Notes

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A One-Step, High-Yield Synthesis of $B_{20}H_{19}^{3-}$ [1]

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The two methods so far reported for the conversion of $B_{10}H_{10}^{2-}$ to $B_{20}H_{19}^{3-}$ and its conjugate base $B_{20}H_{18}^{4-}$ are the direct oxidation with Ce^{4+} at 0°[2] and an indirect route *via* $B_{20}H_{18}^{2-}$.[3] In the ceric ion oxidation the yield of the desired product is low due to the readiness with which it undergoes further oxidation. Thus, when the triethylammonium salt is used, the principal products are boric acid, $[(C_2H_5)_3NH]_2B_{20}H_{18}$, and the double salt $[(C_2H_5)_3NH]_5[B_{20}H_{18} \cdot B_{20}H_{19}]$; consequently the yield cannot exceed 50% of theoretical. Moreover, extraction of the desired salt from the double salt without exchanging the cation for another one, usually tetramethylammonium,[2] is not an easy task as the solubilities of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ and of the double salt are very similar in a number of solvents.

In the course of work on the reactions of $B_{10}H_{10}^{2-}$ with transition metal ions it was found that the reaction with $FeCl_3$ has a very large activation energy. Thus, though at 80° the conversion of $B_{10}H_{10}^{2-}$ to $B_{20}H_{18}^{2-}$ is quantitative and rapid,[4] at room temperature considerable amounts of the $B_{20}H_{19}^{3-}$ intermediate can be isolated. It became apparent that if freshly formed $B_{20}H_{19}^{3-}$ could somehow be removed from contact with the oxidant, the production of $B_{20}H_{18}^{2-}$ could be suppressed even more. One easy way to do this is to have a two-phase reaction system. Owing to the high viscosity of concentrated solutions of $FeCl_3$ a two-phase aqueous system with $FeCl_3$ in one layer and $B_{10}H_{10}^{2-}$ with products of its oxidation in another is very easy to maintain for long periods of time. Very concentrated solutions of both reactants are used as otherwise the reaction rate is dismally slow. If the two-layer system is left undisturbed, oxidation of $B_{10}H_{10}^{2-}$ to $B_{20}H_{19}^{3-}$ takes place at the interface, but before it can undergo further oxidation the $[(C_2H_5)_3NH]_3B_{20}H_{19}$, which is less dense than water, rises to the surface of the upper phase and out of contact with the ferric ion. This upward movement sets up a current in the upper phase which brings fresh $B_{10}H_{10}^{2-}$ into contact with the oxidant below. After a thick layer of solid has accumulated at the surface, it can be skimmed off, or the lower layer containing Fe(III) and Fe(II) salts can be siphoned out and the solid can be separated from the clear upper layer by filtration. Yields of over 70% of the desired product have been obtained in this manner. At the same time, there is very little degradation to boric acid under these conditions so that most of the $B_{10}H_{10}^{2-}$ not converted to $B_{20}H_{19}^{3-}$ or $B_{20}H_{18}^{2-}$ can be recovered from the upper aqueous layer and reused.

Very pure $B_{20}H_{19}[(C_2H_5)_3NH]_3$ can be obtained by simply washing the solid with cold water to remove traces of $[(C_2H_5)_3NH]_2B_{10}H_{10}$ and with acetone or methanol, either one of which dissolves $[(C_2H_5)_3NH]_2B_{20}H_{18}$ very readily. Complete removal of the last one is indicated by the disappearance of the characteristic ultraviolet band at 293 mμ. Should one or two washings fail to remove all of the $B_{20}H_{18}^{2-}$, which might be tied up in the double salt, a 5–10-min refluxing of the solid with acetone or ethanol (not methanol!) followed by filtration yields pure $[(C_2H_5)_3NH]_3B_{20}H_{19}$. The B^{11} nmr spectrum indicates that the *ae* isomer is obtained.[2] This triethylammonium salt, unlike that of $B_{20}H_{18}^{2-}$, is insoluble in cold and hot acetone, cold and hot ethanol, and cold methanol. It dissolves in hot methanol but is not recovered quantitatively owing to the unusually rapid air oxidation to $B_{20}H_{18}^{2-}$ in this solvent. Acetonitrile dissolves readily the triethylammonium salts of both ions, but will not dissolve the tetramethylammonium salt of $B_{20}H_{19}^{2-}$. Consequently, should one want to convert the triethyl- into the more inert tetramethylammonium salt, it is faster and more efficient to add an aqueous solution of $(CH_3)_4NCl$ to an acetonitrile solution of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ and collect the precipitate than to resort to ion exchangers or quantitative titration with $(CH_3)_4NOH$. The cesium salt of the ion is very difficult to isolate in a pure state, since despite the large pK_a of the $B_{20}H_{19}^{3-}$ ion[2] the corresponding salt of the conjugate base is so very insoluble in aqueous and most mixed organo-aqueous solvents that the equilibrium

