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A Novel Method for the Preparation of Diborane from Aluminum, Ethyl Chloride, Boron Oxide and Hydrogen**

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ABSTRACT

A novel method is described for the preparation of diborane from aluminum, ethyl chloride, boron oxide and hydrogen via three steps; deoxyalkylation of boron oxide, hydrogenation of triethylboron and liberation of diborane. The triethylboron was prepared from aluminum, ethyl chloride and boron oxide directly at 85–110°C in 88% yield, with aluminum trichloride as by-product in 95% yield. In the presence of triethylamine and a hydrogen pressure of 130 kg/cm², the triethylboron was hydrogenated at 200°C for 2 hours to produce borane-triethylamine complex in 92% yield. The borane-triethylamine complex was treated again at 80°C with the aluminum trichloride collected from the first step to liberate diborane in 94% yield. The overall reaction yield was 76%.

INTRODUCTION

Borane has been widely used in organic synthesis as a very important hydroborating agent and an excellent reducing agent [1–3]. Around 30 years ago, there was a vital interest in the preparation of diborane. The synthesis of diborane based on the reaction between lithium hydride and the ethyl ether complex of boron trifluoride in good yield was reported by Schlesinger and Brown [4, 5]. The process for the production of diborane from aluminum, ethylene, hydrogen, trialkylboroxine, sodium phenolate, and boron trifluoride was described by Köster [6]. This was a long process involving more than five steps. Aiming at a simplified and economical process, we consequently undertook a study of the preparation of diborane that involves only three steps from simple and cheap starting materials:

$$4Al + 6EtCl + B_2O_3 \rightarrow 2Et_3B + 2AlCl_3 + Al_2O_3 \quad (1)$$

$$2Et_3B + 3H_2 + 2Et_3N \rightarrow 2Et_3N \bullet BH_3 + 6C_2H_6 \quad (2)$$

$$2Et_3N \bullet BH_3 + 2AlCl_3 \rightarrow B_2H_6 + 2Et_3N \bullet AlCl_3 \quad (3)$$

$$4Al + 6EtCl + B_2O_3 + 3H_2 + 2Et_3N \rightarrow B_2H_6 + Al_2O_3 + 2Et_3N \bullet AlCl_3 + 6C_2H_6$$

The triethylamine can be recycled. The consumable starting materials of this method therefore involve only aluminum, ethyl chloride, boron oxide, and hydrogen. The principal advantages of this method are:

1. shorter process with only three steps and in good yield of the overall reaction,
2. cheap and easily available starting materials, and
3. eliminating boron trifluoride or its ethyl ether complex so as to avoid corrosion of the equipment.

We now present a brief account. The details will be reported elsewhere subsequently.

**This was a classified work when it was first done during the period of 1961 to 1964. It was declassified only very recently. The decision to publish this paper and the detailed papers later on in the open literature at this late date (after one fourth of a century!) is based upon the fact that, after perusing the Chemical Abstract up to 1990 thoroughly, we find that this method is still unique among the various methods of the preparation of diborane published so far.

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Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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RESULTS AND DISCUSSION

Trialkylboron

Triethylboron, prepared from aluminum, ethylene, hydrogen, and trialkyl borate *via* two steps, was first reported by Köster [7]. Pursuing a simplified and cheap process with easily available starting materials, we studied the preparation of triethylboron from aluminum, ethyl chloride and boron oxide first *via* two steps:

$$4Al + 6EtCl \rightarrow 2Et_3Al_2Cl_3 \qquad (4)$$

$$2Et_3Al_2Cl_3 + B_2O_3 \rightarrow 2Et_3B + 2AlCl_3 + Al_2O_3 \quad (5)$$

$$4Al + 6EtCl + B_2O_3 \rightarrow 2Et_3B + 2AlCl_3 + Al_2O_3$$

and then *via* only one step as described in reaction (1).

Reaction (4) was effected at 120–160°C and normal pressure by passing purified ethyl chloride vapor into aluminum foil, which was activated by iodine [8]. The yield was 93% or higher. The thickness of aluminum foil used should be 0.4 mm or less. Ethylaluminum sesquichloride could also be used to activate aluminum instead of iodine with almost equally good yield, but the ratio of $Et_2AlCl/EtAlCl_2$ was somewhat lowered.

