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Abstract

Tri-n-propylborane and tricyclopropylborane have been prepared by the action of the appropriate Grignard reagent on borontrifluoride etherate. The Grignard reagents were prepared by the action of the appropriate alkylbromide on magnesium metal. The purification of the alkylboranes was effected by distillation directly from the generator flask and redistillation of the higher boiling material with the final collection of the maximum boiling fraction. Little difference was noticed in the reactions except that the reaction of cyclopropylbromide with magnesium metal required a short initiation period, whereas the n-propylbromide reaction was spontaneous. The previously planned tests for determining the relative acidity of the two compounds were not carried out due to a lack of time.

INTRODUCTION

In recent years, there has been considerable interest in the chemistry of organoboranes (1-15, 17,22,24). Many studies have been devoted to these compounds as acids to test the relative base strengths and effect of steric strain on the borane-donor adducts (1-6). Also much attention has been directed toward the determination of the thermal stability and stability toward oxidation of alkylboranes (7-11, 14,15). However, most of this work has utilized the methyl, halo-methyl, ethyl and a few of the higher alkylboranes.

Some work has been done with the propylboranes, but only as relatively small parts of larger studies (2, 8, 10-13, 16). Furthermore, no work at all has been done in the comparison of the acid strengths of the tripropylboranes. In fact, cyclopropylborane has only been reported once, and was not well-characterized (13).

Because of the greater inductive effect and steric hindrance of the more branched alkyl groups, the order of acidity of the propylboranes, from weakest to strongest, should be, isopropylborane < cyclopropylborane < n-propylborane.

Methods of Determining Relative Acidities

The basis for the acid properties of trialkylboranes is the fact that they possess a sextet of electrons in the vicinity of the boron atom and exhibit a strong tendency to share an electron-

pair with a base, a donor compound, thereby achieving a more stable octet of elections (17). According to the Lewis theory, an acid is an electron-pair acceptor and a base is an electron-pair donor. The acid strength of the acceptor, all other conditions being the same, will be directly proportional to the strength of the boron-donor (B-D) bond. Therefore, to determine the relative acidities of a group of compounds, one need only determine the relative strength of the bond formed between each compound and a referance donor compound.

There are three classical methods for determining the relative bond strengths of addition compounds.

1. Displacement Reactions

Displacement reactions are the simplest means of qualitatively determining relative bond strengths of addition compounds. This method consists, simply of preparing one of the addition compounds, and bringing it into contact with each of the other reactant acids to be tested. The products of these interactions are then analyzed. If the original addition compound is still present in the greatest percentage, it is said to be the one with the stronger B-D bond. However, if the majority of the original acid in the addition compound is displaced, the newly formed addition compound is said to have the stronger bond.

Subsequent reactions are conducted using each possible combination of addition compounds and acids.

2. Gas Phase Thermal Dissociation

Gas phase thermal dissociation study of adducts is one way
of quantitatively determining the relative strengths of the B-D
bonds. Through such investigations, the degree of dissociation,
α, can be determined. From α, Kp, the equilibrium constant,
and ΔH, the heat of dissociation of the B-D bond can be calcu-
lated. This produces three good values for the comparison of the
B-D bond strengths.

There are two methods for making these determinations, "The
Method of Matched Samples", developed by Brown, Taylor, and
Gerstein (18), and "The Method of Approximations", developed by
Brown and Gerstein (19).

(a) "The Method of Matched Samples"

In this method the volumes of two dissociation tensimeters
are matched to within 1 part in 2000. The two compounds are indi-
vidually measured out, one in each tensimeter, at a temperature
and pressure such that van der Waals deviations are negligible.
The sizes of two samples are adjusted until the pressures are equal
to within 1 part in 2000. With the aid of liquid nitrogen the
more volatile of the two compounds is quantitatively transferred
into the tensimeter holding the second component. The two compo-
nents react to form the addition compound. The temperature is
then raised until the material is completely volatilized and

measurements of the pressures exerted by the gaseous products are made at a number of temperatures.

The data obtained permit calculation of α , Kp and ΔH. Using this method one can determine Kp and ΔH with a high degree of precision. However, there are certain disadvantages. (1) The two samples must be matched to within 1 part in 2000. Thus, samples of 20.00 mm. must be matched to within 0.01 mm. This operation is quite tedious. (2) The lowest pressure then can be measured accurately on a manometer is in the neighborhood of 20.00 mm. The minimum pressure exerted by a highly dissociated addition compound, synthesized from two samples of this magnitude, will be in the neighborhood of 40.00 mm. However, to avoid deviation from the perfect gas laws, it would often be desirable to measure the dissociation pressures in a lower pressure range, particularly in the case of addition compounds of relatively low volatility. (3) Impurities of the order of 0.1% in either of the two components may not be detected and can seriously affect the accuracy of the data (19).

