Keywords: oxonium ions · oxygen · layered compounds · tin

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Markovnikov Hydroboration of Perfluoroalkylethylenes**

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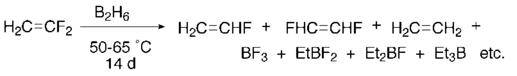
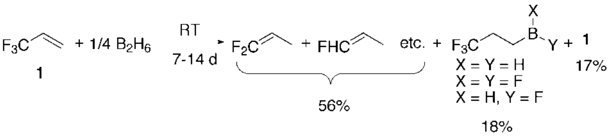
Fluoroorganic compounds are increasingly being used in analytical, biological, medicinal, organic, and polymer chemistry as well as materials science.[1] The introduction of fluorine in place of hydrogen often improves the biological properties of organic compounds.[1] The application of organoboranes has become a routine affair in many synthetic laboratories.[2] Yet, it is surprising that relatively little organoborane chemistry has been utilized to prepare fluoroorganic compounds.[3] For example, the ether-catalyzed hydroboration of olefins has been known for over 40 years.[4] However, there are no reports in the literature describing the liquid-phase addition of borane to fluorine-containing unsaturated molecules. Several gas-phase reactions of diborane with fluoroolefins have been described. The first such study by Barotcha and Stone described the reaction of diborane with tetra-, tri-, 1,1-di-, and monofluoroethylene at high and room temperatures resulting in the formation of a complex mixture of products.[5] For example, the reaction of 1,1-difluoroethylene provided a series of products resulting from the exchange of fluorine and hydrogen between the olefin and borane [Eq. (1)]. Stone and co-workers later reported that the reaction of 3,3,3-trifluoro-1-propene (**1**) with 0.25 equivalents of diborane at room temperature for 1–2 weeks resulted in several products. 1,1-Difluoropropene and its reduced species constituted 56% of the products, and (3,3,3-trifluoro-1-propyl)borane derivatives accounted for another 18% [Eq. (2)]. They reasoned that the former product originated from the addition of borane to the internal carbon atom, followed by a β-elimination [Eq. (3)].[6]



$$H_2C{=}CF_2 \xrightarrow[\text{14 d}]{\substack{B_2H_6 \\ \text{50-65 °C}}} H_2C{=}CHF + FHC{=}CHF + H_2C{=}CH_2 + BF_3 + EtBF_2 + Et_2BF + Et_3B \text{ etc.} \quad (1)$$



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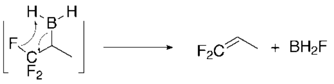
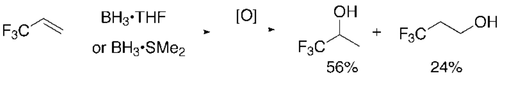


(3)

Several hydroboration agents of differing steric and electronic requirements have since become commercially available.[2] However, none of these have been tested with fluoroolefins. The fascinating results of our systematic study of the hydroboration of perfluoroalkylethylenes ($R_FCH{=}CH_2$) with these reagents are presented herein.

When **1** was treated with one equivalent of $BH_3 \cdot THF$ at room temperature, the ^{11}B NMR spectrum of the mixture after five minutes revealed three peaks at $\delta = 0.12$ (q), 5.5 (t), and 9.5 (d). These correspond to the unchanged $BH_3 \cdot THF$, a monoalkylborane, and a dialkylborane, respectively. The concentration of the dialkylborane increased with time until no further change was observed after four hours. The ^{11}B NMR spectrum now revealed the presence of BH_3, RBH_2, and R_2BH in a ratio of 2.5:4.5:1. Oxidation of the reaction mixture with alkaline H_2O_2 provided a gas chromatographic (GC) yield of 82% for the product alcohols 1,1,1-trifluoro-2-propanol and 3,3,3-trifluoro-1-propanol in a ratio of 7:3 [Eq. (4)]. The reaction of **1** with one equivalent of $BH_3 \cdot SMe_2$ at room temperature followed by oxidation with alkaline H_2O_2 revealed results similar to those realized in hydroboration with $BH_3 \cdot THF$ [Eq. (4)].



(4)

The hydroboration of **1** with $ClBH_2 \cdot SMe_2$ in Et_2O was slow and complete in 24 h. Oxidation of this mixture resulted in a 3:2 ratio of secondary and primary alcohols. The increase in the amount of the primary alcohol may be the result of an enhanced formation of the dihydroborated intermediate. The second hydroboration might be occurring at the terminal carbon atom due to the large bulk of the R_FBHCl reagent formed in the initial hydroboration.

