition inhibits further reduction. However, the hydrazine analysis of the reaction mixture indicated the formation of aldehyde. It suggested that this reagent showed a possibility of partial reduction of carboxylic acids to aldehydes. Indeed we could apply this reagent successfully for the synthesis of aldehyde from the corresponding carboxylic acid. The yield of partial reduction of benzoic acid to the corresponding aldehydes based on GLC analysis was 67% in 6 h. Carboxylic acids react with lithium aluminum hydride[4] very rapidly, but react lithium borohydride[3] was sluggishly. Acid chlorides, such as caproyl chloride and benzoyl chloride, consumed 2 equiv of hydride rapidly to give the corresponding alcohols. Lithium aluminum hydride4 and lithium borohydride[3] also reduce them very rapidly. Acetic, succinic, phthalic anhydrides reacted with lithium gallium hydride at a slow rate, and a similar trend was observed with lithium aluminum hydride[4] and lithium borohydride.[3] The results are summarized in Table 4.

Table 4. Reaction of Lithium Gallium Hydride with Representative Carboxylic Acids and Acyl Derivatives in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Caproic acid[d]	0.5	1.01	1.19	0.18
	1.0	1.01	1.36	0.35
	3.0	1.01	1.41	0.40
	6.0	1.01	1.69	0.68
	12.0	1.01	1.89	0.88
Benzoic acid[d]	0.5	0.99	1.19	0.20
	1.0	0.99	1.34	0.35
	3.0	0.99	1.75	0.76
	6.0	0.99	1.92	0.93
	12.0	0.99	2.24	1.25
Caproyl chloride	0.5	0.00	1.96	1.96
	1.0	0.00	1.96	1.96
Benzoyl chloride	0.5	0.01	2.01	2.00
	1.0	0.01	2.06	2.05
Acetic anhydride[e]	0.5	0.03	0.90	0.87
	1.0	0.03	1.20	1.17
	3.0	0.03	1.54	1.51
	6.0	0.03	1.83	1.80
Succinic anhydride[e]	0.5	0.00	0.91	0.91
	1.0	0.00	1.16	1.16
	3.0	0.00	1.18	1.18
	6.0	0.00	1.22	1.22
	12.0	0.00	1.52	1.52
	24.0	0.00	1.87	1.87
Phthalic anhydride[e]	0.5	0.00	1.79	1.79
	1.0	0.00	2.04	2.04
	3.0	0.00	2.56	2.56
	6.0	0.00	2.68	2.68
	12.0	0.00	2.92	2.92
	24.0	0.00	2.96	2.99

[a-c] See corresponding footnotes in table 1. [d] White gel precipitate formed immediately. [e] Hydride to compound ratio is 6 : 1.

Esters and Lactones. Most of the esters and lactones examined reacted somewhat rapidly, consuming 2 equiv of hydride per mol of compound. However, isopropenyl acetate utilized 3 equiv of hydride slowly. This result indicates an involvement of the double bond. Lithium aluminum hydride[4] with isopropenyl acetate also utilized 3 equiv of hydride for reduction, and it was reduced to isopropyl alcohol and ethanol. Lithium aluminum hydride[4] reacts rapidly with all of the esters and lactones. Whereas, lithium borohydride[3] reacts slowly with esters and lactones. The results are summarized in Table 5.

Alkyl Halides. All of the alkyl halides examined consumed readily 1 equiv of hydride per mol of compound for reduction and were reduced to the corresponding hydrocarbons. Aliphatic halides were rapidly reduced. Aromatic halides appeared to be more readily reduced than aliphatic onces. Alkyl halides are very difficult to reduce by the the most metal hydrides, except for only a few metal hydrides such as lithium aluminum hydride[4] and lithium triethylborohydride.[9c] The results are summarized in Table 6.

Epoxides. Styrene oxide and cyclohexene oxide were reduced rapidly within 3 h. In the case of styrene oxide, the reduction product was only 1-phenylethanol. That is, the reduction of styrene oxide with this reagent gave more hindered alcohols exclusively, resulting from the less hindered site hydride attacks. Epoxides are also readily with lithium aluminum hydride[4] and very slowly with lithium borohydride.[3] The results are summarized in Table 7.