<center>(b) "The Method of Approximations"</center>

This method is based upon the assumption that over the relatively short temperature range that the dissociation is usually studied, the heat of dissociation, ΔH , may be considered to be constant. Therefore, the correct value for the size of the sample

yields a linear relationship between log Kp and 1/T as required
by the equation:

$$\frac{d \ln Kp}{d \ 1/T} = - \ \frac{\Delta H}{R}$$

In this procedure the two components are purified using only
relatively simple precautions. A sample of the addition compound
is synthesized, purified by distillation in the high vacuum appa-
ratus, and introduced into the tensimeter. The temperature is
raised until the sample is completely vaporized. A series of 8
to 10 pressure measurements is then made, usually at 5°C inter-
vals.

A value for the size of the sample is chosen arbitrarily and
used to calculate the equilibrium constant for five different tem-
peratures, approximately evenly spaced over the temperature range.
If the size selected for the sample is too low, a curve drawn
through the calculated equilibrium constants in the usual log K vs.
1/T graph will be concave upward. If the size selected is too
high, the curve will be concave downward. The value for the sample
size is then varied until the calculated equilibrium constants
yield a straight line.

A small fraction of the addition compound may be distilled
away and the determination repeated. If the addition compound is
of satisfactory homogeneity, the results of the two determinations
will be in good agreement (19).

3. Calorimetry

When vapor phase measurements are not applicable, other methods must be employed to determine ΔH. Calorimetry has been used successfully in determinations of ΔH of liquid or solid addition compounds formed from gaseous or liquid reactants (20, 21, 22).

Special calorimeters have been developed for special conditions. Brown and Horowitz developed a mercury-well calorimeter for use in determining the ΔH of liquid reactants forming solid or liquid adducts (20). This calorimeter consists of a glass dewar flask with a pool of mercury in the bottom. A central receptacle dips into the mercury, thus producing two individual compartments. When the temperature has been equalized and the dewar flask evacuated, the reactants are mixed by raising and lowering the central cylinder at a uniform rate.

Another type of calorimeter was developed by Brown and Gintis to handle gaseous and liquid reactants (21). This calorimeter consists of a glass dewar flask with an inner metallic reaction chamber connected to it by metal to glass seals. The liquid reactant is placed in the metallic chamber, the temperature equalized, the air evacuated from the dewar flask, and then the gaseous reactant is allowed to pass into the chamber under its own pressure.

In our work, we employed a modification of the process for preparing alkylboranes first developed by Kraus and Nitsche (25). This modification, employing the appropriate alkylbromide and

magnesium to form a Grignard reagent, which is then reacted with borontrifluoride etherate to form the alkylborane, was used by Long and Dollimore to prepare tri-n-propylborane (12).

$$R\text{-}Br + Mg \longrightarrow R\text{-}MgBr$$
$$R\text{-}MgBr + BF_3 \longrightarrow R_3B + MgBrF$$

We found it most fruitful to purify the alkylborane by distilling the liquid directly from the reaction flask followed by redistillation of the higher boiling material.

Through this procedure we were able to prepare, in good yields, both the tri-n-propyl and tricyclopropylboranes.

We originally planned to form the pyridine adducts of these compounds and subject these adducts to displacement reactions and vapor phase dissociation tests. With the data thus obtained, the relative acidity of the two compounds could be determined.

However, because of a late start, caused by the changing of my topic in December, and an illness which caused termination of work on April 17, the original goals were not realized. Instead we were able only to accomplish the preparation of the two compounds.

Experimental

Preparation of n-propylbromide.

To a 250 ml roundbottom flask was added 52.7 ml (0.7 moles)

of n-propanol, 72.1 g. (0.7 moles) of sodium bromide and 90 ml of water. The flask was then chilled in an ice bath. Concentrated sulfuric acid (70.0 ml) was added to the flask slowly with constant stirring. A reflux condenser was attached and the flask was heated with a heating mantle. The mixture was refluxed moderately for 55 minutes. The condenser was then replaced with a distillation apparatus and the mixture distilled. The fraction boiling between 70.0^{o}C and 72.0^{o}C was collected, washed with water, concentrated sulfuric acid, 10% sodium hydroxide solution, and then redistilled from calcium chloride. The fraction boiling between 70.5^{o}C and 71.5^{o}C was collected. Pure n-propylbromide boils at 70.9^{o}C (26).

Preparation of tri-n-propylborane.

(a) Preparation of n-propylmagnesiumbromide

A 50 ml, 3-necked, pearshaped flask was equipped with 25 ml dropping funnel, reflux condenser, and a magnetic stirrer. Magnesium turnings (2.3 g, 0.098 moles) and 5 ml diethyl ether were placed in the flask. A solution of n-propylbromide (10 g, 0.072 moles) in 10 ml of diethyl ether was put in the dropping funnel. The bromide solution was then added dropwise with constant stirring at such a rate as to keep the mixture refluxing smoothly (approximately 15 minutes). When the reaction subsided, a heating mantle was inserted and the reaction mixture refluxed for 45 minutes (variac setting: 25v). The supernatent solution was drawn off for use in part (b).

