

SYNTHETIC REAGENTS 3

J. S. PIZEY

SYNTHETIC REAGENTS

Volume 3

Diborane;
2,3-Dichloro-5,6-Dicyanobenzoquinone (DDQ);
Iodine;
Lead Tetra-acetate

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Preface to Volume 3

The plan used for the organization of the two earlier volumes in this series is repeated here: four reagents are revised in sufficient depth to provide a full understanding of the synthetic uses of each reagent. The four reagents have been specially chosen for their current importance, their versatility, and their capability to cause the major types of reactions.

The important properties of each reagent, and also the methods for its preparation, are given at the beginning of the respective chapters. The synthetic uses of each reagent are then discussed in extensive surveys which occupy the larger part of the four reviews in the book. Mechanistic ideas have been introduced when it is felt that they will afford a better understanding of the synthetic possibilities or limitations of the reagent.

DIBORANE (C. F. Lane), a most important chemical, effects a large number of reactions including hydroboration and the preparation of alcohols, and reduction. In addition this chapter includes a major survey of the synthetic applications of organoboranes. *2,3-DICHLORO-5,6-DICY-*

ANOBENZOQUINONE (A. B. Turner) is one of the modern breed of quinones and potentially a very useful reagent for dehydrogenation and for the oxidation of certain alcohols and phenols. *IODINE* (J. S. Pizey) in addition to its uses as an iodinating agent may be used in certain cleavage reactions, as an oxidant, and in a number of other reactions. *LEAD TETRA-ACETATE* (R. N. Butler) is one of the most often used and versatile of oxidants and, for example, may be used for acetoxylation and hydroxylation, in oxidative cyclisation and dehydrogenation, and in decarboxylation.

It is hoped that this book will help chemists to determine the types of reaction the reagent will effect and resolve its selectivity: and that it will also indicate the optimum reaction conditions. This will also enable the chemist to find a method for the synthesis of a large number of compounds. The original reference for that method will then (generally) give him the necessary precise synthetic details. Rapid retrieval of information is assisted by a very complete index covering all the compounds and types of reactions.

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Chapter 1

Diborane

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A INTRODUCTION

Diborane, B_2H_6 , was first isolated and characterized by Stock in 1912 [1]. His process involved the preparation and hydrolysis of magnesium boride to give a mixture of higher boron hydrides. Thermal decomposition of the higher boron hydrides then gave B_2H_6 along with other boron hydrides. Although this pioneering work by Stock must be considered truly remarkable [2, 3], the process developed by Stock was extremely tedious and gave exceedingly low yields of diborane.

In 1931, Schlesinger and Burg reported an improved method for the preparation of diborane which involved passing hydrogen and boron trichloride through

a silent electric discharge [4]. The major product was chlorodiborane, B_2H_5Cl , which disproportionated upon fractional distillation to yield diborane and boron trichloride. This procedure was satisfactory for the preparation of micro quantities of diborane, which was all that was required for the studies carried out by Schlesinger and co-workers on the Stock high-vacuum apparatus.

Schlesinger and his students were attracted to the boron hydrides because their formulae, which had been established without a doubt by Stock, did not conform to the then accepted theories of valence and molecular structure. As part of their investigations, the reaction of diborane with the carbonyl group in certain organic compounds was studied by Brown as part of this Ph.D. research [5]. This is the first report on the use of B_2H_6 as a synthetic reagent with potential applications in organic chemistry. The reactions were studied on the high-vacuum line in the absence of a solvent using micro amounts of reactants. Furthermore, relatively complex equipment was required to prepare the diborane. Consequently, although the results are now considered of fundamental importance, at the time the results of this study were of negligible importance to synthetic organic chemistry.

Fortunately, in 1940 a National Defense Project, initiated at the University of Chicago under the direction of Schlesinger and Brown, ultimately resulted in the development of large-scale processes for the preparation of both sodium borohydride and diborane [6]. With only minor modifications these processes are now used commercially in the United States to prepare both sodium borohydride and diborane. Unfortunately, the results of these projects carried out at the University of Chicago during the war were not made public until a series of eleven articles appeared in 1953 [8]. While preparing these articles for publication, Brown again became interested in the use of diborane as a reducing agent for organic compounds. Also, since sodium borohydride had become commercially available and provided a ready source for diborane, it was apparent that diborane should be of utility as a reducing agent for applications in synthetic organic chemistry. A preliminary communication appeared in 1957 [9] which was followed by a full paper [10].

