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Photochemical Reactions of Hexafluoroacetone with Pentaborane(9) and 2,4-Dicarbaheptaborane(7)

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The gas-phase photolysis reaction at 3000 Å of pentaborane(9) and hexafluoroacetone (HFA) has been found to produce in good yields both the basal and apical perfluoropropanol-substituted compounds, $2\text{-}[HO(CF_3)_2C]B_5H_8$ and $1\text{-}[HO(CF_3)_2C]B_5H_8$, and the novel oxygen–boron-bonded perfluoropinacol derivative $1\text{-}[HO(C(CF_3)_2)_2O]B_5H_8$. Similarly, the photolysis of the small carborane $2,4\text{-}C_2B_5H_7$ with HFA results in the formation of both $5\text{-}[HO(CF_3)_2C]\text{-}2,4\text{-}C_2B_5H_6$ and $5\text{-}[HO(C(CF_3)_2)_2O]\text{-}2,4\text{-}C_2B_5H_6$ as major products.

Introduction

We have reported[2] studies of the mercury-sensitized photolysis of a number of small boranes and carboranes and demonstrated that these reactions could be used in certain cases for the high-yield synthesis of boron–boron-linked, multicage compounds. These results prompted our further investigations of the reactions of polyhedral boranes and carboranes with photochemically excited molecules[3] as potential synthetic pathways for the formation of either larger cage systems or new types of substituted derivatives unattainable by more conventional reaction techniques.

Both the thermal and photochemical reactions of hexafluoroacetone (HFA) have been extensively studied with inorganic and organic substrates[4] and have been used to produce a variety of unusual substituted compounds. The chemistry of HFA is governed by the electron-withdrawing inductive effect exerted by the highly electronegative perfluoromethyl groups on the carbonyl function resulting in a weakly polarized, electron-deficient C–O bond that has been suggested[5] to more closely resemble the double bond of a weakly polarized olefin rather than a normal carbonyl group. Direct evidence for this change in polarization with respect to acetone is a 75-cm^{-1} infrared carbonyl shift to a shorter wavelength,[6] a 31 ppm upfield ^{13}C NMR chemical shift,[7] a marked reduction in the gas-phase basicity of the carbonyl oxygen,[8] and an increased reactivity on the carbonyl carbon by weak nucleophiles.[9]

Although the carbonyl group of hexafluoroacetone may undergo addition reactions of R–H thermally,[4,5,8] photochemical excitation enhances its reactivity. The ultraviolet spectrum of HFA shows absorption between 2450 and 3550 Å with a maximum at about 3020 Å,[10] and rate constants for both the fluorescent[11] and phosphorescent[11a,12] emissions are known. While the excited singlet-state molecules have a short radiative lifetime of 48 ns at 3160 Å,[11b] the triplet-state molecules, formed from the excited-state species by intersystem crossing, are relatively long lived (τ = 3.3 ms)[12] and are therefore responsible for HFA's photochemistry. In this study, we have investigated the reactions of triplet-state HFA with both pentaborane(9) and 2,4-dicarbaheptaborane(7) and have shown that these reactions can be used to produce unusual oxygen-containing derivatives of these compounds.

Experimental Section

Materials. Anhydrous hexafluoroacetone (HFA), obtained from the Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., was judged to be pure by comparison of its IR spectrum with that in the literature[6] and was used without further purification. The closo carborane $2,4\text{-}C_2B_5H_7$ was purchased from Chemical Systems Inc. and was purified by vacuum line fractionation until it was shown to be pure by ^{11}B NMR. Pentaborane(9) was vacuum distilled from laboratory stock. Gas–liquid chromatography (GLC) was conducted on a F & M Model 700 gas chromatograph using an 8 ft × 0.25 in. 10% silicone FS-1265 on 60/80 W 700 column. The chromatographic solvent was reagent grade methylene chloride that was degassed and dried over P_2O_5.

Physical Measurements. Boron-11 NMR spectra at 115.5 MHz were obtained on a Bruker WH-360 Fourier-transform spectrometer located in the Mid-Atlantic Regional NMR facility at the University of Pennsylvania. Proton NMR spectra at 250 MHz and carbon-13 NMR spectra at 62.9 MHz were obtained on a Bruker WH-250 Fourier-transform spectrometer. Boron-11 NMR spectra at 31.9 MHz, fluorine-19 NMR spectra at 93.7 MHz, and proton NMR spectra at 99.5 MHz were recorded on a JEOL PS-100 Fourier transform spectrometer; boron-11 and proton spin decoupling were accomplished by using double-resonance techniques with a broad-band noise decoupler. Unit- and high-resolution electron impact (EI) mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. Chemical ionization (CI) mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY.

General Procedure. All operations were performed with use of standard high-vacuum techniques.[13] The radiation source in each experiment was a Griffin-Rayonet photochemical reactor equipped with 16 3000-Å lamps. Photochemical reactions were carried out in an all-glass circulating photolysis apparatus similar to one described previously.[2b,14] The substrates were allowed to equilibrate in the gaseous state before the reaction was initiated. Upon photolysis, the pressure in the apparatus was immediately found to drop while products condensed in the quenching trap (15 °C) beneath the reactor.

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[14] The apparatus described in ref 2b was used without mercury in the photolysis zone, but some mercury vapor was present due to an open manometer.

