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Reducing Characteristics of Potassium Triethylborohydride

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The approximate rates, stoichiometries and products of the reaction of potassium triethylborohydride (KEt_3BH) with selected organic compounds containing representative functional groups under the standard condition (0°C, THF) were examined in order to explore the reducing characteristics of this reagent as a selective reducing agent. Primary alcohols, phenols and thiols evolve hydrogen rapidly whereas secondary and tertiary alcohols evolve very slowly. n-Hexylamine is inert to this reagent. Aldehydes and ketones are reduced rapidly and quantitatively to the corresponding alcohols. Reduction of noncamphor gives 3% *exo*-and 97% *endo*-norboneol. Anthraquinone is cleanly reduced to 9,10-dihydro-9,10-dihydroxyanthracene stage. Carboxylic acids liberate hydrogen rapidly and quantitatively but further reduction does not occur. Anhydrides utilize 2 equiv of hydride to give an equimolar mixture of acid and alcohol. Acid chlorides, esters and lactones are rapidly and quantitatively reduced to the corresponding alcohols. Epoxides are reduced at moderate rates with Markovnikov ring opening to give the more substituted alcohols. Primary amides liberate 1 equiv of hydrogen rapidly. Further reduction of caproamide is slow whereas benzamide is not reduced. Tertiary amides are reduced slowly. Benzonitrile utilizes 2 equiv of hydride in 3 h to go to the amine stage whereas capronitrile takes only 1 equiv. The reaction of nitro compounds undergo rapidly whereas azobenzene and azoxybenzene are reduced slowly. Cyclohexanone oxime rapidly evolves hydrogen without reduction. Phenyl isocyanate utilizes 1 equiv of hydride to proceed to formanilide stage. Pyridine N-oxide and pyridine is reduced rapidly. Disulfides are rapidly reduced to the thiol stage whereas sulfoxide, sulfonic acid are practically inert to this reagent. Sulfones and cyclohexyl tosylate are slowly reduced. Octyl bromide is reduced rapidly but octyl chloride and cyclohexyl bromide are reduced slowly.

Introduction

The discovery of the unique characteristics of lithium trialkylborohydrides in 1972 in the course of a study of the carbonylation of organoboranes aroused considerable interest in the exploration of their utility for organic functional group reductions.[1] As a result, a number of trialkylborohydrides have been developed in recent years as highly attractive reducing agents to achieve chemo-, regio- and stereoselective transformation in organic synthesis.[2] Lithium triethyl-

borohydride ($LiEt_3BH$), unlike the parent compound lithium borohydride ($LiBH_4$), has been proved to be an exceptionally powerful reducing agent.[3] In fact, $LiEt_3BH$ is found to be more powerful than lithium aluminum hydride ($LiAlH_4$) in S_N2 reaction.[4]

Recently the effect of cation on the reactivity of saline borohydrides reduction of carboxylic esters was studied and the order of reactivity was found to be $LiBH_4 > Ca(BH_4)_2 > NaBH_4$. This suggests that potassium triethylborohydride (KEt_3BH) would be a considerably milder reducing agent than $LiEt_3BH$. In order to characterize the reducing properties of KEt_3BH and hopefully find out new selectivities in reduction, we have decided to undertake a systematic study of rates and stoichiometries of the reaction of KEt_3BH with representative organic compounds.

Results and Discussion

Preparation of Standard Solution of KEt_3BH[5] Solutions of KEt_3BH in THF were conveniently prepared by stirring triethylborane with an excess of finely divided potassium hydride (about 0.5 equiv excess) in THF at room temperature for 24 h. The excess potassium hydride settled down and the concentration was determined by hydrolyzing a known aliquot of the solution with THF-water-glycerine (1:1:1) at room temperature and measuring the hydrogen evolved. The yields are quantitative. Such solutions of KEt_3BH in THF are quite stable under a dry nitrogen atmosphere with no change observed in months at room temperature.

$$KH + Et_3B \xrightarrow{THF} \underset{100\%}{KEt_3BH} \quad (1)$$

Procedure for Rate and Stoichiometry Studies The general procedure adopted was to add 5 mmol of the organic compound under examination to 20 mmol of KEt_3BH in appropriate amount of THF to give 20 mL of solution. This made the reaction mixture 1.0 M in hydride and 0.25 M in compound. Any hydrogen evolved was noted. Aliquots were then removed at appropriate intervals of time and analyzed for residual hydride by injecting them into a hydrolyzing mixture of water-glycerine-THF (1:1:1). Simultaneously, a blank was run, in which THF was added, in place of the THF solution of the compound, all other conditions being the same. When hydrogen evolution was continuous, individual experiments were conducted to measure the hydrogen evolution and to determine the residual hydride at different time intervals. In this way, it was possible to estimate both the approximate rate and the stoichiometry of the reaction.

