

THE IDENTIFICATION OF SOME SODIUM  
ALKOXYBOROHYDRIDES

By

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## PART I

### INTRODUCTION

In their study of the alkoxy substituted borohydrides, Brown, Mead, Shoaf, and Subba Rao (1, 2, 3, 4) have investigated the preparation and chemical properties of a number of sodium trialkoxy- and tetraalkoxyborohydrides. They found evidence that  $\text{NaBH}(\text{OMe})_3$  and  $\text{NaBH}(\text{OEt})_3$  in tetrahydrofuran solution readily disproportionate, presumably to  $\text{NaBH}_2(\text{OR})_2$  and  $\text{NaB}(\text{OR})_4$ . The corresponding triisopropoxy- and tertiary-butoxyborohydrides do not disproportionate, probably because steric hindrance prevents the formation of  $\text{NaB}(\text{OR})_4$  when R is isopropyl or tertiarybutyl (4). Indeed it is impossible to construct the tetratertiarybutoxyborohydride ion with the usual Fisher-Hirschfelder-Taylor molecular models (2).

The trialkoxyborohydrides are potentially very useful as selective reducing agents (2, 4, 7). However, the disproportionation products, whatever they may be, are almost certain to have reducing properties different from that of trialkoxyborohydride; their presence could, and probably would, circumvent the desired selectivity in a reduction. It is obviously of interest, then, to learn as much as possible about such disproportionations.

The techniques of x-ray diffraction appear to be a

good method of identifying products of the disproportionation as well as the parent compounds. Brown, Mead, and Freeman at Purdue University approached the problem in this manner, but abandoned the method in order to attack the problem from a more chemical viewpoint, attempting to separate disproportionation products by propitious choice of solvents (7). However, several excellent diffraction patterns were obtained by Freeman from samples prepared by Mead and Shoaf, and have been available to this laboratory. Brown has expressed both a willingness and a desire for this laboratory to attack the problem using x-ray diffraction techniques (5).

Investigation of this apparent disproportionation was undertaken in this research using this method, with the major emphasis to establish definitely the diffraction patterns for the stable compounds in the series  $\text{NaBH}(\text{OR})_3$  and  $\text{NaB}(\text{OR})_4$  where R represents methyl, ethyl, and isopropyl. This involved preparing the compounds, some of which are extremely sensitive to moisture, and obtaining diffraction patterns for them. Methods of preparation are readily available (2, 3).

Data for the patterns obtained are reported and are compared with those obtained by Freeman from samples prepared by Mead and Shoaf.



## PART II

### HISTORICAL

#### Preparation of Alkyl Borate Esters

There are three characteristic reactions by which the alkyl borates are usually prepared: (1) action of an alcohol on boron trichloride, (2) action of an alcohol on an oxide of boron, and (3) esterification of boric acid. Various other methods also have been used to advantage by many investigators. Some of these are modifications of the standard reactions; some are novel.

The initial attempts to use the alcohol-boron trichloride reaction were made by Ebelman and Bouquet (15, 16). Their technique, in which the reactants were heated in a sealed tube, was not very successful. In 1931 Wiberg and Sütterlin (37, 38), using the Stock high-vacuum apparatus at low temperatures, investigated the same reaction and obtained quantitative yields of the triesters with methanol and ethanol.

In 1951 Gerrard and Lappert (17) prepared tributyl and triisobutyl borates in good yields by dissolving three moles of the alcohol in pentane at  $-10^{\circ}$ , treating with one mole boron trichloride in pentane, and allowing the temperature to rise to  $15^{\circ}$ . They also refluxed one mole of a pyridine-

boron trichloride complex in chloroform with three moles of<sup>4</sup> the appropriate alcohol to obtain tritertiarybutyl borate and triacetotertiarybutyl borate (19). Lappert (29) reports that addition of one mole boron trichloride to three moles of an alcohol in the presence of three moles of pyridine at  $-10^{\circ}$  or  $-80^{\circ}$  results in good yields of the triesters.