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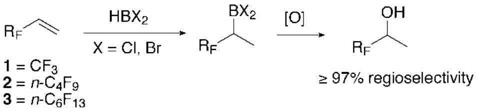
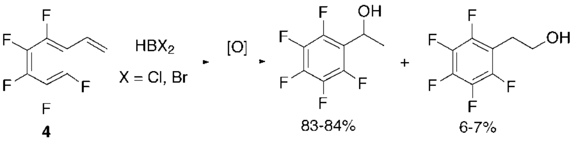
We envisaged that hydroboration with reagents containing only one hydrogen atom on the boron atom, such as 9-borabicyclo[3.3.1]nonane (9-BBN), catecholborane (CB), or dichloroborane, might provide the secondary alcohol selectively. However, 9-BBN was very slow to react with this olefin, even after 24 h. Catecholborane did not show any indication of reaction, even after days. To our gratification, the reaction of Cl_2BH—prepared by liberation from $Cl_2BH \cdot SMe_2$ upon addition of BCl_3[7] or by Matteson's procedure ($BCl_3 + R_3SiH$)[8]—was instantaneous, and oxidation of the organoborane intermediate produced the secondary (Markovnikov) alcohol in 98% isomeric purity (GC) along with 2% of the primary alcohol [Eq. (5)].



(5)

We then conducted the hydroboration of 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (**2**) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene (**3**) with $ClBH_2$ and Cl_2BH. The results of hydroboration were similar, except that the product ratio from the hydroboration with $ClBH_2 \cdot SMe_2$ showed improved regioselectivity as compared to **1**, providing the secondary and primary alcohols in a ratio of 84:16. Cl_2BH achieved essentially quantitative regioselectivity in providing the secondary alcohol [Eq. (5)]. The product alcohols were isolated in 72–86% yields from these olefins.

Subsequently, we studied the hydroboration of a representative perfluoroarylethylene, 2′,3′,4′,5′,6′-pentafluorostyrene (**4**). It has been reported that hydroboration of styrene with $BH_3 \cdot THF$ provides a 4:1 mixture of primary and secondary alcohols.[2] The reaction of **4** with $BH_3 \cdot THF$ at room temperature was complete within five hours, and the ^{11}B NMR spectrum revealed a 4:1 ratio of mono- and dihydroborated products. Oxidation of this mixture provided the secondary and primary alcohols in a 4:1 ratio, which could be isolated in 66% yield. On the contrary, Cl_2BH reacted instantaneously to provide, after oxidation, a 92:8 mixture of the secondary and primary alcohols in 90% [Eq. (6)].



(6)

The hydroboration of **1**–**4** with Br_2BH provided results comparable to those achieved with Cl_2BH. The data are summarized in Table 1.

In conclusion, we have studied the hydroboration of a series of perfluoroalkylethylenes and 2′,3′,4′,5′,6′-pentafluorostyrene with several hydroboration agents. Cl_2BH and Br_2BH hydroborate these olefins with an unprecedented Markovnikov regioselectivity of 92% or higher. The utilization of these fluoroalkylboranes for the synthesis of representative fluoro-organic derivatives is in progress.

Table 1. Hydroboration of perfluoroalkyl(aryl)ethylenes $R_FCH{=}CH_2$ with representative hydroborating agents at room temperature

