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Borane cluster photochemistry
2. Photochemical alcoholysis of the octahydrotriborate(1−) anion

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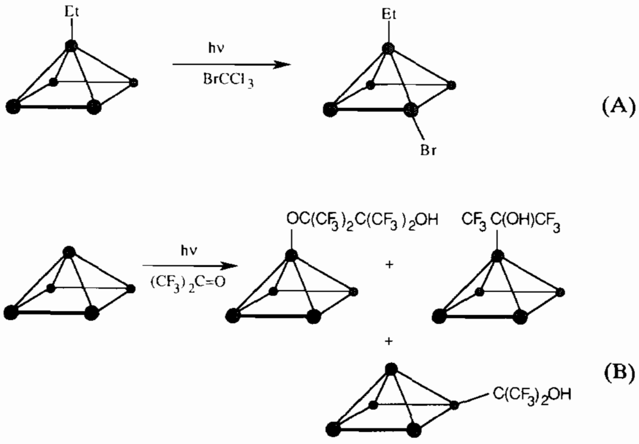
Abstract

The rapid photoinduced alcoholysis of the octahydrotriborate(1−) anion was observed from the UV irradiation of solutions of $(Bu_4N)B_3H_8$ and either ethanol or methanol in THF or chloroform. The octahydrotriborate(1−) anion, which is stable to alcoholysis in the ground state, reacts cleanly and rapidly with the alcohols to give $HB(OC_2H_5)_2$ and $B(OC_2H_5)_3$ products. Photolysis of $(Bu_4N)B_3H_8$ and C_2H_5OD gave both $DB(OC_2H_5)_2$ and $HB(OC_2H_5)_2$, as well as $B(OC_2H_5)_3$. A mechanism is proposed to accommodate these observations.

Introduction

Among the smaller boron hydride compounds, the *arachno*-octahydrotriborate(1−) anion, $B_3H_8^-$, shows exceptional oxidative and hydrolytic stabilities [1]. Indeed, one synthetic route to this borane is the reaction of pentaborane(9) and $NaOCH_3$ in methanolic solutions [2]. By contrast, the hydrolysis and alcoholysis of diborane and pentaborane are facile reactions, and the mechanisms of these reactions have been studied in detail [3–8].

The photochemistry of boron hydrides has received only limited attention [9]. The use of photochemical transformations of the boron hydrides in synthetic preparation and substitution reactions to form other borane species has been mostly neglected. The photochemistry of polyhedral boranes with other reagents is limited to four literature cases [10–13]. Two of these four examples are shown in Scheme 1. In the first paper [10], shown in reaction (A) of Scheme 1, the authors only mention photolysis briefly in the experimental section for the synthesis of 2-Br-1-Et-B_5H_7 by the cophotolysis of 1-Et-B_5H_8 and $BrCCl_3$. The photolysis itself in not described in any further detail in this work. Gaines and Hildebrandt [11] reported the cophotolysis of three organometallic compounds, $[(CO)_4ReBr]$, $[(\eta^5\text{-}C_5H_5)(CO)_2FeI]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3WCl]$, with the octahydrotriborate(1−) anion to produce $[(CO)_4ReB_3H_8]$, $[(\eta^5\text{-}C_5H_5)(CO)FeB_3H_8]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3WB_3H_8]$ complexes, respectively. Later, Astheimer and Sneddon [12] examined the gas-phase photolysis of B_5H_9 and 2,4-$C_2B_5H_7$ with hexafluoroacetone. As shown in reaction (B) of Scheme 1, this process produced both the basal and apical perfluoropropanol-substituted pentaborane or dicarbaheptaborane derivatives in good yields, as well as a novel oxygen–boron-bonded perfluoropinacol derivative of pentaborane. The fourth study examined the photoinduced nucleophilic substitution of perhalogenated *closo*-borane dianions by cyanide, cyanate, azide and halide ions (in the dark these dianions are essentially inert to nucleophiles) [13].



Scheme 1. Intermolecular photochemical reactions of boron hydrides.