Boron trioxide and alcohols were used by Schiff (33) in 1867 and by Counciler (10, 11, 12, 13) in 1878 to prepare several borates. The reaction required twenty-four hours in a digester, generally at a pressure of two atmospheres and temperatures of  $120^{\circ}$  to  $160^{\circ}$ . As early as 1909 boron trioxide was heated with alcohols at atmospheric pressure and  $125^{\circ}$  for twelve hours to obtain the triesters (25). In 1929, also without the aid of an autoclave, good results were obtained using a mixture of borax, hydrochloric acid, and alcohol (26). The same method was employed in 1953 using sulfuric acid instead of hydrochloric acid (32). A specially designed rotating autoclave has permitted reduction of the reaction time from twenty-four to six hours. Yields were also increased (9, 18). Dupire (14) in 1936 refluxed a mixture of boron trioxide and an alcohol with an inert solvent such as toluene, and allowed the condensate to percolate through anhydrous copper sulfate, held in a thimble of a Soxhlet extractor, to remove the water formed.

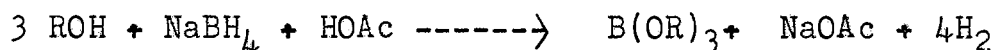
Esterification of boric acid with propyl alcohol to prepare tripropyl borate in 90% yield was reported by

Wuyts and Duquesne (39). Some investigators (38) report that tertiary alcohols do not esterify with boric acid, but Lippincott (30) reported preparing neutral borates of tertiary alcohols by esterification by removing the water formed as an azeotrope with benzene, toluene, petroleum naphtha, or carbon tetrachloride. Removal of water as an azeotrope in esterification was used by other workers about the same time and subsequent to Lippincott's patent (21, 22).

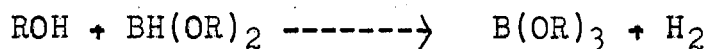
Miscellaneous reactions have been used to prepare borate esters. Examples are: heating dialkylchloroborinates with zinc dust or sodium metal (27), or with trimethylamine (38), to effect disproportionation. Heating tetraalkoxysilanes with boric acid or one of its salts results in the formation of trialkyl borates and silicon dioxide (28). Trimethyl and triethyl borate have been prepared by warming to  $-80^{\circ}$  a frozen equimolar mixture of trialkoxysilane and boron tribromide (28).

Pictet and Geleznoff (32) in 1903 reacted boron triacetate, the mixed anhydride of boric and acetic acids, with an alcohol slightly above room temperature; the ester was recovered by fractional distillation. The method was rapid. Kahovec (24) in 1939 used this method to prepare tritertiarybutyl borate. Others also used similar methods for preparing higher borates from lower ones (9, 18, 20, 39).

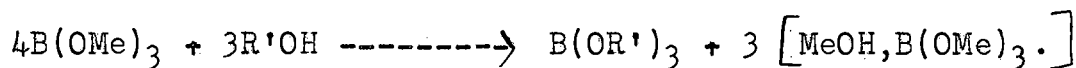
In the presence of one equivalent of acetic acid primary and secondary alcohols react smoothly with sodium borohydride at room temperature according to the reaction:



Tertiary alcohols under the same conditions liberate but three moles of hydrogen, the fourth being released only at higher temperatures (3):



Schiff (33) in 1867 was the first to use alcoholysis for the preparation of trialkyl borates. Trimethyl borate is now readily available and the transesterification by an alcohol proceeds according the equation:



The low boiling point of the methanol-methyl borate azeotrope (54.5°) provides a means of shifting the reaction to completion (3). However, because of the formation of considerable amounts of mixed esters, yields are not too good.

#### Preparation of the Salts of Alkyl Borates

The earliest preparation of the salts of alkyl borates seems to have been done by Cambi (8). He reacted an alkali metal alkoxide with a trialkyl borate to prepare sodium and potassium tetraalkoxyborohydrides. Potassium was replaced by lithium when the tetraalkoxyborohydride in methanol reacted with lithium chloride. Thallium replaced potassium when the tetraalkoxyborohydride reacted with thallium acetate. Calcium metal dissolved in trimethyl borate in methanol to form calcium tetramethoxyborohydride (8).

The most extensive investigations with the complex salts have been reported since 1953. Sodium hydride reacts at moderate temperatures with methyl, ethyl, and butyl borates to form sodium hydride--trialkyl borate adducts which are white, stable solids (3).

