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A Study of Solvents for Sodium Borohydride and the Effect of Solvent and the Metal Ion on Borohydride Reductions[1]

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Isopropyl alcohol and the dimethyl ethers of di- and triethylene glycol are convenient solvents for sodium borohydride. High purity sodium borohydride (99.6 to 99.9%) may be obtained readily by recrystallization from the dimethyl ether of diethylene glycol. Reductions of ketones in this solvent are slow. However, in isopropyl alcohol the reaction is much faster and the rate can be studied conveniently. The reaction follows second-order kinetics with the rate constant decreasing in the order acetone > methyl ethyl ketone > methyl isopropyl ketone > methyl *t*-butyl ketone. Esters are not reduced by sodium borohydride in these solvents. However, the reduction of esters can be brought about by the addition of lithium bromide or anhydrous magnesium chloride or bromide to sodium borohydride in the dimethyl ether of diethylene glycol.

In comparing the reducing properties of sodium borohydride with related alkoxyborohydrides[4] we found our studies severely handicapped by the lack of suitable solvents for sodium borohydride. This reagent is commonly used in water or methanol. However, it undergoes a slow reaction with these solvents which causes no difficulty in most preparative work,[5] but does introduce complications in quantitative studies. Accordingly, we undertook to find other solvents with which the borohydride would undergo no significant reaction.

Isopropyl alcohol and the dimethyl ethers of di- and triethylene glycol proved to be satisfactory solvents.[6] These were utilized for the preparation of pure sodium borohydride and for the study of the reaction of sodium borohydride with ketones and esters.

Results

Solvents.—At 60° a solution of sodium borohydride in methanol rapidly liberates 4 moles of hydrogen.[7] The reaction with ethanol is considerably slower, but even here there is obtained 33% liberation of the available hydrogen in 4 hours (Table I).

TABLE I

REACTION OF SODIUM BOROHYDRIDE WITH METHANOL[a] AND ETHANOL[b] AT 60°

Methanol		Ethanol	
Time, min.	Hydrogen evolved, % calcd.	Time, min.	Hydrogen evolved, % calcd.
1.0	2.2	60	3.4
2.0	8.2	105	9.6
3.0	17.4	165	20
4.0	29	240	33
5.0	40	300	44
7.0	60	360	54
9.0	74	460	67
12.0	88	570	77
16.0	96	660	83
24.0	100	870	90

[a] Solution 1.05 *M* in sodium borohydride. [b] Solution 1.08 *M* in sodium borohydride.

Under the same conditions neither isopropyl nor *t*-butyl alcohol exhibited any tendency toward formation of hydrogen over a 24-hour reaction period. The solubility of sodium borohydride in both of these solvents proved to be relatively low (Table II). However, it was considered that the solubility of sodium borohydride in isopropyl alcohol was sufficiently high to justify adoption of this solvent for a kinetic study of the reduction of ketones.

TABLE II

SOLUBILITY OF SODIUM BOROHYDRIDE

Solvent	Temp., °C.	Solubility, g./l.
Isopropyl alcohol	25	3.7
	60	8.8
t-Butyl alcohol	25	1.1
	60	1.8

We examined the utility of isopropyl alcohol as a solvent for the purification of commercial sodium borohydride, but with only moderate success. In view of the far better success achieved with diglyme as solvent, these studies need not be discussed.

Sodium borohydride proved to be slightly soluble in monoglyme, but very highly soluble in both di- and triglyme. Since the boiling point of diglyme is in a more convenient range, we concentrated our investigation on this substance.

At 40° sodium borohydride dissolves in diglyme to give a solution nearly 3 *M* in borohydride. The solubility decreases at both higher and lower temperatures. A solution, saturated at 40°, deposits long, needle-like white crystals on cooling to 25° or lower. Analysis of the crystals indicate them to be a 1:1 solvate of diglyme and sodium borohydride. The solvate melts at approximately 65° and the solvent may be removed readily under vacuum. The product thus obtained is very pure. In this way sodium borohydride of 99.6–99.9% purity has been obtained in a single operation from commercial product of 80% purity.