$$4Cs^+ + B_{20}H_{19}^{3-} \rightleftharpoons Cs_4B_{20}H_{18}(s) + H^+$$

can only be displaced to the left in strongly acidic solutions; under ordinary conditions, pH >0, if ion exchangers are used or stoichiometric ratios of cation to anion are mixed only $Cs_4B_{20}H_{18}$ is isolated. It is interesting to note in passing that while the solubilities of the cesium salts in water increase in the order $B_{20}H_{18}^{4-} < B_{20}H_{19}^{3-} < B_{20}H_{18}^{2-}$, those of the corresponding tetramethylammonium salts decrease in the same order. The same observations have been recorded for the related series of ions, $B_{20}H_{17}OH^{4-}$, $B_{20}H_{18}OH^{3-}$, and $B_{20}H_{17}OH^{2-}$.

Experimental Section

Materials.—Except for $[(C_2H_5)_3NH]_2B_{10}H_{10}$, which was prepared from $B_{10}H_{14}$ and $(C_2H_5)_3N$ and recrystallized from aqueous ethanol, all inorganic chemicals were reagent grade.

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(1) Research sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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(3) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

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Preparation of $[(C_2H_5)_3NH]_3B_{20}H_{19}$. Method A.—To 30 ml of 0.436 M $[(C_2H_5)_3NH]_2B_{10}H_{10}$ was added 30 ml of 2.1 M $FeCl_3$ and the two were thoroughly mixed. After 3 hr at room temperature, the reaction mixture was filtered and the solid washed repeatedly with cold water until the washings were free of Fe(II) and Fe(III) ions. Subsequently, the wet solid was washed with four 25-ml aliquots of methanol, removed from the filter paper, stirred for 15 min with 50 ml of acetone, and separated by filtration. The resulting white solid weighed 0.5623 g and melted at 163–164° after being kept for 24 hr over P_2O_5 *in vacuo;* its ultraviolet spectrum showed no evidence of $B_{20}H_{18}^{2-}$. Elemental analysis indicated that the water of hydration amounted to no more than 0.4% by weight. The filtrate and the washings were combined, reduced to half the initial volume on a steam bath, allowed to cool to room temperature, and left standing for 24 hr. Filtration of the resulting mixture yielded 2.0932 g of $[(C_2H_5)_3NH]_2B_{20}H_{18}$.

Method B.—With the aid of a pipet 10 ml of 4 M $FeCl_3$ was introduced underneath 15 ml of 0.872 M $[(C_2H_5)_3NH]_2B_{10}H_{10}$, contained in a medium size Petri dish (8 cm in diameter). The two aqueous layers remained undisturbed for 20 hr; then the remaining clear liquid phases were siphoned out, and the residual wet solid was separated by filtration and washed with five 25-ml aliquots of cold water. After drying for 24 hr over P_2O_5 the crude product weighed 2.4378 g. Since its ultraviolet spectrum still exhibited a weak band at 293 $m\mu$ the solid was washed with four 25-ml aliquots of acetone and dried. The resulting product was white, mp 163–164°, and its ultraviolet spectrum showed no evidence of absorption at either 293 or 232 $m\mu$. The weight of the washed material, 2.0252 g, indicated that $[(C_2H_5)_3NH]_3B_{20}H_{19}$ made up over 80% (by mole) of the crude product.

Preparation of $[(C_2H_5)_3NH]_5(B_{20}H_{18}\cdot B_{20}H_{19})$.—A 0.2230-g sample of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ was dissolved in 50 ml of boiling methanol and the solution immediately allowed to cool to room temperature. After 24 hr 0.0942 g of very clear large crystals, melting at 203–204°, was isolated. The product was identified as the double salt by means of its ultraviolet and infrared spectra.[2,3]

Preparation of $[(CH_3)_4N]_3B_{20}H_{19}$.—A 0.5725-g sample of $[(C_2H_5)_3NH]_3B_{20}H_{19}$ in 25 ml of acetonitrile was stirred with 5 ml of 1 M tetramethylammonium chloride for 30 min and filtered. The precipitate was first washed with 10 ml of water, then with two 25-ml aliquots of acetonitrile, and dried over P_2O_5 for 12 hr. The dry product, which was characterized by its ultraviolet and infrared spectra,[2,3] weighed 0.3835 g.