Product Analysis by GLC After having established the approximate rate and stoichiometry of the reaction, we desired to establish the nature of the products wherever it appeared of interest, offering a possibility for selective reduction. Accordingly, seperate reactions on a 2 mmol scale were carried out by using either a stoichiometric amount of the reagent or an excess amount, depending upon the nature of the reaction. The products were identified by GLC comparison with authentic samples, and the yields were determined by GLC utilizing internal standards.

Rate and Stoichiometry Alcohols, Phenols, Amines and Thiols. Primary alcohols liberated hydrogen rapidly, whereas secondary and tertiary alcohol literated very sluggishly, evolving about 20% of hydrogen in 24 h. The rate of hydrogen evolution for alcohols decreases in the order; primary $\gg$ secondary $\geq$ tertiary. This is in agreement with the usual interpretation that the acidity of the hydroxylic hydrogen in these alcohols decreases in this order.[6] In the case of $LiEt_3BH$[3], all of the alcohols examined liberated hydrogen rapidly and quantitatively with exception of 3-ethyl-3-pentanol. Phenol, 2,6-di-*tert*-butylphenol and both of the thiols evolved hydrogen rapidly and quantitatively. n-Hexylamine proved to be inert to this reagent under the experimental condition. The results are summarized in Table 1.

Table 1. Reaction of Potassium Triethylborohydride with Representative Alcohols, Phenols, Amines and Thiols in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
1-hexanol	5 min	1.04	1.04	0.00
	30 min	1.04	1.04	0.00
benzyl alcohol	5 min	1.01	1.01	0.00
	1 h	1.01	1.01	0.00
3-hexanol	30 min	0.03	0.03	0.00
	3 h	0.10	0.10	0.00
	6 h	0.14	0.14	0.00
	24 h	0.23	0.23	0.00
3-ethyl-	30 min	0.03	0.03	0.00
3-pentanol	1 h	0.03	0.03	0.00
	3 h	0.05	0.05	0.00
	6 h	0.08	0.08	0.00
	24 h	0.16	0.16	0.00
phenol	5 min	1.01	1.01	0.00
	1 h	1.06	1.06	0.00
2,6-di-*tert*-	5 min	1.04	1.04	0.00
butylphenol[c]	30 min	1.04	1.04	0.00
	1 h	1.04	1.04	0.00
n-hexylamine	5 min	0.00	0.00	0.00
	1 h	0.00	0.00	0.00
benzenethiol[c]	5 min	1.07	1.07	0.00
	1 h	1.07	1.07	0.00
1-hexanethiol[c]	5 min	1.04	1.04	0.00
	1 h	1.04	1.04	0.00

[a] Five mmol of compound was added to 20 mmol of KEt_3BH in 20 mL of solution (0.25 M in compound and 1.0 M in KEt_3BH).[3] [b] In mmol/mmol of compound. [c] White precipitate within 5 min.

Aldehydes and Ketones. The aldehydes and ketones examined utilized rapidly 1 equiv of hydride to proceed to the alcohol stage. Cinnamaldehyde utilized 1 equiv of hydride rapidly and showed no more uptake of hydride under the experimental condition, indicating rapid reduction to cinnamyl alcohol stage. The results are summarized in Table 2-A. The stereochemistry of cyclic and bicyclic ketones such as 2-methylcyclohexanone, 4-*tert*-butylcyclohexanone, norcamphor and camphor was also examined. Thus 2-methylcyclohexanone was quantitatively reduced to give a mixture of 79.2% *cis*-and 20.8% *trans*-2-methylcyclohexanol. On the other hand, 4-*tert*-butylcyclohexanone gave a mixture of 20% *cis*-and 80% *trans*-4 *tert*-butylcyclohexanol. Norcamphor and

