ionization so that they both produce an average of only one particle per molecule of SbF_5 or SbF_4SO_3F.

Table IV and Figure 8 also give the results of an experiment in which SO_3 was added to a 0.0415 *m* solution of $SbF_4(SO_3F)$ and the freezing point measured. Freezing points interpolated for the compositions $SbF_3(SO_3F)_2$, $SbF_2(SO_3F)_3$, and $SbF(SO_3F)_4$ gave values of ν = 1.6, 2.3, and 3.1, respectively, where ν is the number of moles of particles produced in solution by one mole of solute. Complete ionization of any of these acids would give $\nu = 2$

$$H[SbF_{5-n}(SO_3F)_{n+1}] + HSO_3F = H_2SO_3F^+ + SbF_{5-n}(SO_3F)_{n+1}^- \quad (14)$$

Thus the observed value of $\nu = 1.6$ for $H[SbF_3(SO_3F)_3]$ is consistent with the conclusion from conductometric studies that it is not a strong acid. The observed value of $\nu = 2.3$ for $H[SbF_2(SO_3F)_4]$ indicates that it is probably a strong acid and must be in equilibrium with an appreciable amount of free SO_3

$$H[SbF_2(SO_3F)_4] \rightleftharpoons H[SbF_3(SO_3F)_3] + SO_3 \quad (15)$$

but because polymers are also undoubtedly present it is not possible to interpret the ν value quantitatively. Finally the value of $\nu = 3.1$ indicates complete dissociation of the acid $H[SbF(SO_3F)_5]$ to $H[SbF_2(SO_3F)_4]$ and SO_3, which is consistent with the previous conclusion from the conductometric and n.m.r. studies that the higher fluorosulfates $SbF(SO_3F)_4$ and $Sb(SO_3F)_5$ are extensively if not completely dissociated into sulfur trioxide and lower fluorosulfates.

Acknowledgments.—We thank the Defence Research Board of Canada, the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research, and the Petroleum Research Fund of the American Chemical Society for generous financial assistance. We also thank the Ontario Research Foundation for the award of a fellowship (to R. C. T.) and the East Ham Education Authority, London, England, for the award of a scholarship (to J. B.).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO

The Preparation and Properties of Some Tetracoordinate Boron Compounds. The Pseudo-Metal Ion Concept

BY L. H. TOPORCER, R. E. DESSY,[1] AND S. I. E. GREEN

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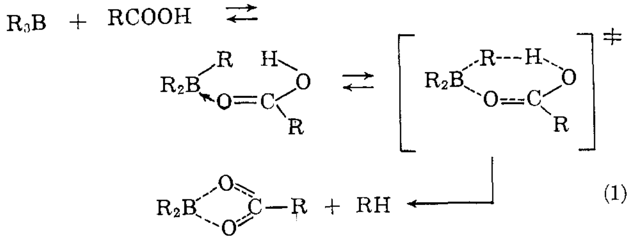
The infrared, ultraviolet, H^1 and B^{11} nuclear magnetic resonance spectra, and polarographic behavior of a series of R_2B complexes possessing tetrahedral geometry indicate that they and similar derivatives can serve as excellent models with which to study chelate characteristics. The R_2B moiety functions as a pseudo-metal ion or atom which permits alteration of total and effective charge without variation in size of the chelate ring and permits placement and surveying of probes to study the electron distribution in the chelates.

Introduction

In a previous publication[2] the kinetics of the cleavage of triethylborane with weak acids were studied, and a mechanism emphasizing the essential prior coordination was proposed which was consistent with available data. The present paper describes a series of investigations on the products of this reaction, and related processes, which yield compounds involving four-coordinate boron.



(1)

Experimental

All melting points were uncorrected and obtained on a Fisher-Johns melting point apparatus. The molecular weight determinations were obtained from a Mechrolab Model 301 osmometer at approximately 0.1 *M* concentrations. A Baird-Atomic Model KM-1 infrared spectrophotometer was used to obtain the infrared spectra, and a Varian A-60 n.m.r. spectrometer was used for the proton n.m.r. spectra. The B^{11} spectra were obtained on a Varian high-resolution spectrometer at 19.3 Mc. The ultraviolet spectra were obtained on a Cary Model 11 recording spectrophotometer. The analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reagents.—Triethylborane was used as obtained from Stauffer Chemical Co., Anderson Chemical Division. Gas chromatographic analysis indicated one major component with a trace of a minor one. The following compounds were obtained from Matheson Coleman and Bell and their method of purification is indicated: 2,4-pentanedione (distilled, b.p. 136°), ethyl acetoacetate [b.p. 66–68° (11 mm.), used as obtained], 1,3-diphenyl-1,3-propanedione (recrystallized from ether), boron trifluoride ethyl ether complex (distilled, b.p. 124°), and 2(1H)-pyridone (recrystallized from benzene, m.p. 106–107°). The 8-quinolinol was Eastman White Label material. Phenylacetylene was used as purchased from Columbia Chemicals Co. Hexafluoroacetylacetone was obtained from K and K laboratories.

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[1] Alfred P. Sloan Fellow.

[2] L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *J. Am. Chem. Soc.*, **87**, 1236 (1965).

