therefore obtained in high yields. While the mechanism of this halogen exchange is unclear, the isomerization of the bicyclo[2.2.2]octyl system[10] under longer reaction times suggests that the halophilic catalyst can promote an internal halogen exchange perhaps involving only partial carbonium ion character.

**Acknowledgment.** This work was supported by the National Research Council of Canada. We wish to thank Dr. J. C. Kauer (E. I. du Pont de Nemours and Co.) for a generous supply of 1,4-dichlorobicyclo-[2.2.2]octane.

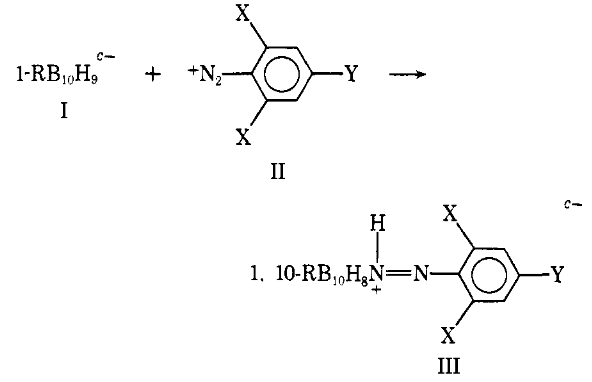
(10) W. v. E. Doering and M. Barber, *J. Amer. Chem. Soc.*, **71**, 1514 (1949); P. v. R. Schleyer, K. R. Blanchard, and C. D. Woody, *ibid.*, **85**, 1358 (1963).

**James W. McKinley, Richard E. Pincock,* W. Bruce Scott**
*Department of Chemistry, University of British Columbia*
*Vancouver 8, Canada*
*Received November 6, 1972*

## A Novel Transfer of the Diazonium Function from Carbon to Boron

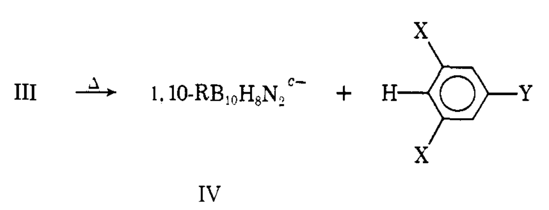
*Sir:*

The azo coupling of aryldiazonium ions with $B_{10}H_{10}^{2-}$ has been shown to be a useful pathway to apically substituted $B_{10}H_{10}^{2-}$ derivatives[1]



(1)

We wish to report a novel method of generating the diazonium function at boron by the thermal decomposition of III.



(2)

IV

IIIa, R = H; X = Y = Br; $c = 1$
b, R = $^+S(CH_3)_2$; X = Y = Br; $c = 0$
c, R = $^+N(CH_3)_3$; X = H; Y = Br; $c = 0$
d, R = H; X = H; Y = $NO_2$; $c = 1$
e, R = H; X = H; Y = Br; $c = 1$
IVa, R = H; $c = 1$
b, R = $^+S(CH_3)_2$; $c = 0$
c, R = $^+N(CH_3)_3$; $c = 0$

The usefulness of this method is enhanced by the fact that the diazonium function has been shown to be the most synthetically useful substituent on the $B_{10}H_{10}^{2-}$ cage since it can be displaced by a wide variety of nucleophiles.[2,3] In addition, the method presented here is the only method yet reported of obtaining the monodiazonium $1\text{-}B_{10}H_9N_2^-$. This compound should prove extremely useful as a precursor to monosubstituted $B_{10}H_{10}^{2-}$ derivatives. The overall reaction may be considered to be a transfer of the diazonium function from the phenyl ring to the $B_{10}H_{10}^{2-}$ cage. The $1\text{-}B_{10}H_9N_2^-$ ion was prepared by dissolving $(CH_3)_4N^+$IIIa in dry acetonitrile (~20 ml/g) and heating at reflux under $N_2$ for 3 hr. The acetonitrile was then removed *in vacuo*, and the solid was washed with diethyl ether to remove the 1,3,5-tribromobenzene formed (identified by infrared spectra). The solid residue was then extracted into acetone and filtered with decolorizing charcoal. Recrystallized $(CH_3)_4N^+$IVa (65% yield) was obtained by adding ethanol to the filtrate and slowly removing the solvent on a rotary evaporator. *Anal.* Calcd for $C_4H_{21}B_{10}N_3$: C, 21.90; H, 9.65; B, 49.28; N, 19.15. Found: C, 22.14; H, 9.82; B, 49.56; N, 19.48. In a similar manner $1,10\text{-}(CH_3)_2SB_{10}H_8N_2$ was synthesized starting with IIIb. After the solvent was removed the reaction mixture was heated to 40° under high vacuum to first remove the tribromobenzene, and then the product was separated from the residue by chromatography on silica gel and recrystallized from ethanol (yield 45%). The product was identified by comparison of the infrared and $^{11}B$ spectra with those of the known compound.[4]