Heating a saturated solution of sodium borohydride to higher temperatures results in the precipitation of a finely divided white crystalline solid which proved to be unsolvated sodium borohydride. The material obtained in this way was of

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[1] Addition Compounds of the Alkali Metal Hydrides. III.

[2] Research assistant on a National Science Foundation Grant, 1953–1954.

[3] Parke, Davis and Co. Fellow at Purdue University, 1952–1955.

[4] H. C. Brown and E. J. Mead, THIS JOURNAL, **75**, 6263 (1953).

[5] S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

[6] These names are exceedingly long and very awkward for common use. It is proposed that the terms monoglyme, diglyme, triglyme, etc., be utilized as common names for the dimethyl ethers of mono-, di- and triethylene glycol, respectively.

[7] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

slightly lower purity, 98.6–99.3%, than that achieved by the previous procedure.

Either of these two procedures provides a convenient route to sodium borohydride of the purity desired for research work.

The solubility data are summarized in Table III.

TABLE III

SOLUBILITY OF SODIUM BOROHYDRIDE IN DIGLYME[6]

Temp., °C.	Solubility, M[a] From 0 to 100°	From 100 to 0°
0	0.350	
20	0.88	
25	1.26	1.36
30	1.88	1.93
35	2.66	2.59
40	2.91	2.45
45	2.62	2.04
50	1.43	
60	0.70	0.60
80	0.201	0.192
100	0.116	0.112

[a] The solution was exceedingly viscous at temperatures near the maximum solubility and it proved difficult to attain equilibrium, especially when the solution was in contact with unsolvated sodium borohydride precipitated from the hot solution (from 100 to 0°).

Reduction of Ketones.—Garrett and Lyttle recently showed that kinetic data obtained for the reaction of sodium borohydride with 3*α*-hydroxy-11*α*-acetoxypregnan-20-one in methanol were in good agreement with a second-order rate equation which they derived on the assumption that the reductions proceed *via* a stepwise formation of new C–H and B–O bonds in which the first step is rate determining.[8]

We have observed that the reaction of sodium borohydride with acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl *t*-butyl ketone proceeds at a rate convenient for kinetic studies in isopropyl alcohol at 0°. The data for typical experiments are shown in Fig. 1 with the rate constants listed in Table IV.

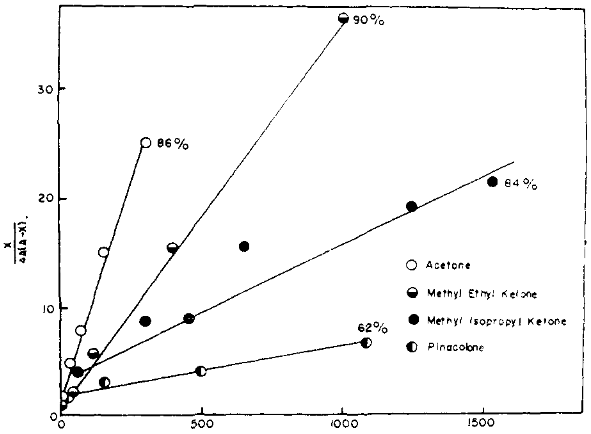

Fig. 1.—Sodium borohydride reduction of ketones in isopropyl alcohol at 0°.

In contrast to the very rapid reaction in isopropyl alcohol, the reaction of sodium borohydride with acetone in diglyme and triglyme proved to be exceedingly slow, both at 0 and at 25°. Even after 96 hours the reaction was far from complete.

TABLE IV

SPECIFIC SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF SODIUM BOROHYDRIDE WITH KETONES IN ISOPROPYL ALCOHOL AT 0°

Ketone	Concentration, M Borohydride	Ketone	Rate constants, k_2, l. mole^{-1} min.$^{-1}$
Acetone	0.061	0.244	0.078
Methyl ethyl	.061	.240	.0358
Methyl isopropyl	.064	.253	.0149
Methyl *t*-butyl	.061	.243	.0050

The reaction is catalyzed by water, isopropyl alcohol and especially by triethylamine. The catalytic effect of triethylamine was exceedingly interesting and it was studied in some detail. In the presence of this material 25% of the available hydride (*i.e.*, one hydride per borohydride ion) disappears within the first few minutes with no further loss of hydride over periods of several hours. Typical data are summarized in Table V.

