

SYNTHESIS OF FLUOROPHENYL AND 3-FLUOROBENZYL DERIVATIVES OF DECABORANE AND THE ELECTRON PROPERTIES OF 5- AND 6-DECABORANYL GROUPS

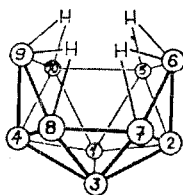
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Reaction of $(F-C_6H_4BH_2)_2$ with anions $B_9H_{14}^-$ gave 6-(3- or 4-fluorophenyl)decaboranes in low yields. Alkylation of the decaborane anion $B_{10}H_{13}^-$ produced a mixture of 5- and 6-(3-fluorobenzyl) decaboranes(13), which was treated with dimethyl sulphide to separate the 6-isomer. The ^{19}F NMR spectra of these compounds and the σ constants calculated from them suggest that the decaboranyl group has a weak electron-withdrawing character, manifesting itself by both the inductive and the resonance effects.

A typical representative of *nido*-boranes, *i.e.* compounds of the general formula B_nH_{n+4} , where the orbital unsaturation produces unusual bonding properties, is decaborane, $B_{10}H_{14}$ (I). Although many papers deal with both the quantum-chemical

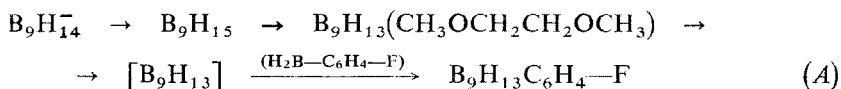


I

calculation of electron distribution in its molecule¹ and the reactivity of this compound², we considered it of interest to study interaction of the benzene ring and this pseudoaromatic system, and to estimate the polar effects of the decaboranyl group. As a measure of the polar effect of a particular group we chose the value of its σ constant. Taft and coworkers^{3,4} discovered a correlation between the chemical shift of the fluorine signal in the ^{19}F -NMR spectra of substituted 3- and 4-fluorobenzene and the constants σ_I and σ_R^0 of the substituents; this correlation was used in the present paper. Our syntheses of model compounds, 3- and 4-fluorophenyldecaboranes, have been guided by experience with the preparation of phenyldecaborane⁵ and the results published by Schaeffer and coworkers⁶; these authors found

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that in the reaction of diborane with tetramethylammonium tetradecahydronona-borate(1-) the insertion of a boron atom occurs and the decaborane skeleton is formed. The needed 6-(fluorophenyl)decaboranes were obtained (in low yields) by the following reactions.



The assumed structure of the boron skeleton, with an aromatic ring bound to boron at position 6, is in agreement with the ^{11}B -NMR spectra of these compounds. The reaction scheme (A), involving the formation of the unstable borane B_9H_{13} , has been deduced by us from the following facts:

As was found by Schaeffer and coworkers⁷, nonaborane *i*- B_9H_{15} in ether can be quantitatively converted into a compound $\text{B}_9\text{H}_{13}\text{L}$. Pyrolysis of this compound in gaseous phase gives the unstable B_9H_{13} (ref.⁸), whose existence is postulated even in the mechanism propounded for the formation of octadecaborane, $\text{B}_{18}\text{H}_{22}$ (ref.⁹). Because of its high reactivity the structure of B_9H_{13} has not yet been determined, but is supposed^{9,10} to have the same boron skeleton as the above-mentioned compound $\text{B}_9\text{H}_{13}\text{L}$. Consequently, the unequivocal incorporation of another boron atom into position 6 is a logical completion of an icosahedral skeleton.

Attempts at synthesis of phenyldecaborane by reaction of bromobenzene with decaborane ended in failure. Surprisingly, the main product of the reaction was a mixture of the isomeric 1- and 2-bromodecaboranes.

Alkylation of the decaborane anion $\text{B}_{10}\text{H}_{13}^-$ by a benzyl halide is known¹¹ to substitute alkyl for the hydride hydrogen at position 6, and, to some extent, at position 5 of the decaborane skeleton¹². This method enabled us to synthesize 5- and 6-(3-fluorobenzyl)decaboranes and use them as model compounds to determine the σ_1 constants of the 5- and 6-decaboranyl groups; in these compounds the resonance effect of the decaboranyl group on the electronic system of the aromatic ring is absent, since the two systems are separated by a methylene group.