For the carboranes, however, it has been established that UV irradiation can effect reactions between these

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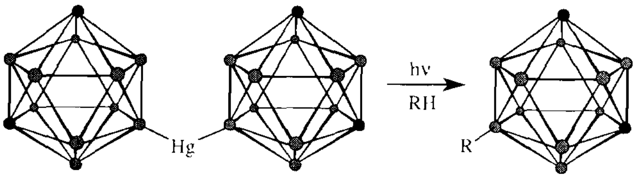


Scheme 2. Photochemical alkylation of *closo*-$(1,7\text{-}C_2H_2B_{10}H_9)_2Hg$.

clusters and otherwise inert solvents. The clean alkylation of carboranes was achieved by the photolysis of bis-carboranyl mercury complexes with the desired alkane as the solvent. Specifically, $9\text{-R-}1,7\text{-}C_2H_2B_{10}H_9$ were prepared in 45–90% yields by UV photolysis of $(1,7\text{-}C_2H_2B_{10}H_9)_2Hg$ and $1,7\text{-}C_2B_{10}H_9Tl(O_2CCF_3)_2$ in RH ($R = Ph$; C_6F_5; $1,4\text{-}Me_2C_6H_3$) as shown in Scheme 2 [14]. No similar reactions for small-cage boranes have been reported.

Earlier studies in our laboratory, however, have revealed interesting photochemistry of chlorohydrocarbon solutions of the octahydrotriborate(1−) anion [15]. In this paper, we report that the UV irradiation of octahydrotriborate (1−) anion and alcohols in THF or chloroform provides clean, rapid, and total alcoholysis of this robust boron hydride. Deuterated alcohols (Et-OD and Me-OD) were employed to probe the mechanism of this phenomenon. The photo-products were identified by ^{11}B and ^{1}H NMR spectroscopy.

Experimental

Materials

All solvents used were reagent grade or better. Chloroform (Fisher) was shaken with concentrated H_2SO_4, washed with water, dried over K_2CO_3, distilled under a nitrogen atmosphere, and stored over 4 Å molecular sieves [16]. Tetrahydrofuran (Fisher) was freshly distilled from sodium/benzophenone under a nitrogen atmosphere.

Ethanol (Pharmco), ethanol-d (95% C_2H_5OD, 5% D_2O; Cambridge Isotope Laboratories), methanol (Fisher) and boric acid (Fisher) were used as received. Tetrabutylammonium octahydrotriborate (1−) was prepared by a modification of the procedure developed by Cruikshank *et al.* [2].

The manipulation of all reactions was carried out using standard inert-atmosphere techniques [17].

Instruments

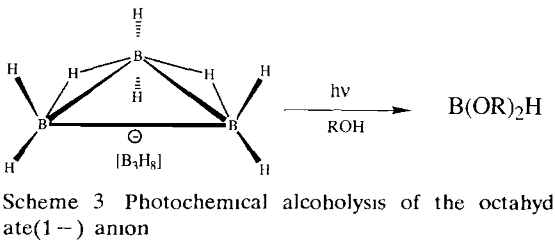
All photochemical reactions were performed with a water-cooled quartz immersion-well photochemical reactor (Ace no. 7841) with a Conrad-Hanovia 450W mercury-vapor lamp as light source (Ace no. 7825-34). The outer jacket was fitted with two ground-glass joints. Boron (^{11}B) NMR spectra were recorded on a Cryomagnetics spectrometer operating at 80.26 MHz Spectra were referenced to BBr_3 at +40.0 ppm (downfield relative to $BF_3{:}O(C_2H_5)_2$). Proton-decoupled spectra were obtained with a wide-band frequency generator operating at 250 MHz.

Methods

The solutions in this study were approx. 0.01 M $(Bu_4N)B_3H_8$ dissolved in 1–2% (vol./vol.) alcohol/solvent mixtures. In a typical reaction, 0.21 g (0.75 mmol) of $(Bu_4N)B_3H_8$ was dissolved in 50 ml of dry degassed THF. To this solution was added 2.0 ml (1.6 g, 34 mmol) of ethanol and the mixture irradiated for a total of 3 h at room temperature. The progress of each reaction was monitored by periodically removing samples of the solution via syringe for ^{11}B NMR analysis. Control solutions of $(Bu_4N)B_3H_8$ and ethanol or methanol were stirred in the dark for several hours. No changes were observed in the ^{11}B NMR resonance for $(Bu_4N)B_3H_8$ in the control solutions and the starting triborane compound was recovered unchanged.