Sodium tetraalkoxyborohydrides are prepared by reaction of equimolar amounts of borate ester with the corresponding sodium alkoxide. Sodium is first dissolved in the alcohol under a dry nitrogen atmosphere. The borate is then added at a rate slow enough to avoid sharp rises in temperature (2).

Sodium borohydride reacts readily with both methanol and ethanol at their boiling points to form the corresponding tetraalkoxy salt (3):



PART III  
EXPERIMENTAL

I. Chemicals and Reagents

The sodium borohydride, a product of Metal Hydrides Inc., of Beverly, Mass., was labeled 98% and was used without further purification.

Sodium hydride and trimethyl borate were also products of Metal Hydrides Inc., but were not labeled as to purity. They were used without purification.

Portions of Fisher research grade methanol and Mathieson, Coleman, and Bell white label 2-propanol were purified immediately before each use by distilling three times from fresh calcium hydride through a twelve-bubble Snyder column directly into the reaction flask. The only opening to the atmosphere was protected by an activated alumina drying agent.

Pure absolute ethanol from U. S. Industrial Chemicals Co. was used. The first portion taken from a sealed bottle was used without purification, but subsequent portions were dried as described for methanol.

Tetrahydrofuran from Eastman (yellow label-purity not specified) was allowed to stand several hours over potassium hydroxide pellets and then twice distilled from fresh pellets and once from calcium hydride.

The glacial acetic acid was Fisher reagent grade.

The standard hydrochloric acid solution was prepared by dilution of Baker and Adamson reagent grade concentrated hydrochloric acid, and was standardized against recrystallized borax (sodium tetraborate decahydrate, Fisher reagent grade) using methyl red as an indicator.

The sodium hydroxide solution was prepared by dilution of Fisher reagent 5N solution, and standardized against potassium hydrogen phthalate using phenolphthalein as an indicator. It was stored in a polyethylene bottle equipped with a soda-lime tube.

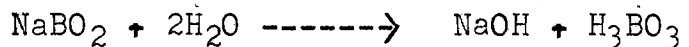
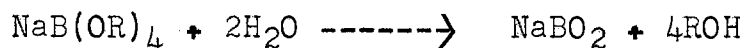
The mannitol from Brothers Chemical Co. was not labeled as to grade.

## EXPERIMENTAL

### II. Analytical Procedure

The method used in the titration of the tri- and tetra-alkoxyborohydrides was that of Brown, Mead and Shoaf (3).

Sodium determinations were obtained by measuring the total base obtainable after hydrolyzing a weighed sample in distilled water by titrating with standard hydrochloric acid (0.1 N) to a methyl red end-point (approx. pH 5.3). Boron was then determined by adding mannitol and back-titrating with standard base (0.1 N NaOH) to a phenolphthalein end-point (pH 7.8 to 8.0). The addition of mannitol causes boric acid to titrate as though monobasic.



For the standardization of the hydrochloric acid, borax was recrystallized twice from distilled water, and dried at 105° until a constant weight was obtained. With continuous magnetic stirring, an accurately weighed sample of borax was titrated from a 50-ml. burette, estimating to the nearest 0.02 ml. The weight of sample was large enough so that more than 10 ml. of titrant was required; thus



the normality could be expressed with four significant figures and accurate to three digits. Each analytical weight used was calibrated against a set of class M weights and corrections applied when necessary.

## EXPERIMENTAL

### III. Preparations

The methods used to prepare these compounds are those of Brown, Mead, and Shoaf (2, 3).

Sodium tetramethoxy- and tetraethoxyborohydride may be prepared by two procedures:

(1) the reaction of equimolar amounts of the trialkyl borate ester and the metal alkoxide and (2) the reaction of the corresponding alcohol and sodium borohydride at the boiling point of the alcohol. The procedure based on sodium borohydride was chosen because it offered considerable advantage in yield, ease of operation, and convenience.