Preparation of Diethylboron Acetylacetonate.—Into a three-necked flask equipped with condenser and nitrogen sweep was placed 50 ml. of anhydrous tetrahydrofuran (THF). After the apparatus was flushed with nitrogen, 3 g. (0.03 mole) of 2,4-pentanedione and 3.15 g. (0.032 mole) of triethylborane were added by the use of a hypodermic syringe. The mixture immediately turned light yellow. Upon refluxing, gas evolution was evident through the Gilman trap. The gas was measured by a crude Zerewitinoff method. After 3 hr. of refluxing the approximate amount of gas was obtained for the liberation of 1 mole of gas per mole of 2,4-pentanedione. The infrared analysis indicated that the gas was ethane. The yellow reaction mixture was transferred to a mini-lab distillation apparatus and the THF solvent was stripped. Distillation gave 4.2 g. (84% yield) of a yellow liquid [b.p. 69–70° (2.9 mm.), $n^{22}\text{D}$ 1.4655].

Anal. Calcd. for $C_9H_{17}BO_2$: C, 64.3; H, 10.1; B, 6.4; mol. wt., 168. Found: C, 63.4; H, 10.4; B, 6.3; mol. wt., 175 in benzene.

The infrared obtained on a neat sample gave strong bands at 1585 cm.$^{-1}$ ($C—O\rightarrow B<$), 1532 cm.$^{-1}$ ($C=C$ conj.), and 1360 cm.$^{-1}$ ($B—O—$).[3] There was no normal carbonyl peak present.

Preparation of Diethylboron 1,3-Diphenyl-1,3-propanedionate.—Into a flask equipped with condenser and N_2 sweep were placed 50 ml. of anhydrous diglyme (Ansul 141) and 2.7 g. (0.01) mole of 1,3-diphenyl-1,3-propanedione. The system was flushed with nitrogen and 4 ml. (2.8 g., 0.0286 mole) of triethylborane was added by the use of a hypodermic syringe. The reaction mixture immediately turned to a yellow-orange color. Upon refluxing for 4 hr. the approximate amount of gas evolved for 1 mole of gas per mole of 1,3-diphenyl-1,3-propanedione was obtained by a crude Zerewitinoff method. The orange reaction mixture was cooled and transferred to a double Schlenk tube. After the diglyme solvent and the excess of triethylborane were stripped by the use of a vacuum pump an orange solid remained. The crude material (2.8 g.) had m.p. 90–93°. Two recrystallizations from anhydrous pentane gave 1.8 g. (51%) of product melting at 92–93°. A mixture melting point with 1,3-diphenyl-1,3-propanedione was 65–69°. It should be noted that the above reaction went quite slowly, if at all, when tetrahydrofuran solvent was used.

Anal. Calcd. for $C_{19}H_{21}O_2B$: C, 78.2; H, 7.2; B, 3.7; mol. wt., 292. Found: C, 77.3; H, 7.5; B, 3.6; mol. wt., 280 in C_6H_6.

The infrared spectrum on a Nujol mull did not show any uncoordinated carbonyl peak but showed a strong peak at 1585 cm.$^{-1}$ ($C—O\rightarrow B<$); ultraviolet spectrum: $\lambda_{\max}$ 266 cm.$^{-1}$ (ϵ 9400), 311 cm.$^{-1}$ (ϵ 17,500), and 401 cm.$^{-1}$ (ϵ 6150).

Reaction of Triethylborane with Ethyl Acetoacetate.—Using procedures previously described 3.65 ml. (3.7 g., 0.029 mole) of ethyl acetoacetate was allowed to react with 4.5 ml. (3.15 g., 0.032 mole) of triethylborane in 10 ml. of anhydrous diglyme solvent. Within 1 hr. of refluxing the expected amount of gas was obtained (1 mole per mole of ethyl acetoacetate). The infrared analysis of the gas indicated that it was ethane. The mixture turned slightly yellow during refluxing. Stripping of the solvent and distillation through a mini-lab apparatus gave 4.6 g. (82%) of a colorless liquid, b.p. 64–65° (0.8 mm.), $n^{21}\text{D}$ 1.4559. A positive flame test was obtained for boron.

The reaction would not proceed using THF as solvent. However, the same product was obtained in the absence of a solvent.

Anal. Calcd. for $C_{10}H_{19}O_3B$: C, 60.6; H, 9.7; mol. wt., 198. Found: C, 60.7; H, 9.6; mol. wt., 192 in C_6H_6.

The infrared spectrum obtained from a thin film showed a peak that indicated a trace of free carbonyl. Also characteristic peaks were found at 1590 cm.$^{-1}$ ($C—O\rightarrow B<$) and 1530 cm.$^{-1}$ ($C=C$).

Preparation of Diphenylboron Acetylacetonate.—Diphenylborinic anhydride was prepared by the method of Coates and Livingstone,[4] and the diphenylboron chloride was prepared by the method of Abel, *et al.*[5] The method of preparation for the diphenylboron acetylacetonate was similar to that used by Gerrard, *et al.*,[6] for the preparation of 2-ethoxycarbonyl-1-methyl vinyl diphenylboronite. Into 20 ml. of pentane in a double Schlenk tube was placed 2.1 g. (0.011 mole) of diphenylboron chloride. The tube was flushed with nitrogen and then 1.08 ml. (1.05 g., 0.011 mole) of 2,4-pentanedione was added dropwise with a hypodermic syringe. The reaction was exothermic and HCl was given off. The pentane was stripped and a white solid that turned pink upon standing remained. The solid was dissolved into benzene and then pentane was added. At first a red oil came out of solution. The solvents were transferred to the other side of the Schlenk tube and were removed. A pink solid remained again. This solid was dissolved into benzene and removed from the tube. The red oil on the one side was removed from the Schlenk tube and the benzene solution returned to the tube. Then pentane was added to precipitate the solid. Three recrystallizations from dry diethyl ether gave 2.0 g. (71%) of a white solid (m.p. 116–117°).