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Nuclear Magnetic Resonance in Polycyclic Compounds. III. Evidence for P^{31}–H^1 Spin–Spin Sign Changes in the PCH Bonds of a New Polycyclic Phosphine

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There exists a substantial body of evidence which suggests strongly that the absolute sign of the phosphorus–hydrogen coupling constant is positive in compounds such as $P(CH_3)_3$ and $P(CH_2CH_3)_3$ and negative in phosphonium salts and trialkylphosphine chalcogenides such as PR_4^+ and OPR_3, respectively.[2] That a change in sign of J_{PCH} from three- to four-coordinate phosphorus compounds of this type takes place has been known with fair certainty for some time.[3] Such a sign change was demonstrated recently by the observation that J_{PCH} for $P(CH_3)_3$ passed through zero as $Al(CH_2CH_3)_3$ was added to form the labile but slightly dissociated 1:1 adduct.[4]

We present evidence here which is consistent with a decrease in the absolute magnitude of J_{PCH} to zero as the new polycyclic phosphine $P(CH_2O)_3CCH_3$[5] (I) is converted to $Fe(CO)_4(I)$ or *trans*-$[Fe(CO)_3(I)_2]$ followed by a progressive increase upon oxidation of I to $SP(CH_2O)_3CCH_3$ (II) and $OP(CH_2O)_3CCH_3$ (III). Moreover, these changes parallel those we observed earlier for J_{POCH} in the analogous derivatives of $P(OCH_2)_3CCH_3$.[6]

Experimental Section

Preparation of $P(CH_2O)_3CCH_3$ (I).—This polycycle was synthesized following a preparation we reported earlier for $P(CH_2O)_3CH$ (IV)[7] except that the methanol produced was removed by a nitrogen flush as soon as the temperature of the reaction mixture reached 90°. The oily residue which solidified on cooling was sublimed twice under vacuum at 60° to give a 60% yield of colorless crystals.

Anal. Calcd for $C_5H_9O_3P$: C, 40.54; H, 6.07. Found: C, 40.27; H, 5.90. The mass spectrum obtained at a source temperature of 200° exhibited a parent peak corresponding to mass 148 as expected.

Preparation of $SP(CH_2O)_3CCH_3$ (II).—A mixture of 1.0 g of I (6.7 mmoles) and 0.20 g of sulfur (6.7 mg-atoms) was heated in a sealed tube for 1 hr at 110°. An acetone extract of the residue upon concentration and addition of methanol gave a white solid which sublimed at 60° under vacuum to give a 33% yield of II as colorless crystals. A medium band at 744 cm^{-1} characteristic of the P=S group was observed in Nujol in the infrared spectrum.

Anal. Calcd for $C_5H_9O_3PS$: C, 33.22; H, 5.00. Found: C, 33.28; H, 5.07.

Preparation of $OP(CH_2O)_3CCH_3$ (III).—To 1.0 g of I (6.7 mmoles) dissolved in 10 ml of absolute ethanol containing about 3 g of Linde 4A Molecular Sieve was added 0.8 g of 30% hydrogen peroxide (6.7 mmoles of H_2O_2). After standing 15 min at room temperature, the mixture was filtered and the solution concentrated under vacuum to 5 ml. Cooling this solution to 0° gave a 20% yield of III as colorless crystals after several hours. A strong infrared band at 1200 cm^{-1} observed in $CHCl_3$ is assigned to the P=O stretching mode.

Anal. Calcd for $C_5H_9O_4P$: C, 36.59; H, 5.49. Found: C, 37.18; H, 5.48.

Preparation of $P(CH_2O)_3CH$ (IV), $SP(CH_2O)_3CH$ (V), and $OP(CH_2O)_3CH$ (VI).—Compounds IV and VI were prepared as described earlier.[7] The thiophosphine V was prepared in the same way as was II. The product sublimed at 40° under vacuum to give a 28% yield of colorless crystals.

Preparation of $Ni(CO)_2(I)_2$.—This complex was prepared by

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[1] Alfred P. Sloan Fellow.

[2] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966), and references therein.

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[4] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966).

[5] The new compound $P(CH_2O)_3CCH_3$ (I) is named 4-methyl-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane. The names of the derivatives $SP(CH_2O)_3CCH_3$ (II) and $OP(CH_2O)_3CCH_3$ (III) are the same except they are preceded by 1-sulfo and 1-oxo, respectively.

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[7] E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Am. Chem. Soc.*, **88**, 1140 (1966).