

Dehydration of $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$: an Improved Preparation of Icosaborane Oxide, $(\text{B}_{10}\text{H}_{13})_2\text{O}$

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6,6'-bis(nido-decaboranyl)oxide, $\text{B}_{10}\text{H}_{13}\text{OB}_{10}\text{H}_{13}$, was originally obtained [1] by reaction of 6,9-bis(di-alkyl sulphido) dodecahydrodecaborane, $\text{B}_{10}\text{H}_{12}(\text{R}_2\text{S})_2$ ($\text{R} = \text{CH}_3$ or C_2H_5), with sulphuric acid. It has been shown in more recent work [2] that 6-hydroxy-nido-decaborane, $\text{B}_{10}\text{H}_{13}\text{OH}$, is formed in addition to $(\text{B}_{10}\text{H}_{13})_2\text{O}$. The structure of $(\text{B}_{10}\text{H}_{13})_2\text{O}$ 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 $(\text{B}_{10}\text{H}_{13})_2\text{O}$ by dehydration of $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$ has never been reported. $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$ is a strong acid; hydrates such as $\text{H}_2\text{B}_{10}\text{H}_{10}\cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{B}_{10}\text{H}_{10}\cdot 2\text{H}_2\text{O}$ have been characterized during the dehydration [5]. Further drying has given a solid residue from which a compound of formula $\text{B}_{10}\text{H}_{14}\text{O}$ has been isolated by sublimation under vacuum. According to our results, it is probable that this compound was 6- $\text{B}_{10}\text{H}_{13}\text{OH}$.

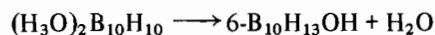
Results and Discussion

$(\text{B}_{10}\text{H}_{13})_2\text{O}$ is obtained with a 60% yield by dehydration of an easily available material, $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$, prepared by ion exchange from $\text{B}_{10}\text{H}_{10}^{2-}$ salts. Starting from the acidic solution, the first stage is the formation of 6- $\text{B}_{10}\text{H}_{13}\text{OH}$ by evaporation of water under vacuum; benzene is then added to the reaction mixture and it dissolves the 6- $\text{B}_{10}\text{H}_{13}\text{OH}$. Benzene is evaporated in the second stage; the residue is a white solid from which 6,6'- $(\text{B}_{10}\text{H}_{13})_2\text{O}$ can be extracted with hexane at room temperature.

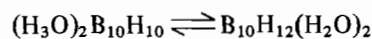
Although the preparation of $(\text{B}_{10}\text{H}_{13})_2\text{O}$ from $\text{B}_{10}\text{H}_{12}(\text{R}_2\text{S})_2$ and from $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$ is very different, the mechanisms leading to the final product appear to be similar. It has been shown [2] that $\text{B}_{10}\text{H}_{13}\text{OH}$ is an intermediate which reacts with $\text{B}_{10}\text{H}_{12}(\text{Et}_2\text{S})_2$ to give the oxide. It has also been demon-

strated 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 $\text{B}_{10}\text{H}_{13}\text{OH}$ with a bis-ligand seems also the best way to account for the results, the bis-ligand being here $\text{B}_{10}\text{H}_{12}(\text{H}_2\text{O})_2$.

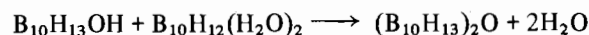
The formation of 6- $\text{B}_{10}\text{H}_{13}\text{OH}$ must be related to the general case of opening the $\text{B}_{10}\text{H}_{10}^{2-}$ cage in acidic medium; $\text{B}_{10}\text{H}_{12}(\text{R}_2\text{S})_2$ [6, 7] and $\text{B}_{10}\text{H}_{14}$ [8] can be prepared under these conditions.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



6,9- $\text{B}_{10}\text{H}_{12}(\text{H}_2\text{O})_2$ 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 $\text{B}_{10}\text{H}_{12}(\text{R}_2\text{S})_2$ from $(\text{H}_3\text{O})_2\text{B}_{10}\text{H}_{10}$ and R_2S . One possibility is that $\text{B}_{10}\text{H}_{12}(\text{H}_2\text{O})_2$ is present in low concentration because of the equilibrium



6,6'- $(\text{B}_{10}\text{H}_{13})_2\text{O}$ should be formed by the reaction



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 $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ 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

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; $6\text{-B}_{10}\text{H}_{13}\text{OH}$ was the only boron compound present in the benzene solution. Benzene was evaporated at 10^{-3} torr and new fractions of benzene ($3 \times 10 \text{ cm}^3$) were added and evaporated under the same conditions. The white solid thus obtained was extracted with n-hexane ($3 \times 10 \text{ cm}^3$) at room temperature, and 0.61 g of crude $(\text{B}_{10}\text{H}_{13})_2\text{O}$ were obtained (60% yield). The solid was sublimed at 10^{-6} torr and $100\text{--}110^\circ\text{C}$. ^{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 $6\text{-B}_{10}\text{H}_{13}\text{OH}$ (singlet at 6.9 ppm and doublets at 15.1, 33.3, 51.1 and 62.6 ppm with $\text{B}(\text{OMe})_3$ 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].

$(\text{B}_{10}\text{H}_{13})_2\text{O}$ 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 stretch-

ing vibrations are in the $1850\text{--}2100 \text{ cm}^{-1}$ range; only weak and broad bands appeared by IR at 1900 and 1980 cm^{-1} .

The melting point of sublimed $6\text{-}(\text{B}_{10}\text{H}_{13})_2\text{O}$ 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 ($139\text{--}140^\circ\text{C}$) [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.

References

- 1 S. Hermanek, J. Plešek and B. Stibr, *Collect. Czech. Chem. Commun.*, **33**, 691 (1968).
- 2 N. N. Greenwood, M. J. Hails, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 953 (1985).
- 3 N. N. Greenwood, W. S. McDonald and T. R. Spalding, *J. Chem. Soc., Chem. Commun.*, 1251 (1980).
- 4 J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, **38**, 93 (1980).
- 5 E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth and H. C. Miller, *Inorg. Chem.*, **3**, 445 (1964).
- 6 M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams and J. M. Makhlof, *J. Am. Chem. Soc.*, **89**, 3361 (1967).
- 7 G. Guillevic, J. Dazord, H. Mongeot and J. Cueilieron, *J. Chem. Res. (S)*, 402 (1978).
- 8 H. Mongeot and H. R. Atchekzai, *Z. Naturforsch., Teil B:*, **36**, 313 (1981).
- 9 Wang Guang-Chang, Lü Yi-Xin and Dai Li-Xin, Huang Xiu Yun, *Acta Chim. Sinica*, **39**, 251 (1981).
- 10 G. Guillevic, J. Dazord, H. Mongeot and J. Cueilieron, *J. Chem. Res.*, 4864 (1978).