Anal. Calcd. for $C_{17}H_{17}BO_2$: C, 77.3; H, 6.5; B, 4.1; mol. wt., 264. Found: C, 77.0; H, 6.4; B, 4.1; mol. wt., 246 in C_6H_6.

The infrared spectrum obtained on a Nujol mull indicated one C–O absorption present at 1585 cm.$^{-1}$.

Preparation of Diphenylethynylboron Acetylacetonate.—The path pursued was to prepare the triphenylethynylboron and allow it to react with acetylacetone to cleave one phenylethynyl group. Therefore, the triphenylethynylboron was prepared in the manner reported by Ashby.[7]

The phenylethynyllithium was prepared by reaction of 0.16 mole of phenylacetylene with 0.16 mole of *n*-butyllithium in pentane solvent. The phenylethynyllithium was added to 28.2 g. (0.2 mole) of $BF_3\cdot(C_2H_5)_2O$ in 100 ml. of a 50–50 mixture of ether and pentane in a 1-l. round-bottom flask equipped with stirrer, condenser, and argon sweep. The addition time was approximately 30 min. and the reaction vessel was cooled in a Dry Ice–acetone bath. While the reaction mixture was at −70°, 10 g. (0.1 mole) of acetylacetone was added. The mixture with an insoluble solid present was allowed to warm to room temperature and was heated to reflux. The reaction mixture was filtered and the solvent stripped by use of a vacuum pump. When concentrating the solvent and heating under vacuum, the mixture turned black. The black material was then run through a chromatography column using Woelm neutral alumina and a solvent mixture of benzene–ligroin (40–60°). Fractions containing phenylacetylene, acetylacetone, a white solid, and a black oil were obtained. The white solid (1.2 g.), diphenylethynylboron acetylacetonate, was recrystallized from ether, m.p. 123–124°. A positive flame test for boron was observed.

Anal. Calcd. for $C_{21}H_{17}O_2B$: mol. wt., 312. Found: mol. wt., 303.

The infrared spectrum obtained from a KBr pellet indicated a single C–O absorption at 1575 cm.$^{-1}$. The proton n.m.r. spectrum was consistent with the formulation of diphenylethynylboron acetylacetonate.

Reaction of Diphenylboron Chloride with 1,3-Diphenyl-1,3-propanedione.—Using a similar procedure as above, 2.23 g. (0.011 mole) of diphenylboron chloride in 30 ml. of anhydrous pentane was allowed to react with 2.48 g. (0.011 mole) of 1,3-diphenyl-1,3-pentanedione. The reaction was exothermic and HCl was given off. A yellow solid was obtained. The solid was washed three times with ether in the Schlenk tube which removed a maroon-colored impurity. The solid was recrystallized from dry benzene to give 3.7 g. (86%) of a yellow solid (m.p. 229–231°).

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[4] G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 4909 (1961).

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[6] W. Gerrard, M. F. Lappert, and R. Shafferman, *ibid.*, 3648 (1958).

[7] E. C. Ashby and W. E. Foster, *J. Org. Chem.*, **29**, 3225 (1964).

Anal. Calcd. for $C_{22}H_{21}BO_2$: C, 83.5; H, 5.5; B, 2.8; mol. wt., 388. Found: C, 83.3; H, 5.6; B, 3.0; mol. wt., 391 in benzene.

The infrared spectrum of a Nujol mull indicated only one C–O absorption, at 1575 cm.$^{-1}$; ultraviolet spectrum: λ_{max} 279 cm.$^{-1}$ (ϵ 13,000), 304 cm.$^{-1}$ (ϵ 11,500), and 393 cm.$^{-1}$ (ϵ 12,400).

Preparation of Boron Difluoride Complex of Acetylacetone.— The following preparation is somewhat similar to the method of Morgan and Tunstall,[8] which involved the passing of BF_3 into a concentrated solution of acetylacetone in benzene.

Into a round-bottom flask equipped with N_2 sweep and dropping funnel was placed 10.13 g. (0.07 mole) of $BF_3\cdot(C_2H_5)_2O$ (0.07 mole). Then 7 ml. (7 g., 0.07 mole) of acetylacetone was added dropwise. Hydrogen fluoride was evolved. The reaction mixture became warm and turned dark brown. After the HF was removed the mixture was transferred to a distillation apparatus. First, the ether was stripped and then 8.1 g. (78%) of a light brown liquid [b.p. 121° (1–1.5 mm.)] that solidified upon standing was obtained. After six recrystallizations from anhydrous diethyl ether 1.8 g. (17%) of a white crystalline solid (m.p. 39–40°) was obtained. Since the reported melting point of this compound[8] was 43°, the C and H analyses were checked.

Anal. Calcd. for $C_5H_7O_2BF_2$: C, 40.7; H, 4.8. Found: C, 40.5; H, 4.8.

The infrared spectrum obtained on a KBr pellet indicated only one carbonyl absorption (1580 cm.$^{-1}$).