Results and discussion

The photolysis of $(Bu_4N)B_3H_8$ in ethanol/chloroform was found to quantitatively convert the octahydrotriborate(1−) anion to $HB(OC_2H_5)_2$ very rapidly (see Scheme 3). The reactions in our study were followed primarily by ^{11}B NMR spectroscopy and representative spectra are shown in Fig. 1 and complete data are given in Table 1. Complete conversion of the starting $(Bu_4N)B_3H_8$ compound to $HB(OC_2H_5)_2$ was essentially complete within several minutes. Our assignment of the downfield resonance as $HB(OC_2H_5)_2$ was initially by a comparison of the ^{11}B NMR chemical shifts for the observed resonance and the literature value for $HB(OC_2H_5)_2$ [18]. The assignment of this resonance to $HB(OC_2H_5)_2$ was confirmed by an observed shift of this resonance upfield by 25 ppm upon addition of triethylamine. The intermediates in the alcoholysis of diborane (i.e. dialkoxyboranes) can be isolated as adducts of amines and similar shifts in these amine adducts ^{11}B NMR resonances have been reported [20]. Continued irradiation of the diethoxyborane photoproduct



Scheme 3 Photochemical alcoholysis of the octahydrotriborate(1−) anion

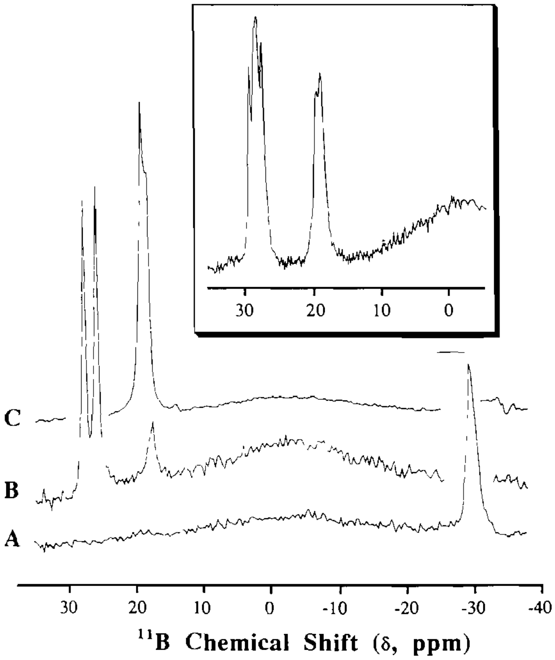


Fig. 1. The ^{11}B NMR spectra for the products from the photochemical alcoholysis reactions of the octahydrotriborate(1 −) anion. (A) Spectrum of $(Bu_4N)B_3H_8$ in ethanol/chloroform prior to irradiation. (B) Spectrum of $(Bu_4N)B_3H_8$ in ethanol/chloroform after 6 min of irradiation. The large doublet at 28.6 ppm arises from $HB(OC_2H_5)_2$. The small peak at 19.1 ppm is from $B(OC_2H_5)_3$. (C) ^{1}H-decoupled ^{11}B NMR spectrum of the mixture after 60 min and after having been spiked with boric acid. The spectrum shows resonances present from both $B(OC_2H_5)_3$ and boric acid Insert: spectrum of $(Bu_4N)B_3H_8$ in ethanol-d/chloroform after irradiation. Resonances arising from $HB(OC_2H_5)_2$ (doublet at 28 6 ppm), $DB(OC_2H_5)_2$ (broad singlet at 28 6 ppm), and $B(OC_2H_5)_3$ (singlet at 19.1 ppm) are observed.

(*c.* 1 h) led to the formation of triethoxyborane, $B(OC_2H_5)_3$.