Olefin	R_F	Reagent	Solvent	Reaction time [h][a]	Product alcohol yield [%][b]	*sec:pri*[c]
1	CF_3	$BH_3 \cdot SMe_2$	Et_2O	3	79[d]	70:30
1	CF_3	$BH_3 \cdot THF$	THF	4	82[d]	71:29
1	CF_3	$BH_2Cl \cdot SMe_2$	Et_2O	24	80[d]	59:41
1	CF_3	$BHCl_2 \cdot SMe_2$	hexane	inst.	81[d]	**98:2**
1	CF_3	$BHCl_2$	hexane	inst.	81[d]	**98:2**
1	CF_3	$BHBr_2$	hexane	inst.	85[d]	**97:3**
2	n-C_4F_9	$BH_3 \cdot SMe_2$	Et_2O	3	71	84:16
2	n-C_4F_9	$BH_3 \cdot THF$	THF	4	73	85:15
2	n-C_4F_9	$BH_2Cl \cdot SMe_2$	Et_2O	24	68	84:16
2	n-C_4F_9	$BHCl_2 \cdot SMe_2$	hexane	inst.	75	**99:1**
2	n-C_4F_9	$BHCl_2$	hexane	inst.	85	**≥ 99**[e]
2	n-C_4F_9	$BHBr_2$	hexane	inst.	86	**99:1**
2	n-C_4F_9	9-BBN	THF		very slow reaction	
2	n-C_4F_9	CB	THF		no perceivable reaction	
3	n-C_6F_{13}	$BH_3 \cdot SMe_2$	Et_2O	3	72	80:20
3	n-C_6F_{13}	$BH_3 \cdot THF$	THF	4	74	83:17
3	n-C_6F_{13}	$BH_2Cl \cdot SMe_2$	Et_2O	24	74	84:16
3	n-C_6F_{13}	$BHCl_2 \cdot SMe_2$	hexane	inst.	77	**≥ 99**[e]
3	n-C_6F_{13}	$BHCl_2$	hexane	inst.	77	**≥ 99:1**[e]
3	n-C_6F_{13}	$BHBr_2$	hexane	inst.	80	**99:1**
4	C_6F_5	$BH_3 \cdot THF$	THF	5	66	79:21
4	C_6F_5	$BHCl_2 \cdot SMe_2$	hexane	inst.	90	**92:8**
4	C_6F_5	$BHBr_2$	hexane	inst.	90	**94:6**

[a] inst. = instantaneous. [b] Yields of isolated product unless otherwise stated. [c] Determined by GC analysis. [d] Yields determined by GC analysis. [e] No primary alcohol was detected.

Experimental Section

All operations were carried out under an inert atmosphere.[9] A typical experimental procedure for the hydroboration of **3** with Cl_2BH is as follows. Trimethylsilane (1.48 g, 20 mmol) was added to a solution of BCl_3 (20 mL, 1.0 M in hexanes, 20 mmol) and **3** (6.92 g, 20.0 mmol), precooled to −78 °C. The hydroboration was completed essentially instantaneously as shown by the ^{11}B NMR spectrum ($\delta = 60.4$). The solution was brought to room temperature, treated with water (5 mL), and neutralized with saturated Na_2CO_3. The volatile components were removed under vacuum, and the residue was dissolved in diethyl ether and oxidized with NaOH (20.0 mmol) and H_2O_2 (20.0 mmol). The crude product was analyzed by GC using a Carbowax 20 column. No primary alcohol was detected. Distillation (76 °C/25 Torr) provided 5.61 g (77%) of 3,3,4,4,5,5,6,6,6-nonafluoro-2-hexanol.

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Ta_4BTe_8: Tantalum Telluride Cluster Chains with Encapsulated Boron Atoms[**]

Holger Kleinke, E. Wolfgang Finckh, and Wolfgang Tremel[*]

Clusters of the types $M_6X_{12}{}^{n+}$ and $M'_8X_8{}^{m+}$ have been known for many years for Group 5 and 6 transition elements.[1, 2] For the more common M_6X_{12} type, various binary and ternary niobium and tantalum compounds have been made that contain $M_6X_{12}{}^{2+/3+}$ clusters along with different halide anions.[3, 4] The electronic rules for the stability of these cluster compounds are mainly dictated by the (idealized) cubic symmetry and the connectivity within the cluster cores. The $M_6X_{12}{}^{n+}$ cluster phases are generally stable for electron counts between 14 and 16;[5] typical electron counts for M_6X_8 clusters range between 19 and 24 with an upper limit of 24.[6] Given the generality that something close to these "magic" electron counts is required for cluster stability, it is clear that the M_6X_8 type is preferred for Group 6 chalcogenides, as observed in the Chevrel phases,[7] whereas the M_6X_{12} type is adopted by Group 5 halides such as Ta_6Cl_{15}.[8]

Analogous clusters of the Group 3 and 4 elements will be seriously electron deficient, but this shortage may be compensated for by encapsulating heteroatoms in the center of the cluster where the heteroatoms donate their electrons to the (otherwise) empty cluster orbitals.[9] Alternatively, to electronically saturate electron-deficient cluster species, counterreduction of the clusters may be achieved by the inclusion of cations into the cluster network.[10] The knowledge of the electronic and structural principles has lead to the discovery of an enormous variety of centered early transition metal halide clusters during the past decade.[11]