Preparation of Boron Difluoride Complex of 1,3-Diphenyl-1,3-propanedione.—Into a three-necked round-bottom flask equipped with condenser and N_2 sweep were placed 20 ml. of dry diglyme (Ansul 141) and 2 g. (0.01 mole) of 1,3-diphenyl-1,3-propanedione. To this mixture was added 1.2 ml. of $BF_3\cdot(C_2H_5)_2O$ (0.65 g., 0.01 mole, BF_3). The reaction mixture was heated to reflux for 20 min. and became black. After stripping the HF, ether, and diglyme, the solid was transferred into the double Schlenk tube. An attempt to remove the dark color by ether washings was not totally successful. The pale yellow-green solid was recrystallized from dry benzene several times, but this did not seem to remove any more of the dark impurity. Finally, purification by sublimation gave 1.6 g. (67%) of a light yellow solid (m.p. 193–194°). The reported melting points were 191°[8] and 189–190°.[9] The infrared spectrum was obtained on a KBr pellet. There was no normal carbonyl peak, but a shifted one at 1590 cm.$^{-1}$ ($C—O \rightarrow B$).

Preparation of Diethylboron Hexafluoroacetylacetonate.— Into a round-bottom flask equipped with condenser and argon sweep were placed 3.44 g. (0.017 mole) of hexafluoroacetylacetone and 2.1 g. (0.02 mole) of triethylborane. The mixture turned orange immediately. After refluxing for 2 hr. the correct amount of gas (1 mole of gas per mole of hexafluoroacetylacetone) was obtained. The infrared analysis on the gas identified it as ethane. The deep mixture was distilled through the mini-lab. distillation apparatus to give 2.3 g. (50%) of a blood-red liquid, b.p. 120–121°. The liquid was quite air-sensitive and therefore was always handled in an argon atmosphere. Upon exposure to air a colorless liquid resulted. The infrared spectrum obtained on neat liquid indicated only one C–O absorption, at 1570 cm.$^{-1}$. The structure was confirmed by proton n.m.r.

Reaction of Triethylborane with 8-Hydroxyquinoline.—Into a flask equipped with condenser and N_2 sweep were placed 50 ml. of dry THF, 4 ml. (2.8 g., 0.029 mole) of triethylborane, and 4.5 g. (0.029 mole) of 8-hydroxyquinoline. A yellow color formed immediately and gas evolution was evident through the Gilman trap. The mixture was left at room temperature for 2 hr. and then heated to reflux for 20 min. The approximate amount of gas (ethane) was obtained for 1 mole of gas per mole of 8-hydroxyquinoline. After transferring the mixture to a double Schlenk tube and stripping the THF solvent a yellow solid was obtained. Recrystallization of the yellow solid from ether and from ligroin (40–60°) still gave a solid with a 5° m.p. range. Thus, the material was distilled from a mini-lab apparatus to give a yellow liquid [b.p. 150–152° (1.5 mm.)] which solidified upon standing (m.p. 52–53°). The 5.0 g. of product represented an 82% yield. A characteristic green flame for boron was obtained when the product was burned.

Anal. Calcd. for $C_{13}H_{16}BON$: C, 73.3; H, 7.6; mol. wt., 213. Found: C, 72.4; H, 7.3; mol. wt., 198, 206 in benzene.

Reaction of Triethylborane with 2(1H)-Pyridone.—Into a round-bottom flask equipped with N_2 sweep and condenser were placed 50 ml. of anhydrous THF and 3.9 g. (0.041 mole) of 2(1H)-pyridone. To this was added 9 ml. (6.3 g., 0.065 mole) of triethylborane dropwise. Gas evolution was quite rapid and the reaction was exothermic. The correct amount of gas (1 mole per mole of 2-pyridone) was obtained. Infrared analysis of the gas indicated that ethane was evolved. After refluxing the reaction mixture for 1 hr. the contents were transferred to a Schlenk tube and the solvent was stripped. The white solid that remained was recrystallized from chloroform. The solid was quite air-sensitive.

The molecular weight was obtained in anhydrous benzene using an argon atmosphere: calcd., 162.8; found, 311. Thus, it was concluded that the compound was dimeric.

The infrared spectrum in $HCCl_3$ indicated one C–O absorption (as in starting material) at 1700 cm.$^{-1}$.

Reaction of Triethylborane with 2-Pyrrolidone.—Into a flask equipped with condenser and N_2 sweep were placed 20 ml. of anhydrous THF and 3.15 g. (0.0322 mole) of triethylborane. To this was added 2.5 g. (0.0286 mole) of 2-pyrrolidone. The mixture was refluxed for 0.5 hr. and 1 mole of gas (ethane) per mole of pyrrolidone was obtained. The solvent was stripped and 3.5 g. (80%) of a solid was collected. The solid could not be distilled. An approximate melting point of 50° was obtained on the air-sensitive solid. After drying under vacuum for 24 hr. the molecular weight was obtained on a sample using anhydrous benzene as solvent: calcd., 153; found, 160. A green flame indicated the presence of boron. The proton n.m.r. spectrum was in agreement with the proposed structure of the compound.

Reaction of Triethylborane with Acetamide.—Into a three-necked round-bottom flask equipped with N_2 sweep were placed 50 ml. of THF and 4 ml. (2.8 g., 0.0286 mole) of triethylborane. Then 1.7 g. (0.0286 mole) of acetamide was added. The reaction mixture was left at room temperature for 8 hr. during which time ethane gas was evolved (1 mole per mole of acetamide). The solvent was stripped and a polymeric type residue remained. Upon distillation, a clear liquid which turned to a rubbery solid was collected [b.p. ~98° (0.7 mm.)]. The solid was air-sensitive and would become moist when exposed.

The molecular weight was obtained in benzene under an argon sweep: calcd., 127; found, 245, 233. Therefore it was concluded that the product was a dimer, $[CH_3CONHB(C_2H_5)_2]_2$.