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Table I. ^{11}B NMR Data

compd[a]	δ, ppm (*J*, Hz)[b]	rel area	assignt
2-[HO$(CF_3)_2$C]B_5H_8 (I)[e]	−8.4 (s)[c]	1	B(2)
	−13.3 (165)	2	B(3,5)
	−15.0 (165)	1	B(4)
	−52.1 (178)	1	B(1)
1-[HO$(CF_3)_2$C]B_5H_8 (II)[e]	−12.9 (168)[d]	4	B(2-5)
	−41.6 (s)[c]	1	B(1)
1-[HO$(C(CF_3)_2)_2$O]B_5H_8 (III)[f]	−14.2 (165)	4	B(2-5)
	−19.9 (s)	1	B(1)
5-[HO$(CF_3)_2$C]-2,4-$C_2B_5H_6$ (IV)[f]	15.9 (s)	1	B(5)
	2.8 (184)	1	B(3)
	−3.6 (182)	1	B(6)
	−20.2 (182)	2	B(1,7)
5-[HO$(C(CF_3)_2)_2$O]-2,4-$C_2B_5H_6$ (V)[f]	15.9 (s)	1	B(5)
	2.8 (184)	1	B(3)
	−3.3 (170)	1	B(6)
	−20.3 (186)	2	B(1,7)

[a] All samples run in C_6D_6 solvent. [b] All chemical shifts relative to external $BF_3\cdot O(C_2H_5)_2$; a negative sign indicates an upfield shift. [c] s = singlet. [d] Proton-spin-decoupled spectrum shows quartet with $J_{^{11}B_{apical}-^{11}B_{basal}}$ = 20.8 Hz with peak separations of 19.5, 21.5, and 21.5 Hz. [e] 32.1-MHz spectrum. [f] 115.5-MHz spectrum.

Table II. ^1H NMR Data

compd[a]	δ, ppm (J_{B-H}, Hz)[b]	rel area	assignt
I[c]	2.73 (164)	3	B-H(3-5)
	2.41	1	-OH
	1.20 (176)	1	B-H(1)
	−1.96	2	B-H-B
	−2.33	2	B-H-B
II[d]	2.66 (166)	4	B-H(2-5)
	2.43	1	-OH
	−2.20	4	B-H-B
III[c]	4.00	1	-OH
	2.49 (162)	4	B-H(2-5)
	−2.29	4	B-H-B
IV[e]	4.48	2	C-H(2,4)
	4.41	1	-OH
	4.24	1	B-H(3)
	3.61	1	B-H(6)
	0.55 (185)[f]	2	B-H(1,7)
V[e]	4.44	3	C-H(2,4), B-H(3)
	4.26	1	-OH
	3.61	1	B-H(6)
	0.58 (185)[f]	2	B-H(1,7)

[a] All samples were run in pure C_6D_6 solvent. [b] Positive shifts are downfield from $(CH_3)_4Si$. [c] 250-MHz spectrum. [d] 99.5-MHz spectrum. [e] 99.5-MHz spectrum, ^{11}B spin decoupled. [f] Only coupling constant measurable from coupled spectrum.

Table III. 93.7-MHz ^{19}F NMR Data

compd[a]	δ, ppm (J_{F-F}, Hz)[b]	assignt
I	−75.1 (s)[c]	-C$(CF_3)_2$OH
II	−75.3 (s)[c]	-C$(CF_3)_2$OH
III[f]	−66.8 (h, 10)[d,e]	-OC$(CF_3)_2$C-
	−71.0 (h, 10)[d]	-C$(CF_3)_2$OH
IV	−72.6	-C$(CF_3)_2$OH
V[f]	−67.4 (h, 10)[d,e]	-OC$(CF_3)_2$C-
	−70.9 (h, 10)[d]	-C$(CF_3)_2$OH

[a] All samples were run in pure C_6D_6 lock. [b] All shifts upfield from external CCl_3F. [c] Singlet. [d] Heptet. [e] Heptet structure sharpens upon ^{11}B spin decoupling. [f] Both peaks of equal area.

Table IV. Infrared Spectra (cm^{-1})

compd	bands
I[a]	3410 (w), 2605 (s), 1445 (m), 1360 (m), 1280 (vs), 1230 (vs), 1155 (m), 1110 (m), 1040 (w), 995 (w), 820 (w, br), 740 (w, br), 690 (w, br)
II[b]	3420 (w), 2600 (s), 1435 (m), 1386 (m), 1320 (w), 1260 (vs), 1220 (vs), 1154 (m), 1109 (w), 1031 (m), 985 (w), 890 (w, br)
III[c]	3480 (m), 2625 (s), 1440 (w), 1345 (vw), 1300 (m), 1240 (vs), 1210 (vs), 1120 (m), 1090 (w), 1015 (vw), 983 (m), 940 (w), 915 (m), 874 (m), 765 (vw), 744 (w), 717 (m)
IV[a]	3500 (w), 2600 (s), 1410 (m, sh), 1360 (s), 1260 (vs), 1140 (m), 1060 (m), 990 (m), 943 (m), 885 (s), 800 (m), 745 (m), 713 (m)

[a] Conditions: Gas samples; 10-cm length; 2-cm o.d.; NaCl windows. [b] Conditions: Solution $CHCl_3$ vs. $CHCl_3$; NaCl windows. [c] Conditions: Thin film on NaCl plates.

The greatest pressure change was found to take place during the first $^1/_2$ h, but photolysis was usually continued for an additional 3 h to ensure complete consumption of the HFA. The quenching trap was then frozen at −196 °C, and the noncondensables were pumped away. The volatile reaction materials were then separated with use of vacuum line fractionation techniques[13] as described below.