A systematic study of the influence of temperature, ratio of the reactants, and molecular ratio of $Et_2AlCl/EtAlCl_2$ in the product ethylaluminum sesquichloride on this reaction was made. Finally, the optimum conditions for reaction (5) were chosen as reaction temperature 170–180°C, B_2O_3: ethylaluminum sesquichloride = 1.0:2.0, and ratio of Et_2AlCl to $EtAlCl_2$ = 45:55. Besides, the vacuum dehydration of boric acid to make B_2O_3 was specifically studied, since an active boron oxide of large surface area, high porosity, fine skeletal structure and a loose appearance was indispensible for the successful operation of this reaction. When all the above conditions were fulfilled, the yield was 92%, which was much better than that disclosed by Jenkner [9].

Animated by the excellent results of the two step process, we ventured to prepare the triethylboron *via* one step. The influences of the thickness of the aluminum foil, the molecular ratio of Al to B_2O_3, the molecular ratio of C_2H_5Cl to Al, and temperature of reaction (1) were methodically studied. The optimum reaction conditions were finally found as:

reactants ratio = C_2H_5Cl: Al: B_2O_3 = 6.6:4:1
temperature = 85–110°C
pressure = atmospheric
activator = iodine

It was necessary also that reaction (1) was carried out under vigorous mechanical stirring. A study was made on the influence of the purity of the ethyl chloride. The commercial ethyl chloride we used contained usually minor amount of methyl chloride, which would produce diethylmethylboron, which in turn would influence the yield of the hydrogenation reaction to be discussed below. Thus, ethyl chloride containing no methyl chloride is recommended.

With a 99.5% purity of ethyl chloride and the above mentioned reaction conditions, the triethylboron was isolated by distillation from the reaction mixture in 88% yield. The purity of triethylboron in this product was gas-chromatographically analyzed to be 98–99%. This one-step method is obviously much better than the two-step method because the process is simplified. It is noteworthy that the reaction temperature of the one-step method is much lower than that of the two-step method.

The by-product aluminum chloride was collected in 95% yield in two parts. About 49–55% aluminum trichloride was condensed as sublimate on the wall of the reaction flask during the distillation of the triethyl boron. The rest of the aluminum trichloride could be extricated by the thermal decomposition (up to 850°C) of a brown-colored residue, which was considered to be mainly aluminum oxychloride (AlOCl) by chemical analysis, and which was left in the reaction flask after distillation of triethylboron. The aluminum trichloride could be reused in reaction (3).

Hydrogenation

It was reported by Köster [10] that, in the presence of triethylamine, triethylboron was hydrogenated at 200°C, 300 atmospheres for ten hours to produce borane-triethylamine complex in essentially quantitative yield. This reaction was reinvestigated by us. The effect of the reaction time, initial hydrogen pressure, and purity of the starting material on the yield of the product borane-triethylamine complex was studied individually. It was found that the reaction time could be reduced to 2–4 hours with even better yield. For a longer reaction time, the intricacies of the thermal decomposition of borane-triethylamine complex caused deterioration of the product. The initial hydrogen pressure could be reduced to 130 Kg/cm^2 or even lower, as long as the partial pressure of hydrogen was kept at 60 Kg/cm^2 or higher during the entire hydrogenation process. The purity of the starting material triethylboron was of importance. With $(C_2H_5)_2BCH_3$ as impurity, the yield would be reduced. In view of the fact that a longer reaction time would lower the yield, the thermal stability of borane-triethylamine complex was also studied. It was found that at 220°C and 100 Kg/cm^2 hydrogen pressure, the thermal decomposition of the complex was obvious in two hours. Finally, the optimum reaction conditions for this reaction were chosen as: 200°C, 130 Kg/cm^2 initial hydrogen pressure, and two hours. The yield was 92% or higher as determined by chemical analysis of the boron content as well as by the liberated hydrogen volume from the hydrolyzed (by concentrated sulfuric acid) product [11].