Benylation of the decaborane anion $\text{B}_{10}\text{H}_{13}^-$ by 3-fluorobenzyl bromide under the given conditions led to a 40% substitution on the atom at position 5 (determined from integral intensities in the ^{19}F -NMR spectrum). As we were unable to separate the mixture of the two isomers by crystallization from hexane and pentane and/or by chromatography, the mixture was treated with dimethyl sulphide; only the 5-derivative reacted, giving the 5-substituted bis(dimethylsulphide)decaborane(12), and the unreacted 6-derivative was extracted into hexane. The ^{11}B -NMR spectra of the mixture of the 5- and 6-isomers, as well as of the pure 6-isomer, were identical in character with the spectra of unsubstituted 5- and 6-benzyldecaboranes and their mixture¹², and were consistent with the propounded structures of the compounds prepared.

From the measured values of relative chemical shifts of fluorine in 6-(fluorophenyl)-decaboranes we calculated, by the method of Taft and coworkers³, the values of σ_I and σ_R for the decaboranyl group: $\sigma_I = 0.12 \pm 0.04$, $\sigma_R = 0.12 \pm 0.05$. The intervals of accuracy refer to a confidence interval of 95%; the intervals were estimated by the method described¹³.*

The data show that the 6-decaboranyl group is a weak electron acceptor. The electron withdrawing character of this group is due to its weak $-I$ effect, indicated by the value of σ_I , and to its resonance effect, as follows from the statistically significant value of σ_R (supposed to be a measure of the resonance interaction of a group with an aromatic system). Compared to the 1-*o*-carboranyl group¹⁶ the decaboranyl group is a weaker electron acceptor, but its electron withdrawing character is enhanced by the resonance effect, which is not so in the former. From the ¹⁹F chemical shifts of fluorine in 3-fluorobenzyldecaboranes we analogously calculated the values of the constant $\sigma_I(\text{CH}_2\text{X})$: -0.14 ± 0.04 for $\text{X} = 5\text{-B}_{10}\text{H}_{13}$, and 0.12 ± 0.04 for $\text{X} = 6\text{-B}_{10}\text{H}_{13}$. The accuracy refers again to the 95% confidence interval. The values of σ_I for the decaboranyl groups were estimated by Charton's method¹⁷, the transmittance coefficient of the CH_2 group was considered equal to 0.4 (ref.¹⁸), for $\text{X} = 6\text{-B}_{10}\text{H}_{13}$ $\sigma_I(\text{X}) = 0.45$, for $\text{X} = 5\text{-B}_{10}\text{H}_{13}$ $\sigma_I(\text{X}) = -0.20$. The value for the 6-decaboranyl group is significantly different statistically from that deduced from the ¹⁹F-NMR spectra of 6-(3-fluorophenyl)decaborane, $\sigma_I = 0.12$, although both suggest that the 6-decaboranyl group is an electron acceptor, as a result of its induction mechanism. The difference in solvation of the two model compounds does not seem to be a probable cause of the discrepancy, since in the non-polar solvents employed the chemical shift of fluorine was not much dependent on concentration of the solute or on the nature of the solvent.

Whether or not Charton's method was applicable in this case is questionable. Some authors¹⁹ ascribe changes in the chemical shift of fluorine in aromatic systems to electrostatic polarisation of electrons of the C—F bond, and consider the inductive effect of electrons to be negligible. The decaboranylmethyl group, compared to the decaboranyl group, has a considerable conformation freedom. In addition, the decaboranyl group has an unusually high dipole moment (3.5 D, ref.²). It is possible that in the case of this group with heteroatoms the inductive and the resonance effects of the substituent in the aromatic system are accompanied by other strong effects, which mask the damping power of the CH_2 bridge.