Cophotolyses of HFA and B_5H_9. When equal molar quantities (14.0 mmol) of B_5H_9 and $(CF_3)_2CO$ were placed in the apparatus (*V* = 1.84 L), the pressure equilibrated to 28 cm without a reaction of the substrates. Upon photolysis, the pressure steadily dropped to 17 cm over the course of the first $^1/_2$ h, indicating a condensation of the lower volatile substrates without substantial formation of higher volatile products. The reaction was continued for 3 h while the pressure dropped an additional 3 cm. After the product quenching trap was frozen at −196 °C for $^1/_2$ h, 7 cm of noncondensables was pumped away. The remaining liquid was then fractionated overnight through traps maintained at −78 and −196 °C. The trap at −196 °C was found to contain only B_5H_9 (2.4 mmol), indicating that no HFA survived the reaction. The products isolated in the −78 °C trap (1.6191 g) were combined with 2 mL of CH_2Cl_2 and analyzed by GLC on the 10% silicone column operating isothermally at 55 °C. The major products eluted from the chromatograph were as follows: 2-[HO$(CF_3)_2$C]B_5H_8 (I): $R_V = 0.35$ (relative to that for $B_{10}H_{14}$, 1.0); 54.9%; liquid; calcd mass $^{19}F_6{}^{16}O^{12}C_3{}^{11}B_5{}^1H_9$ 230.1023, found mass 230.1000 ^{13}C NMR 1:3:3:1 quartet, 123.9 ppm ($J_{^{13}C-^{19}F}$ = 285.4 Hz, downfield relative to $(CH_3)_4Si$). Anal. Calcd: B, 23.58. Found: B, 23.04. 2:2′-$[B_5H_8]_2$: $R_V = 0.59$; 2.0%. 1-[HO$(CF_3)_2$C]B_5H_8 (II): R_V = 0.83; 19.6%; mp 54–55 °C (sealed capillary, uncorrected); calcd mass $^{19}F_3{}^{16}O^{12}C_2{}^{11}B_5{}^1H_9$ $[(M - CF_3)^+]$ 161.1071, found mass 161.1079. Anal. Calcd: B, 23.58; C, 15.72; H, 3.93. Found: B, 23.00; C, 15.85; H, 4.04. $B_{10}H_{14}$: $R_V = 1.00$; 1.0%. 1-[HO$(C(CF_3)_2)_2$O]B_5H_8 (III): R_V = 1.50; 13.7%; liquid; CI *m/e* = 229 for $(M - (CF_3)_2COH)^+$. Anal. Calcd: B, 13.67. Found: B, 14.35. Uncharacterized minor products at R_V = 0.21, 0.46, and 1.70 accounted for the remaining 8.8% of the products. The absolute yields, based on total consumed B_5H_9, were (I) 40.7%, (II) 14.5%, and (III) 10.2%. Hence, 25.2% B_5H_9 and 49.5% $(CF_3)_2CO$ were lost to polymerization, noncondensibles, or involatile materials.

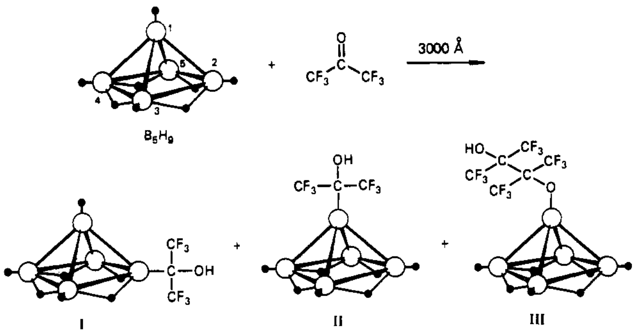
The known compounds, 2:2′-$[B_5H_8]_2$ and $B_{10}H_{14}$, were identified by spectroscopic comparison with genuine substances. Infrared and boron-11, fluorine-19, and proton NMR data of the new pentaborane(9) derivatives are presented in Tables I–IV.

In an alternate workup to the one described above, the products were fractionated through a series of traps maintained at −10, −23, −41, −78, −95, and −196 °C and analyzed by GLC. Contained at −196 °C were traces of fluorocarbons while the −95 °C trap held only unreacted B_5H_9. At −78 °C was a 6:4 mixture of I and B_5H_9; however, the −41 °C trap contained 90% I. The fractions at −23 and −10 °C yielded 6:4 and 2:7 mixtures of II:III, respectively. Isolation of large quantities of these compounds was greatly facilitated by such fractionations before further purification by GLC.

In separate experiments, 5.9 mmol of B_5H_9 and 11.8 mmol of HFA (1:2 ratio) were reacted as above to yield a 0.4962-g product mixture and 3.4 mmol of unreacted B_5H_9. Chromatographic analysis showed the products to be 44.0% I, 14.7% II, and 19.1% III. When the B_5H_9:HFA ratio was changed to 3.8:1, 12.9 mmol of B_5H_9 and 3.4 mmol of HFA yielded 0.6715 g of the product mixture, while leaving 8.7 mmol B_5H_9 unreacted. The products consisted of 40.0% I, 22.2% II, and 20.0% III.

When the reaction was allowed to continue for longer times (e.g., 12 h), the amounts of 2:2′-$[B_5H_8]_2$ and $B_{10}H_{14}$ produced were increased. This effect may be due to the mercury-sensitized photolysis

Scheme I



of pentaborane(9)[2,15] since the low-pressure 3000-Å lamps used also produce some amount (15%) of 2537-Å radiation.