#### A. Preparation of sodium tetramethoxyborohydride.

A 6.25-gram sample of sodium borohydride was placed in a 100-ml. round-bottom flask equipped with a teflon-covered stirring bar. A 55-ml. sample of methanol was distilled into the flask. After introducing a positive pressure of dry nitrogen to exclude atmospheric moisture, the flask was connected to an apparatus which consisted of a Claissen head and condenser leading to a fraction cutter. The outlet to the cutter was equipped so that it could be opened either to the atmosphere or to a trap, manometer, and

vacuum pump. Heating was done by a Glas-Col mantle sitting on a magnetic stirrer so that continuous stirring could be obtained. The methanol-sodium borohydride slurry was heated to the boiling point at atmospheric pressure with the outlet protected by a drying tube. Gentle reflux was continued until reaction had ceased. The excess methanol was then taken off at reduced pressure and a white solid remained.

While introducing a positive pressure of dry nitrogen, the reaction flask was disconnected from the apparatus and kept closed to the atmosphere. In a dry box, the white crystalline solid was quickly powdered in an agate mortar and bottled. A portion was sealed in a capillary for the x-ray powder study, and another portion was analyzed for sodium and boron content. Calculated for  $C_4H_{12}O_4BNa$ :

Na, 14.55; B, 6.85. Found: Na, 14.48; B, 6.84.

B. Preparation of sodium tetraethoxyborohydride.

While flooding the flask with a positive pressure of dry nitrogen, a 4.1-gram sample of sodium borohydride was quickly added to 150 ml. of absolute ethanol in a 250-ml. flask connected to the apparatus described above. After the slurry had refluxed twelve hours, no solid sodium borohydride remained. Excess ethanol was removed at reduced pressure and a white crystalline solid remained. It was heated at reduced pressure for several hours to insure dryness, and in the dry box it was powdered and bottled. An x-ray capillary was prepared and a portion

of the material was analyzed. Calculated for  $C_8H_{20}O_4BNa$ : Na, 10.74; B, 5.05. Found: Na, 10.90; B, 5.04.

C. Preparation of sodium tetraisopropoxyborohydride.

One gram of sodium metal was dissolved in excess 2-propanol at its boiling point in a flask protected from the atmosphere. To assure that all alkoxide would be reacted, a slight molar excess of triisopropyl borate (8.15 grams, 10.8 ml.) was added from a closed dropping funnel. A white, gelatinous precipitate formed immediately. The excess alcohol was removed at reduced pressure. There remained a white crystalline solid which was powdered and bottled in the dry box. An x-ray capillary was prepared and a portion of the material was analyzed. Calculated for  $C_{12}H_{28}O_4BNa$ : Na, 8.52; B, 4.01. Found: Na, 9.10; B, 4.27.

D. Preparation of sodium triisopropoxyborohydride.

One gram of sodium hydride was added to 20 ml. (slight molar excess) of triisopropyl borate in 100 ml. of dry tetrahydrofuran as an inert medium. This was refluxed for 168 hours, after which time the tetrahydrofuran was removed at reduced pressure. There remained a white solid which was powdered and bottled in the dry box. An x-ray capillary was prepared and a portion of the material was analyzed. Calculated for  $C_9H_{22}O_3BNa$ : Na, 10.85; B, 5.11. Found: Na, 10.45; B, 5.08.

E. Preparation of triisopropyl borate.

A 15.66-gram sample of sodium borohydride was added to 175 ml. of 2-propanol in a three-necked flask connected to the Snyder column. With continuous stirring by an iron bar and magnetic stirrer, a 24-ml. portion of glacial acetic acid was added at a slow rate from a pressure-equalized dropping funnel. The slurry was refluxed eighteen hours; the hydrogen evolved was measured through a gas flowmeter and vented into the hood. Excess 2-propanol was distilled at atmospheric pressure and the remaining product was fractionated through the twelve-bubble Snyder column. A 60-ml. cut taken at 74-76° and 75 mm. Hg was retained for preparations.

## EXPERIMENTAL

### IV. Equipment

The x-ray source was a Norelco x-ray diffraction unit (type 12045/3) adapted for Debye-Scherrer powder cameras of 114.59-mm. diameter. During all exposures, a copper target and a nickel filter were used at 35 kilovolts and 20 milliamps.

Patterns were measured on a Norelco "film illuminator-measuring device" type no. 52022.

X-ray capillaries were prepared in the dry box by dipping the open end of the capillary tube into the powdered material. Vibrations, set up by rasping the capillary tube with a file, caused the material to be packed into the closed end of the tube. Immediately upon removal of the tube from the dry box, the open end was sealed with a small flame of a micro burner. The tube was aligned in the camera in the usual manner.