Discussion

In the previous study concerning the reaction of organoboranes with carboxylic acids (eq. 1), it was found that the nucleophilic character of the acid was of greater importance than inherent acidity, a conclusion in agreement with the observation that weaker acids accomplished B–C cleavage more readily than stronger acids. The pre-rate-determination coordination step serves two functions in preparing for transmission across the high-energy barrier to reaction-activation of the incipient carbanion by bond weakening and enhancement of the electrophilic character of the proton. Thus, even relatively weak acids (pK_a = 10–25) are capable of cleaving B–C bonds, provided the intramolecular nucleophilic (N, O, S) and electrophilic (H) sites are in proper geometric relationship to one another. For example,

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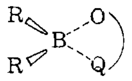
[8] G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

[9] C. R. Hauser, F. C. Frostick, Jr., and E. H. Man ,*J. Am. Chem. Soc.*, **74**, 3231 (1952).

1,3-diketones,[10,11] acyclic amides,[11] 2-pyrolidone,[11] 2-pyridone,[11] 8-hydroxyquinoline,[11] 1-imino-3-ketones,[10a] and 1,3-diketo esters[11] react readily with organoboranes, while 4-pyridone and phenol–pyridine mixtures do not.

The products of such reactions involving 1,3-diketones, 8-hydroxyquinoline, 1,3-diketoesters, and pyrolidone, as will be shown below, involve structures such



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as 1 where Q is an oxy or nitrogen function.

Similar compounds may also be prepared *via* more difficult routes involving R_2BCl[12] or $(RBO)_3$[13] and BF_3.[8,9]

Such materials offer a unique view of a coordination compound in which the pseudo-metal ion unit, R_2B- (R = R or X) may be altered with respect to charge without alteration of size and where the high energy of available orbitals forbids π-bonded interactions. Thus, effects of R on the physical characteristics of the chelating ligand, and *vice versa*, may be attributed to inductive processes acting on and through the boron atom. The difficulties to be encountered in interpretation of data derived from transition metal coordination compounds are illustrated in the reported studies of the metal complexes of 1,3-diketones.[14]

The following physical measurements of compounds described by formula **1** have been examined and evaluated: (1) H^1 n.m.r. of the chelate ring, (2) B^{11} n.m.r. of the complexes, (3) ultraviolet spectra of the chelate ring, (4) polarographic and controlled potential reductions of the complexes, and (5) H^1 n.m.r. of the R units (when possible).

In all of the cases described in the tables to follow, molecular weight measurements on isolated materials dissolved in benzene revealed monomeric species. This, of course, in itself, does not distinguish between tetrahedral or trigonal geometry. However, H^1 n.m.r. involving observation of the chelate ring indicated that if open chain form was present, it was in rapid equilibrium with chelate form. Infrared spectroscopy (mull, KBr, or neat) revealed only *one* C–O absorption (shifted from normal C–O)[3a] and B^{11} resonance data in various solvents (neat, C_6H_6, THF) were identical. This would seem to confirm the tetrahedral geometry implied above.

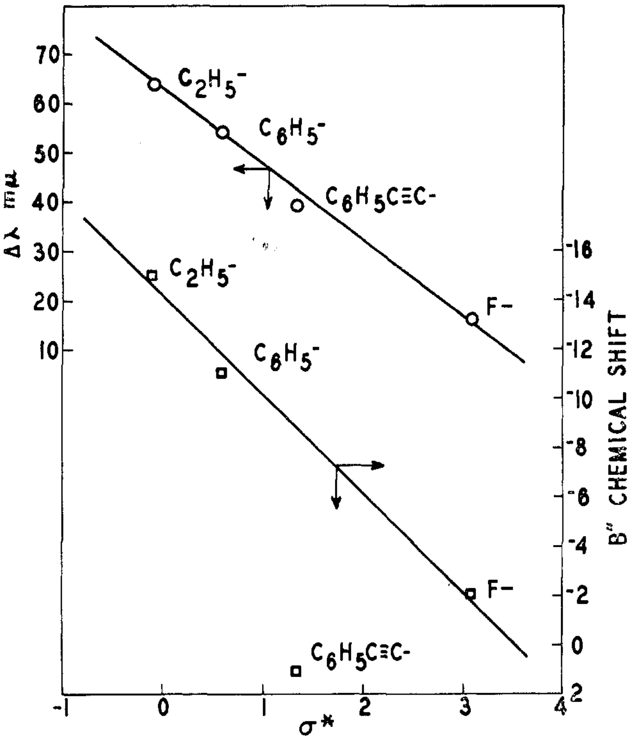
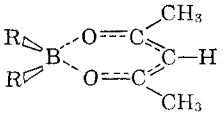


Figure 1.

The series



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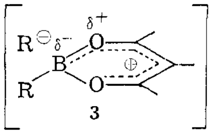
(R = C_6H_5, C_2H_5, $C_6H_5C\equiv C$, F) (Table I) shows that the methine hydrogen and methyl hydrogen chemical shifts are sensitive to R, in the order to be expected from inductive effects, although the positioning of phenyl and ethyl is rather close. On the other hand, B^{11} resonance data[15] (Tables I and II, Figure 1) show that as the σ^* (Taft) value of R increases (increasing $-I$ effect), the B^{11} resonance moves to higher field. Although the number of points is minimal, a linear Taft correlation is observed with the phenylethynyl compound being an exception, undoubtedly due to a high diamagnetic anisotropy contribution.[18]

At first glance the slope is the opposite from that which might be expected. One possible and likely interpretation is that as R is made more electron-withdrawing, donation to the pseudo-metal atom by the chelate ring is increased with possible contributions from rehybridization[19] such that electron shielding at boron is increased. Alternatively no-bond resonance contributions similar to that shown below may be involved.