Cophotolysis of HFA and $2,4\text{-}C_2B_5H_7$. In a typical reaction, 5.0 mmol of $2,4\text{-}C_2B_5H_7$ and 10 mmol of HFA were photolyzed for 3 h. The initial pressure (16 cm) dropped to 5 cm after $^1/_2$ h and dropped only another 1 cm during the next 3 h. After 2 cm of noncondensables was pumped away, the products were fractionated through −63, −95, and −196 °C traps. Contained at −95 °C was 0.4 mmol of unreacted $2,4\text{-}C_2B_5H_7$ while the −196 °C trap contained only a trace of unidentified material. The products at −63 °C (1.1971 g) were analyzed by GLC on the silicon column operating at 35 °C. Two major products were isolated. $5\text{-}[HO(CF_3)_2C]\text{-}2,4\text{-}C_2B_5H_6$ (IV): $R_V = 0.27$ (relative to that for $B_{10}H_{14}$, 1.0); 20.0%; liquid; calcd mass $^{19}F_6{}^{16}O^{12}C_5{}^{11}B_5{}^{1}H_6$ $[(M - {}^1H)^+]$ 251.0865, found 251.0795. $5\text{-}[HO(C(CF_3)_2)_2O]\text{-}2,4\text{-}C_2B_5H_6$ (V): $R_V = 1.08$; 45.5%; liquid. Uncharacterized minor products appeared in the chromatogram in the relative amounts: R_V = 0.12, 1.8%; 0.17, 5.5%; 0.20, 3.6%; 0.88, 7.3%; 1.53, 1.8%; 1.65, 3.6%; 1.76, 3.6%. The absolute yields of the two major products based on consumed $2,4\text{-}C_2B_5H_7$ were (IV) 20.7% and (V) 27.8%. Infrared and boron-11, fluorine-19, and proton NMR data for IV and V are presented in Tables I–IV.

Results

The cophotolysis of gaseous mixtures of hexafluoroacetone with pentaborane(9) at 3000 Å was found to produce both the basal and apical fluoropropanol, $-C(CF_3)_2OH$, derivatives in 41 and 15% yields, respectively, based on consumed pentaborane(9). In addition, an unusual apically substituted perfluoropinacol, $-O(C(CF_3)_2)_2OH$, species was formed and isolated in 10% yield (Scheme I).

Initial isolation of the compound $2\text{-}[HO(CF_3)_2C]B_5H_8$ (I) was most easily accomplished by collecting the photolysis products passing a −23 °C trap and condensing at −41 °C. This fraction was found to contain 90% I, which was then purified by GLC to yield a volatile air- and moisture-sensitive liquid. The elemental composition of I is supported by both the mass spectral and analytical data, while the NMR and infrared data clearly support its formulation as $2\text{-}[HO(CF_3)_2C]B_5H_8$. The ^{11}B NMR spectrum exhibits a singlet of intensity 1 at −8.4 ppm arising from the substituted boron, B(2), along with doublets at −13.3, −15.0, and −52.1 ppm (2:1:1) for the boron atoms B(3,5), B(4), and B(1), respectively, each connected to a terminal hydrogen. The proton NMR data (Table II) also support basal substitution and, in addition, show a resonance assigned to the hydroxyl group at 2.41 ppm. The presence of the OH moiety is also indicated by an IR stretch at 3410 cm^{-1}. The fluorine-19 NMR spectrum contains only a sharp singlet at −75.1 ppm due to the perfluoromethyl groups. Equivalent CF_3 groups are also indicated by the observation of a single resonance in the carbon-13 NMR spectrum at 123.9 ppm (J_{C-F} = 285 Hz).

The corresponding apical isomer, $1\text{-}[HO(CF_3)_2C]B_5H_8$ (II), is isolated from the chromatograph as an air- and moisture-sensitive white solid (mp 54–55 °C). It is significantly less volatile than I, stopping at −23 °C during vacuum-line fractionation. The proposed formula is supported by the analytical data, but the mass spectrum of $1\text{-}[HO(CF_3)_2C]B_5H_8$ does not show a parent ion under either EI or CI conditions. Instead, the highest ion observed in both spectra is m/e = 161, which may be interpreted as $(M - CF_3)^+$. The ^{11}B NMR spectrum of II consists of a singlet of intensity 1 at −42.6 ppm arising from apical substitution and a doublet of intensity 4 at −12.9 ppm for the equivalent basal resonances. Upon proton decoupling, the basal resonance exhibits the quartet structure which is characteristic of homonuclear spin–spin coupling between the apex boron and the four basal borons (J_{B-B} = 20.8 Hz). The proton NMR spectrum is also consistent with apical substitution, showing the terminal protons at 2.66 ppm (1:1:1:1 quartet (J_{B-H} = 166 Hz)) and one broad resonance of equal intensity at −2.20 ppm due to four equivalent bridge hydrogens. The presence of the OH group is indicated in the proton NMR (2.43 ppm) and the IR spectrum (3420 cm^{-1}). A sharp singlet in the ^{19}F NMR spectrum, similar to that observed for I, is again characteristic of the $-C(CF_3)_2OH$ moiety.