This investigation of the reduction of organic compounds by Brown and Subba Rao was responsible for the discovery of hydroboration which was first reported in 1956 [11]. Hydroboration provides a convenient method for the preparation of organoboranes. Thus, this development has kindled vigorous activity in the study of organoboranes as intermediates in organic syntheses. Both hydroboration and the chemistry of organoboranes have been reviewed by Brown and others [7, 12-19]. Also, the use of diborane for the reduction of organic compounds was briefly discussed by Brown [20, 21] and, recently, was the subject of an extensive review [22].

The molecular structure, molecular properties, physical properties and preparation of diborane are covered in a recent review [23]. Also, the reaction chemistry of diborane has been reviewed with the emphasis being on the reaction of diborane with inorganic elements and inorganic compounds [24]. However,

a comprehensive review devoted exclusively to the use of diborane and related borane complexes as synthetic reagents in organic chemistry has not appeared.

In this review the literature is covered through mid-1975. Originally, it was hoped that every reference which describes a synthetic application of a borane reagent could be included in this review. However, it became apparent, early in the literature searching, that such a comprehensive coverage would be difficult to obtain. Thus, a number of limiting factors have, by necessity, been introduced. The review deals exclusively with the use of diborane and borane-Lewis base complexes as synthetic reagents in organic chemistry. The substituted boranes; such as, bis(3-methyl-2-butyl)borane [25, 26], 2,3-dimethyl-2-butylborane [27-29], 9-borabicyclo[3,3,1] nonane (9-BBN) [30, 31], catecholborane [32, 33], and the chloroborane etherates [34], which are also useful synthetic reagents, are not covered in this chapter. To be consistent and objective it was decided that a publication must meet at least one of the following criterions before it would be cited in this review, (1) the reference must illustrate the selectivity of the reagent, (2) the reference must provide some insight into the mechanisms by which the reagent operates, or (3) the reference must contain a detailed experimental section.

A large number of borane reactions involve the use of the borane-tetrahydrofuran reagent, which will be abbreviated as $\text{BH}_3\text{-THF}$. It should be understood that in all cases where $\text{BH}_3\text{-THF}$ is discussed, the reagent is actually a solution of the borane-tetrahydrofuran complex in tetrahydrofuran.

B THE REAGENT

1. Preparation

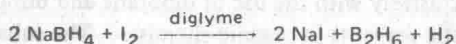
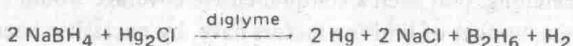
Diborane, $\text{BH}_3\text{-THF}$, borane-methyl sulphide (BMS), and various borane-amine complexes are all available commercially. A comprehensive coverage of the preparative chemistry of diborane is included in a recent review by Long [23]. Thus, only a short discussion of the more convenient methods of preparation will be given here.

Since sodium borohydride is available commercially at a reasonable price, this chemical is the starting material of choice for the preparation of diborane. For the vacuum-line preparation of small quantities of high-purity diborane, the Schlesinger-Burg process has been replaced by several more convenient procedures. Diborane can be prepared in a vacuum line in good yield from the reaction of sodium borohydride and concentrated sulphuric acid [35]. Sulphur dioxide, which is formed as a by-product, can be eliminated by the use of methane-sulphonic acid in place of sulphuric acid [35]. To obtain a purer sample, phosphoric acid is also recommended in place of sulphuric acid [36]. A detailed literature procedure is available for the reaction of potassium borohydride with 85% orthophosphoric acid [37]. The yield is only 40-50%, but the purity of the



diborane prepared by this method is excellent, and only a trace amount of carbon dioxide (<0.1%) is observed in some cases.