We were initially concerned that the upfield singlet for $B(OC_2H_5)_3$ might have been boric acid ($B(OH)_3$ ^{11}B NMR resonance occurs at + 18.8 ppm). Spiking our samples with boric acid produced a new signal nearly one ppm downfield of our observed product signal. Furthermore, dialkoxyboranes are known to react with alcohols in the dark to form trialkoxyboranes [7]. Upon standing in the dark for several hours, the resonance attributed to $HB(OC_2H_5)_2$ (at + 28.6 ppm) slowly disappeared while the resonance for $B(OC_2H_5)_3$ (at + 19.1 ppm) grew stronger. We attribute the increased rate of conversion to triethoxyborane for the illuminated mixture to warming of the solution by the mercury lamp. Despite a rapid flow of cooling water in the reactor, the outside of the reaction cell was found to be warm by the end of the experiment.

Switching the solvent from chloroform to THF was found to greatly retard the rate of the alcoholysis reaction. After 3 h of irradiation, some $B_3H_8^-$ starting material still remained, although approximately two-thirds of the diethoxyborane photoproduct had been converted to triethoxyborane. In the chloroform system, no triethoxyborane appeared until all the $B_3H_8^-$ had been consumed.

There was no evidence of the unknown $H_2B(OC_2H_5)$ compound in any of our photoreactions. Monoalkoxyborane has not been detected during the alcoholysis of diborane [7, 8] or pentaborane [7], wherein the ethanol was slowly introduced to an excess of the borane. Shapiro and co-workers [8] attempted to generate this elusive derivative in a different fashion by adding a trace amount of triethoxyborane to diborane, yet only diethoxyborane was observed. Kinetic studies done earlier by their laboratory [4] on the analogous diborane hydrolysis (leading to $B(OH)_3$) showed that the reaction of borane (BH_3) with water to form H_2BOH was the rate-determining step [8]. Hence, any $HB(OC_2H_5)_2$ formed would quickly go to $H_2B(OC_2H_5)$. It is worth noting that in a thermal study on the ethanolysis of diborane, these workers did not observe 'any appreciable quantity' of triethoxyborane until all the diborane was converted to the diethoxyborane compound. While we observe the same step-wise conversion in our ethanol/chloroform system, triethoxyborane quickly becomes the predominate species in the ethanol/THF system, well before all the octahydrotriborate(1 −) is consumed. This result is not particularly surprising, since our photo-

TABLE 1. ^{11}B NMR data for the compounds prepared in the photochemical alcoholysis of the octahydrotriborate(1 −) anion

Compound	Solvent	^{11}B resonance (δ in ppm)	Coupling	Reference
$HB(OC_2H_5)_2$	$CHCl_3$	28.6(d)	J(B–H) = 163 Hz	this work
	THF	28.0(d)	J(B–H) = 163 Hz	this work
	diethyl ether	27.3(d)	J(B–H) = 161 Hz	18
$B(OC_2H_5)_3$	$CHCl_3$	19.1(s)		this work
	THF	20.1(s)		this work
	(neat)	18.1(s)		19
$DB(OC_2H_5)_2$	$CHCl_3$	28.6(br)	J(B–D) not resolved	this work

chemical alcoholysis is presumably preceding via a different mechanism (*vide infra*).

What is striking about the NMR spectra of these photochemical reactions is the absence of any other boron-containing species, especially with chloroform as a solvent. Our laboratory had previously discovered that the photochemical irradiation of octahydrotriborate(1 −) in chlorohydrocarbon solvents, including chloroform, leads to the clean chlorination of the cluster without degradation [15]. However, under the conditions outlined in 'Experimental', the rate of alcoholysis of octahydrotriborate (1 −) appears to be more than an order of magnitude greater than the rate of chlorination. Thus, the lack of chlorinated triborane derivatives can be attributed to the very rapid photoinduced reaction of the cluster with the ethanol, precluding any reaction with the solvent chlorohydrocarbon. Regardless, the very clean conversion of the octahydrotriborate(1 −) to a single series of products is noteworthy.