Table 2-A. Reaction of Potassium Triethylborohydride with Representative Aldehydes and Ketones in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
caproaldehyde	5 min	0.04	1.06	1.02
	1 h	0.04	1.07	1.03
benzaldehyde	5 min	0.09	1.11	1.02
	1 h	0.09	1.13	1.04
2-heptanone	5 min	0.00	1.09	1.09
	1 h	0.00	1.09	1.09
norcamphor	5 min	0.00	1.02	1.02
	1 h	0.01	1.01	1.00
acetophenone	5 min	0.00	1.00	1.00
	1 h	0.00	1.03	1.03
benzophenone	5 min	0.00	1.04	1.04
	1 h	0.00	1.07	1.07
cinnamaldehyde	5 min	0.02	1.01	0.99
	30 min	0.02	1.01	0.99
	1 h	0.02	1.05	1.03
	3 h	0.02	1.11	1.09
	6 h	0.02	1.08	1.06
	24 h	0.02	1.11	1.09

[a,b] See the corresponding footnotes in Table 1.

Table 2-B. Stereoselective Reduction of Cyclic and Bicyclic Ketones with KEt_3BH[a,b]

ketone	temp °C	less stable isomer	ratio of less stable isomer, % KEt_3BH[3]	ratio of less stable isomer, % $LiEt_3BH$[3]
2-methyl-cyclohexanone	0	*cis*	79.2	75
4-*tert*-butyl-cyclohexanone	0	*cis*	20	
norcamphor	0	*endo*	97	99
d-camphor	0	*exo*	97	

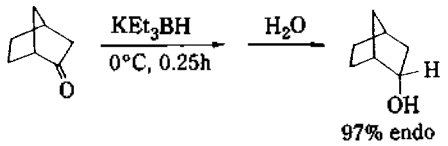
[a] Reaction mixtures were 0.25 M in ketones at 0°C. A 1.1:1 ratio for reagent-ketone was used. [b] The yields of alcohols were quantitative.

Table 3. Reaction of Potassium Triethylborohydride with Representative Quinones in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used	hydride used for reduction[b]
p-benzoquinone[c]	30 min	0.36	1.43	1.07
	1 h	0.36	1.45	1.09
	3 h	0.36	1.48	1.12
	6 h	0.36	1.48	1.12
anthraquinone[d]	5 min	0.07	2.07	2.00
	1 h	0.07	2.08	2.01

[a,b] See the corresponding footnotes in Table 2. [c] Immediate color change to dark green, and then to light brown in 5 min. [d] Reverse addition. Color changed to reddish brown.

d-camphor were reduced with excellent stereoselectivity, yielding 97% *endo*-and 3% *exo*-norboneol (eq 2), and 97% *exo*- and 3% *endo*-borneol respectively. These results are very similar to those of $LiEt_3BH$[3]. The results are summarized in Table 2-B.



97% endo (2)

Table 4. Reaction of Potassium Triethylborohydride with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
caproic acid[c]	5 min	1.00	1.00	0.00
	1 h	1.01	1.01	0.00
benzoic acid[d]	5 min	1.02	1.02	0.00
	24 h	1.03	1.03	0.00
acetic anhydride	5 min	0.15	2.14	1.99
	1 h	0.15	2.14	1.99
succinic	5 min	0.20	2.13	1.93
anhydride	1 h	0.20	2.17	1.97
	3 h	0.20	2.21	2.01
phthalic	5 min	0.15	2.05	1.91
anhydride	1 h	0.15	2.14	1.99
caproyl	5 min	0.21	2.23	2.01
chloride[c]	1 h	0.21	2.23	2.01
benzoyl	5 min	0.03	2.04	2.01
chloride[c]	1 h	0.04	2.03	1.99

[a,b] See the corresponding footnotes in Table 1. [c] The solution turned milky immediately. [d] Precipitate formed in 5 min.

Quinones. p-Benzoquinone rapidly utilized 1.43 equiv of hydride, of which 0.36 equiv of hydride was utilized for hydrogen evolution, with only slow further uptake of hydride. The hydride uptake observed does not correspond to clean reduction either to hydroquinone or to 1,4-dihydroxycyclohexadiene. Anthraquinone, on the other hand, rapidly utilized 2 equiv of hydride without significant hydrogen evolution, indicating a clean reduction to 9,10-dihydro-9,10-dihydroxyanthracene. Similar results are observed in the reaction of the compound with $LiFt_3BH$[3], and Li9-BBNH[7]. The results are summarized in Table 3.