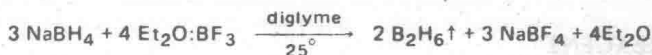
Another potentially useful vacuum-line preparation of diborane involves the reaction of sodium borohydride in diglyme with either mercurous chloride or iodine [38]. The yield by either of these methods is very good (88–98%) and



the purity of the diborane is excellent (no detectable impurities). Unfortunately, a detailed experimental procedure is not available and there is no indication if these methods are useful on a preparative scale.

Although diborane is available commercially in steel cylinders and can be handled safely by adequately trained personnel, it must be considered a very hazardous material. When large amounts of diborane are required for a preparative scale organic transformation, it is generally much safer to generate the diborane as needed and pass it directly into a reaction mixture. Alternatively, the reagent can be purchased in the form of a borane–Lewis base complex, such as BH_3 –THF or BMS. Both of these reagents are stable but still reactive and can be safely and easily handled.

The reaction of sodium borohydride with boron trifluoride, as developed by Brown and coworkers, is probably the most convenient method available for the



preparative scale generation of diborane. The reaction was studied extensively by Brown and Tierney [39] and experimental procedures for generating diborane have been reported [39, 40]. Further refinements in the process were later introduced [41], and a detailed experimental procedure is now available [42].

In addition to the use of externally generated diborane or the use of preformed borane–Lewis base complexes for organic reactions, these reagents can also be prepared *in situ* in the presence of a reactive compound. A variety of procedures for the *in situ* generation of diborane were developed for use in the hydroboration reaction [43]. However, the presence of strong Lewis acids, such as boron trifluoride or aluminium chloride, can sometimes result in the formation of unexpected by-products (*vide infra*). Also the starting material may react with the basic alkali metal borohydride (*vide infra*). Consequently, for exploratory work it is usually wise to first use either externally generated diborane or preformed BH_3 –THF. Almost invariably this results in fewer side reactions and a higher purity product.

2. Physical and chemical properties

The physical, chemical and molecular properties of diborane were summarized in two recent reviews [23, 24]. Also, a complete compilation of the major physical

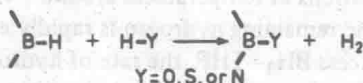
and thermodynamic properties of diborane is available in a concise graphical format [44]. The property data covered include critical constants, vapor pressure, heat of vaporization, heat capacity, density, viscosity, surface tension, thermal conductivity, heat of formation, and free energy of formation. The properties of $\text{BH}_3\text{-THF}$ and BMS are discussed in the present review in the section dealing with borane-Lewis base complexes.

Sodium borohydride [45] and lithium aluminium hydride LAH [46] are both widely utilized for the selective reductions of organic compounds. These reagents react principally by nucleophilic attack on an electron-deficient center. Conversely, borane, which is already electron-deficient, is believed to function through attack on an electron-rich center in the functional group [5, 47]. Thus, diborane and borane complexes are acidic-type reducing agents which exhibit markedly different selectivity than the basic-type reducing agents, sodium borohydride and LAH [9]. This interesting difference in the reducing activity of diborane and sodium borohydride prompted an extensive study of the reduction of organic compounds with borane-ether complexes [10, 48].

In addition to the Lewis acid character of borane, other important chemical properties have enhanced the utility of borane complexes as synthetic reagents. Many reactions involving borane complexes have unusually low activation energies. Consequently, most reactions occur readily at room temperature or below. These low temperatures favor clean reaction mixtures with a minimum of side products. The solubility of diborane in ether solvents means that the reactions are usually homogeneous, proceed without induction periods, and are easily controlled. Finally, the inorganic by-product of a borane reaction is usually an inert, water-soluble borate salt, which can be washed away over a broad pH range. All of these chemical and physical properties combine to make diborane one of the most chemically versatile compounds known.

3. Reaction with acidic hydrogens

Boron hydrides and other metal hydrides react rapidly and quantitatively with various acidic hydrogens (H-Y), liberating one mole of hydrogen per equivalent



of hydride. Both the acidity of the hydrogen and the ability of the donor atom Y to share a pair of electrons, influence the rate of these reactions [48].

