

A Novel Synthesis of $nido-[8-HO-7-CB_{10}H_{12}]^-$ Anion

SHAH ALAM KHAN

P.C.S.I.R. Laboratories, Jamrud Road, Peshawar, Pakistan.

(Received 16th December, 1990, revised 6th April, 1991)

Summary: A *nido-closo-nido* interconversion reaction of 7-Me₃N-*nido*-7-CB₁₀H₁₂ is discussed. $Nido-[8-HO-7-CB_{10}H_{12}]^-$ anion is obtained from the reaction of 7-Me₃N-*nido*-7-CB₁₀H₁₂ with sodium hydride. At ambient temperature the initial product is the deprotonated species, *nido*-[7-Me₃N-7-CH₁₀H₁₁], but after reflux and hydrolysis the isolated product is the *nido*-[8-HO-7-CH₁₀H₁₂] anion with the *closo*-[2-CB₁₀H₁₁] as an intermediate. The results unambiguously show [OH] substitution at B (8) position.

Introduction

Substitution of the monocarbon - carborane species derived from *nido*-[7-CB₁₀H₁₃] anion has been achieved under various experimental conditions. In our previous paper [1], chlorine and deuterium substitutions of 7-Me₃N-*nido*-7-CB₁₀H₁₂ were achieved by the electrophile induced nucleophilic method, whereas this paper reports the synthesis of *nido*[8-HO-7-CB₁₀H₁₂] anion (I) (Fig. 1) through a *nido-closo-nido* sequence of reaction which resulted in substitution at B (8).

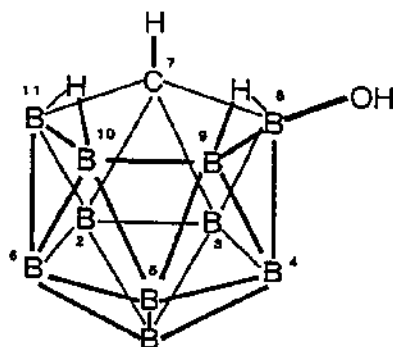


Fig.1: Structure of $nido-[8-HO-7-CB_{10}H_{12}]^-$

(I) is a new ionic species although its neutral molecule, 7-Me₃N- HO-*nido*-7-CB₁₀H₁₁, has been reported elsewhere [2], in which the position of the

(OH) substituent was not established unambiguously. The compound has been fully characterised by elemental analysis, ¹H, ¹¹B and 2-D ¹¹B-¹¹B n.m.r spectroscopy.

Experimental

Physical Measurements

IR spectra were recorded as mulls in nujol between KBr plates on a Perkin-Elmer 457 Grating Infrared spectrometer (ν_{max} in cm^{-1}), mass spectra on an A.E.I. MS9 spectrometer and NMR spectra were recorded on Bruker WH 360 spectrometer (¹H 360 MHz, ¹¹B 115.5 MHz) ion solutions in CD₃CN. Chemical shifts are given in δ [ppm, referenced to TMS (¹H) and BF₃ · O Et₂ (¹¹B)]; positive shifts downfield]. Two-dimensional (2-D) ¹¹B-¹¹B NMR spectra were produced on samples via procedures described elsewhere [3]. TLC was carried out on plates made in the laboratory as required from silica gel [Kieselgel 60 G (Merck); detection by iodine vapours] in dichloromethane.

Chemicals and Synthesis

7-Me₃N-*nido*-7-CB₁₀H₁₂ was prepared by the previously reported method [4]. NaH in mineral oil

was washed with dry Et₂O prior to use. Tetrahydrofuran was dried over Na and then distilled from Na/benzophenone before use. Other commercially available chemicals were reagent grade and were used as purchased. The synthesis and standard isolation procedure was conducted strictly in an inert atmosphere.

Synthesis of (I)

7-Me₃N-7-CB₁₀H₁₂ (0.5g, 2.6 mmole) and excess sodium hydride (0.25 g, 10.4 mmole) were refluxed in dry THF for 24 hrs. The cooled solution was filtered in a nitrogen-filled glovebox. Solvent was removed *in vacuo*. The ¹¹B n.m.r monitored at this stage, showed the boron product to be *closo*-[2-CB₁₀H₁₁]⁻. Addition of water and precipitation with Me₄N Cl gave a quantitative yield of the product (I) (TLC on SiO₂ eluted with 25% CH₃CN- 75% CH₂Cl₂ showed a single component, R_f 0.4. ¹¹B NMR: δ_B 10.1[s, 1B, B(8)], -5.2[d, 1B, B(5)], -9.6 [d, 1B, B(3)], -12.1 [d, 1B, B(11)], -13.8 [d, 1B, B(2)], -20.6 [d, 1B, B(10)], -24.4 [d, 1B, B(4)], -26.2 [d, 1B, B(9)], -30.0 [d, 1B, B(1)], -37.3 [d, 1B, B(6)]. (Found: C, 26.6; H, 11.3; N, 6.1; C₅H₂₅ B₁₀NO requires: C, 26.9; H, 11.3; N, 6.10).