TABLE V

REACTION OF SODIUM BOROHYDRIDE WITH ACETONE IN DIGLYME AS SOLVENT[a]

Time	Hydride reacted, % calcd. No catalyst 0°	No catalyst 25°	Water, 25° 0.25 M	Water, 25° 1.0 M	Isopropyl alcohol, 1.0 M 25°	Triethylamine, 1.0 M 25°
5 min.		14	18	24	16	25
30 min.			23	49	25	24
60 min.		16	33	57	34	25
180 min.	11	25	44	69	53	25
12 hr.[b]	15	47				
24 hr.[b]	20	64	83	91	89	54
48 hr.[b]	27	80			93	59
96 hr.[b]	40	86			95	64

[a] The solutions were 1.0 M in acetone and 0.25 M in sodium borohydride. [b] After three hours the solutions developed color and it is probable that condensation of the acetone introduces a complication to the reaction.

It was noted that after 3–6 hours the solutions developed color and the rate of hydride utilization increased. Accordingly, the experiments were repeated and the solutions analyzed both for hydride and for residual acetone (by analysis with 2,4-dinitrophenylhydrazine). The data clearly show that triethylamine catalyzes a rapid reaction of acetone with sodium borohydride, presumably

TABLE VI

REACTION OF SODIUM BOROHYDRIDE WITH ACETONE IN DIGLYME AS SOLVENT[a]

Time, min.	Hydride and acetone reacted, % calcd. No catalyst, 25° Hydride	No catalyst, 25° Acetone	No catalyst, 0° Hydride	No catalyst, 0° Acetone	Triethylamine, 0.8 M, 0° Hydride	Triethylamine, 0.8 M, 0° Acetone
5	15.4	22.5	9.0	15.5	27.0	27.4
30	16.3	23.5	11.3	20.5	25.9	23.8
60	18.0	24.4	12.9	23.1	26.0	24.6
180	19.6	26.2	14.7	23.8	25.6	23.8
360			15.0	31.1	26.0	24.9
720	31.5	35.5	17.2	30.3	32.4	

[a] The solutions were 0.8 M in acetone and 0.20 M in sodium borohydride.

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(8) E. R. Garrett and D. A. Lyttle, THIS JOURNAL, **75**, 6051 (1953).

to form the unknown monoisopropoxyborohydride, and that acetone appears to disappear somewhat more rapidly than hydride, presumably as a result of self-condensation. The data are presented in Table VI.

Reduction of Esters.—In ether solvents lithium borohydride readily reduces esters[9] whereas such reductions have not been reported for sodium borohydride.[5] It appeared that this difference in the two borohydrides might be the result of a difference in solubility, since sodium borohydride is essentially insoluble in the ether solvents previously utilized. Accordingly, we examined the possibility that esters might be reduced by sodium borohydride in either isopropyl alcohol or diglyme as solvents.

It was observed that a reaction mixture of 35 mmoles of ethyl benzoate and 25 mmoles of sodium borohydride in 125 cc. of isopropyl alcohol lost but 12% of the available active hydrogen in 6 hours at 75°. A similar reaction mixture in diglyme lost less than 10% of the available hydrogen in 24 hours at 75°. On the other hand, lithium borohydride was observed to reduce esters easily in diglyme under the same conditions. Consequently, the differences in the reactivity of sodium and lithium borohydrides observed in the past do not have their origin in the difference in the solubility of the two salts.

Recently, Kollonitsch, Fuchs and Gabor reported that they had successfully reduced esters by utilizing a mixture of sodium borohydride and lithium chloride in ethanol.[10] Better yields were obtained utilizing lithium iodide or magnesium iodide and a suspension of sodium borohydride in tetrahydrofuran. We therefore examined the utility of isopropyl alcohol and diglyme for such reductions.