The direct measurement of the volume of hydrogen gas produced upon hydrolysis of a boron hydride provides a convenient and accurate method for the determination of either the purity of a boron hydride or the concentration of a boron hydride in an appropriate solvent [49]. Also, a simple, rapid, and quantitative procedure for determining acidic hydrogens in organic materials based upon hydrogen evolution from a large excess of $\text{BH}_3\text{-THF}$ [50] has been developed. The method is especially valuable for hydroxyl group determinations, and a precision of about 1% is possible.

In reactions of diborane with compounds containing acidic hydrogens, hydrogenolysis of the C-Y bond is usually not observed. Upon hydrolysis the alcohol, amine, thiol, or related functional group is regenerated unchanged. However, in a few specialized cases those benzylic alcohols which can readily form carbonium ions are transformed by diborane into the corresponding hydrocarbons (cf. Section C3). Even though the alcohol, thiol, and amine groups are normally recovered unchanged, their presence and reactivity must be considered when carrying out a borane reaction, i.e. sufficient borane reagent must be added to compensate for loss of hydride activity upon reaction with acidic hydrogens. Consequently, an understanding of the reactivity of borane reagents towards alcohols, thiols, and amines is important.

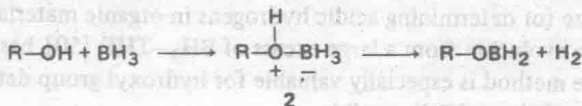
(a) Alcohols

The hydrolysis of diborane with simple alcohols proceeds in stages. The first two hydrides react rapidly, but the third is so slowly hydrolyzed that the intermediate dialkoxymorane can be isolated. Using this reaction, dimethoxymorane (1) was



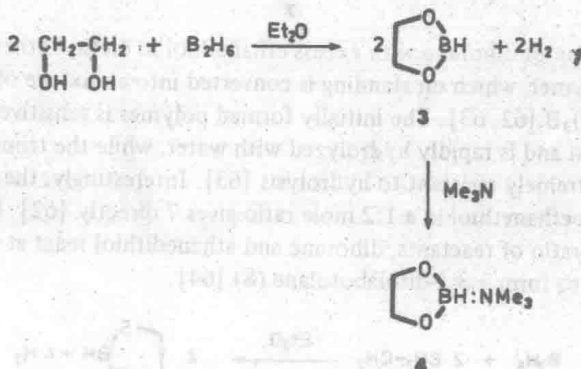
first isolated and characterized by Burg and Schlesinger [51]. No evidence was found for dimerization of (1). Even in the presence of excess diborane, there was no indication of the formation of monomethoxymorane. Later investigations by Lehmann and coworkers, on the preparation of dimethoxymorane [52], diethoxymorane [53] and diisopropoxymorane [54], substantiated the earlier results. For example, Lehmann found that when ethanol is added to a large excess of diborane, there is no detectable formation of EtOBH_2 by ir analysis [53]. Also, the diborane is quantitatively converted into diethoxymorane before there is any detectable formation of triethoxymorane. Even with excess ethanol, the rate of formation of triethoxymorane (triethyl borate) from diethoxymorane is slow at room temperature [55]. Stoichiometric evidence is also available which indicates that $\text{HB}(\text{OH})_2$ is formed as an intermediate in the hydrolysis of diborane in aqueous solutions at temperatures around -70° [56]. Upon warming to room temperature, the remaining hydrogen is rapidly evolved.

In the presence of excess BH_3 -THF, the rate of hydrogen evolution for alcohols decreases in the order: primary > secondary > tertiary [48]. The acidity of the hydroxylic hydrogen also decreases in this order. A factor, in addition to the acidity of the hydrogen, must be involved in these reactions because BH_3 -THF reacts relatively slowly with phenol. The results can be rationalized by prior co-ordination of BH_3 with alkoxy oxygen to give the intermediate (2) which decomposes with evolution of hydrogen. Mass spectro-

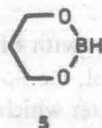


metric evidence is now available for the existence of an intermediate donor-acceptor adduct (2) in the reaction of borane with 2-propanol [57]. Also, stoichiometric evidence points to the formation of a dihydrate of diborane (empirical formula $B_2H_6 \cdot 2 H_2O$) in the reaction of diborane with water at -130° [58].