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[10] (a) B. M. Mikhailov and T. N. Bubnov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1883 (1960); *Chem. Abstr.*, **55**, 16416 (1961); (b) M. F. Hawthorne and M. Reintjis, *J. Am. Chem. Soc.*, **86**, 5016 (1964).

[11] Present work.

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[13] M. J. S. Dewar and R. C. Dougherty, *Tetrahedron Letters*, **16**, 907 (1964).

[14] (a) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958); (b) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963); (c) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).

[15] Onak and Williams[16] have shown that in a series of closely related compounds, B^{11} chemical shifts may be considered proportional to the electron shielding around the boron nucleus. A comprehensive survey by Schaeffer[17] supports this view also.

[16] T. P. Onak and R. E. Williams, *J. Phys. Chem.*, **67**, 1740 (1963).

[17] H. Steinberg and A. L. McCloskey, "Progress in Boron Chemistry," Vol. 1, Pergamon Press, New York, N. Y., 1964, p. 420.

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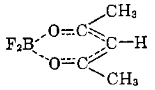
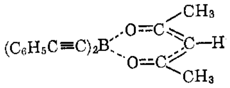
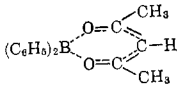
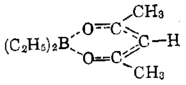
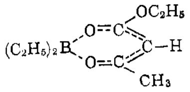
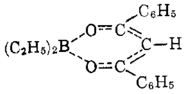
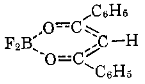
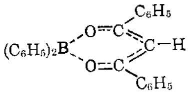
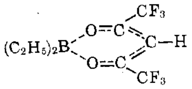
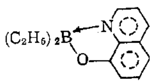
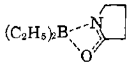
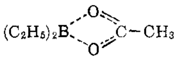
TABLE I

PROTON N.M.R.

Compound	Solvent standard[a]	=CH- τ	-CH$_3$ τ	Comments	B^{11} chemical shift, p.p.m.[b]
	HCCl$_3$–TMS	4.0	7.7	...	− 2.0 (THF)
	DCCl$_3$–TMS	4.15	7.8	10-proton aromatic multiplet centered at τ 2.58	+ 1.2 (THF)
	CCl$_4$–TMS	4.66	7.98	Aromatic multiplet centered at τ 3.1	−10.8 (THF)
	HCCl$_3$–TMS	4.58	8.05	High-field multiplet resolved into a quartet and triplet patterns centered at τ 9.50 (CH$_2$) and 9.25 (CH$_3$) with $J_{H'-H'} \sim$ 5–6 c.p.s.	−14.2 (THF) −14.7 (neat) −14.7 (C$_6$H$_6$)
	Neat TMS	5.13	8.08	Quartet and triplet centered at τ 5.77 and 8.72 with $J_{H'-H'}$ = 7 c.p.s. Higher-field multiplet which resolved into a quartet and triplet pattern centered at τ 9.52 and 9.26 with $J_{H'-H'}$ = 5–6 c.p.s.	−15.0 (THF) −14.4 (neat)
	CCl$_4$–TMS	3.42	...	10-proton aromatic multiplet centered at τ 1.9 and 2.55, also a 10-proton ethyl multiplet having τ_{CH_2} 9.37 and τ_{CH_3} 9.18	−14.5 (THF)
	THF–TMS	...	...	Aromatic multiplet centered at τ 1.8 and 2.5, -CH proton not observed, apparently shifted into aromatic region	−2.7 (THF)
	HCCl$_3$–TMS	3.4		Aromatic multiplet centered at τ 2.45 and 2.65	...
	Neat TMS (ext. std.)	3.78	...	10-proton high-field multiplet centered at τ 9.1	−20.3 (THF)
$(C_2H_5)_3B$	Neat TMS (ext. std.)	...	...	High-field multiplet consisting of basic quarter and triplet patterns centered at τ 8.8 and 8.98, respectively, with $J_{H'-H'}$ = 4.5–5 c.p.s.	−80.3 (THF)
	CCl$_4$–TMS	...	...	Sharp 10-proton singlet at τ 9.41 and 6-proton multiplets centered at τ 1.8 and 2.8	−14.4 (C$_6$H$_6$)
$[(C_2H_5)_2B(HNCOCH_3)]_2$	HCCl$_3$–TMS	...	...	10-proton multiplet centered at τ 9.18 (with a broad singlet at τ 9.1) and a 3-proton singlet at τ 7.86. NH proton was not well-characterized.	...
	HCCl$_3$–TMS	...	...	2-proton triplet at τ 6.45 with $J_{H'-H'}$ = 6 c.p.s., 4-proton multiplet centered at τ 7.8 and a 10-proton multiplet at τ 9.3 with a strong broad singlet at τ 9.08	−46.5 (C$_6$H$_6$)
$[(C_2H_5)_2B(C_5H_4NO)]_2$	DCCl$_3$–TMS	...	...	Aromatic multiplets (4 protons) centered at τ 2.22 and 3.4 and a broad singlet (10 protons) at τ 9.22	...
	...	...	...	...	−47.8 (C$_6$H$_6$)

[a] TMS is tetramethylsilane. [b] With reference to $BF_3 \cdot (C_2H_5)_2O$.