Carboxylic Acids and Acyl Derivatives. Carboxylic acids instantly evolved 1 equiv of hydrogen to form their potassium salts. The reaction mixtures became milky immediately, and a precipitate was observed in 5 min in the case of benzoic acid. No further hydride uptake was observed with both caproic acid and benzoic acid. This result suggests that KEt_3BH can be utilized for the selective reduction of other easily reducible functional groups in the presence of carboxylic acids. Such a behavior of carboxylic acids has also been noted in the reaction with $LiEt_3BH$[3] and Li9-BBNH[9]. Acid anhydrides rapidly consumed 2 equiv of hydride without further uptake of hydride, corresponding to the reduction to the carboxylic acid and alcohol stage. It should be possible to utilize this characteristics for the conversion of cyclic anhydride to lactone. Acid chloride utilized 2 equiv of hydride rapidly to proceed to the corresponding alcohol

Table 5. Reaction of Potassium Triethylborohydride with Representative Esters and Lactones in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
ethyl caproate	5 min	0.00	2.03	2.03
	1 h	0.03	2.03	2.00
ethyl benzoate	5 min	0.08	2.04	1.96
	1 h	0.08	2.12	2.04
phenyl acetate	5 min	0.08	2.11	2.03
	1 h	0.08	2.11	2.03
γ-butyrolactone	5 min	0.04	2.15	2.11
	1 h	0.04	2.15	2.11
phthalide[c]	5 min	0.04	2.08	2.04
	1 h	0.04	2.08	2.04
isopropenyl	5 min	0.03	2.70	2.67
acetate	30 min	0.03	2.94	2.91
	1 h	0.03	2.92	2.89
	3 h	0.03	2.92	2.89

[a,b] See the corresponding footnotes in Table 1. [c] Color changed to yellow.

Table 6. Reaction of Potassium Triethylborhydride with Representative Epoxides in Tetrahydrofuran at 0°C

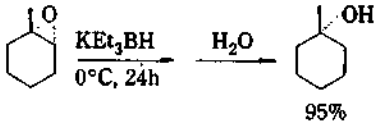
compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
1,2-butylene	5 min	0.02	0.98	0.96
oxide	1 h	0.02	1.00	0.98
styrene oxide[c]	5 min	0.03	1.02	0.99
	1 h	0.03	1.05	1.02
cyclohexene	5 min	0.00	0.14	0.14
oxide	30 min	0.00	0.41	0.41
	1 h	0.00	0.52	0.52
	3 h	0.00	0.85	0.85
	6 h	0.00	1.00	1.00
1-methyl-1,2-	5 min	0.00	0.19	0.19
cyclohexene	30 min	0.00	0.45	0.45
oxide[d]	1 h	0.00	0.58	0.58
	3 h	0.00	0.54	0.54
	6 h	0.00	0.94	0.94
	12 h	0.00	1.03	1.03

[a,b] See the corresponding footnotes in Table 2. [c] The product was a mixture of 97% of 1-phenylethanol and 3% of 2-phenylethanol. [d] 1-Methylcyclohexanol was obtained in a 95% yield, without contaminating 2-methylcyclohexanols.

stage. The results are summerized in Table 4.

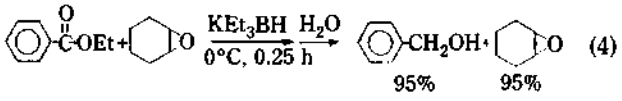
Esters and Lactones. Ethyl caproate and ethyl benzoate consumed 2 equiv of hydride within 5 min. Phenyl acetate, γ-butyrolactone and phthalide also utilized 2 equiv of hydride rapidly to proceed to the corresponding alcohol and diol stage, respectively. Isopropenyl acetate utilized 2.9 equiv of hydride in 30 min with no further uptake of hydride thereafter. Presumably, the acetate group was reduced to the ethanol stage (two hydride) and the isopropenyl group to the isopropyl alcohol stage (one hydride). This result is similar to those of $LiEt_3BH$[3] and Li9-BBNH[7]. The possibility of partial reduction of a carboxylic acid ester to the corresponding aldehyde with potassium triethylborohydride was also explored. Accordingly, an equimolar amount of the reagent was slowly added to a solution of ethyl benzoate in THF at −15°C. After quenching, it was revealed that 11% of benzaldehyde and 32.3% of benzyl alcohol were formed. The results are summerized in Table 5.