Cyclic dialkoxyboranes are formed by the reaction of diborane with 1,2- and 1,3-diols. For example, 1,3,2-dioxaborolane (3) can be prepared through the reaction of ethylene glycol with diborane in diethyl ether and can be isolated as



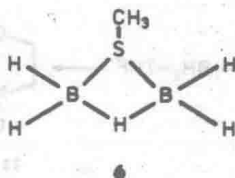
the trimethylamine adduct (4 [59]. The corresponding 1,3,2-dioxaborinane (5) can also be prepared from 1,3-propanediol [60].



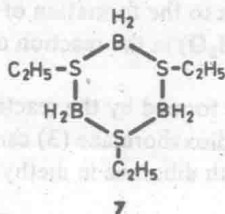
The reaction of borane with polyalcohols apparently results in a chelation which must enhance the reactivity of the boron hydride. Thus, hydrolysis of all three hydrides occurs very rapidly in the presence of a polyglycol, such as glycerol or mannitol [49].

(b) Thiols

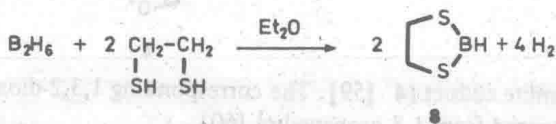
The ability of sulphur to bring *d* orbitals into hybridization with *s*- and *p*-orbitals to form multiple bonds apparently exerts a pronounced effect on the products obtained through the reaction of diborane with alkanethiols. Thus, the first reported alkylthio derivative of diborane, methylthiodiborane [61], has the structure (6) based on nmr data [62]. In this and other alkylthio derivatives of



diborane, the alkylthio group occupies exclusively a bridging position, e.g. structure (7) [62].



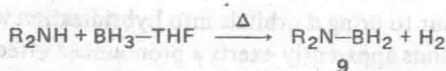
The reaction of diborane with excess ethanethiol in diethyl ether at 25° yields a viscous polymer, which on standing is converted into a mixture of the trimer (7) plus (EtS)₃B [62, 63]. The initially formed polymer is sensitive to atmospheric oxygen and is rapidly hydrolyzed with water, while the trimer (7) is stable in air and extremely resistant to hydrolysis [63]. Interestingly, the reaction of diborane and ethanethiol in a 1:2 mole ratio gives 7 directly [62]. With the proper mole ratio of reactants, diborane and ethanedithiol react at room temperature to form 1,3,2-dithiaborolane (8) [64].



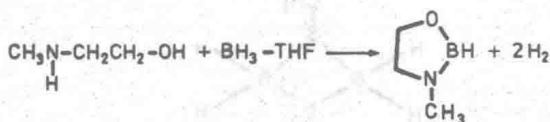
(c) Amines

Primary and secondary amines react with BH₃-THF at 0° with the slow evolution of hydrogen [48]. With phenol, the slow evolution of hydrogen is presumably due to its weakly basic character which opposes formation of the prior addition complex (2). On the other hand, amines readily form such addition complexes. Thus, the slow evolution of hydrogen must be caused by the low acidity of the hydrogen atoms attached to nitrogen.

At higher temperatures an increased rate of hydrogen evolution is observed. Primary or secondary amines react with BH₃-THF in refluxing THF to give monoaminoboranes (9) [65]. Even in the presence of a large excess of amine, no



additional hydrogen evolution is observed. However, the amino-alcohol (10) reacts with BH₃-THF under otherwise identical conditions to give the heterocyclic compound (11) [65].



10

11

Other functional groups, which contain acidic hydrogens, such as carboxylic acids and primary and secondary amides, react with borane with evolution of hydrogen. However, since these groups react further with borane, they will be discussed in later sections dealing with the reduction of these functional groups.

4. Borane-Lewis base complexes

The high reactivity of diborane is presumably due to its ready dissociation into borane (BH_3) [66]. The borane molecule behaves as a strong electron-pair acceptor (Lewis acid) forming co-ordination complexes with suitable electron donors (Lewis bases). Of the various known complexes, the borane-amine, borane-ether, and borane-alkyl sulphide complexes are all particularly interesting because of their wide range of physical and chemical properties.

