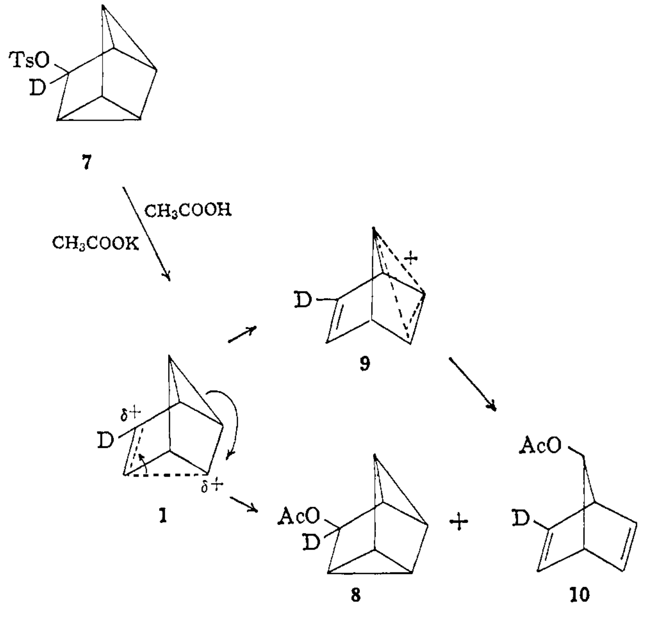
of a mixture of **6a** (10%) and **6b** (90%). Since the ratio of tricyclic olefin (**6b**) to norbornadiene was within experimental error of that usually found[11b,12] upon reduction of the 7-norbornadienyl cation, we believe it to be the source of **6b** and the norbornadiene. *We further propose that* **6a** *results from reduction of the ion,* **1**, *at C-5.* We are prompted by the comments of a referee to add, however, that this conclusion is based on the assumption that all of the hydrocarbon product arises from a carbonium ion intermediate. Since the actual yield of **6a** is very low, our position is somewhat compromised. On the other hand, a direct displacement by deuteride on **2c**, which seems to be the best alternative to ionization, would be predicted to be more important in anhydrous diglyme. In fact, no **6** was obtained in this solvent.[1]

Quite remarkably, a significant amount of the quadricyclic cation **1** isomerizes to the more stable 7-norbornadienyl cation (**9**) before it is trapped by hydride. We have found, by solvolysis of 7-deuterioquadricyclic *p*-toluenesulfonate (**7**), that this isomerization undoubtedly follows the general rearrangement path suggested by both Richey[2] and ourselves.[1] Our version of this sequence is indicated by the following equation. Solvolysis of **7** (2–3 days) at 25° in acetic acid containing an excess of potassium acetate gave a 75% yield (isolated) of a product consisting of an approximately 50:50 mixture of **8** and **10**. The kinetic isotope effect, k_H/k_D, was found to be a standard 1.18. Both the quadricyclic acetate **8** and the 7-norbornadienyl acetate (**10**) contained one deuterium by mass spectral analysis and by analysis of their nmr spectra. The nmr spectra also served to establish, unequivocally, the location of the deuterium. It should be kept in mind that this method, of course, is not capable of great accuracy. For example, about 5% or less of 7-norbornadienyl acetate containing deuterium *anti* to the acetoxy would have escaped detection.



Nonetheless, this experiment has revealed some rather interesting features of the ions involved. For one, the hydrogens of the quadricyclic cation are not scrambled by rearrangement, thus ruling out a structure in which the positive center is delocalized over two or more equivalent carbons. Furthermore, the isomerization of the quadricyclic ion to the 7-norbornadienyl ion is highly (perhaps completely) stereospecific and, in addition, the 7-norbornadienyl ion, once it is formed, retains its configuration.

Acknowledgment. We thank Mr. E. W. Anderson for the determination of some of the nmr spectra.

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Chelate Adducts Containing a Bidentate Electron-Pair Acceptor. 1,2-Bis(difluoroboryl)ethane

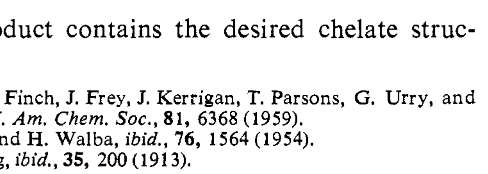
Sir:

Chelate formation is a common phenomenon in coordination chemistry where many complexes are known in which a polyfunctional donor ligand is attached to a central metal acceptor. We wish to report an analogous situation in which a polyfunctional acceptor, $F_2B\text{-}CH_2\text{-}CH_2\text{-}BF_2$, is apparently coordinated to a central donor atom.