Epoxides. 1,2-Butylene oxide and styrene oxide utilized 1 equiv of hydride rapidly to proceed to the alcohol stage. But cyclohexene oxide and 1-methyl-1,2-cyclohexene oxide were reduced slowly, completing the reduction in 12 h. In the case of $LiEt_3BH$[3], on the other hand, all of epoxides examined were reduced rapidly. The ring opening of the epoxides proceeds at the less hindered sides of the compounds with good regioselectivity. Thus styrene oxide gave 1-phenylethanol (97%) and 2-phenylethanol (3%) and 1-methyl-1,2-cyclohexene oxide gave 1-methylcyclohexanol (95%) exclusively.



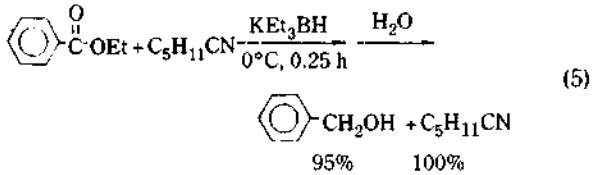
(3)

Since the reduction of cyclohexene oxide is relatively slow compared to the rapid reduction of ester, it was thought that the selective reduction of ester in the presence of cyclohexene oxide might be possible. As shown below, ethyl benzoate was reduced to benzyl alcohol quantitatively, leaving cyclohexene oxide intact. The results are summerized in Table 6.



(4)

Amides and Nitriles. Primary amides reacted almost instantly to evolve 1 equiv of hydrogen; further hydrogen evolution does not occur even over extended periods of time. While caproamide then underwent a slow reduction, benzamide was inert to this reagett. N,N-Dimethylcaproamide was reduced slowly utilizing 1.21 equiv of hydride in 24 h, however the reduction of N,N-dimethylbenzamide was considerably faster than N,N-dimethylcaproamide and completed in 24 h. Thus KEt_3BH reduces tertiary amides much slower than $LiEt_3BH$[3]. KEt_3BH reduced N,N-dimethylbenzamide to benzyl alcohol in 98% yield, similar to $LiEt_3BH$. Capronitrile took up one hydride in 3 h, and no further reduction was observed. We observed nearly 50% of capronitrile remained unreacted after 3 h reaction. This suggests the reaction underwent similar to $LiEt_3BH$[3]. On the other hand, benzonitrile consumed 2 equiv of hydride to be reduced to the amine state in 3 h. Although capronitrile is reduced rather rapidly, it was possible to reduce ester selectively in the presence of capronitrile. As shown below, ethyl benzoate was reduced to benzyl alcohol quantitatively, leaving capronitrile intact. The results are summerized in Table 7.



(5)

Nitro Compounds and Their Derivatives. 1-Nitro-

Table 7. Reaction of Potassium Triethylborohydride with Representative Amides and Nitriles in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
caproamide[c]	5 min	1.13	1.13	0.00
	30 min	1.13	1.25	0.12
	1 h	1.13	1.49	0.36
	3 h	1.13	1.67	0.54
	6 h	1.13	1.69	0.56
	24 h	1.13	1.92	0.79
benzamide[d]	5 min	1.04	1.04	0.00
	24 h	1.04	1.04	0.00
N,N-dimethyl-	5 min	0.00	0.00	0.00
caproamide	30 min	0.00	0.03	0.03
	1 h	0.00	0.11	0.11
	3 h	0.00	0.19	0.19
	6 h	0.00	0.39	0.39
	12 h	0.00	0.58	0.58
	24 h	0.00	1.21	1.21
N,N-dimethyl-	5 min	0.10	0.10	0.00
benzamide	30 min	0.10	0.15	0.05
	1 h	0.10	0.46	0.36
	3 h	0.10	0.71	0.61
	6 h	0.10	0.95	0.85
	24 h	0.10	2.07	1.97
capronitrile	5 min	0.00	0.64	0.64
	1 h	0.00	0.81	0.81
	3 h	0.00	0.98	0.98
	24 h	0.00	0.96	0.96
benzonitrile[e]	5 min	0.00	0.96	0.96
	30 min	0.00	1.67	1.67
	1 h	0.00	1.94	1.94
	3 h	0.00	2.01	2.01

[a,b] See the corresponding footnotes in Table 1. [c] Solution becomes turbid within 5 min[d] Immediate white precipitate. [e] Immediate color change to redviolet within 5 min.

propane rapidly evolved 1 equiv of hydrogen, forming a white precipitate with no hydride being consumed for reduction. Presumably, the active α-hydrogen was involved in this reaction. Nitrobenzene rapidly utilized 2 equiv of hydride for reduction with slight hydrogen evolution, and no further uptake of hydride was apparent. Azobenzene was slowly reduced, utilizing 1 equiv of hydride for reduction in 24 h. Azoxybenzene was also slowly reduced. The reducing characteristics of KEt_3BH with these compounds are very similar to those of $LiEt_3BH$[3]. The results are summerized in Table 8.