Table 5. Reaction of Lithium Gallium Hydride with Representative Esters and Lactones in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Ethyl caproate	0.5	0.00	1.80	1.80
	1.0	0.00	1.90	1.90
	3.0	0.00	2.01	2.01
	6.0	0.00	2.01	2.01
Ethyl benzoate	0.5	0.06	1.75	1.69
	1.0	0.06	1.79	1.73
	3.0	0.06	2.01	1.95
	6.0	0.06	2.01	1.95
γ-Butyrolactone	0.5	0.00	0.91	0.91
	1.0	0.00	1.48	1.48
	3.0	0.00	1.60	1.60
	6.0	0.00	1.94	1.94
	12.0	0.00	2.01	2.01
	24.0	0.00	2.01	2.01
γ-Valerolactone	0.5	0.01	1.89	1.88
	1.0	0.01	1.98	1.97
	3.0	0.01	1.98	1.97
Phthalide	0.5	0.00	1.48	1.48
	1.0	0.00	1.51	1.51
	3.0	0.00	1.57	1.57
	6.0	0.00	1.70	1.70
	12.0	0.00	1.97	1.97
	24.0	0.00	1.98	1.98
Phenyl acetate	0.5	0.07	2.07	2.00
	1.0	0.07	2.07	2.00
Isopropenyl acetate	0.5	0.02	2.45	2.43
	1.0	0.02	2.47	2.45
	3.0	0.02	2.69	2.67
	6.0	0.02	2.88	2.86
	12.0	0.02	2.95	2.93

[a-c] See corresponding footnotes in table 1.

Table 6. Reaction of Lithium Gallium Hydride with Representative Alkyl Halides in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Butyl chloride	0.5	0.00	0.47	0.47
	1.0	0.00	0.71	0.71
	3.0	0.00	0.93	0.93
	6.0	0.00	0.94	0.94
Butyl bromide	0.5	0.00	0.69	0.69
	1.0	0.00	0.96	0.96
	3.0	0.00	1.06	1.06
	6.0	0.00	1.06	1.06
Butyl iodide	0.5	0.03	0.86	0.83
	1.0	0.03	1.00	0.97
	3.0	0.03	1.01	0.98
Benzyl chloride	0.5	0.16	0.97	0.81
	1.0	0.16	1.27	1.11
	3.0	0.16	1.27	1.11

[a-c] See corresponding footnotes in table 1.

Table 7. Reaction of Lithium Gallium Hydride with Representative Epoxides in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Styrene oxide	0.5	0.00	0.48	0.48
	1.0	0.00	0.71	0.71
	3.0	0.00	0.94	0.94
	6.0	0.00	0.94	0.94
1,2-Butylene oxide	0.5	0.07	1.10	1.03
	1.0	0.07	1.10	1.03
Cyclohexene oxide	0.5	0.02	0.65	0.63
	1.0	0.02	0.87	0.85
	3.0	0.02	0.99	0.97
	6.0	0.02	0.99	0.97

[a-c] See corresponding footnote in table 1.

Table 8. Reaction of Lithium Gallium Hydride with Representative Amides and Nitriles in Diethyl Ether at 0 ℃

Compound[a]	Time, h	Hydrogen evolved[b,c]	Hydride used[b,c]	Hydride used for reduction[b,c]
Caproamide	0.5	0.89	2.72	1.83
	1.0	1.08	2.99	1.91
	3.0	1.11	3.02	1.91
Benzamide	0.5	0.29	0.53	0.24
	1.0	0.50	0.61	0.11
	3.0	1.03	1.23	0.20
	6.0	1.03	1.59	0.56
N,N-Dimethylcaproamide	0.5	0.01	0.02	0.01
	1.0	0.01	0.02	0.01
	3.0	0.01	0.02	0.01
N,N-Dimethyl-Benzamide	0.5	0.03	0.53	0.50
	1.0	0.03	0.91	0.88
	3.0	0.03	1.47	1.44
	6.0	0.03	1.99	1.96
Capronitrile	0.5	0.15	0.53	0.38
	1.0	0.15	0.74	0.56
	3.0	0.15	1.20	1.05
	6.0	0.15	1.52	1.37
	12.0	0.15	1.76	1.61
Benzonitrile[d]	0.5	0.18	2.43	2.25
	1.0	0.18	2.21	2.03
	3.0	0.18	2.21	2.03

[a-c] See corresponding footnotes in table 1. [d] Color changed to yellow.