Substituting C_2H_5OD for C_2H_5OH in chloroform again permitted rapid photochemical alcoholysis of the borane to di- and triethoxyborane products. The $\{^1H\}^{11}B$ NMR spectrum of the photolyzed solution was similar to the spectrum of the C_2H_5OH reaction mixture. However, in the proton-coupled ^{11}B NMR spectrum, the doublet centered at $\delta = 28.5$ from $HB(OC_2H_5)_2$ was joined by a broad singlet at $\delta = 28.6$ (see Fig. 1). The two signals were assigned to the two substituted diethoxyboranes, $HB(OC_2H_5)_2$ and $DB(OC_2H_5)_2$ (see Table 1). Since deuterium is an $I = 1$ nucleus, a triplet from B–D coupling would be expected. No B–D coupling was observed, however, in the ^{11}B spectrum. This was consistent with deuterium labelling studies of pentaborane(9), in which B–D coupling was not observed in the ^{11}B NMR spectra [21, 22]. We did observe some broadening of the resonance, however, as observed by other workers [21, 22, 32].

The results of our isotope studies are similar to those of other boranes reported by Shapiro and Weiss [7]. They sought to understand the mechanism of the non-photochemical alcoholysis by the isotopic ethanolysis of diborane(6), tetraborane(10) and pentaborane(9). Diborane, which has only B–H–B bonds, reacts with alcohols to give one molecule of H_2 per 'hydridic' hydrogen. Alcoholysis of the higher boranes, which have B–B bonds as well as B–H–B bonds, generates more hydrogen than corresponds to the number of 'hydridic' hydrogen. These workers noted that the number of excess moles of hydrogen that are formed represent the number of B–B bonds that must be broken. In their experiment, the incremental addition of C_2H_5OH or C_2H_5OD to diborane(6) produced only $HB(OC_2H_5)_2$ whereas the introduction of C_2H_5OD to tetraborane(10) or pentaborane(9) yielded both $HB(OC_2H_5)_2$ and $DB(OC_2H_5)_2$. They concluded that a deuteride is created from the alcoholic deuterium during the rupture of a boron–boron bond, with the ethoxide group bonding to the other boron atom.

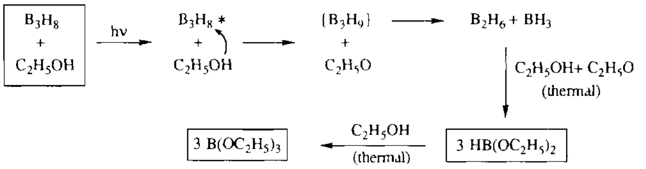


Fig 2 Proposed mechanism for the photochemical ethanolysis of octahydrotriborate(1 −) anion

Our mechanism for the ethanolysis of octahydrotriborate(1 −) is presented in Fig. 2. In the ground state, $B_3H_8^-$ is believed to a weaker base than ethoxide ion. This is consistent with the observation that ground state and excited state acid–base equilibrium constants for a variety of species can be quite different [23]. Therefore, $B_3H_8^-$ in the excited state may be a strong enough nucleophile to abstract a proton from ethanol to give transient B_3H_9. Triborane(9) is often invoked as an intermediate in the pyrolysis of diborane to produce the higher boranes and is believed to be in equilibrium with diborane(6) and borane(3) [24]. These two smaller boranes, once formed *in situ*, would undergo the non-photochemical ethanolysis as described above. The transfer of deuterium from C_2H_5OD to $B_3H_8^-$ to give B_3H_8D would account for the presence of $DB(OC_2H_5)_2$. Future work on the photolysis of octahydrotriborate(1 −) with other proton sources may assist in the further elucidation of this mechanism for alcoholysis.

Conclusions

We have demonstrated that photochemical irradiation of the octahydrotriborate(1 −) anion can induce alcoholysis of this borane, as is observed thermally for the other lower boron hydrides. The photochemistry is both very rapid and very clean. The starting material is consumed within minutes, and diethoxy- and triethoxyborane are the only observed boron-containing products.

Acknowledgements

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