Table II

Physical Data on R_2BAcAc Complexes

	σ^{*a}	B^{11}, p.p.m.[b]	$\Delta\lambda$, mμ	$-E_{1/2}$, v.[c,d]
BF_2	+3.1	− 2.0	16	2.08
$B(C{\equiv}CC_6H_5)_2$	+1.35	+ 1.2	39	2.16
$B(C_6H_5)_2$	+0.6	−11.0	54	2.40
$B(C_2H_5)_2$	−0.1	−15.0	64	2.66

[a] Values taken from M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13, pp. 617, 619. [b] With reference to $BF_3\cdot(C_2H_5)_2O$. [c] With reference to 1 × 10^{-3} Ag^+/Ag. [d] Acetylacetone reduces at 2.98 v.

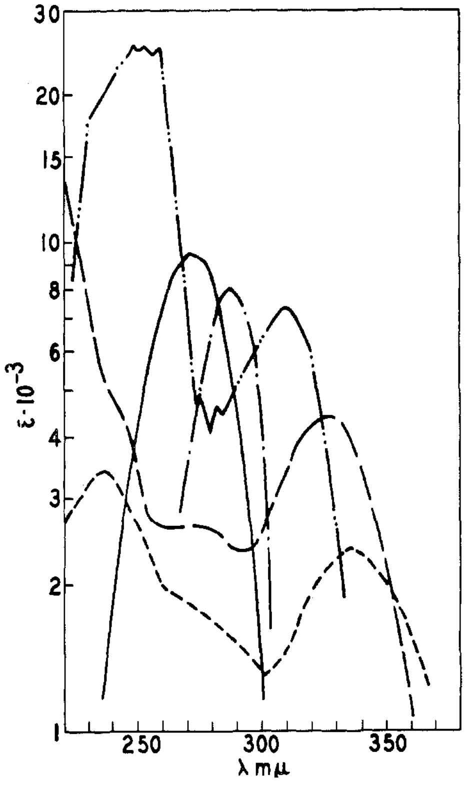


Figure 2.—Legend: ———, acetylacetone; – –, diphenylboron acetylacetonate; –·–, diethylboron acetylacetonate; —·—, difluoroboron acetylacetonate; —···—, diphenylethynylboron acetylacetonate.

An interesting correlation between hydrolytic stability and B^{11} chemical shift values appears to be involved, as evidenced by qualitative studies. The compounds with higher B^{11} shielding are the most resistant to hydrolysis. A similar situation in borate esters has been reported by Onak.[16] In light of the mechanistic work reported on the R_3B–RCOOH systems,[2] the source of this correlation is that as the boron becomes more shielded, attack by the nucleophile of the hydrolyzing entity is retarded.

Paralleling the B^{11} observation is the fact that the ultraviolet spectra (270–340 mμ) of the series in the region attributable to $\pi \rightarrow \pi^*$ (chelate ring) transitions show a linear Taft correlation (σ^* *vs.* $\Delta\lambda = \lambda_{\max}^{\text{chelate}} - \lambda_{\max}^{CH_3COCH_2COCH_3}$) with a negative slope (Figures 1 and 2, Table II).

The electrochemical behavior of R_2BAcAc (where AcAc = 2,4-pentanedione and R = F, $C_6H_5C{\equiv}C$, C_6H_5, C_2H_5) was also studied. Both polarographic and controlled potential electrolysis studies in monoglyme using tetrabutylammonium perchlorate as supporting electrolyte were pursued. Three-electrode geometry was employed. Reduction of these compounds is highly irreversible "electrochemically," but diffusion controlled. For example: $(C_6H_5)_2BAcAc$ shows a cathodic wave at −2.40 v. *vs.* 1 × 10^{-3} Ag^+/Ag (n = 1). Controlled potential electrolysis at −2.48 v. gave a solution having an anodic wave at −1.0 v. Controlled electrolysis on this solution at −0.3 v. regenerated $(C_6H_5)_2BAcAc$. Other data appear in Table II.

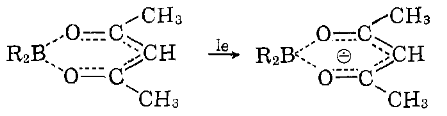
Also a polarographic study was conducted on the 1,3-diphenyl-1,3-propanedionate compounds. The data are shown in Table III. Two marked differences were noted in these compounds as compared to the acetylacetonate derivatives. They are: (a) two one-electron reductive steps are now observed and (b) the electrolysis at the first wave (n = 1) gave highly colored solutions. In particular, electrolysis of the fluoro, phenyl, and ethyl compounds (n = 1) gave colored solutions of turquoise, green, and green to orange, respectively. After electrolysis the phenyl and fluoro derivatives could be reoxidized back to starting material.

Table III

Polarographic Data on the 1,3-Diphenyl-1,3-propanedionate Compounds

R_2B	$-E_{1/2}$, v.[a]
F_2B	1.60 and 2.66
$(C_6H_5)_2B$	1.71 and 2.74
$(C_2H_5)_2B$	1.90 and 2.80

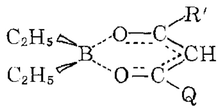
[a] With reference to 10^{-3} Ag^+/Ag.