Amides and Nitriles. Caproamide evolved 1 equiv of hydrogen rapidly, and reduction also proceeded rapidly. However benzamide consumed only 0.56 equiv of hydride for reduction in 6 h. For the tertiary amides, *N,N*-dimethylcaproamide was inert to this reagent, but *N,N*-dimethylbenzamide was reduced moderately in 6 h consuming 2 equiv of hydride. Capronitrile was reduced moderately. On the other hand, benzonitrile was reduced to the amine stage rapidly. Nitriles react with lithium aluminum hydride[4] in 3 h,

Table 9. Reaction of Lithium Gallium Hydride with Representative Nitro Compounds and Their Derivatives in Diethyl Ether at 0 ℃

Compound^a	Time, h	Hydrogen evolved^{b,c}	Hydride used^{b,c}	Hydride used for reduction^{b,c}
1-Nitropropane^d	0.5	1.04	2.87	1.83
	1.0	1.04	2.87	1.83
Nitrobenzene^d	0.5	1.00	2.78	1.78
	1.0	1.00	2.90	1.90
	3.0	1.00	2.90	1.90
Azobenzene^e	0.5	0.00	0.01	0.01
	6.0	0.00	0.01	0.01
Azoxybenzene^f	0.5	0.00	0.03	0.03
	6.0	0.00	0.03	0.03

$^{a-c}$See corresponding footnotes in table 1. ^{d}Color changed to brown. ^{e}Color changed to dark brown. ^{f}Color changed to dark green.

Table 10. Reaction of Lithium Gallium Hydride with Representative Nitrogen Compounds in Diethyl Ether at 0 ℃

Compound^a	Time, h	Hydrogen evolved^{b,c}	Hydride used^{b,c}	Hydride used for reduction^{b,c}
Cyclohexanone oxime	0.5	0.46	2.02	1.56
	1.0	0.47	2.02	1.55
	3.0	0.47	2.17	1.76
	6.0	0.47	2.51	2.04
	12.0	0.47	2.51	2.04
Pyridine	0.5	0.01	0.02	0.01
	3.0	0.01	0.02	0.01
Pyridine N-oxide	0.5	0.00	0.00	0.00
	1.0	0.00	0.05	0.05
	3.0	0.00	0.11	0.11
Phenyl isocyanate	0.5	0.00	1.76	1.76
	1.0	0.00	1.93	1.95
	3.0	0.00	1.95	1.95

$^{a-c}$See corresponding footnotes in table 1.

Table 11. Reaction of Lithium Gallium Hydride with Representative Sulfur Derivatives in Diethyl Ether at 0 ℃

Compound^a	Time, h	Hydrogen evolved^{b,c}	Hydride used^{b,c}	Hydride used for reduction^{b,c}
Dibutyl disulfide^d	0.5	0.86	1.82	0.96
	1.0	1.03	2.05	1.02
	3.0	1.03	2.05	1.02
Diphenyl disulfide^d	0.5	0.88	1.78	0.90
	1.0	0.99	1.98	0.99
	3.0	0.99	1.98	0.99
Diphenyl sulfone	0.5	0.01	0.02	0.01
	3.0	0.01	0.04	0.03
Methanesulfonic acid	0.5	1.04	1.05	0.01
	1.0	1.04	1.05	0.01
p-Toluenesulfonic acid monohydrate	0.5	2.98	3.00	0.02
	1.0	2.98	3.00	0.02
Dimethyl sulfoxide	0.5	0.02	1.00	0.98
	1.0	0.02	1.06	1.04
	3.0	0.02	1.06	1.04

$^{a-c}$See corresponding footnote in table 1. ^{d}White gel precipitate formed immediately.

but do not react with lithium borohydride.[3] The results are summarized in Table 8.

Nitro Compounds and Their Derivatives. 1-Nitropropane and nitrobenzene consumed 2.9 equiv of hydride rapidly, of which 1.9 equiv was for reduction, and no further reduction was apparent. However, in the reaction of lithium aluminum hydride,[4] 1-nitropropane and nitrobenzene consume 6 and 5 equiv of hydride, respectively with a half of hydride being utilized for reduction and the other half for the hydrogen evolution. However, lithium borohydride[3] reacts very slowly with these compounds. Azobenzene and azoxybenzene were inert to gallium hydride, and also inert to lithium borohydride.[3] The results are summarized in Table 9.