So far, a corresponding chalcogenide interstitial cluster chemistry does not exist. McCarley[12] as well as Simon and Köhler[13] developed a systematic chemistry of the "reduced" niobates and molybdates such as $NaMo_4O_6$.[14] The structures of these materials are based on isolated and fused M_6O_{12} units whose inherent electron deficiency is compensated for by charge-balancing cations. In contrast, the structures of early transition metal sulfide, selenide, or telluride clusters are almost exclusively based on Mo_6Q_8 cluster units. Alternative cluster topologies are infinite chains of interpenetrating icosahedral[15] or face-sharing square-antiprismatic units;[16] Ta_2S_2C, which contains layers of edge-sharing C-centered Ta_6 octahedra, is a notable exception.[17]

Here we report on the synthesis, structure, and properties of an unusual centered M_6X_{12} chalcogenide cluster phase. From structural chemistry it is well known that size effects and radius ratios control the structure of materials to a major extent. Similarly, the size of the heteroelement determines the structure of compounds in the sytem M-A-Te (M = Nb, Ta; A = Group 13 element). In attempts to replace gallium (covalent radius $r_{cov} = 1.26$ Å) in the ternary phase $Ta_{13}Ga_3Te_{24}$[18] by the isoelectronic, but much smaller, group homologue boron ($r_{cov} = 0.88$ Å) leads to the formation of the novel cluster compound Ta_4BTe_8 with an interstitial boron atom.[19]

The structure of Ta_4BTe_8 is shown in Figure 1.[20] Ta_4BTe_8 crystallizes in the space group *Pbam* with two formula units per unit cell, and all atoms are situated on mirror planes perpendicular to *c* at $z = 0$ and $\frac{1}{2}$. The structure consists of Ta_6BTe_{12} clusters, whose twofold axis is along the viewing direction and which contain a B atom in the center. The individual clusters are condensed by sharing of common edges. As a result, linear chains of centered edge-sharing Ta_6-octahedra are obtained which are coordinated by Te atoms above all free edges and exhibit the connectivity ${}^{1}_{\infty}[\mathrm{Ta1}_{4/2}\mathrm{Ta2}_2(\mathrm{B})\mathrm{Te1}^{\mathrm{i}}_{4/2}\mathrm{Te2}^{\mathrm{i}}_{4/2}\mathrm{Te3}^{\mathrm{a}}_{2}\mathrm{Te4}^{\mathrm{i-a}}_{4/2}]$, according to the nomenclature of Schäfer and von Schnering.[2] Figure 2 shows in

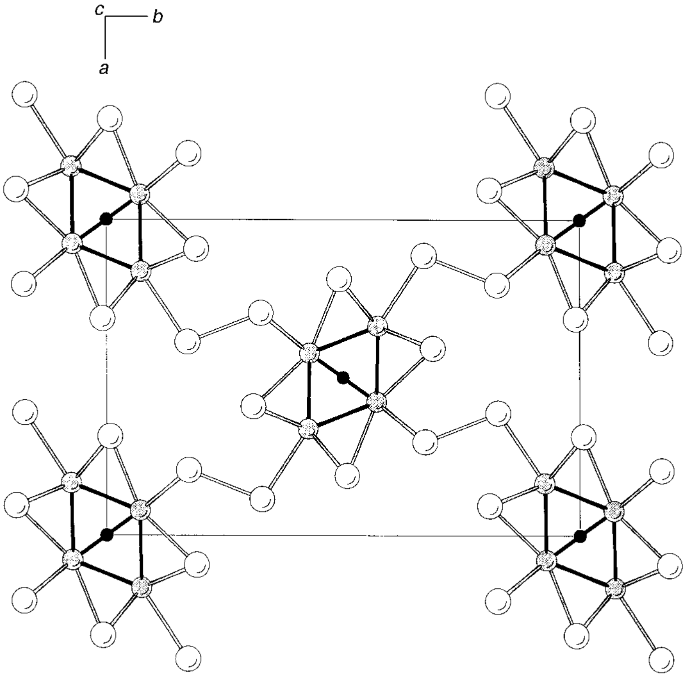

Figure 1. View of the Ta_4BTe_8 structure along *c* (Te: white open spheres, Ta: gray spheres, B: black spheres).

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