The chlorinated ion, $1\text{-}(1\text{-}Br\text{-}4\text{-}N_2Ph)B_{10}Cl_9^{2-}$, was prepared by passing $Cl_2$ through an acetonitrile solution of IIIe in the presence of excess NaH at 0° in a manner similar to that previously reported.[5] *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}Cl_9N_2C_6H_4Br$: C, 22.14; H, 3.73; B, 14.23; Br, 10.52; Cl, 42.01; N, 7.37. Found: C, 22.60; H, 3.82; B, 13.69; Br, 10.69; Cl, 41.95; N, 7.17. This compound was subsequently protonated by strong acid to form the monoanion which was found to be unreactive toward thermal decomposition in refluxing acetonitrile. All attempts to chlorinate IIIa in the absence of NaH resulted in the formation of partially chlorinated IVa, even at low temperatures. However, 1-chloro-2,4,6-tribromobenzene, in addition to $1,3,5\text{-}C_6H_3Br_3$, was isolated from the reaction mixture and identified by its mass spectrum. This suggests the existence of a second pathway for the formation of the $B\text{-}N_2^+$ function which involves electrophilic attack of $Cl_2$ on the phenyl carbon bonded to azo nitrogen.

The 80.5-MHz $^{11}B$ nmr spectrum of $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ in acetonitrile contained a singlet and three doublets of area ratios 1:1:4:4 at +13.4, −22.0 (146), +17.2 (133), +25.8 (140) [chemical shifts, ppm relative to $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (Hz)]. The singlet at 13.4 ppm is assigned to the apical boron attached to the diazonium group. This very high field chemical shift for an apical boron atom in the $B_{10}H_{10}^{2-}$ system is quite likely due to the strong electron-withdrawing character of the diazonium function.[3] The infrared spectrum of this salt contains a band at 2230 cm$^{-1}$ assigned to $-^+N{\equiv}N$ and the ultraviolet spectrum

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(1) M. F. Hawthorne and F. P. Olsen, *J. Amer. Chem. Soc.*, **86**, 4219 (1964); **87**, 2366 (1965).

(2) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 115 (1964).

(3) W. H. Knoth, *J. Amer. Chem. Soc.*, **88**, 935 (1966).

(4) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, **4**, 280 (1965).

(5) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

exhibits absorptions at 273 (14,200) and 219 (9210) [$\lambda_{\max}$ ($\epsilon$)].

The thermal decomposition of the azo-coupled species to produce the diazonium-substituted borane product was found to proceed more rapidly and with fewer complications in the case of the 2,4,6-tribromophenyl arylazo system than the other substituted phenyl derivatives examined. In addition, the polarity of the solvent correlated with the rate of product formation. Polar solvents, such as acetonitrile, gave a faster reaction than less polar solvents such as ethyl acetate and diglyme. These observations suggest that the reaction proceeds *via* ionic intermediates rather than by a concerted transfer of the hydrogen from nitrogen to carbon. The unprotonated ion, $1\text{-}(1\text{-Br-4-N}_2\text{Ph})\text{B}_{10}\text{H}_9{}^{2-}$, was stable toward thermal decomposition and did not form the $\text{B–N}_2{}^+$ function. This observation demands that a proton be present to effect an electrophilic attack at azo carbon. Further work is in progress and will be reported elsewhere.

**Acknowledgment.** The authors wish to thank Dr. R. J. Wiersema for measuring $^{11}$B nmr spectra and Professor F. A. L. Anet for use of the 80-MHz nmr spectrometer. This research was supported in part by the Office of Naval Research and the National Science Foundation under Grant No. GP-14372X1.