After exposure from two to four hours, the films were developed five minutes (according to contrast desired), fixed for twenty minutes, and washed for two hours. After drying, each was labeled and placed in a protective cellophane cover.

Measurement was done in the usual manner for Straumanis film mounting. Values were calculated for  $2\theta$  (correction for shrinkage was 1.0043),  $\theta$ ,  $\sin \theta$ ,  $\sin^2 \theta$ ,  $d$ , and  $1/d^2$ .

## PART IV

### RESULTS AND CONCLUSIONS

X-ray diffraction data obtained in this research are reported in tables V through XIV. A comparison of values of  $\text{Sin}^2 \theta$  is listed in tables I through IV. These show close agreement between the patterns of compounds prepared in this research and those of compounds prepared by Mead and Shoaf. Only sodium tetramethoxy- and tetraethoxyborohydrides could be prepared by the two methods mentioned on page 12.

The sodium tetramethoxyborohydride listed on the left in Table I was prepared by method two on page 12. The results of the analysis are reported on page 13. These represent a deviation of 0.5% from the calculated value for sodium and 0.15% for boron. The compound prepared by the interaction of sodium methoxide and trimethyl borate (method one page 12) contained 13.27% sodium (8.2% deviation) and 6.48% boron (5.4% deviation). However, none of the major lines is missing, although fewer lines were present in the pattern, and it is not seriously altered. All except three lines are common to the other two patterns.

The preparation and analysis of the compound listed on the left in table II is given on page 13 and 14. The result of the analysis shows a deviation of 1.5% for sodium and

0.2% for boron. The pattern for the sample listed in the center of the table shows good agreement for the lines that are present. However, three major lines are missing. Since the results of analysis showed 12.8% sodium (19% deviation) and 6.22% boron (23% deviation), considerable hydrolysis may have taken place prior to or during the x-ray exposure. Exceptional agreement of the major lines for the other two patterns is noteworthy.

The results of the analysis for sodium tetraisopropoxyborohydride in table III are reported on page 14. A deviation of 6.8% for sodium and 6.5% for boron is considered acceptable for such a hindered molecule. Five major lines are in excellent agreement.

The analysis of sodium triisopropoxyborohydride reported on page 14 reveals a deviation of 3.7% for sodium and 0.59% for boron. Although this compound is stable toward disproportionation, it seems to be the most sensitive to hydrolysis by moisture and requires the greatest care in handling. The values of table IV show the least agreement of the compounds investigated. The results of this research indicate the patterns for the tetraisopropoxy and triisopropoxy salt to be practically identical, but the chemical analysis leaves little doubt that the patterns were of the indicated compounds.

Considering the difficulties involved in handling these compounds and their sensitivity toward atmospheric



moisture, the deviations in sodium and boron content are within allowable limits, with the exception of the sodium tetraethoxyborohydride reported in table II and IX. This was listed to show that some correspondence to other patterns is retained even when considerable hydrolysis takes place. In other cases where the deviations were of the order of plus or minus 5%, the patterns were not seriously altered, confirming the conclusion that the patterns are of the specified compounds.

Table I

Comparison of  $\text{Sin}^2 \theta$  Values of Sodium Tetramethoxyborohydride

<u>Prepared from <math>\text{NaBH}_4 + \text{MeOH}</math></u>	<u>Prepared from <math>\text{NaOMe} + \text{B(OMe)}_3</math></u>	<u>Prepared by Mead and Shoaf</u>
0.0177	0.0184	0.0183
0.0203	0.0208	0.0211 0.0216
0.0229	0.0238	
0.0256	0.0262	
0.0277	0.0278	
0.0308	0.0315	0.0310
0.0338	0.0345	0.0345
0.0364	0.0371	0.0377
0.0404	0.0408	0.0404
0.0457		0.0425
0.0487		0.0499
	0.0537	
0.0569	0.0585	0.0577
0.0652	0.0636	0.0661
0.0723		0.0741
0.0778		0.0788
0.0864		0.0894
0.0945		0.0955
0.0986		0.0991
0.1060		0.1071
0.1114		0.1126