Other Nitrogen Compounds. Cyclohexanone oxime rapidly liberated 1 equiv of hydrogen, without undergoing reduction under the experimental condition. Consequently, the formation of oximes would provide another means for protecting carbonyl compounds toward KEt_3BH. Such a trend was also observed in the reaction with $LiEt_3BH_3$, Li9-BBNH[7] and Lin-$BuBH_3$[8]. Phenyl isocyanate was rapidly reduced, utilizing 1 equiv of hydride, corresponding to reduction to the formanilide stage. Pyridine is reduced rapidly consuming 2.0 hydrides in 1 h, whereas quinoline took up 1.0 hydride in 3 h. Further reductions were very slow in both

Table 8. Reaction of Potassium Triethylborohydride with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
nitropropane[c]	5 min	1.00	1.00	0.00
	1 h	1.01	0.01	0.00
nitrobenzene[d]	5 min	0.31	2.26	1.95
	30 min	0.31	2.28	1.97
	1 h	0.31	2.30	1.99
	6 h	0.33	2.34	2.01
azobenzene[e]	5 min	0.01	0.17	0.16
	1 h	0.01	0.28	0.27
	3 h	0.02	0.44	0.42
	6 h	0.02	0.64	0.62
	24 h	0.02	0.99	0.97
azoxybenzene[f]	5 min	0.05	0.27	0.22
	30 min	0.05	0.51	0.46
	1 h	0.05	0.75	0.70
	3 h	0.06	0.96	0.90
	6 h	0.06	1.48	1.42
	24 h	0.06	2.18	2.12

[a,b] See the corresponding footnotes in Table 1. [c] Immediate white precipitate. [d] Color change to orange. [e] Color change to dark green. [f] Color change to reddish brown within 12 h.

Table 9. Reaction of Potassium Triethylborohydride with Representative Other Nitrogen Compounds in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
cyclohexanone	5 min	1.04	1.08	0.04
oxime	1 h	1.04	1.08	0.04
	6 h	1.05	1.09	0.04
	24 h	1.05	1.09	0.04
phenyl	5 min	0.02	1.01	0.99
isocyanate[c]	1 h	0.02	1.03	1.01
pyridine	5 min	0.00	1.73	1.73
	30 min	0.00	1.82	1.82
	1 h	0.00	1.99	1.99
	3 h	0.00	2.09	2.09
	24 h	0.00	2.17	2.17
quinoline	5 min	0.00	0.15	0.15
	30 min	0.00	0.37	0.37
	1 h	0.01	0.63	0.62
	3 h	0.02	1.01	0.99
	6 h	0.02	1.17	1.15
	24 h	0.02	1.27	1.25
pyriding	5 min	0.00	2.24	2.24
N-oxide[d]	30 min	0.04	2.32	2.28
	1 h	0.04	2.32	2.28
	3 h	0.04	2.40	2.36
	6 h	0.04	2.42	2.38
	24 h	0.04	2.58	2.54

[a,b] See the corresponding for footnotes in Table 2. [c] Color change to yellow. [d] Color change to reddish brown, then to orange.

Table 10. Reaction of Potassium Triethylborohydride with Representative Sulfur Compounds and Alkyl Halides in Tetrahydrofuran at 0°C