The difunctional acid 1,2-bis(difluoroboryl)ethane was synthesized according to a reported method (vapor pressure at 0° 154.6 mm obsd, lit[1] 156 mm; mp −31.2° obsd, lit[1] −31°; mol wt 128 obsd, 126 calcd).[1] Addition of this acid to dimethyl ether or to tetrahydrofuran led to 2:1 compounds as the only stable adducts, *e.g.*, $C_2H_4B_2F_4 \cdot 2OC_4H_8$.

Much more interesting behavior was observed for bis(triphenylmethyl) ether where a 1:1 compound was indicated by tensimetric titration and also by weight gain. The resulting air-sensitive golden yellow crystals melted at 113–114°. *Anal.* Calcd: C, 76.46; H, 5.45; B, 3.44; F, 12.10. Found: C, 76.26; H, 5.65; B, 3.24; F, 11.84. The infrared spectrum showed a complete absence of B–F stretching frequencies for trigonally bonded boron (1350–1380 cm^{-1}), while new peaks (*ca.* 1050 cm^{-1}) attributable to B–F vibrations of tetrahedrally bonded boron were present. Clearly, both ends of the bidentate acid are coordinated. Twin absorption maxima at 430 and 410 mμ in methylene chloride solutions of the compound showed the presence of the triphenylmethyl cation.[2] Thus, a Lewis acid cleavage of bis(triphenylmethyl) ether has occurred which is analogous to the known protolytic cleavage.[3] The simplest reaction consistent with these data is

$F_2B\text{-}CH_2\text{-}CH_2\text{-}BF_2 + (C_6H_5)_3C\text{-}O\text{-}C(C_6H_5)_3 =$



$$[(C_6H_5)_3C]^+ \left[(C_6H_5)_3C\text{-}O \begin{matrix} \diagup BF_2\text{-}CH_2 \\ \quad\quad\quad | \\ \diagdown BF_2\text{-}CH_2 \end{matrix} \right]^- \quad (1)$$

where the product contains the desired chelate structure.

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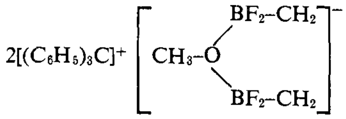
[1] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **81**, 6368 (1959).

[2] G. Branch and H. Walba, *ibid.*, **76**, 1564 (1954).

[3] M. Gomberg, *ibid.*, **35**, 200 (1913).

In a similar experiment, tensimetric titration of triphenylmethyl methyl ether in toluene solution with the acid showed the formation of a 1:1 complex. The resulting yellow compound was less stable in methylene chloride solution than the product of eq 1. Equilibrium measurements in dilute methylene chloride solutions indicate that at low $F_2B-CH_2-CH_2-BF_2$ concentrations a 2:1 adduct forms, but in the presence of a large excess of acid the 1:1 complex predominates.

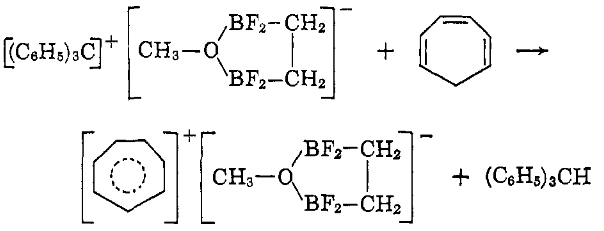
$C_2H_4B_2F_4 \cdot 2(C_6H_5)_3C\text{-}O\text{-}CH_3 + C_2H_4B_2F_4 =$



(2)

The true nature of the anion was not elucidated by the form of the equilibrium constant because ion clusters formed in the low dielectric constant solvent are not distinguishable from high molecular weight substances.

To circumvent the complications introduced by the equilibrium shown in eq 2, a tropenium (tropylium) derivative was prepared *via* hydride exchange (eq 3).[4] A 0.357-mmole sample of the acid was added to a solution of 0.308 mmole of triphenylmethyl methy ether in methylene chloride. An excess of 1,3,5-cycloheptatriene was added, whereupon a white crystalline precipitate formed. The reaction mixture was filtered and washed with pentane. Vacuum evaporation of the solvent and excess reagents from the filtrate gave 0.309 mmole of triphenylmethane which was characterized by an infrared spectrum and melting point: mp 92.0°, lit. 92.5°. Also, a flame test on this methylene chloride soluble product indicated the absence of boron. The infrared and ultraviolet spectra of the precipitate matched those cited in the literature for the $C_7H_7^+$ cation.[5,6] Significantly, the only infrared absorption frequencies characteristic of B–F stretching motions were in the 1000-cm^{-1} region which is symptomatic of four-coordinated boron. Thus, the general correctness of reaction 3 is established, but just as in reactions 1 and 2 there is the possibility of a polymeric anion.



