

tained from the product in method B. However, immediate treatment with concentrated potassium hydroxide followed by precipitation with a large excess of ethanol gave $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii in almost quantitative yield.

Preparation of $(Me_4N)_2B_{20}H_{17}OH$. To a solution of 2.00 g. (4.43 mmoles) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in 100 ml. of 0.2 N hydrochloric acid at 0° was added slowly 20 ml. (10.0 mmoles) of 0.5 N ferric chloride solution. The reaction mixture was stirred for 10 hr. after which a saturated solution of tetramethylammonium chloride was added until no further precipitation occurred. The pale yellow $(Me_4N)_2B_{20}H_{17}OH$ was collected and recrystallized from hot water. There was obtained 1.5 g. (85%) of $(Me_4N)_2B_{20}H_{17}OH$. The compound absorbed in the ultraviolet at λ_{max} 300 μ (ϵ 12,000) and λ_{max} 230 μ (ϵ 16,000). The

infrared spectrum contained a B-H stretching band at 2480 cm^{-1} (vs) and an OH stretching band at 3560 cm^{-1} (m). Other bands occurred at 1410 (m), 1290 (m), 1200 (m), 1170 (s), 1090 (s), 1075 (s), 1020 (w), 986 (w), 948 (vs), 909 (w), 889 (m), 875 (s), 855 (w), 826 (s), 811 (m), 775 (s), 738 (s), 692 (s), and 678 (s) cm^{-1} .

Anal. Calcd. for $(Me_4N)_2B_{20}H_{17}OH$: C, 24.09; H, 10.16; N, 7.02; B, 54.26. Found: C, 24.50; H, 10.95; N, 6.27; B, 55.11.

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The Electronic Properties of the 1,2- and 1,7-Dicarbaclododecaborane(12) Groups Bonded at Carbon

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The electronic properties of the 1,2- and 1,7-dicarbaclododecaborane(12) groups bonded at carbon have been examined with the aid of the following data: (1) nitration of the phenyl ring in [1,2-dicarba-1-clovdodecaboranyl(12)]benzene with mixed acid and determination of the ortho, meta, and para isomer ratios; (2) the determination of the pK_a values of *m*- and *p*-[1,2-dicarba-1-clovdodecaboranyl(12)]benzoic acids and anilinium ions; (3) determination of the ^{19}F chemical shifts relative to fluorobenzene of *m*- and *p*-[1,2- and 1,7-dicarba-1-clovdodecaboranyl(12)]fluorobenzenes. The data obtained provide no evidence for ground-state extension of electron delocalization by interaction of the aryl group with the highly delocalized 1,2-dicarba-1-clovdodecaboranyl(12) group, but did provide evidence for ground-state extension of electron delocalization by weak electron donation from the 1,7-dicarba-1-clovdodecaboranyl(12) isomer to the aryl group. The chemical equilibrium data for the 1,2-dicarba-1-clovdodecaboranyl(12) group were correlated with approximately the same Hammett σ constants ($\sigma_m \cong 0.47$, $\sigma_p \cong 0.49$) in both series of equilibria. The ^{19}F data correlated with σ_I constants of $+0.375 \pm 0.010$ and $+0.194 \pm 0.010$ for the 1,2- and 1,7-dicarba-1-clovdodecaboranyl(12) groups, respectively. The σ_R^0 constants $+0.003 \pm 0.005$ and -0.039 ± 0.005 were similarly obtained for the 1,2- and 1,7-dicarba-1-clovdodecaboranyl(12) substituents, respectively.

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Introduction

The reaction of $B_{10}H_{14}$ with ligands such as acetonitrile produces $B_{10}H_{12}(\text{ligand})_2$ ³ derivatives which react with substituted acetylenes to produce 1,2-dicarba-1-clovdodecaboranyl(12) (hereafter α -carboranyl)^{4,5} derivatives. The latter compounds possess the geometry of a nearly regular icosahedron with the carbon atoms in neighboring positions.⁶ The α -carboranyl derivatives normally rearrange at 400–450° to 1,7-dicarba-1-clovdodecaboranyl(12) (hereafter, β -carboranyl)^{5,7} derivatives which differ from their α isomers in that the carbon atoms in the icosahedron are separated from each other by a pair of boron atoms.⁸ The organic chemistry of the α - and β -carboranyl systems has been investigated⁹ and evidence has accumulated which

(3) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

(4) (a) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); (b) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. K. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963); (c) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); (d) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963); (e) M. M. Fein, D. Grafstein, J. E. Paus-tian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963); (f) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1874 (1964).

(5) In previous literature the 1,2 and 1,7 isomers were referred to as *o*- and *m*-carborane, respectively. These isomers will be referred to as the α and β isomers, respectively, in this paper to avoid confusion with the standard nomenclature for phenyl derivatives.

(6) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964).

(7) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(8) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(9) (a) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963); (b) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963); (c) R. P. Alexander and H.