Addition of equimolar amounts of lithium chloride to solutions of sodium borohydride in isopropyl alcohol resulted in the quantitative precipitation of sodium chloride and the formation of lithium borohydride solutions. In contrast to the high stability of sodium borohydride in isopropyl alcohol, the corresponding solutions of lithium borohydride were unstable and liberated hydrogen slowly. For example, a solution 0.5 *M* in lithium borohydride at 82° evolved hydrogen as indicated: 2 hr., 10%; 6 hr., 21%; 12 hr., 28%; 24 hr., 56%. Addition of lithium isopropoxide to the solution had no effect upon the rate of hydrogen evolution.

It was possible to demonstrate the reduction of esters under these conditions. However, the reaction required considerable excess of borohydride to replace that lost in the side reaction with the solvent and it was considered that the procedure would therefore be of low utility.

In diglyme, however, the addition of lithium bromide proved highly effective in bringing about reduction of the ester. Lithium chloride is much less soluble in the solvent and this salt was therefore much less effective. The experimental procedure which finally was developed is quite simple and should have high utility for ester reductions in synthetic work.

To a 1.0 *M* solution of sodium borohydride in diglyme there was added an equivalent quantity of solid lithium bromide. After 30 min., the ester was added and the reaction mixture heated to 100°. In cases where a 100% excess of borohydride was present, a reaction time of 1 hr. was ample to ensure essentially quantitative reaction, whereas with 20% excess reagent, a reaction time of 3 hr. was found desirable.

Utilizing these procedures a practically quantitative uptake of hydrogen (2 moles of hydride per mole of ester) was demonstrated for ethyl acetate, ethyl stearate, ethyl benzoate, ethyl *p*-chlorobenzoate and ethyl cinnamate. Nitrobenzene reacted vigorously under these conditions; however, no attempt was made to characterize the reaction products.

On a preparative scale a 91% yield of *p*-chlorobenzyl alcohol was obtained in the reduction of 0.4 mole of ethyl *p*-chlorobenzoate.

The results of these studies are summarized in Table VII.

TABLE VII

HYDRIDE UTILIZATION IN THE REACTION OF ESTERS WITH SODIUM BOROHYDRIDE–LITHIUM BROMIDE IN DIGLYME AT 100°

	—Reactants, mmoles[a]—				
Ester	Ester	Sodium borohydride	Lithium bromide	Time, hr.	Ester reduction,[b] %
Ethyl acetate	5.0	5.0	5.0	1.0	96
	5.0	5.0	5.0	1.0	98
Ethyl stearate	5.0	5.0	5.0	1.0	97.4
	5.0	5.0	5.0	1.0	100
Ethyl benzoate	5.0	5.0	5.0	1.0	93.2
Ethyl cinnamate	5.0	5.0	5.0	1.0	95.5
	5.0	5.0	5.0	1.0	96.6
Ethyl benzoate	8.0	5.0	5.0	1.0	90
	8.0	5.0	5.0	2.0	97
	8.0	5.0	5.0	3.0	100
Ethyl *p*-chlorobenzoate	8.8	5.0	5.0	3.0	100
	8.1	5.0	5.0	3.0	99.8
Ethyl cinnamate	8.0	5.0	5.0	3.0	98.2
	8.0	5.0	5.0	3.0	97.5
Nitrobenzene	8.0	5.0	5.0	..[c]	

[a] Diglyme solution, 1.0 *M* in borohydride. [b] Calculated from hydride utilization at end of reaction. [c] Very vigorous reaction. No residual hydride.

Anhydrous magnesium chloride and bromide possess only a small solubility in diglyme (0.013 *M* for magnesium chloride and 0.078 *M* for the bromide, both at 100°). However, the addition of equivalent amounts of the solid salts to diglyme solutions of sodium borohydride brings about the reduction of esters. In this way ethyl stearate was reduced in 4 hours at 100° to 1-octadecanol in 74% yield and ethyl *p*-nitrobenzoate was reduced in 3–4 hours at 40–50° to *p*-nitrobenzyl alcohol in 57% yield. These do not represent maximum yields, since no attempt was made to ascertain optimum conditions.