These borane-Lewis base complexes provide a convenient source of borane for use as a synthetic reagent. Another reason for discussing these complexes is that all organic reductions with borane probably involve the initial formation of a donor-acceptor adduct between borane and the functional group undergoing reduction. Thus, a borane-carbonyl complex (12) was proposed as an intermediate in the first report of a borane reduction [5]. This complex (12), once formed, is presumed to undergo a rapid rearrangement. Recently, convincing



12

evidence was reported which shows that the first formed intermediate in the reaction of diborane with acetone is the donor-acceptor adduct [57]. Arguments were also presented which suggest that the formation of this adduct (12) is not a 'dead-end' reaction in the overall process, i.e. the adduct is the first formed intermediate and it subsequently reacts to give a product *via* a hydride rearrangement [57].

(a) Amine complexes

The borane-amine complexes are very useful reagents which have many important laboratory and industrial applications [67].

The first borane-amine complex was reported in 1937 and was prepared by the direct reaction of diborane with trimethylamine [68]. Since then almost all



structural types of amines have been used to prepare borane-amine complexes. A wide variety of these complexes are now available commercially.

An important feature of the borane-amine complexes is their broad range of physical properties. Liquid, low-melting solid, and high-melting solid borane-amines are known. The borane-amines also have low vapor pressures and can be purified by distillation and/or recrystallization. Another very useful property of

Table 1. Physical Constants for the Borane-amine Complexes

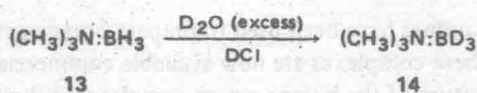
Borane-amine	mp, °C	bp, °C (mm Hg)	Reference
Borane- <i>tert</i> -butyl amine	96	decomp.	[67]
Borane- <i>NN</i> -diethylaniline	-30 to -27		[69]
Borane-dimethylamine	36	49(0.01)	[70]
Borane-2,6-lutidine	110-111		[71]
Borane-morpholine	93-95		[69]
Borane- <i>N</i> -phenylmorpholine	97-99		[69]
Borane-pyridine	10-11	decomp.	[72]
Borane-triethylamine	-4	100-101 (12)	[73]
Borane-trimethylamine	94-94.5	172	[68]

the borane-amines is their solubility in a wide variety of solvents [67, 69]. The physical constants of some of the typical complexes are summarized in Table 1.

All of the borane-amines listed in Table 1 are stable indefinitely at room temperature and are unaffected by dry air. The borane-amines prepared from primary and secondary amines are surprisingly resistant to loss of hydrogen. Borane-*tert*-butylamine does not lose hydrogen until heated to its melting point and borane-morpholine loses only 11.5% hydrogen after 20 hr at 69° in THF [69]. Borane-dimethylamine reportedly shows no evidence of thermal instability when heated to 110° [70]. An attempted distillation of borane-pyridine at reduced pressure resulted in violent decomposition [74]. However, this complex has been stored for a year at room temperature without any detectable signs of deterioration [75].

Only the borane complexes with *N* arylamines (*N*-phenylmorpholine and *NN*-diethylaniline) are hydrolyzed by water and alcohols [69]. These two borane-amines react with atmospheric moisture. However, by careful and rapid handling, they may be transferred in air with only minimal loss of hydride activity. Naturally, an inert atmosphere and dry aprotic solvents must be used for the borane-*N*-arylamines. All of the other borane-amines are unaffected by hydrolytic solvents at neutral pH after a minimum of twelve hours at 25° [69]. Hydrolysis does occur in a 1M hydrochloric acid medium in 50% water-50% ethylene glycol [69].

The active hydrogens of borane-trimethylamine (13) undergo a rapid exchange with deuterium when the borane-amine is stirred with acidic deuterium oxide [76]. The exchange occurs much faster than hydrolysis. For example, after six



hours, the deuterium content of the borane-amine is 98% while less than 6% has hydrolyzed [76]. Subsequently, this procedure was used to prepare large quantities of borane-*d*₃-trimethylamine (14) which was used in the first