The product $1\text{-}[HO(C(CF_3)_2)_2O]B_5H_8$ (III) cannot be separated by vacuum-line fractionation from II because it slowly passes at −10 °C trap. However, chromatographic separation is readily accomplished to yield a low-volatility air- and moisture-sensitive liquid. The proposed formulation is supported by analysis, but the EI mass spectrum of III contained only a strong ion at m/e = 69 (CF_3^+), and the CI spectrum showed a strong ion at m/e = 229, corresponding to a $-(CF_3)_2COB_5H_8$, $[M - (CF_3)_2COH]^+$, fragment. The NMR and infrared data strongly support $1\text{-}[HO(C(CF_3)_2)_2O]B_5H_8$ as the structure. The ^{11}B NMR spectrum consists of a doublet, intensity 4, at −14.2 ppm (basal borons) and a singlet at −19.9 ppm (substituted apical boron). The large downfield shift relative to B_5H_9 for the apical resonance is, in fact, the largest such shift ($\Delta\delta$ = −32 ppm) of any known apically substituted pentaborane(9) derivative and is consistent with both the deshielding effect of the directly bonded oxygen atom and the electron-withdrawing inductive effect of the highly electronegative perfluoromethyl groups. The proton-decoupled ^{11}B NMR spectrum did not show $^{11}B_{apical}-{}^{11}B_{basal}$ coupling for the basal resonance; however, similar absence of coupling is exhibited by $1\text{-}IB_5H_8$ and $1\text{-}(CH_3)_3SiB_5H_8$.[16] In addition, the ^{19}F NMR data (see below) indicate that long-range $^{11}B-{}^{19}F$ coupling is present, perhaps obscuring the expected quartet structure. The proton NMR data (Table II) is similar to that for II, indicating apical substitution, but the hydroxyl resonance is shifted downfield to 4.00 ppm. The shift differences associated with the OH group in such fluorocarbon substitutents have previously been known to be highly solvent and concentration dependent.[5] The existence of the hydroxyl group is further confirmed by the infrared spectrum (3480 cm^{-1}). The ^{19}F NMR spectrum contains two septets (J_{F-F} = 10 Hz) of equal area at −66.8 and −71.0 ppm with the downfield resonance being substantially broadened. However, in the ^{11}B spin-decoupled ^{19}F NMR spectrum the −66.8 ppm septet sharpens, supporting its assignment to the $-(CF_3)_2CO-$ group directly bonded to the pentaborane cage. Similar fluorine chemical shift data have been observed for $(CH_3)_2(\text{Ö})P[O(C(CF_3)_2)_2OH]$ (δ_F = −68.5, −70.0)[17] and $(C_6H_4O_2)(\text{Ö})P[O(C(CF_3)_2)_2OH]$ (δ_F = −66.5, −69.1),[18] the latter pair of resonances being reported as septets with J_{F-F} = 10 Hz.

Additional experiments using B_5H_9:HFA ratios of 1:2 and 3.8:1 showed only slight differences in the relative product

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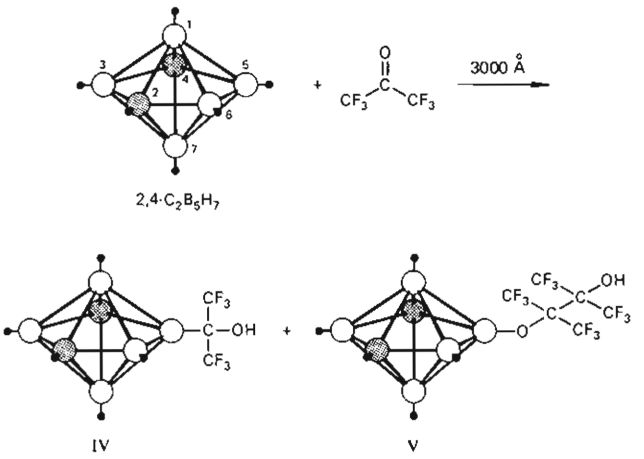
Scheme II



distributions. It can therefore be concluded that a relative increase in the amount of excited-state HFA molecules only increases the rate of reaction without affecting the nature of the products. A similar observation was also made for the reaction between cyclohexane and HFA.[5]

The cophotolysis of HFA and the closo carborane 2,4-$C_2B_5H_7$ at 3000 Å resulted in the perfluoropropanol and perfluoropinacol carborane derivatives. The two major products were 5-[$HO(CF_3)_2C$]-2,4-$C_2B_5H_6$ (IV) and 5-[$HO(C(CF_3)_2)_2O$]-2,4-$C_2B_5H_6$ (V), isolated in 21 and 28% yields, respectively, based on consumed 2,4-$C_2B_5H_7$ (Scheme II). Although the predominant substitution occurred at the 5-position, GLC and NMR evidence support other isomers as trace products.

Compound IV is a volatile air- and mositure-sensitive liquid. Its EI mass spectrum shows a strong B_5^+ envelope pattern with high-mass cutoff consistent with $m/e = (M-H)^+$. The facile loss of hydrogen in the mass spectrum may be associated with a weakening[8] of the O–H bond due to intramolecular hydrogen bonding to fluorine. The ^{11}B NMR spectrum consists of a singlet at 15.9 ppm due to B(5) substitution along with doublets at 2.8, –3.6, and –20.2 ppm attributed to B(3), B(6), and B(1,7), respectively. The ^{11}B spin-decoupled proton NMR spectrum contains cage C–H resonances at 4.48 ppm along with an OH resonance at 4.41 ppm. The appropriate B–H resonances appear at 4.24, 3.61, and 0.55 ppm (1:1:2) and are assigned to BH(3), BH(6), and BH(1,7), respectively. The ^{19}F NMR spectrum indicates equivalent fluorines at –72.6 ppm (singlet), and the IR spectrum confirms the hydroxyl presence (3500 cm^{-1}).