Results and Discussion

It has been reported [5] that *nido*-[7-CB₁₀H₁₃]⁻ is obtained from the reaction of 7-Me₃N- *nido*-7-CB₁₀H₁₂ with sodium hydride. In an attempt to

prepare the said anion by the reported method, it was found that the reaction is significantly more complex, and the products depend on the conditions of the reaction. At ambient temperature the initial product is the deprotonated species *nido*[7-Me₃N-7- CB₁₀H₁₁]⁻ [6], but after reflux and work-up the isolated product was the *nido*[8-HO-7-CB₁₀H₁₂]⁻ anion (I) with the *closo*-[2-CB₁₀H₁₁]⁻ [6] as an intermediate.

Initial reaction with sodium hydride at room temperature results in the removal of ene bridge proton and involves an unsatable *nido*-[7-Me₃N-7-CB₁₀H₁₁]⁻ anion which is then deaminated at reflux temperature subsequently it rearranges to the stable[2- CB₁₀H₁₁]⁻ *closo* isomer. A diamond - square-diamond "dsd" type of rearrangement has been reported [7].

Cage opening occurs after hydrolysis of the *closo* isomer to give the *nido*-[8-HO-7-CB₁₀H₁₂]⁻ anion. It is reasonable to suggest that the terminal proton at B(8) gives bridging between B (8) and B(9) with the attack of [OH]⁻ on B(8). The second bridging between B(10) and B(11) results from a proton produced from H₂O and a similar rearrangement occurs.

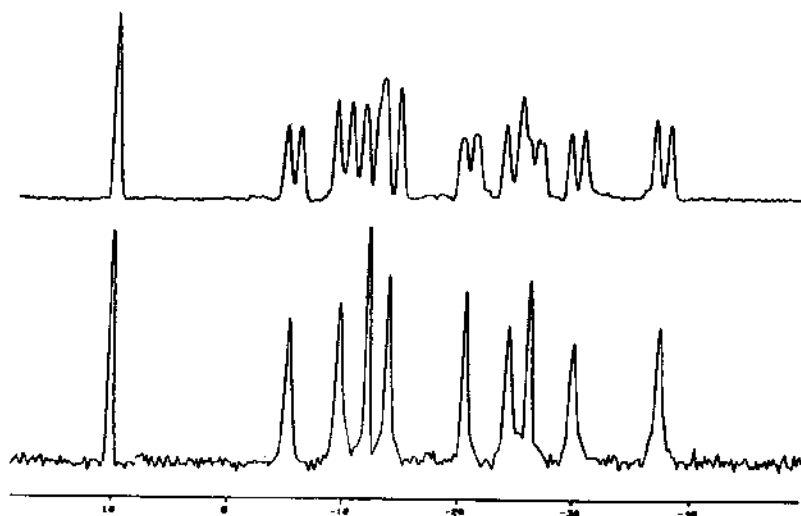
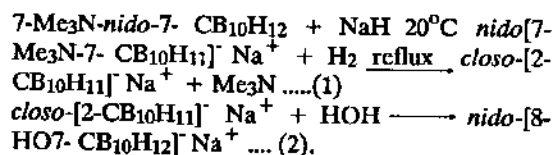


Fig.2: 115.5 MHz ¹¹B and ¹¹B [¹H] n.m.r. spectra of *nido*-[8-Ho-7-CB₁₀H₁₂]⁻.

The 115.5 MHz ^{11}B and ^{11}B - ^1H n.m.r. spectra of (I) (Fig. 2) gave a low-field (high frequency) singlet at 10.1 ppm attributed to the HO-substituted B (8) atom. The ^{11}B - ^1H n.m.r. spectrum further showed ten resonances of equal area ratios.