Liberation of Diborane

The liberation of diborane by the reaction between borane triethylamine complex and the ethyl ether complex of boron-trifluoride was explored by Köster [12] who reported a nearly quantitative yield. In our investigation, aluminum trichloride was obtained as a by-product in reaction (1). The more economical and less corrosive features of aluminum trichloride in contrast with the ethyl ether complex of boron trifluoride influenced us to try reaction (3) for the liberation of diborane.

Diethyl ether, methyl phenyl ether, carbon tetrachloride, liquid paraffin, and benzene as solvent for the reaction were tried one after another. It was found that benzene was the best among them. The reaction of borane-triethylamine complex with aluminum trichloride in benzene at 80°C produced diborane in 94% yield. The reaction temperature was controlled at constant value throughout the run. This result was in sharp contrast with the result of Köster [12], who claimed that, with ethyl ether as solvent, the yield was only 40% due to the fact that the boron hydride partially reduced the aluminum trichloride to aluminum hydride. We indeed found that, with carbon tetrachloride as solvent, trichloromethane was detected in the product and the yield of diborane was reduced to only 8%. A material balance for diborane was also conducted to give the result that around 94% of diborane was collected in the liquid nitrogen cold trap, around 5% of BH_3 remained in the reaction flask as liquid residue and around 0.9% of diborane was carried over in the vent gas. Therefore, the reaction was almost quantitative.

EXPERIMENTAL

All manipulations of the ethylaluminum sesquichloride, boric oxide, triethylboron, borane-triethylamine complex, aluminum trichloride and diborane were performed in a nitrogen-filled dry box. All equipment used in these experiments, when assembled, were flash flamed and allowed to cool under a nitrogen atmosphere. Preparation of triethylboron and diborane were carried out in a nitrogen atmosphere. Preparation of borane-triethylamine complex was carried out under a hydrogen atmosphere.

Preparation of Triethylboron from Aluminum, Ethyl Chloride and Boric Oxide

A mixture of boric oxide (13.0 g, 0.221 mol) made from boric acid, aluminum foil (0.05 mm thickness, 23.9 g, 0.884 mol) and iodine (0.3 g, 0.00236 mol) was strongly stirred at 80°C for 20 minutes for aluminum activation. The vapor of purified ethyl chloride (94.9 g, 1.46 mol) was passed into the mixture at 85–110°C. The feeding of the ethyl chloride vapor was kept at such a rate that it was absorbed by the reaction mixture throughout. The reaction mixture was heated to 170–220°C to distill out crude product, which was redistilled to afford 19.0 g (88% yield) of triethylboron: bp, 94.5–95.5°C.

Aluminum trichloride (65.4 g) as a part of the by-product was collected from the wall of the reaction flask. The other part (48.7 g) of aluminum trichloride was collected from the thermal decomposition (up to 850°C) of a brown residue in the reaction flask. Total aluminum trichloride obtained was 114.1 g (96.8% yield).

Hydrogenation of Triethylboron in the Presence of Triethylamine

The borane-triethylamine complex was prepared by hydrogenation of triethylboron (39.9 g, 0.408 mol) in the presence of triethylamine (41.2 g, 0.408 mol) at 200°C and 130 kg/cm^2 of hydrogen in an autoclave. The crude product was distilled to give borane-triethylamine complex (46.8 g, 92% yield): bp, 90–92°C/10 mmHg.

Reaction of Borane-triethylamine Complex with Aluminum Trichloride

To a solution of aluminum trichloride (7.66 g, 0.0574 mol) collected from reaction (1) in 16 mL of benzene was added dropwise borane-triethylamine complex (6.48 g, 0.0564 mol) at 80°C in dry nitrogen atmosphere over a period of 5 minutes. The mixture was stirred for 3 hours. The liberated diborane was collected by a trap in a liquid nitrogen bath, or absorbed by acetone for chemical analysis [13] in 94% yield based both on H and on B.

Anal. Calcd. for B_2H_6:B:H=1:3. Found:B:H=1:3.01.

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