However, the obtained values of σ_I for the 5- and 6-decaboranyl groups are qualitatively in agreement with their distributions of electron densities, determined by quantum-chemical calculations¹. In addition, they confirm that these electron characteristics are operative even in the transition states of substitution reactions on the deca-

* From the original experimental data^{3,4,15} we obtained the following statistical characteristics for the plot of σ_I vs δ_m^F : $r = 0.991$, $s_{xy} = 0.246$, $\psi^{14} = 0.13$; for σ_R vs $(\delta_p^F - \delta_m^F)$: $r = 0.985$, $s_{xy} = 1.428$, $\psi = 0.19$. The calculated values were used to estimate the errors in σ .

borane skeleton. In accordance with these ideas nucleophilic substitution proceeds preferentially on the boron atom at position 6 of this skeleton.

EXPERIMENTAL

^{11}B -NMR spectra were measured on an apparatus Varian XL 100, the values of δ are related to $\text{BF}_3(\text{OC}_2\text{H}_5)_2$. ^{19}F -NMR spectra were measured on the same apparatus, with the aid of decoupling of protons of the aromatic ring. The measurements were carried out on 0.2M solutions of the compounds in deuteriochloroform. The values of δ^{F} relate to fluorobenzene as internal standard. The dependence of the chemical shift, δ^{F} on concentration of a compound was negligible, in agreement with the reported data^{3,4}. The maximum dispersion variance of δ^{F} values for four measurements was 0.04 p.p.m. All measurements refer to 37°C. IR spectra were measured in an apparatus Beckman IR 20A, mass spectra in an LKB apparatus at 70 eV and an emitter temperature of 150°C. Thin-layer chromatography ran on Silufol plates with starch as binder (Kavalier, Votice, Czechoslovakia); the spots were detected with iodine vapour and aqueous silver nitrate spray.

Bis(3-fluorophenyl)diborane and Bis(4-fluorophenyl)diborane

3-Fluorophenylboric acid, prepared from tributyl borate²⁰ and 3-fluorophenylmagnesium bromide²¹, was esterified with butanol²⁰. The dibutyl ester thus obtained, b.p. 60–80°C/2 Torr, was reduced with diborane, according to Michailov and coworkers²², to bis(3-fluorophenyl)diborane (30% yield), which was used directly for further work. Analogously, 4-fluorophenylboric acid gave its dibutyl ester, b.p. 70–75°C/1 Torr, which was reduced with diborane to bis(4-fluorophenyl)diborane (30% yield).

Reaction of Bis(3-fluorophenyl)diborane with KB_9H_{14}

To 6 g (40 mmol) of a freshly prepared powder of KB_9H_{14} (ref.²³) was added by condensation 5 l of dry hydrogen chloride. After 20 minutes' stirring of the mixture at -110°C the excess of HCl was distilled off and 25 ml of dry 1,2-dimethoxyethane was distilled in. The mixture was stirred for another 30 min at -70°C . The suspension was then mixed with a solution of 27 mmol of bis(3-fluorophenyl)diborane in 10 ml of 1,2-dimethoxyethane. The temperature was raised in the course of 3 h to -30°C , in which time about 500 ml of H_2 (uncorrected) was liberated. Continued elevation of the temperature in 8 h up to 70°C gave rise to a yellow solution. The solvent was removed and the product was distilled *in vacuo* (10^{-3} Torr). Thin-layer chromatography revealed that the main constituent of the first fraction (2.7 g), distilling at a bath temperature of 50–60°C, was decaborane, 60% of the second fraction (3.7 g), distilling at a bath temperature of 150–180°C, was $\text{B}_{18}\text{H}_{22}$, which was partially separated from a pentane solution of this fraction by freezing; the rest of the second fraction was decaborane and a compound of R_{F} 0.50 (Silufol, hexane–benzene 1 : 1). This compound was isolated from the mixture (0.5 g) chromatographically on a column packed with silica gel (200 g); the eluent was hexane with a linearly increasing concentration of benzene. The fractions were analysed by thin-layer chromatography. The sought compound was present in a fraction containing also $\text{B}_{10}\text{H}_{14}$, which was removed by sublimation at $100^\circ\text{C}/1$ Torr, 4 hours. Distillation at $60^\circ\text{C}/10^{-5}$ Torr gave 80 mg of the oily product. The procedure was not optimized. The mass spectrum of 3-fluorophenyldecaborane exhibited a molecular cut off at $m/e = 218$, corresponding to $^{12}\text{C}_6^{1}\text{H}_{17}^{11}\text{B}_{10}^{19}\text{F}_1 + \text{ion}$. The ^{11}B -NMR spectrum had 6 signals of relative intensities 1 : 3 : 2 : 2 : 1 : 1, *viz.* a singlet at -21.5 p.p.m. and doublets at -10.5 , -1.6 , 3.1 , 32.4 and 37.3 p.p.m., respectively. The ^{19}F -NMR