Other Nitrogen Compounds. Cyclohexanone oxime consumed readily 2 equiv of hydride for reduction in 6 h at 0 ℃, suggesting the ready reduction to cyclohexylamine. It is interesting the strong hydride, lithium aluminum hydride showed 90% reduction in 24 h at 0 ℃.[4] Whereas lithium aluminum hydride4 reacts slowly consuming 4 equiv of hydride, 2 for reduction and 2 for hydrogen evolution. And lithium borohydride[3] reacts very slowly. Phenyl isocyanate was rapidly reduced to hydroxymethylaniline stage in 1 h. It reacts rapidly with lithium aluminum hydride[4] and slowly with lithium borohydride.[3] Pyridine and pyridine *N*-oxide were essentially inert to this reagent. Lithium aluminum hydride[4] and lithium borohydride[3] react very slowly with these compounds. The results are summarized in Table 10.

Sulfur Compounds. Disulfides were reduced rapidly to the corresponding thiols, utilizing 2 equiv of hydride, one for reduction and the other for hydrogen evolution. Lithium aluminum hydride[4] shows the similar results. However, they are essentially inert to lithium borohydride. Diphenyl sulfone was essentially inert to lithium gallium hydride. Similarly, the compounds are also inert to lithium borohydride.[3] However, lithium aluminum hydride[4] reacts very slowly. Sulfonic acids liberated hydrogen quantitatively, but no reduction was observed at this reaction conditions. Lithium aluminum hydride[4] and lithium borohydride[3] also show the same results. The results are summarized in Table 11.

Conclusion

The present study has turned up significant differences in reducing characteristics of lithium metal hydrides. The reducing power of gallium hydride lies somewhere between aluminohydride and borohydride. From these results, lithium gallium hydride appeared to be useful reagent for (1) partial reduction of carboxylic acids to aldehydes, (2) the reduction of alkyl halides to hydrocarbons, and (3) the selective reduction of various organic functional groups.

Experimental

Materials. Most of the organic compounds utilized in this study were commercial product of the highest purity. They were further purified by distillation or recrystallization when necessary. All glassware was dried thoroughly in a drying oven and cooled under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solutions.

General Procedure for Determination of Rates and Stoichiometry. A 50-mL flask was oven-dried and cooled in a dry stream of nitrogen. The flask was equipped with reflux condenser connected to a gas buret. The flask was immersed in an ice bath, and 5.14 mL of diethyl ether was introduced into the reaction flask, followed by 1.86 mL of a 0.54 M solution of $LiGaH_4$ in diethyl ether. Finally, 1 mL (1.0 mmol) of a 1.0 M solution of compound was injected into the reaction flask. Now the reaction mixture was 0.125 M in $LiGaH_4$ (0.5 M in hydride) and 0.125 M in compound. At appropriate time intervals, 1 mL of aliquot was withdrown and quenched in a 2 N H_2SO_4-THF, Et_2O, H_2O (1 : 1 : 2) hydrolyzing mixture. The hydrogen evolved was measured volumetrically. For the reaction of compounds with active hydrogen, the hydrogen evolved was collected in a gas buret and the volume of hydrogen was measured.

The reduction of styrene oxide is described as a representative procedure. A 50 mL flask was oven-dried and cooled in a dry stream of nitrogen, The flask was equipped with a sidearm and a reflux condenser connected to a gas buret. The flask was immersed in an ice bath, and 4.14 mL of diethyl ether was introduced in to the reaction flask, followed by 1.86 mL (1 mmol) of a 0.54 M solution of $LiGaH_4$ in diethyl ether. Finally, 2 mL (1 mmol) of a 0.5 M solution of styrene oxide was injected into the reaction flask. No hydrogen evolution was observed. After 30 min at 0 ℃, hydrolysis of a 1 mL aliquot of the reaction mixture indicated 0.44 mmol of residual hydride, which means that 0.48 mmol of hydride per mmol of styrene oxide had been used. After 1 h, 0.71 mmol of hydride per mmol of the compound had been consumed. After 3 h, 0.94 mmol of hydride per mmol of the compound had been consumed and after 6 h, analysis showed no difference in hydride consumption. These results are summarized in Table 7.

Product Identification

The following reduction of styrene oxide and analysis of the reaction product is representative. Utilizing the general procedure described above, 1 mmol of lithium gallium hydride and 1 mmol of styrene oxide in 8 mL of diethyl ether solution containing naphthalene as an internal standard were permitted to react for 6 h at 0 ℃. The reaction mixture was then treated with 10 mL of 1 N sulfuric acid. The organic layer was separated, and analysis GLC on a 10% Carbowax 20 M column, 7 ft×0.125 in., showed 100% 1-phenylethanol.

Acknowledgment. We are grateful to the Foundation of Hanyang University for financial support and to professor N. M. Yoon for his endless help.

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