Dehydration of $(H_3O)_2B_{10}H_{10}$: an Improved Preparation of Icosaborane Oxide, $(B_{10}H_{13})_2O$

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6,6′-bis(nido-decaboranyl)oxide, $B_{10}H_{13}OB_{10}H_{13}$, was originally obtained [1] by reaction of 6,9-bis(dialkyl sulphido) dodecahydrodecaborane, $B_{10}H_{12}(R_2S)_2$ ($R = CH_3$ or C_2H_5), with sulphuric acid. It has been shown in more recent work [2] that 6-hydroxy-nido-decaborane, $B_{10}H_{13}OH$, is formed in addition to $(B_{10}H_{13})_2O$. The structure of $(B_{10}H_{13})_2O$ has been determined by X-ray [3] and ^{11}B NMR [4]. This compound is extremely resistant towards inorganic acids and their halogenides. It has been shown recently [2] that it can be used to prepare new clusters containing boron and metals such as nickel, palladium and platinum.

To our knowledge, the formation of $(B_{10}H_{13})_2O$ by dehydration of $(H_3O)_2B_{10}H_{10}$ has never been reported. $(H_3O)_2B_{10}H_{10}$ is a strong acid; hydrates such as $H_2B_{10}H_{10}\cdot4H_2O$ and $H_2B_{10}H_{10}\cdot2H_2O$ have been characterized during the dehydration [5]. Further drying has given a solid residue from which a compound of formula $B_{10}H_{14}O$ has been isolated by sublimation under vacuum. According to our results, it is probable that this compound was 6-$B_{10}H_{13}OH$.

Results and Discussion

$(B_{10}H_{13})_2O$ is obtained with a 60% yield by dehydration of an easily available material, $(H_3O)_2B_{10}H_{10}$, prepared by ion exchange from $B_{10}H_{10}^{2-}$ salts. Starting from the acidic solution, the first stage is the formation of 6-$B_{10}H_{13}OH$ by evaporation of water under vacuum; benzene is then added to the reaction mixture and it dissolves the 6-$B_{10}H_{13}OH$. Benzene is evaporated in the second stage; the residue is a white solid from which 6,6′-$(B_{10}H_{13})_2O$ can be extracted with hexane at room temperature.

Although the preparation of $(B_{10}H_{13})_2O$ from $B_{10}H_{12}(R_2S)_2$ and from $(H_3O)_2B_{10}H_{10}$ is very different, the mechanisms leading to the final product appear to be similar. It has been shown [2] that $B_{10}H_{13}OH$ is an intermediate which reacts with $B_{10}H_{12}(Et_2S)_2$ to give the oxide. It has also been demonstrated that the conversion of the hydroxide to the oxide does not take place, even in the presence of H_2SO_4 or P_4O_{10}. In our case, the reaction of $B_{10}H_{13}OH$ with a bis-ligand seems also the best way to account for the results, the bis-ligand being here $B_{10}H_{12}(H_2O)_2$.

The formation of 6-$B_{10}H_{13}OH$ must be related to the general case of opening the $B_{10}H_{10}^{2-}$ cage in acidic medium; $B_{10}H_{12}(R_2S)_2$ [6, 7] and $B_{10}H_{14}$ [8] can be prepared under these conditions. Addition occurs always in positions 6 and 9 and the reaction can be written

$$(H_3O)_2B_{10}H_{10} \longrightarrow 6\text{-}B_{10}H_{13}OH + H_2O$$

6,9-$B_{10}H_{12}(H_2O)_2$ can be obtained by the same process. This compound has never been characterized but its existence has been postulated [9]; it is supposed to be the main intermediate in the formation of $B_{10}H_{12}(R_2S)_2$ from $(H_3O)_2B_{10}H_{10}$ and R_2S. One possibility is that $B_{10}H_{12}(H_2O)_2$ is present in low concentration because of the equilibrium

$$(H_3O)_2B_{10}H_{10} \rightleftharpoons B_{10}H_{12}(H_2O)_2$$

6,6′-$(B_{10}H_{13})_2O$ should be formed by the reaction

$$B_{10}H_{13}OH + B_{10}H_{12}(H_2O)_2 \longrightarrow (B_{10}H_{13})_2O + 2H_2O$$