(3)

To settle this question, cryoscopic molecular weight measurements were performed on freshly prepared tetramethylene sulfone solutions of the tropylium salt.[7] The resulting solutions slowly decomposed as indicated by changes in freezing point depression and the development of a yellow coloration. Therefore, it was not possible to obtain sufficiently accurate data to establish a reliable ion-pairing constant. However, an average molecular weight of 211 ± 31 was determined for four solutions in the 0.05 to 0.20 *m* range; the formula weight is 248. For comparison, the apparent molecular weight of a similar salt, tetrapropylammonium tetrafluoroborate, was investigated and found to be 207 in a 0.101 *m* tetramethylene sulfone solution. The formula weight of this salt is 273. Thus, molecular weight and infrared data indicate a chelate structure for the tropenium salt and a similar structure is inferred for the other salts.

While the foregoing observations establish a *chelate structure*, they do not prove a *chelate effect*. In our current work we are employing displacement experiments to test for this effect.

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[4] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

[5] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

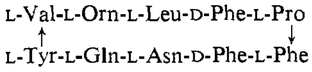
[6] K. M. Harmon and S. Davis, *ibid.*, **84**, 4359 (1962).

[7] R. L. Burwell, Jr., and C. H. Langford, *ibid.*, **81**, 3799 (1959).

Synthesis of Tyrocidine A

Sir:

Tyrocidine A is an antibiotic cyclic peptide isolated as its hydrochloride in 1952 by Battersby and Craig[1] from the cultured filtrate of *Bacillus brevis.* Its structure has been proposed by Craig and his colleagues to be I_n.[2] It is of interest to note that the pentapeptide sequence L-Val-L-Orn-L-Leu-D-Phe-L-Pro is also found in gramicidin S[3] and tyrocidines B[4] and C.[5] Although the partial syntheses of the open-chain peptides related to tyrocidine A have been reported,[6] the complete synthesis has not been accomplished.



L-Val-L-Orn-L-Leu-D-Phe-L-Pro
L-Tyr-L-Gln-L-Asn-D-Phe-L-Phe

I_n

We wish to report the synthesis of the cyclic decapeptide (I_s) having the structure of I_n and on the identity of I_s with natural tyrocidine A in chemical and biological properties.[7] *p*-MZ-L-Phe-D-Phe-OEt (II), mp 126–128°, $[\alpha]D$ −2.8°, was prepared, in a yield of 79%, by coupling *p*-methoxybenzyloxycarbonyl-L-phenylalanine with D-phenylalanine ethyl ester by the mixed anhydride method.[8] II was treated with hydrazine to

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[1] A. R. Battersby and L. C. Craig, *J. Am. Chem. Soc.*, **74**, 4019 (1952).

[2] A. R. Battersby and L. C. Craig, *ibid.*, **74**, 4023 (1952); A. Paladini and L. C. Craig, *ibid.*, **76**, 688 (1954).

[3] A. R. Battersby and L. C. Craig, *ibid.*, **73**, 1887 (1951).

[4] T. P. King and L. C. Craig, *ibid.*, **77**, 6627 (1955).

[5] M. A. Ruttenberg, T. P. King, and L. C. Craig, *Biochemistry*, **4**, 11 (1965).

[6] R. Schwyzer, *et al.*, *Helv. Chim. Acta*, **42**, 972 (1959); *Chimia*, **14**, 366 (1960).

[7] Satisfactory analyses and chromatographic data were obtained for all crystalline compounds described here. Melting points were uncorrected. $[\alpha]D$ refers to a solution in dimethylformamide at 20° except the cyclic decapeptide hydrochlorides, $I_s \cdot HCl$ and $I_n \cdot HCl$. The abbreviations are as follows: Z, benzyloxycarbonyl; *p*-MZ, *p*-methoxybenzyloxycarbonyl; BOC, *t*-butyloxycarbonyl; NHNH$_2$, hydrazide.

[8] J. R. Vaughan, Jr., *J. Am. Chem. Soc.*, **73**, 3547 (1951); J. R. Vaughan, Jr., and J. A. Eichler, *ibid.*, **75**, 5556 (1953); R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951); T. Wieland and H. Bernhard, *Ann.*, **572** 190 (1951).