It therefore appears that ester reductions can be achieved in diglyme solution by utilizing sodium borohydride with an equivalent amount of lithium

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(9) R. F. Nystrom, S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 3245 (1949).

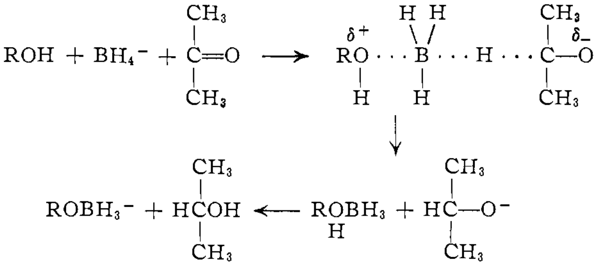
(10) J. Kollonitsch, P. Fuchs and V. Gabor, *Nature*, **173**, 125 (1954).

bromide, magnesium chloride or magnesium bromide.

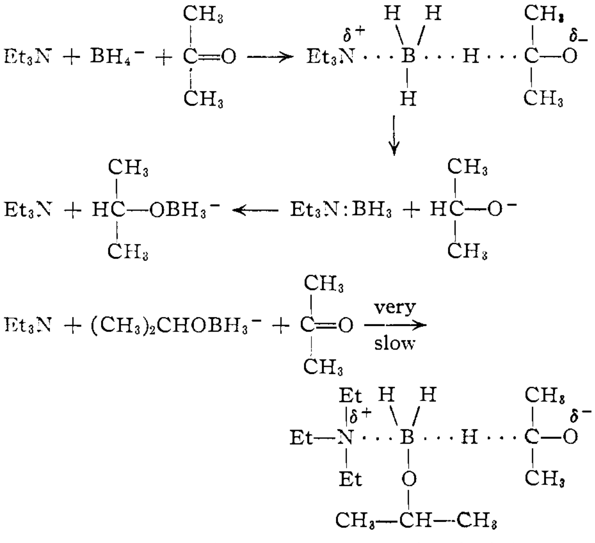
Discussion

The very high solubility of sodium borohydride in diglyme and triglyme should make these solvents very useful for studying the reactions of sodium borohydride. The ready preparation of high purity sodium borohydride from the technical material already has eliminated a major difficulty in making quantitative studies of the reactions of sodium borohydride.

The large difference in the rate of reaction of sodium borohydride with ketones in isopropyl alcohol and diglyme is noteworthy. It indicates that the solvent must be involved in some manner in the transfer of the hydride ion to the carbonyl group.[11]



In terms of this hypothesis, the slow reaction in diglyme would be attributed to the poor donor properties of the ether oxygen atoms in the solvent molecules as compared to those of the oxygen atoms in isopropyl alcohol. On this basis, the catalytic activity of triethylamine would be attributed to the high donor properties of the nitrogen atom in the amine, with the reaction coming essentially to a halt after the transfer of the first hydride ion because of the conflicting steric requirements of the isopropoxyborohydride ion and the triethylamine.



The reaction of acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl *t*-butyl ketone reveals a decrease in rate with increasing steric requirements of the alkyl group. The borohydride reaction shows promise of providing a useful tool for the investigation of the effects of structure on the reactivity of carbonyl groups.[8,12,13]

The reaction kinetics in isopropyl alcohol show the reaction rate to be first order in borohydride and in ketone. The kinetics must mean that the first transfer of hydride must be rate-determining, with subsequent transfers occurring much faster. This conclusion can be rationalized on the basis that transfers of hydride ion from the relatively weak Lewis acids, the alkoxyborines, must be much easier than its transfer from the strong acid, borine. This effect must be sufficiently important as to overcome the expected steric hindrance effects of the accumulated isopropoxy groups on the borohydride ion.[14]

The results clearly show that under identical conditions lithium borohydride is a more powerful reducing agent than is sodium borohydride. Consequently, it must be concluded that in these reactions the chemistry of borohydride ion cannot be considered independent of the metal ion with which it is associated.[15]

Finally, the use of lithium bromide with sodium borohydride in diglyme permits the formation of a reducing system which is intermediate between sodium borohydride and the more powerful lithium aluminum hydride. The reagent should make possible a number of selective reductions not now conveniently accomplished by these two reagents.