(2)

The high cathodic reduction potentials and the known high energy of possible available empty orbitals on boron indicate that the electron is probably exclusively associated with a π^* orbital of the chelate ring (eq. 2). Its exact location is being explored *via* e.s.r. It is obvious that there is a direct parallel between this oxidation–reduction system and a report on the polarographic behavior of metal acetylacetonates.[20]

Examining the series, where the pseudo-metal ion



4

R′ = Q = C_6H_5, CH_3, CF_3 and R′ = CH_3, Q = C_2H_5

remains the same and the chelate ring substituents are altered, the B^{11} resonance (Table I) indicates that the pseudo-metal atom demands electron donation of and from the ring in a fixed amount which is a function

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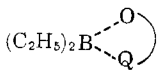
(20) H. Dehn, V. Gutman, and G. Schöber, *Montash Chem.*, **93**, 453 (1962).

of R but not of R′ and Q, presumably within the limits of the capability of the chelate ring. The B^{11} chemical shift value is invariant at −15 p.p.m. for R′, Q = CH_3, CH_3; C_6H_5, C_6H_5; CH_3, OC_2H_5. (A similar lack of effect on alteration of the chelate ring in the F_2B series is also noted.) As might be expected the methyl, methylene H^1 resonances are unaltered by chelate substitution in these series.

It is interesting, but not surprising, therefore that the B^{11} chemical shift for the R′, Q = CF_3, CF_3 derivative is shifted downfield (−20.3 p.p.m.), suggesting that the CF_3 group has affected the limit of the donating ability of the carbonyl.

On the other hand, when the basic structure (**5**) (ring size or heteroatom) of the chelate is altered, effects on both B^{11} and H^1 n.m.r. of the CH_3CH_2B unit are seen.



5

With respect to the CH_3CH_2 data, there seems to be a unique opportunity for it to serve as a probe to ascertain the electronegativity of the B unit. Dailey and Shoolery[21] have shown that the chemical shift difference, $\tau_{CH_3} - \tau_{CH_2}$, was approximately linearly dependent on the electronegativity of the atom in the substituent which was directly bonded to the ethyl group. In the present case, the ethyl group in the acetylacetonates is a quartet–triplet multiplet, while in the 8 hydroxyquinoline and pyrrolidone products it is a singlet. Similar results have been reported where the boron atom (trigonal) was attached to a nitrogen atom.[22]

One other area of this investigation that has not been adequately explained and which deserves attention is the observation that the B^{11} resonance of the diethylboron derivatives is a function of the chelate ring size. In the five- and six-membered chelate (hydroxyquinoline and acetylacetone) rings the B^{11} resonance is 14.5 p.p.m. downfield from $BF_3 \cdot (C_2H_5)_2O$ and in the four-membered ones[23,24] (acetate and pyrrolidone) it is 47 p.p.m. downfield. For reference, trigonal triethylborane has a shift of −84 p.p.m.

It is felt that this approach of using an incipient organometal cation as a pseudo-metal ion in which charge properties and hybridization can be altered without affecting size and in which probes may be placed on the metal atom involved will permit a more detailed study of chelating agents. It is hoped that this preliminary study will excite work in other laboratories.

Acknowledgment.—The authors express their appreciation to the following agencies for financial support during this investigation: Army Research Office (Durham), and the National Science Foundation. We are indebted to Dr. R. Schaeffer and Dr. Litzow, Indiana University, Bloomington, Ind., for their assistance and cooperation in obtaining the B^{11} nuclear magnetic resonance spectra, and to Anderson Chemical Division, Stauffer Chemical Co., for supplying the triethylborane. The authors are also grateful to Dr. W. Kitching for some of the polarographic data.

(21) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

(22) S. J. Brois, *Tetrahedron Letters*, **7**, 345 (1964).

(23) Diethylboron acetate shows one C–O absorption. Its molecular weight in benzene could not be determined due to its air sensitivity. However, derivatives involving homolog acids were monomeric. It is assumed that the diethylboron derivative is monomeric.

(24) The tables also show data for compounds which are dimeric in benzene; for example the products derived from the acetamide and 2-pyridone reactions. The exact structures of these materials are unknown.

Notes

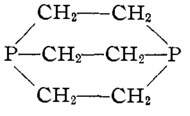
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Polycyclic Group V Ligands. II. 2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane and Derivatives[1]

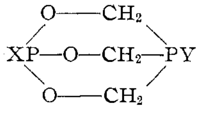
BY K. J. COSKRAN AND J. G. VERKADE

Received May 24, 1965

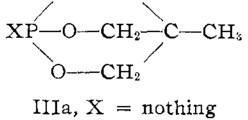
In 1959, Mann[2] reported the synthesis of 1,4-diphosphabicyclo[2.2.2]octane (I). We wish to report the synthesis of the analogous compound, 2,6,7-trioxa-1,4-diphosphabicyclo[2.2.2]octane (IIa) in which the bridgehead phosphorus atoms are chemically different. Also reported are the 1,4-dioxo (IIb), the 1-sulfo (IIc), and the 1-sulfo-4-oxo (IId) derivatives of IIa. These compounds were synthesized in order to evaluate their donor properties with a variety of Lewis acids. Although Mathews has reported the synthesis of the phosphonium salt $[CH_3CH_2P(CH_2CH_2)_3COH]Br$,[3] compound IIc and $P(CH_2O)_3CH$, the orthoformate analog



I



IIa, X = nothing, Y = nothing
IIb, X = O, Y = O
IIc, X = S, Y = nothing
IId, X = S, Y = O



IIIa, X = nothing
IIIb, X = O
IIIc, X = S

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(1) For part I in this series see J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(2) R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).

(3) D. A. Mathews, *Dissertation Abstr.*, **24**, 977 (1963).