compound[a]	time	hydrogen evolved[b]	total hydride used[b]	hydride used for reduction[b]
di-n-butyl-	5 min	1.04	1.94	0.91
disulfide[c]	1 h	1.04	2.10	1.06
diphenyl	30 min	1.02	2.10	1.08
disulfide[d]	1 h	1.02	2.10	1.08
methyl p-tolyl	5 min	0.00	0.00	0.00
sulfide	1 h	0.00	0.00	0.00
	3 h	0.00	0.02	0.02
dimethyl	5 min	0.00	0.01	0.01
sulfoxide	1 h	0.00	0.10	0.10
	3 h	0.00	0.09	0.09
	24 h	0.00	0.08	0.08
diphenyl	5 min	0.00	0.07	0.07
sulfone[e]	30 min	0.00	0.18	0.18
	1 h	0.00	0.26	0.26
	3 h	0.00	0.32	0.32
	6 h	0.00	0.63	0.63
	24 h	0.00	0.80	0.80
methanesulfonic	5 min	1.08	1.08	0.00
acid	1 h	1.08	1.08	0.00
p-toluenesul-	5 min	3.14	3.14	0.00
fonic acid	24 h	3.14	3.14	0.00
monohydrate[f]				
cyclohexyl	5 min	0.19	0.23	0.04
tosylate	30 min	0.19	0.49	0.30
	3 h	0.19	0.49	0.30
	6 h	0.20	0.66	0.46
	24 h	0.20	0.68	0.48
1-chloro-	15 min	0.00	0.34	0.34
octane	1 h	0.00	0.52	0.52
	3 h	0.00	0.98	0.98
	6 h	0.00	1.05	1.05
1-bromooctane	5 min	0.00	0.98	0.98
	1 h	0.00	0.97	0.97
cyclohexyl	30 min	0.01	0.05	0.04
bromide	1 h	0.01	0.11	0.10
	3 h	0.02	0.22	0.20
	6 h	0.02	0.37	0.35
	24 h	0.02	0.42	0.40

[a,b] See the corresponding footnotes in Table 1. [c] Milky solution. [d] Immediate white precipitate. [e] Color change to light yellow. [f] Color change to violet within 5 min, then to white precipitate in 3 h.

cases. This suggests the partial reductions of the heterocyclic rings. We are going to study more in detail in near future. Pyridine N-oxide also reacted rapidly, utilizing 2.58 equiv of hydride, without significant hydrogen evolution. The results are summerized in Table 9.

Sulfur Compounds and Alkyl Halides. Disulfides were rapidly reduced to the thiol stage, utilizing 2 equiv of hydride, one for reduction and one for hydrogen evolution. Methyl *p*-tolyl sulfide and dimethyl sulfoxide were essentially inert to this reagent. Diephenyl sulfone was reduced slowly. On heating the reaction mixture of diphenyl sulfone at reflux, ethylbenzene was detected in 64% yield in 3 h. Such a trend was also observed with $LiEt_3BH$[9]. Sulfonic acid rapidly evolved hydrogen but no significant hydride uptake for reduction was observed. Cyclohexyl tosylate reacted slowly with KEt_3BH. Among the alkyl halides examined, 1-bromooctane was reduced rapidly in 5 min, whereas 1-chlorooctane was reduced moderately in 3-6 h. However, cyclohexyl bromide reacted with this reagent very slowly. The results are summerized in Table 10.

Conclusion

A systematic study of the reaction of representative organic compounds with KEt_3BH in THF at 0°C has been completed. The results clearly reveal that KEt_3BH is a moderately powerful reducing agent in comparison to $LiEt_3BH$, an exceptionally powerful reducing agent, although the difference in these two reagents is only the metal ion. Thus the reactions of secondary and tertiary alcohols, cyclohexene oxides, tertiary amides, and alkyl halide with KEt_3BH are substantially slower than those with $LiEt_3BH$. KEt_3BH is an excellent selective reducing agent of ester functional group in the presence of other functional groups such as cyclohexene oxide and aliphatic nitrile.

Experimental

Materials. Tetrahydrofuran was distilled from benzophenone-sodium metal and stored under the nitrogen. Potassium hydride and triethylborane obtained from Fluka and Aldrich, respectively, were used without further purification. In this study, all of the compounds used were commercially available products of the highest purity. Among these compounds, some were purified just before use by distillation or recrystallization when necessary. All glassware was dried thoroughly in a oven and cooled under a dry stream of nitrogen. All reduction experiments were carried out under a dry nitrogen atmosphere, and hypodermic syringes were used to transfer the solutions.

Standard Solution of KEt_3BH[5]. In a dry 500 m*l* flask, fitted with a rubber syringe cap and a reflux condenser connected to a mercury bubbler, were placed about 375 mmol (50% excess) of potassium hydride in mineral oil. The mineral oil was removed by washing with sufficient pentane. And then 250 mL of 1.0 M solution of triethylborane in THF was added to potassium hydride. The mixture was stirred at room temperature for 24 h in order to ensure completion.[5] In order to obtain a concentrated solution, appropriate volume of THF was evaporated. After settling down potassium hydride, the concentration of a clear solution was determined by hydrolyzing an aliquot with a mixture of THF-water-glycerine (1:1:1). The concentration was found to be 1.5 ~ 2.0 M.