**Richard N. Leyden, M. Frederick Hawthorne***
*Contribution No. 3106, Department of Chemistry*
*University of California*
*Los Angeles, California 90024*
*Received January 12, 1973*

## Observation by ESCA of Inequivalent Fluorines in $ClF_3$, $SF_4$, and $PF_5$

*Sir:*

X-Ray photoelectron spectroscopy (ESCA) is rapidly developing as a method for studying how valence electrons redistribute themselves when atoms are formed into molecules. Recent studies[1,2] have shown that charges on atoms in molecules can be extracted from core-level binding energy shifts and that these charges are in good agreement with both theoretical expectations and with other kinds of chemical evidence. We report here the application of this technique to the molecules $ClF_3$, $SF_4$, and $PF_5$. Of particular interest is the result that the inequivalent fluorines in these molecules can be distinguished in the photoelectron spectra. For $SF_4$ and $ClF_3$ the lines due to the two kinds of fluorines are clearly resolved. For $PF_5$ the lines are not resolved, but the asymmetry of the photoelectron peak clearly indicates the inequivalence of the two kinds of fluorine. We believe this to be the first demonstration that ESCA can be used to distinguish between atoms that differ only in their geometric orientation with respect to the same central atom.

Each of these molecules has the structure of a trigonal bipyramid with each having two axial fluorines. For $PF_5$ there are three equatorial fluorines; for $SF_4$, two equatorial fluorines and one equatorial lone pair; for $ClF_3$, one equatorial fluorine and two equatorial lone pairs. In each case the bond length for the axial fluorines is longer than that for the equatorial fluorines. The axial bonds are thought to be three-center bonds and more ionic than the equatorial bonds.[3] The axial fluorines are expected, therefore, to have higher negative charges than the equatorial ones and, consequently, lower binding energies for their core electrons.

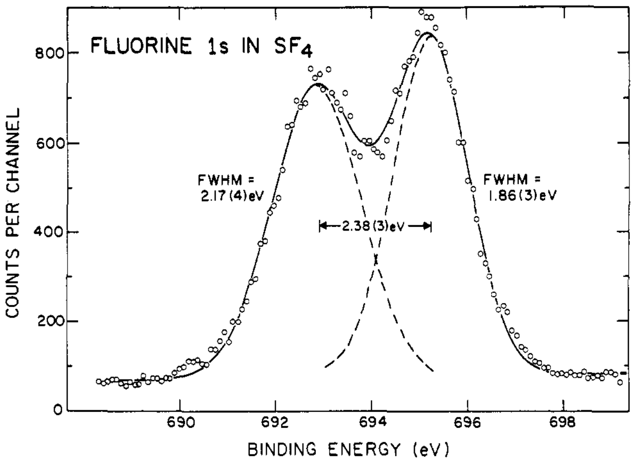

Figure 1. X-Ray photoelectron spectrum of fluorine 1s electrons in $SF_4$, Al K$\alpha$ radiation.

The X-ray photoelectron spectra of the fluorine 1s levels in these compounds in the gas phase were measured in our cylindrical mirror electron spectrometer[4] using aluminum K$\alpha$ X-rays. Pressures in the gas cell were approximately 0.1 Torr. The materials were purchased commercially and were used without further purification. According to the manufacturers the purities were $ClF_3$, 98%; $SF_4$, 90–94%; $PF_5$, 99%. Because of the reactivity of these compounds it is important to establish that the peaks appearing in the spectra are not due to reaction products. Our experience over the months previous to these experiments with xenon fluorides and interhalogens indicates that such reactive materials quickly consume the substances in the spectrometer that they are likely to react with. After the first few minutes of running, the spectrum is that of the pure compound. In each case we have also examined the region of the 2p or 2s electrons for the central atom and have found no evidence for contamination with impurities.

The photoelectron spectrum for the fluorine 1s electrons in $SF_4$ is shown in Figure 1. We see the clear resolution of the two peaks arising from the two kinds of fluorines. We have analyzed these results by fitting two gaussian peaks to the data. First we note that the area ratio of the fitted peaks is 1 to within about 2%, in agreement with expectations. The peak corresponding to the higher binding energy electrons has the narrower width, in accord with chemical effects on line widths that have been reported by us[5] and by others.[6] The splitting between the two peaks is 2.38 ± 0.03 eV. Because there are equal numbers of the two kinds of fluo-

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(1) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, **94**, 6565 (1972).

(2) G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, *ibid.*, **94**, 8009 (1972).

(3) R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962).

(4) P. H. Citrin, R. W. Shaw, Jr., and T. D. Thomas in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 105.

(5) R. W. Shaw, Jr., and T. D. Thomas, *Phys. Rev. Lett.*, **29**, 689 (1972).

(6) R. M. Friedman, J. Hudis, and M. L. Perlman, *ibid.*, **29**, 692 (1972).