(b) Preparation of tri-n-propylborane.

The solution from part (a) and 5 ml of ether were added
to a 50 ml, 3-necked flask filled with dry nitrogen and equipped
with a dropping funnel, reflux condenser, and magnetic stirrer.
Borontrifluoride etherate (5.0 ml, 0.025 moles) and 5 ml of ether
were put in the dropping funnel. The etherate was added to the
reaction flask dropwise with stirring at such a rate as to keep
the mixture refluxing moderately. When the reaction subsided,
a heating mantle was inserted and the mixture refluxed for 45
minutes.

Two methods were used to purify the tri-n-propylborane. In
the first method the mixture was allowed to cool after the reflux,
then hydrolyzed with a solution of 20 ml of concentrated hydro-
chloric acid in 80 ml of water. This destroyed the excess
Grignard reagent. The resulting two phase solution was syphoned
into a separatory funnel, and the water layer drawn off. The
ether layer, containing the borane, was transferred into a one
piece distillation apparatus (consisting of a short stillhead,
a condenser, and an adapter) which had previously been filled with
dry nitrogen. The system was connected to a mercury blow-out
manometer to allow air free distillation at atmospheric pressure.
The ether solution was then distilled. However, in many attempts
to isolate the tri-n-propylborane through this procedure negli-
gible yields were obtained. In the second, and more successful

method, the mixture was cooled after reflux, and the reflux con-
denser replaced with a nitrogen filled distillation apparatus.
This apparatus consisted of a short stillhead, condenser, adapter,
and a "cow" fitted with four collection flasks. The apparatus
was again attached to the manometer and the mixture distilled to
dryness. The fraction boiling above 100°C was collected for
further purification. The maximum temperature of this distilla-
tion was approximately 125°C. This high boiling material was re-
distilled in a similar apparatus with the material boiling be-
tween 155°- 157°C being collected. Pure tri-n-propylborane boils
at 156°C (26).

Preparation of tricyclopropylborane.

(a) Preparation of Cyclopropylmagnesiumbromide.

This preparation was effected using a similar apparatus and
procedure to that used for tri-n-propylborane. In this case 9.69 g
(0.0802 moles) of cyclopropylbromide and 2.5 g (0.103 moles) of
magnesium turnings were used to prepare the Grignard reagent.
However, to initiate the reaction, approximately one-half of the
bromide solution was added to the magnesium turnings and the mix-
ture heated for 10 minutes. After the initiation of the reaction,
the remainder of the previous procedure was followed.

(b) Preparation of Tricyclopropylborane.

For this preparation the previously prepared Grignard re-
agent and 5 ml (0.023 moles) of borontrifluoride etherate were
used and the procedure for the preparation of tri-n-propylborane
was followed. In the purification process, the first fraction
collected boiled between 58°C and 120°C. In the final purifi-
cation the maximum boiling fraction was collected; boiling point
124°C.

Results and Discussion

Though the original goals of the project were not realized,
we do believe that some progress was made. The major difficulty
was the inability to obtain significant yields with a procedure
previously producing good yields (7, 12). This failure was proba-
bly caused by the use of an inadequate distillation apparatus.
It is now believed that the apparatus used was not designed to
distill liquids as viscous as the ones we attempted to distill.
It seems that the distillate might have blocked the narrow adapt-
er delivery tube, so that equilibrium was never established in
the system.

The chief contribution of this work, we believe, is the pre-
paration of tricyclopropylborane in a manner not previously applied
to its preparation. Though we have no absolute criterion of
purity, we believe that we have prepared the cyclopropyl compound
through a slight modification of the classical method used by

Long and Dollimore to prepare tri-n-propylborane. The only modi-
fication we employed was the use of a short (approximately 10
minutes) heating period necessary to initiate the reaction form-
ing the cyclopropylmagnesiumbromide.

The necessity of the initial heating in the Grignard reaction,
which with the n-propyl compound is spontaneous, seems to indicate
that the cyclopropyl group is less reactive. In a study of the
n-propyl versus cyclopropylphosphenes, Denny and Gross indicated
that both groups seemed to produce equal inductive effects (27).
In this light, it seems most likely, that the inactivity we experi-
enced was caused by the increased steric hindrance of the cyclo-
propyl group.

As was mentioned before, we were not absolutely sure of the
purity of our products. However, had time permitted, we had
planned to purify the alkylboranes by a displacement process.
This procedure would have consisted of preparing a convenient ad-
duct of the alkylboranes, and using diborane, a stronger acid,
to displace the alkylboranes, producing the diborane adduct and
the pure alkylboranes. With these purified alkylboranes, the pre-
viously described tests for acidity were to be carried out to
determine the relative acidity of the propylboranes.

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