Table II

Comparison of  $\sin^2 \theta$  Values for Sodium Tetraethoxyborohydride

<u>Prepared from</u> <u>NaBH<sub>4</sub> + EtOH</u>	<u>Prepared from</u> <u>NaOEt + B(OEt)<sub>3</sub></u>	<u>Prepared by</u> <u>Mead and Shoaf</u>
0.0370		0.0380
0.0418		0.0418
0.0561		0.0564
0.0670		0.0683
0.0723		0.0732
0.0821	0.0826	0.0821
0.0965	0.0975	0.0975
0.1119	0.1169	0.1126
		0.1215
0.1355		0.1363
0.1452		0.1452
	0.1602	
0.1693	0.1641	0.1693
	0.1733	
0.1853	0.1813	0.1846
	0.1949	0.1908
0.2146	0.2146	0.2146
0.2248	0.2247	0.2247
	0.2306	
0.2424	0.2365	0.2424
0.2500		0.2515
0.2606	0.2621	0.2606
	0.2668	

Table III

Comparison of  $\sin^2 \theta$  Values for Sodium Tetraisopropoxyborohydride

<u>Prepared from</u> <u>NaOi-Pr + B(Oi-Pr)<sub>3</sub></u>	<u>Prepared by</u> <u>Mead and Shoaf</u>
0.0320	0.0321
0.0345	0.0340
	0.0358
0.0525	0.0530
0.0593	0.0602
0.0723	0.0718
	0.0746
0.0797	
0.1092	
0.1147	

Table IV

Comparison of  $\sin^2 \theta$  Values for Sodium Triisopropoxyborohydride

<u>Prepared from</u> <u>NaH + B(Oi-Pr)<sub>3</sub></u>	<u>Prepared by</u> <u>Mead and Shoaf</u>
	0.0239
	0.0278
0.0320	0.0308
0.0345	
	0.0457
	0.0482
0.0525	0.0545
0.0593	
	0.0670
0.0723	0.0741
0.0806	

Table V

## X-Ray Powder Diffraction Data for Sodium

Tetramethoxyborohydride Prepared from  $\text{NaBH}_4 + \text{MeOH}$ 

<u>Line no.</u>	<u>Intensity*</u>	<u>d</u>	<u><math>\text{Sin}^2 \theta</math></u>
1		5.78	0.0177
2		5.40	0.0203
3		5.08	0.0229
4	2	4.81	0.0256
5	2	4.66	0.0272
6	1	4.38	0.0308
7		4.18	0.0338
8		4.03	0.0364
9		3.83	0.0404
10		3.60	0.0457
11	4	3.49	0.0487
12	3	3.23	0.0569
13		3.01	0.0652
14		2.86	0.0723
15	6	2.76	0.0778
16		2.62	0.0864
17		2.50	0.0945
18	5	2.45	0.0986
19	5	2.36	0.1060
20		2.30	0.1114
21		2.27	0.1147

\* The lowest number signifies the most intense line.

Table VI

X-Ray Powder Diffraction Data for  
Sodium Tetramethoxyborohydride  
Prepared from NaOMe + B(OMe)<sub>3</sub>

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u>sin<sup>2</sup> <math>\theta</math></u>
1		5.68	0.0184
2		5.33	0.0208
3		5.00	0.0238
4	1	4.75	0.0262
5		4.60	0.0278
6	2	4.34	0.0315
7		4.14	0.0345
8		4.00	0.0371
9	4	3.81	0.0408
10		3.33	0.0537
11		3.18	0.0585
12	3	3.05	0.0636

Table VII  
 X-Ray Powder Diffraction Data for  
 Sodium Tetramethoxyborohydride  
 Prepared by Mead and Shoaf

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u><math>\sin^2 \theta</math></u>
1		5.68	0.0183
2		5.30	0.0211
3	1	5.23	0.0216
4	2	4.37	0.0310
5		4.14	0.0345
6		3.86	0.0377
7		3.83	0.0404
8		3.73	0.0425
9		3.45	0.0499
10	4	3.20	0.0577
11	3	2.99	0.0661
12		2.82	0.0741
13		2.74	0.0788
14		2.57	0.0894
15		2.49	0.0955
16		2.44	0.0991
17	5	2.35	0.1071
18		2.29	0.1126