The second product isolated from the HFA/2,4-$C_2B_5H_7$ cophotolysis is proposed to be 5-[$HO(C(CF_3)_2)_2O$]-2,4-$C_2B_5H_6$ (V) from the NMR data. The ^{11}B spin-decoupled proton NMR spectrum (Table II) is similar to that of compound IV above and is consistent with 5-substitution, the hydroxyl group appearing at 4.26 ppm. The presence of the perfluoropinacol moiety, $-O(C(CF_3)_2)OH$, is clearly indicated by two septet resonances at –67.4 and –70.9 ppm, the former resonance sharpening upon ^{11}B spin decoupling. The ^{11}B NMR spectrum is also characteristic of substitution at the 5-position, with the appropriate singlet of intensity 1 occurring at 15.9 ppm. It should be noted that the resonances arising from the substituted borons, B(5), in both compounds IV and V are shifted approximately the same amount ($\Delta\delta$ = 21 ppm) downfield. This is in contrast to the analogous pentaborane(9) derivatives, where it was observed that the apical resonance in the oxygen-bonded perfluoropinacol compound III was shifted considerably farther downfield than in the carbon-bonded perfluoropropanol derivative II. Similar differences in chemical shifts upon substitution have previously been observed between the methyl and chloro derivatices of B_5H_9 and 2,4-$C_2B_5H_7$. Thus, for both 5-CH_3-2,4-$C_2B_5H_6$ and 5-Cl-2,4-$C_2B_5H_6$ the chemical shifts of the B(5) resonances are similar (11.3[19] and 12.8 ppm[20]), while for 1-$CH_3B_5H_8$ and 1-ClB_5H_8, the chemical shifts of the B(1) resonances are quite different (–45.3 vs. –28.7 ppm).[21]

Discussion

In the current study, the radical reactivity of excited-state hexafluoroacetone molecules was studied in the presence of B_5H_9 or 2,4-$C_2B_5H_7$. When the gaseous substrates were allowed to mix in the absence of light, no reaction was detected; however, upon ultraviolet irradiation (3000 Å) lower volatility products formed quickly. The products were found to consist of two types. Those consisting of a one-to-one condensation of reactants were shown to be perfluoropropanol derivatives containing a B–C linkage. When the product contained 2 equiv of HFA/boron cage, a perfluoropinacol moiety was formed connected by a B–O bond. The electron-deficient borane and carborane cages are known to be generally unstable toward oxygen-containing compounds. It is not surprising, therefore, that, to our knowledge, compounds I–III are the first pentaborane derivatives containing a hydroxyl group. Compound III is only the second example[22] of a compound containing an oxygen atom bonded directly to a pentaborane cage. Similarily, compounds IV and V are the first hydroxyl-containing 2,4-$C_2B_5H_7$ derivatives, while V is the first B–O-bonded derivative.

Although the compound perfluoropinacol, $[HOC(CF_3)_2]_2$, is well-known, reports of compounds containing the $-O(C(CF_3)_2)_2OH$ moiety are relatively scarce. Such derivatives have recently been selectively prepared by the reaction of the monosodium or -potassium salt of perfluoropinacol with various reagents.[23a] For example, the reaction between $HO[C(CF_3)_2]_2O^-K^+$ and $(CH_3)_2SO_4$ resulted in a synthesis of $HO[C(CF_3)_2]_2OCH_3$ in good yield.[23a] In addition, compounds of the general formula $HO[C(CF_3)_2]O(\ddot{O})PRR'$ (R, R' = CH_3, OH, OCH_3, $OCH(CH_3)_2$, OC_2H_5, $O_2C_6H_4$) have been isolated from the moisture or alcohol degradation of the corresponding dioxaphosphoranes.[16,17,23b,c] This report is, in fact, the first synthesis of [$HO(C(CF_3)_2)_2O$–]-substituted compounds directly from HFA, although it should be noted that similar reactions have been observed between HFA and trialkylphosphines,[24] where an oxidative addition of 2 equiv of HFA forms carbon–carbon-bonded cyclic compounds:

$$R_3P + 2(CF_3)_2CO \rightarrow [(CF_3)_2CO]_2PR_3$$

Although no previous boron-bonded $-O(C(CF_3)_2)_2OH$ derivatives are known, the closely related dioxaborolane $[(CF_3)_2CO]_2BC_6H_5$ has been synthesized.[25]

Previous studies of the reactions of boron compounds directly with HFA have been reported. Diborane was found to be unreactive to HFA thermally by gas-phase, fast-flow (10^4 cm/s) techniques at 180 °C and 4.5 torr pressure;[26] however,

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under photolytic conditions, B_2H_6 and HFA reacted to form small, unmeasured quantities of B_4H_{10} as the only boron-containing product.[27] The photochemical reaction of borazine with HFA produced[28] two boron-substituted (perfluoroalkyl)borazine derivatives, $H_2[(CF_3)_2HCO]B_3(NH)_3$ and $H_2[(CF_3)_3CO]B_3(NH)_3$, and the borate, $B(OCH(CF_3)_2)_3$; however, no evidence was obtained for the formation of any boron–carbon-bonded species.