Experimental Part

Purification of Diglyme.—Two liters of commercial diglyme (Ansul ether, No. 141) was stirred with 20 g. of calcium hydride to remove moisture. The product was distilled over calcium hydride and the fraction boiling between 160–162° at 740 mm. was collected. To the distillate there was added 10 g. of lithium aluminum hydride and the material was distilled under reduced pressure (75° at 35 mm.) under nitrogen.

Purification of Sodium Borohydride.—Commercial sodium borohydride (Metal Hydrides, Inc., and Callery Chemical Co.) was utilized. Various samples analyzed from 79 to 94% in purity. The following procedures are typical of those used for the purification through the solvate A and the unsolvated salt B.

A. Sodium borohydride, 10.1 g. (79% purity), was added to 120 ml. of freshly distilled diglyme in a dry 3-necked flask fitted with a stirrer, nitrogen inlet and outlet. The mixture was stirred for 30 minutes at 50° until the solid had dissolved except for a small amount of insoluble material. The stirring was halted, the solution permitted to settle, and the supernatant liquid was forced under nitrogen pressure through a sintered glass filter into a dry flask. The residual solution was separated from the solid by centrifugation and added to the bulk of the solution. When the solution was permitted to cool slowly from 50° to room temperature and then 0° long white needles separated. The solution was decanted from the crystals. The solvated crystals in the flask weighed 67.7 g. On pumping at 60° for 4 hr., there was obtained 7.23 g. of 99.7% sodium borohydride. Recovery of active hydrogen in the original technical product was 90%.

B. The solution of sodium borohydride in diglyme was prepared as above. The filtered solution was heated at 80°

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[11] L. W. Trevoy and W. G. Brown, This Journal, 71, 1675 (1949).

[12] Work in progress with Dr. K. Ichikawa.

[13] E. H. Jensen, "A Study of Sodium Borohydride," Nyt Nordisk Forlag, Arnold Busck, Copenhagen, 1954.

[14] We recently have succeeded in preparing sodium triisopropoxy borohydride and have demonstrated that its reaction with acetone is far greater than the corresponding reaction of the parent compound.

[15] Even in isopropyl alcohol the reaction of acetone with lithium borohydride is considerably faster than with sodium borohydride (work in progress with K. Ichikawa).

for 2 hr. A fine white precipitate was obtained. It was collected on a sintered glass filter under a nitrogen atmosphere. Residual solvent was removed from the precipitate by pumping at 60° for 2 hr. There was obtained a 78.7% yield of sodium borohydride of 99.3% purity.

Kinetic Studies of Sodium Borohydride and Ketones.—Solutions of sodium borohydride in isopropyl alcohol were standardized by the iodate method.[16] These were mixed with solutions of the ketone in the same solvent maintaining a mole ratio of $NaBH_4$/ketone of $^1/_4$. The reactions were carried out under a nitrogen atmosphere in an ice-bath. At appropriate intervals of time, aliquots were removed and analyzed for residual hydride by the iodate procedure. The rate data were treated with the aid of the expression

$$kt = x/4a(a - x)$$

where a is the initial concentration of borohydride ion and x is its concentration at time t. Typical results are shown in Fig. 1.

Determination of Solubility.—Sodium borohydride was stirred under nitrogen with isopropyl and *t*-butyl alcohol at 25 and 60°. Samples were removed and analyzed[16] for borohydride content. When the value became essentially constant, it was considered that saturation had been achieved. The results are summarized in Table II.