Table VIII  
 X-Ray Powder Diffraction Data for  
 Sodium Tetraethoxyborohydride  
 Prepared from  $\text{NaBH}_4 \cdot \text{EtOH}$

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u><math>\text{Sin}^2 \theta</math></u>
1	1	3.99	0.0370
2	1	3.76	0.0418
3	3	3.25	0.0561
4		2.97	0.0670
5	4	2.86	0.0723
6	2	2.69	0.0821
7	6	2.48	0.0965
8		2.29	0.1119
9	5	2.09	0.1355
10		2.02	0.1452
11		1.87	0.1693
12		1.79	0.1853
13		1.66	0.2146
14		1.62	0.2248
15		1.56	0.2424
16		1.54	0.2500
17		1.51	0.2606

Table IX

X-Ray Powder Diffraction Data for

Sodium Tetraethoxyborohydride

Prepared from NaOEt + B(OEt)<sub>3</sub>

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u>Sin<sup>2</sup> <math>\theta</math></u>
1	1	2.68	0.0826
2		2.60	0.0874
3		2.46	0.0975
4	2	2.25	0.1169
5		1.92	0.1602
6		1.90	0.1641
7	3	1.85	0.1733
8		1.81	0.1813
9		1.74	0.1949
10		1.71	0.2044
11		1.66	0.2146
12		1.62	0.2247
13		1.60	0.2306
14		1.58	0.2365
15		1.50	0.2621
16		1.49	0.2668

Table X  
X-Ray Powder Diffraction Data for  
Sodium Tetraethoxyborohydride  
Prepared by Mead and Shoaf

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u>Sin<sup>2</sup> <math>\theta</math></u>
1	1	3.95	0.0380
2	1	3.76	0.0418
3	3	3.24	0.0564
4		2.94	0.0683
5	4	2.84	0.0732
6	2	2.68	0.0821
7		2.46	0.0975
8		2.29	0.1126
9		2.21	0.1215
10	5	2.08	0.1363
11		2.02	0.1452
12		1.87	0.1693
13		1.79	0.1846
14		1.76	0.1908
15		1.66	0.2146
16		1.62	0.2248
17		1.56	0.2424
18		1.53	0.2515
19	6	1.51	0.2606

Table XI

X-Ray Powder Diffraction Data for  
Sodium Tetraisopropoxyborohydride  
Prepared from ~~NaO*i*-Pr~~ + B(O*i*-Pr)<sub>3</sub>

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u>Sin<sup>2</sup> <math>\theta</math></u>
1	2	4.30	0.0320
2	1	4.14	0.0345
3	4	3.36	0.0525
4	5	3.16	0.0593
5	3	2.86	0.0723
6		2.72	0.0797
7		2.33	0.1092
8		2.27	0.1147

Table XII  
X-Ray Powder Diffraction Data for  
Sodium Tetraisopropoxyborohydride  
Prepared by Mead and Shoaf

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u>Sin<sup>2</sup> <math>\theta</math></u>
1	1	4.30	0.0321
2	2	4.18	0.0340
3	3	4.07	0.0358
4	4	3.34	0.0530
5	5	3.14	0.0602
6	5	2.87	0.0718
7		2.82	0.0746

Table XIII  
 X-Ray Powder Diffraction Data for  
 Sodium Triisopropyborohydride  
 Prepared from  $\text{NaH} \cdot \text{B}(\text{O}i\text{-Pr})_3$

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u><math>\sin^2 \theta</math></u>
1	2	4.30	0.0320
2	1	4.14	0.0345
3	4	3.35	0.0525
4	5	3.15	0.0593
5	3	2.86	0.0723
6		2.70	0.0806

Table XIV  
X-Ray Powder Diffraction Data for  
Sodium Triisopropoxyborohydride  
Prepared by Mead and Shoaf

<u>Line no.</u>	<u>Intensity</u>	<u>d</u>	<u><math>\sin^2 \theta</math></u>
1		4.97	0.0239
2	2	4.61	0.0278
3	1	4.39	0.0308
4		3.60	0.0457
5	4	3.50	0.0482
6		3.30	0.0545
7	3	2.97	0.0670
8		2.82	0.0741

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