Experimental

General

Except for the aqueous solution, the products were handled in a glove box in an argon atmosphere. ^{11}B NMR spectra were recorded on a XL-100 Varian instrument, IR spectra on a 457 Perkin Elmer instrument and Raman spectra on a PHO Coderg spectrometer equipped with a Spectra Physics argon laser emitting at 514.5 nm. X-ray diffraction patterns were measured on a Philips powder chamber of 360 mm diameter. Melting point was determined on a Setaram DSC 111 instrument.

Synthesis

3 g of $(Et_4N)_2B_{10}H_{10}$ prepared by pyrolysis of Et_4NBH_4 according to a published method [10] were dissolved in 15 cm^3 of water. The solution was passed through a column containing 200 cm^3 of a strong acid ion exchange resin (Duolite C 20 H). The acidic solution was collected and its volume was reduced to 5 cm^3 at room temperature in a rotating evaporator connected to a water aspirator. The remaining water was evaporated under vacuum, without heating, in a vessel equipped with magnetic stirrer. We stopped pumping when a yellow product

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was obtained (the pressure in the reaction vessel was 10^{-6} torr). Then 15 cm^3 of benzene were added to this product and the mixture was stirred; 6-$B_{10}H_{13}OH$ was the only boron compound present in the benzene solution. Benzene was evaporated at 10^{-3} torr and new fractions of benzene (3 × 10 cm^3) were added and evaporated under the same conditions. The white solid thus obtained was extracted with n-hexane (3 × 10 cm^3) at room temperature, and 0.61 g of crude $(B_{10}H_{13})_2O$ were obtained (60% yield). The solid was sublimed at 10^{-6} torr and 100–110 °C. ^{11}B NMR spectra of the product dissolved in n-hexane were the same before and after sublimation.

Characterization

The ^{11}B NMR spectra of 6-$B_{10}H_{13}OH$ (singlet at 6.9 ppm and doublets at 15.1, 33.3, 51.1 and 62.6 ppm with $B(OMe)_3$ as external standard) were in complete agreement with published data [2]; the IR spectra exhibited a band at 3570 cm^{-1} assignment to the OH stretching vibration [2].

$(B_{10}H_{13})_2O$ was also easily characterized from published data concerning X-ray [1, 3], IR [1] and ^{11}B NMR [2] (we obtained a singlet at –2.9 ppm and doublets at 13.2, 30.1, 52.4 and 61.5 ppm). Elemental analysis gave a 0.12 H:B ratio (calculated 0.12). The Raman spectrum of the solid was scanned in the range 100 cm^{-1} –3000 cm^{-1}. The main lines were: 154(w), 225(w), 366(w), 400(w), 472(w), 560(w), 585(w), 637(m), 710(vs), 720(m), 755(m), 769(w), 849(w), 863(s), 880(w), 907(w), 960(w), 1025(w), 1078(w), 1500(w), 1885(w,br), 1906(m,br), 1925(m,br), 1970(m,br), 2055 (m,br), 2539(s), 2550(s) and 2580(vs). The B–H–B bridges were easier to characterize by Raman scattering than by IR. The frequencies of the corresponding stretching vibrations are in the 1850–2100 cm^{-1} range; only weak and broad bands appeared by IR at 1900 and 1980 cm^{-1}.

The melting point of sublimed 6-$(B_{10}H_{13})_2O$ was determined by DSC in stainless steel crucibles sealed in a dry argon atmosphere. No change was observed by use of different scanning speeds (2° per min or 5° per min). The maximum position of the melting peak was at 137 °C which is in good agreement with published results (139–140 °C) [1, 2]. However, a usual melting point determination by DSC produced a value of 132 °C for this point. This temperature is more correct for consideration but it cannot be compared with the melting points determined in open air capillary tubes.

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