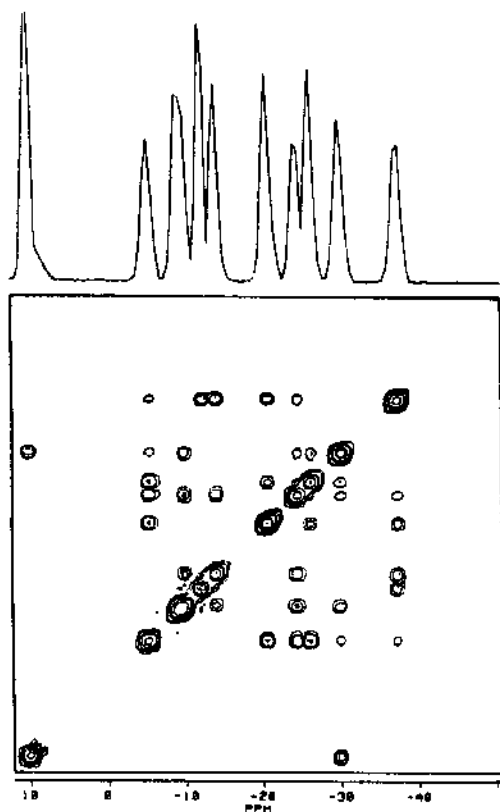


Fig.3: 115.5 MHz 2-D ^{11}B - ^{11}B (COSY) n.m.r. spectrum of nido-[8-HO-7-CB₁₀H₁₂]- in CD₃CN.

The 360 MHz ^1H n.m.r. spectrum displayed singlets at $\delta + 3.07$ p.p.m. (relative area; 12) due to the cation, $[\text{Me}_4\text{N}]^+$, at $\delta + 2.25$ ppm (relative area; 1) corresponding to the [OH] group and at $\delta + 1.4$ ppm. (relative area; 1) corresponding to the [CH] group. Results of the 360 MHz ^1H - ^{11}B

n.m.r. spectrum were consistent with the nine terminal hydrogens and two bridge hydrogens.

Table-1: Cross-peaks as indicated in the 2-B ^{11}B - ^{11}B NMR spectrum of nido-[8-HO-7-CB₁₀H₁₂]⁻ $[\text{Me}_4\text{N}]^+$

B(8) [B(4) ^s]
B(5) [B(10) ^s , B(1) ^m , B(9) ^s , B(6) ^w]
B(3) [B(8) ^w , B(2) ^m , B(1) ^s , B(4) ^m]
B(11) [B(2) ^s , B(6) ^l]
B(2) [B(3) ^m , B(1) ^m , B(6) ^s]
B(10) [B(5) ^s , B(9) ^m , B(6) ^m]
B(1) [B(5) ^m , B(3) ^s , B(2) ^m , B(4) ^w , B(6) ^w]
B(9) [B(5) ^s , B(10) ^m , B(4) ^m]
B(4) [B(8) ^s , B(5) ^w , B(3) ^m , B(1) ^w , B(9) ^m]
B(6) [B(5) ^w , B(11) ^s , B(2) ^s , B(10) ^m , B(1) ^w]

^sAtoms giving cross-peaks with the observed atoms (on diagonal) are listed in brackets with right superscripts indicating relative intensities of the off-diagonal interactions (s-strong, m-medium, w-weak interaction). Observed atoms (Off brackets) are listed upfield.

The 115.5 MHz 2-D ^{11}B - ^{11}B n.m.r. spectrum (fig. 3) showed a strong correlation between the oxygen-coordinated B(8) and the high field resonance of B(4) atoms (Table 1).

References

1. S.A. Khan, *J.Chem.Soc.Pak.*, submitted for publication.
2. W.H. Knoth, *J.Am.Chem.Soc.*, **89**, 1274 (1967).
3. S. Hermanek, J. Fusek, B. Stibr, J. Plasek and T. Jelinek, *Polyhedron* **5**, 1303 (1986).
4. J. Plesek, T. Jelinek, E. Drdakova, S. Hermanek and B. Stibr, *Coll.Czech.Chem.Comm.*, **49**, 1559 (1984).
5. D.E. Hyatt, F.R. Scholer, L.J. Tedd and J.L. Warner, *Inorg.Chem.*, **6**, 2229 (1967).
6. W.H. Knoth, *Inorg.Chem.*, **10**, 598 (1971).
7. R.J. Wiersema and M.F. Hawthorne, *Inorg.Chem.*, **12**, 785 (1973).