The 1:1 solvate of sodium borohydride with diglyme was prepared and used for the solubility determination. In a flask fitted with a mercury-sealed stirrer, nitrogen inlet and outlet there was placed 100 g. of the solvate and 40 cc. of the purified solvent. The reaction mixture was stirred at the appropriate temperature for periods of time (4–6 hr.) sufficient to attain equilibrium. Samples of the solution were removed and analyzed for sodium by titration with standard acid, using methyl red as indicator. In this way the solubility was determined at a number of temperatures as these were increased from 0 to 100° (Table III). The process was repeated in the reverse direction. The check determinations were satisfactory except at temperatures in the vicinity of the maximum solubility (Table III). Here the very high viscosity of the solutions made it difficult to achieve true equilibrium as well as to remove representative samples for analysis.

Reduction of Esters.—The various reagents were mixed in small flasks and heated under nitrogen for appropriate intervals of time. When isopropyl alcohol was used as solvent, the hydrogen evolved was collected and measured. At the end of the reaction, aqueous hydrochloric acid was added and the residual hydride determined as hydrogen. Hydride utilized in the reduction was taken as the difference between the hydrogen collected during and after the reaction and that obtained in blank runs without ester present.

A similar procedure was used for the reductions in diglyme. However, in this case hydrogen was not evolved during the course of the reaction. A portion of the results are given in Table VII.

In reductions utilizing magnesium chloride and magnesium bromide it was observed that the results depended upon the particular preparation of the halide. Thus successful reductions were achieved with anhydrous magnesium chloride prepared by heating the hexahydrate at 100° for 4 hr. and then at 175–200° for 2 hr., both in a steady stream of hydrogen chloride. Chloride analysis indicated a purity of 95%. On the other hand, commercial anhydrous magnesium chloride (Dow) specified to be 97% pure proved to be much less active.

Reduction of Ethyl *p*-Chlorobenzoate.—Sodium borohydride, 0.25 mole, and 250 cc. of diglyme were placed in a 500-ml. round-bottomed, 3-necked flask fitted with a stirrer. After the sodium borohydride had dissolved, 0.25 mole of finely ground lithium bromide was added and the mixture stirred for 30 min. To the reaction flask there was then added 0.40 mole of ethyl *p*-chlorobenzoate (b.p. 235–236° at 740 mm., $n^{20}D$ 1.5240) and the reaction mixture was heated on a steam-bath for 3 hours. The contents then were poured onto 500 g. of crushed ice containing 50 cc. of concentrated hydrochloric acid. Fine, shiny flakes of *p*-chlorobenzyl alcohol precipitated which were collected on a filter, washed with water until free of acid, dried and weighed. The product weighed 51.7 g. (91% yield), m.p. 73–74°. Recrystallization from hot water yielded 48.5 g. (85% yield), m.p. 74–75°.

Reduction of Ethyl Stearate.—In the flask were placed 0.2 mole of ethyl stearate (b.p. 198–199° at 10 mm., m.p. 31°) and 125 cc. of a 1.0 *M* solution of sodium borohydride in diglyme. To the reaction mixture was added 7.0 g. (0.07 mole) of anhydrous magnesium chloride. After stirring for several minutes at room temperature, the flask was heated on a steam-cone for 4 hr. The product was poured into a beaker containing crushed ice and hydrochloric acid. A white precipitate of 1-octadecanol was obtained. This was collected on the filter, washed and recrystallized from hot aqueous ethanol to give 20.0 g. of product, m.p. 58–59°, a yield of 74%.

Reduction of Ethyl *p*-Nitrobenzoate.—The reaction mixture was prepared as described above, using 39.5 g. (0.20 mole) of ethyl *p*-nitrobenzoate (m.p. 56–57°). The reaction mixture was stirred at room temperature for one hour, with occasional cooling to keep the temperature from rising. The contents turned reddish-brown in color. At the end of 1 hr., the flask was placed in a 40° bath and stirred for 2 hr. The temperature then was raised to 50° for 30 min. The reaction product then was poured into a beaker containing crushed ice and dilute acid. The product was extracted with ether and the ether removed. The crude material then was recrystallized twice from hot water to give 17.4 g. of *p*-nitrobenzyl alcohol, pale brown needles, m.p. 92–93°, a yield of 57%.

LAFAYETTE, INDIANA

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[16] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).