spectrum contained a singlet at -0.24 p.p.m. The IR spectrum (5% solution in CCl_4 , 0.1 mm cell of NaCl) consisted of bands at (cm^{-1}): 3065 vw ($\nu\text{C—H}$ arom.), 2580 s ($\nu\text{B—H}$), 1980 w ($\nu\text{B—H—B}$), 1945 w ($\nu\text{B—H—B}$), 1900 w ($\nu\text{B—H—B}$), 1870 w ($\nu\text{B—H—B}$), 1610 m, 1580 s, 1560 shm, 1500 s, 1485 s, 1450 n, 1418 s, 1410 shs, 1300 w, 1260 vs ($\nu\text{C—F}$), 1230 w, 1170 n ($\delta\text{C—H}$ arom.), 1160 m ($\delta\text{C—H}$ arom.), 1100 m, 1075 shm, 1015 m, 1005 shs, 995 s, 965 shw ($\nu\text{B—B}$) 955 w, 930 w ($\delta\text{B—H}$), 900 w, 885 wsh, 880 m, 860 m, 703 m, 690 s ($\delta\text{C—H}$ arom.), 675 shm.

In the same way bis(4-fluorophenyl)diborane was converted into 4-fluorophenyldecaborane (92 mg). The mass spectrum of this compound exhibited a molecular cut-off at m/e 218, corresponding to $^{12}\text{C}_6\text{ }^1\text{H}_{17}\text{ }^{11}\text{B}_{10}\text{ }^{19}\text{F}_1 + \text{ion}$. The ^{11}B -NMR spectrum consisted of six signals of relative intensities 1 : 3 : 2 : 2 : 1 : 1 at -22.5 , -10.0 , -1.44 , 4.0 , 32.0 and 38.0 p.p.m. The ^{19}F -NMR spectrum had a singlet at -3.85 p.p.m. The IR spectrum (5% solution in CCl_4 , 0.1 mm NaCl cell, contained the following bands (cm^{-1}): 3035 w ($\delta\text{C—H}$ arom.) 2960 m ($\nu\text{C—H}$ arom.), 2580 vs ($\nu\text{B—H}$), 1990 vw ($\nu\text{B—H—B}$), 1945 w ($\nu\text{B—H—B}$), 1900 w ($\nu\text{B—H—B}$), 1600 s, 1555 m, 1510 s, 1495 shs, 1445 m, 1410, 1395 m, 1303 M, 1260 vs ($\nu\text{C—F}$), 1230 s ($\delta\text{C—H}$ arom.) 1160 s ($\delta\text{C—H}$ arom.), 1095 vs, 1015 vs, 995 shs, 975 shm, 952 m, 920 m ($\delta\text{B—H}$), 910 m, 863 m, 863 m, 830 s ($\delta\text{C—H}$), 705 m ($\delta\text{B—H}$), 680 m ($\delta\text{B—H}$).