The formation of the products observed in the cophotolysis of HFA with B_5H_9 or 2,4-$C_2B_5H_7$ can be understood given the known free-radical chemistry of HFA. Howard, Sargeant, and Krespan[5] have proposed a chain reaction model consistent with their experimental observations. The reaction sequence shown by eq 1–8 adapts their model to the reaction of excited-state HFA molecules with pentaborane(9).

initiation

$$(CF_3)_2CO \xrightarrow{h\nu} (CF_3)_2CO^* \text{ } (n \rightarrow \pi^* \text{ transition})^{10} \quad (1)$$

$$(CF_3)_2CO^* + B_5H_9 \rightarrow (CF_3)_2\dot{C}OH + B_5H_8\cdot \quad (2)$$

propagation

$$B_5H_8\cdot + (CF_3)_2CO \rightarrow B_5H_8C(CF_3)_2O\cdot \quad (3)$$

$$B_5H_8\cdot + (CF_3)_2CO \rightarrow B_5H_8O\dot{C}(CF_3)_2 \quad (4)$$

$$B_5H_8C(CF_3)_2O\cdot + B_5H_9 \rightarrow B_5H_8C(CF_3)_2OH + B_5H_8\cdot \quad (5)$$

$$B_5H_8O\dot{C}(CF_3)_2 + B_5H_9 \rightarrow B_5H_8OC(CF_3)_2H + B_5H_8\cdot \quad (6)$$

termination

$$2B_5H_8\cdot \rightarrow (B_5H_8)_2 \quad (7)$$

$$B_5H_8O\dot{C}(CF_3)_2 + (CF_3)_2\dot{C}OH \rightarrow B_5H_8O[C(CF_3)_2]_2OH \quad (8)$$

[others]

The reaction is presumed to proceed via an excited HFA molecule, whose oxygen atom abstracts[10] a hydrogen atom from the boron cage to initiate the chain reaction (eq 2). Then there are two competing propagation sequences (eq 3–6), where the pentaborane radical adds to the carbonyl group at either the carbon atom (eq 3) or the oxygen atom (eq 4). The relative stability and reactivity of these intermediate radicals are important. It is expected that the chain intermediate isopropyl radical $B_5H_8O(CF_3)_2C\cdot$ is more stable than the isopropoxyl radical $B_5H_8(CF_3)_2CO\cdot$ because of electron donation from oxygen[29] and the interaction with the perfluoromethyls.[30] On the other hand, alkoxy radicals are efficient hydrogen abstraction agents.[31] Thus, since the isopropyl radical is a long-lived poor hydrogen atom abstractor, it would be expected that the reaction in eq 5 is fast relative to that in eq 6. The reaction of $B_5H_8O(CF_3)_2C\cdot$ with another long-lived species present in the reaction, $(CF_3)_2\dot{C}OH$, may result in the formation of the observed product, $B_5H_8O[C(CF_3)_2]_2OH$ (eq 8). The formation of this product may also occur according to eq 9 and 10 in an alternate propagation sequence.

$$B_5H_8O\dot{C}(CF_3)_2 + (CF_3)_2CO \rightarrow B_5H_8O[C(CF_3)_2]_2O\cdot \quad (9)$$

$$B_5H_8O[C(CF_3)_2]_2O\cdot + B_5H_9 \rightarrow B_5H_8O[C(CF_3)_2]_2OH + B_5H_8\cdot \quad (10)$$

Certainly, the overall energy relationships between the C-alkylation sequence (eq 3 and 5) and the O-alkylation sequence (eq 4 and 6) can be altered by the nature of R–H. Thus, the hydrogen abstraction step would be reaction controlling. This is supported by the reactions of HFA with compounds containing easily abstractable hydrogen atoms which have been shown to produce oxygen-bonded products, such as aldehydes,[5] silanes,[5,32,33] germanes,[32] and tin hydrides.[32]

The results obtained herein may also be compared with the borazine/HFA photolysis[28] where O-alkylation predominates due to a weaker boron–hydrogen bond relative to that in pentaborane(9). The stronger B–H terminal bonds in B_5H_9 vs. borazine are evidenced by considerably shorter bond lengths (1.181 (2) and 1.186 (2)[34] vs. 1.258 (14) Å[35]), higher IR B–H stretching frequencies (2610 and 2598 vs. 2535 and 2520 cm^{-1}),[36,37] and greater B–H NMR coupling constants (175 and 165 vs. 133 Hz).[38] Therefore, as for cyclohexane,[5] C-alkylation is prevalent for B_5H_9.

It should be noted, that the isolation of 2:2′-$[B_5H_8]_2$ among the products does not necessarily confirm the termination step in eq 7. Although mercury atoms are known to have only a minor effect on the lifetime of triplet-state HFA molecules,[12] excited-state mercury atoms have been shown to promote mercury-sensitized borane dehydrodimerizations.[2,15] Since some mercury vapor was present in the apparatus, the relative increase in the amounts of 2:2′-$[B_5H_8]_2$ and $B_{10}H_{14}$ upon long reaction times may well have arisen from the reaction of pentaborane(9) with triplet-state mercury atoms formed by the absorption of 2537-Å radiation.