Procedure for Study of the Rate and Stoichiometry. The reduction of accetophenone is representative. KEt_3BH solution (13.9 m*l*, 20 mmol in hydride) and 3.6 m*l* of THF were introduced into a dried 50 mL flask, fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a gas buret. The flask was maintained at 0°C and 2.5 m*l* (5 mmol) of 2.0 M solution of acetophenone in THF was injected slowly. Then hydrogen evolution was monitored. In this way, a solution was obtained which was 1.0 M in hydride and 0.25 M in acetophenone. Upon addition of the compound, no hydrogen evolution

observed. After 5 min, 4.0 m*l* of the reaction mixture was removed and injected into a hydrolyzing mixture of THF-water-glycerine (1:1:1). The hydrogen evolved was 3.0 mmol, indicating that 1.0 mmol of hydride had been used per mmol of acetophenone. Therefore, 1.0 mmol of hydride had been used for reduction per mmol of acetophenone. Another 4.0 mL of the reaction mixture was also removed and hydrolyzed after 30 min. The amount of hydride used for reduction was 1.03 mmol. After 1 h, it was also 1.03 mmol. It was shown that reduction of acetophenone was over in 5 min.

Procedure for Product Analysis by GLC. The reduction of 1-methyl-1.2-cyclohexene oxide is representative. The setting-up was the same as the previous part. 1 m*l* of solution containing 1 mmol of 1-methyl-1.2-cyclohexene oxide and 0.5 mmol of dodecane as a internal standard in THF was placed in a 50 mL flask and then 0.65 m*l* of THF was introduced. The mixture was maintained at 0°C and then 2.35 m*l* (4.0 mmol) of KEt_3BH solution was added dropwisely. After 24 h, excess hydride was destroyed with 0.5 mL of water and oxidized by the addition of 0.8 mL of 2 N NaOH, followed by 0.8 mL of 30% H_2O_2 for 2~3 h. The aqueous layer was saturated with K_2CO_3 and subjected to GLC analysis on a 10% carbowax 20 M column, 10 ft × 0.125 in. It was revealed that KEt_3BH reduced 1-methyl-1,2-cyclohexene oxide to 1-methylcyclohexanol (95%) exclusively.

Procedure for Competitive Reaction. The reaction of ethyl benzoate in the presence of cyclohexene oxide is representative. The experimental set-up was the same as the rate study. To a well-stirred mixture of 2 mmol of ethyl benzoate and cyclohexene oxide was added 2.14 mL (4.4 mmol) of KEt_3BH solution at 0°C. After 15 min, the remaining hydride was destroyed with 0.5 mL of water and 1 mL (1.0 mmol) of naphthalene in THF as an internal standard was added. After warming the reaction mixture to room temperature, it was oxidized by the addition of 1.0 mL of 2 N NaOH and 1.0 mL of 30% H_2O_2 for 2~3 h. Then the aqueous layer was saturated with K_2CO_3 and the dry THF layer was subjected to GLC analysis. The column used was the same as the previous section. GLC analysis showed the formation of 95% benzyl alcohol and cyclohexene oxide remained intact.

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Vibrational Spectroscopic Study of Benzenethiol on Silver Surface

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Vibrational spectroscopy has been applied to the benzenethiol molecule adsorbed on the silver surface. The results of infrared and Raman spectral studies have led to the conclusion that benzenethiol is chemisorbed dissociatively on the silver surface by rupture of S-H bond and the benzenethiolate formed upon adsorption is bound to silver via its sulfur atom. It seemed more likely that benzenethiol is adsorbed as being inclined to the silver surface. On contact with oxygen, the geometry of the adsorbed species appeared to bear a resemblance to that of silver benzenethiolate salt. The infrared bands of adsorbed species remained with little decrease of intensity even after the prolonged evacuation at 673 K, indicating that benzenethiol is very strongly chemisorbed to the silver surface.

Introduction

Understanding the interactions between sulfur compounds and various metals has been of a great concern in catalytic chemistry[1]. Catalyst poisoning by sulfur compounds is a serious problem in a number of applications[2]. Despite the realization that sulfur adversely affects catalyst performance, there is little understanding of the poisoning mechanism[3].

Vibrational spectroscopy has been widely used in surface and catalysis studies[4]. The most general approach of vibra-

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