Reaction of Bromobenzene with Decaborane and Aluminium Bromide

A mixture of decaborane (6.0 g, 49 mmol), bromobenzene (26 ml) and AlBr_3 (15 g) was heated 1 h to 100°C with an evolution of HBr . Then it was refluxed for 2.5 h, diluted with 50 ml of dichloromethane, decomposed by the addition of water and filtered. The separated organic phase was diluted with 50 ml of hexane and placed in a freezing box; 1.8 g of a solid separated; this was identified as $2\text{-BrB}_{10}\text{H}_{13}$ by TLC on silica gel (hexane as eluent; prior to sample application the plate was exposed to vapour of trichloroacetic acid for 5 min) and by its IR spectrum²⁴. The parent liquor was chromatographed on a silica gel column with hexane as eluent. In addition to the unreacted starting substances there was obtained a compound (0.9 g) which was identified by TLC and the IR spectrum²⁴ as $1\text{-BrB}_{10}\text{H}_{13}$. Further elution, with benzene, gave a fraction from which a crop of crystals separated. Sublimation of the crystals gave another 0.2 g of $2\text{-BrB}_{10}\text{H}_{13}$. The total yield of 2-bromodecaborane was 21%.

Fluorobenzyldecaborane(13)

Adhering to a described procedure¹¹, a fresh solution of $\text{B}_{10}\text{H}_{13}\text{Na}$, prepared from 11.8 g (97 mmol) of $\text{B}_{10}\text{H}_{14}$ and 3.2 g (133 mmol) of 85% NaH in 100 ml of ether, was treated with approx. 12 ml (100 mmol) of 3-fluorobenzyl chloride. Repeated distillation of the crude product at 100°C and 10^{-4} Torr gave 2 g (96%) of $3\text{-F—C}_6\text{H}_4\text{CH}_2\text{B}_{10}\text{H}_{13}$. Thin-layer chromatography of this preparation gave two spots, R_F 0.35 and R_F 0.40 (hexane-benzene 1 : 1). For $\text{C}_7\text{H}_{19}\text{B}_{10}\text{F}$ (230.4) calculated: 46.95% B, 36.48% C, 8.31% H; found: 46.80% B, 36.40% C, 8.20% H. The ^{11}B -NMR spectrum: a clear singlet at -23.9 p.p.m., intensity c. 0.5, and a broad obscure signal at 0.0 p.p.m., intensity c. 3.5, associated with the boron atoms at positions 5, 7, 8 and 10 of the decaborane skeleton. The ^{19}F -NMR spectrum: singlets at -0.25 and 0.36 p.p.m. in CDCl_3 at -0.19 and 0.38 p.p.m. in C_6D_6 .

The mixture (0.5 g) was dissolved in dimethyl sulphide (40 ml). After two months' standing at room temperature dimethyl sulphide was distilled off *in vacuo* and the remaining oily residue was extracted with pentane. After evaporation of pentane from the extract, distillation at 100°C 10^{-4} Torr gave 80 mg of an oil, which proved chromatographically pure. Its ^{11}B -NMR spectrum consisted of 7 signals of relative intensities 1 : 2 : 1 : 2 : 2 : 1 : 1 at -23.9 , -10.8 , -9.1 , -1.0 , 1.5 ,

33.9 and 38.0 p.p.m., respectively. The IR spectrum (5% solution in 0.1 mm NaCl cell) showed bands at (cm^{-1}): 3040 vw ($\nu\text{C—H}$ arom.), 2965 m (νCH_2), 2910 shm (νCH_2), 2865 w (νCH_2), 2580 vs ($\nu\text{B—H}$), 1990 vw, 1935 w ($\nu\text{B—H—B}$), 1905 w ($\nu\text{B—H—B}$), 1860 vW ($\nu\text{B—H—B}$), 1620 s, 1500 shs, 1490 vs, 1450 s, 1415 m, 1263 s, 1230 s ($\nu\text{C—F}$), 1142 s ($\delta\text{C—H}$ atom.), 1095 shs, 1080 s, 1020 s, 1005 s, 995 s, 960 shm ($\nu\text{B—B}$), 960 m, 945 m, 920 m ($\delta\text{B—H}$), 900 w, 885 m, 863 m, 840 w, 705 m ($\delta\text{B—H}$), 690 m ($\delta\text{C—H}$ arom.), 685 m ($\delta\text{B—H}$).

The ^{19}F -NMR spectrum exhibited a singlet at -0.25 p.p.m. in CDCl_3 .

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