The hexafluoroacetone molecule is known to exhibit electrophilic character[4,5,39] and is therefore expected to attack at the position of greatest ground-state electron density, that being the apical position for B_5H_9[40] and the 5-position for 2,4-$C_2B_5H_7$.[41] The observation of 1-$[HO(CF_3)_2C]B_5H_8$ and 1-$[HO(C(CF_3)_2)_2O]B_5H_8$ among the major pentaborane/HFA cophotolysis products is consistent with this expectation. Surprisingly, 2-$[HO(CF_3)_2C]B_5H_8$ is also produced in large, but less than statistical, amounts. Lewis-based-catalyzed isomerizations of apically substituted alkylpentaboranes to the more thermodynamically favorable basal isomers are well-known.[42] It is possible, therefore, that 2-$[HO(CF_3)_2C]B_5H_8$ is not an initial reaction product but a result of a photochemical isomerization, perhaps occurring upon condensation of the

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pentaborane radical with hexafluoroacetone (eq 3 and 4). The absence of any 2-$[HO(C(CF_3)_2)_2O]B_5H_8$ may be a reflection of its low thermodynamic stability with respect to that of the apical isomer, and in fact, irreversible basal to apical isomerization for the pentaborane derivative 1-$(CF_3)_2PB_5H_8$ has previously been observed.[43] Alternatively, the absence of 2-substituted product may be due to decomposition resulting from oxygen bonding at the base. This latter explanation is consistent with the observation that 2-$CH_3OB_5H_8$ decomposes rapidly in the liquid phase.[22] In the reaction products of the 2,4-$C_2B_5H_7$/HFA cophotolysis, the strong preference for 5-position substitution is analogous to the known electrophilic methylation of 2,4-$C_2B_5H_7$ using Friedel–Crafts conditions.[19]

The reactions described above further exemplify the utility of photochemical techniques for the facile synthesis of novel polyhedral borane and carborane derivatives and suggest that the full potential of such photochemical approaches in this area has not been realized. Work is currently under way in this laboratory directed toward the development of other photochemical synthetic procedures for the production of new types of boron cluster compounds.

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Registry No. I, 91384-71-3; II, 91384-72-4; III, 91384-73-5; IV, 91384-74-6; V, 91384-75-7; $(CF_3)_2CO$, 684-16-2; B_5H_9, 19624-22-7; 2,4-$C_2B_5H_7$, 20693-69-0.

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Kinetics of the Stepwise Oxidation of Manganese(II) by Peroxodiphosphate (PDP) in Aqueous Perchloric Acid. Catalysis by Silver(I)

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The kinetics of the title reaction was investigated under isolated conditions ([Mn(II)] << [PDP]) at $I = 0.58$ M. The kinetics of the first stage of the reaction, during which Mn(II) is oxidized to Mn(IV) via a stable Mn(III) species, were monitored by following the increase in absorbance of Mn(IV) at 400 nm, where the other species in the reaction have negligible absorbance. The reaction exhibits an induction period followed by a binomial dependence of the type $a + b$[Mn(III)], a first-order dependence on [Ag(I)], and a complex dependence on [PDP]. It is also observed that further oxidation of Mn(IV) to Mn(VII) occurs only when the former is stoichiometrically formed from Mn(II). The plots of absorbance vs. time at 400 nm were found to pass through a steep maximum, after which the descending portions were linear. When [Mn(II)] was varied, with all other parameters kept constant, the maxima of the plots of absorbance vs. time obey Beer's law. The descending linear portions of these plots correspond to the oxidation of Mn(IV) to Mn(VII). An analysis of these plots suggests that this stage of the oxidation process exhibits a zero-order dependence on [Mn(IV)], first-order dependence on [Ag(I)], and a complex dependence on [PDP]. When the kinetic runs were monitored by following the increase in absorbance of Mn(VII) at 525 nm, the zero-order rate constants (k_0) were found to be identical with those evaluated from the slopes of the descending portions of the absorbance vs. time plots at 400 nm. The results for this stage of oxidation conform to the rate law $-d[Mn(IV)]/dt = d[Mn(VII)]/dt = k_0K_1K_2[PDP][Ag^+][H^+]/(1 + K_1[H^+] + K_1K_2[PDP][H^+])$, where K_1 and K_2 correspond to the equilibrium constants for the equilibria

$$H_2P_2O_8^{2-} + H^+ \xrightleftharpoons{K_1} H_3P_2O_8^- \qquad H_3P_2O_8^- + Ag^+ \xrightleftharpoons{K_2} \text{complex}$$

The k_0 values were found to be $(1.20 \pm 0.10) \times 10^{-4}$, $(1.85 \pm 0.10) \times 10^{-4}$, and $(2.33 \pm 0.14) \times 10^{-4}$ s^{-1} at 25, 30, and 35 °C, respectively.

Of the oxidation states of manganese the +7, +4, +3, and +2 states are known to be stable in acid solution while +5 and +6 are known to be stable in alkaline medium. The kinetics of oxidation of Mn(II) to Mn(VII) by periodate and peroxodisulfate ions has been reported[1,2] without much information on the nature of the intermediate oxidation states of manganese. The peroxodisulfate ion is isoelectronic and isostructural with peroxodiphosphate ion (PDP), which in recent years has been reported to be an oxidizing agent for a variety of substrates. Creaser and Edwards have extensively reviewed the oxidation reactions of this ion and the nature of its species under different pH conditions.[3] Edwards et al. and Gupta et al.[4-9] were mainly responsible for the use of this salt in kinetic studies on the oxidation of inorganic substrates. While most of the peroxodisulfate oxidations were known to be catalyzed by Ag(I) ion, similar studies with PDP as oxidizing agent are comparatively scarce. Santappa et al.[10] have reported the use of Ag(I) ion as a catalyst in the oxidation of water by PDP. In this paper, we report the results of our kinetic study on the oxidation of Mn(II) by PDP catalyzed

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