Table I. Ionization Constants for Substituted Anilinium Ions

| Substituent | λ_{\max} | D_{ti}^a | D_{ui}^b | D_{pi}^c | C_X/C | pK_a |
|-----------------------------------|------------------|------------|------------|------------|---------|-------------------|
| <i>m</i> -OCH ₃ | 236 | 0.018 | 0.775 | 0.120 | 0.135 | 4.48 |
| <i>p</i> -Cl | 238 | 0.017 | 1.379 | 0.352 | 0.246 | 4.18 |
| <i>m</i> -Cl | 236 | 0.015 | 1.188 | 0.600 | 0.500 | 3.67 ^d |
| <i>m</i> -NO ₂ | 232 | 0.287 | 1.496 | 1.360 | 0.110 | 2.76 |
| <i>m</i> -[α -Carboranyl] | 236 | 0.038 | 1.170 | 0.752 | 0.370 | 3.44 |
| <i>p</i> -[α -Carboranyl] | 255 | 0.055 | 1.493 | 1.056 | 0.304 | 3.31 |

^a D_{ti} , observed optical density in a 30% H₂SO₄-40% MeOH solution. ^b D_{ui} , observed optical density in a 40% MeOH-60% H₂O solution. ^c D_{pi} , observed optical density in a 5×10^{-3} M H₂SO₄-40% MeOH-60% H₂O solution. ^d Literature value, used as reference aniline; see W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3072 (1962). $pK_a^A - pK_a^B = \log C_A/C_{AH^+} + \log C_B/C_{BH^+}$; $C_X/C = (D_{ti} - D_{pi})/(D_{ti} - D_{ui})$; $C_X/C + C_{XH^+}/C = 1$; $(C_X/C)(C_{XH^+}/C) = C_X/C_{XH^+}$.

suggests that the α - and β -carboranyl groups are strongly electron attracting.¹⁰ In view of the highly delocalized nature of both carborane species, it was desirable to examine their electronic effects more closely and to test appropriate systems for possible carboranyl-aryl π overlap. Accordingly, we have examined the isomer distribution of the [α -carboranyl]nitrobenzenes produced in the mixed acid nitration of [α -carboranyl]benzene,¹¹ determined the effective Hammett σ constants¹² for the α -carboranyl group, and determined the inductive σ constant, σ_I , and the reactivity resonance effect parameter,¹³ σ_R^0 , for both the α -carboranyl and the β -carboranyl groups. The pK_a values of the *m*- and *p*-[α -carboranyl]benzoic acids and anilinium ions were employed in the evaluation of the Hammett σ constants, and the ¹⁹F chemical shifts relative to fluorobenzene of the *m*- and *p*-[α - and β -carboranyl]fluorobenzenes were employed in the evaluation of σ_I and σ_R^0 .

Results and Discussion

The mixed acid nitration of [α -carboranyl]benzene was carried out at 25° for 10 hr. using a two-phase (CH₂Cl₂-mixed acid) reaction medium. Analysis of the reaction products using gas-liquid chromatography revealed 4% *o*-, 26% *m*-, and 70% *p*-[α -carboranyl]nitrobenzenes. No dinitro derivatives were detected. The *m*- and *p*-[α -carboranyl]nitrobenzenes were characterized by elemental analysis and ¹H n.m.r. spectra. The *ortho* isomer was not separated in sufficient quantities to allow its characterization. The successful nitration of the aryl portion of [α -carboranyl]benzene without disruption of the boron hydride system provides an excellent demonstration of the chemical stability of the α -carborane system.

The *m*- and *p*-[α -carboranyl]anilines, required for the determination of the corresponding anilinium ion acidities, were prepared by catalytic reduction of the corresponding nitro compounds using the method of

Schroeder, *Inorg. Chem.* **2**, 1107 (1963); (d) D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963); (e) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963); (f) S. Papetti and T. L. Heying, *ibid.*, **3**, 1448 (1964).

(10) (a) S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *ibid.*, **3**, 1444 (1964); (b) L. I. Zakharin, V. I. Stanko, V. A. Brattsev, and U. A. Chapovskii, *Dokl. Akad. Nauk SSSR*, **157**, 1149 (1964).

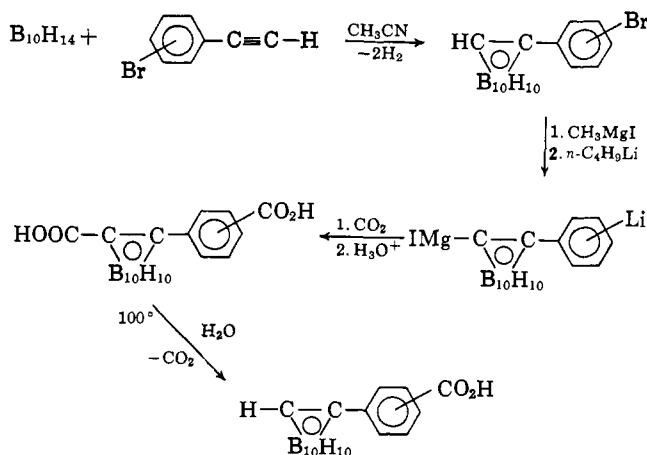
(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter XI.

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(13) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

Brown and Brown.¹⁴ Table I reports the apparent pK_a values of a series of *meta*- and *para*-substituted anilinium ions including the *m*- and *p*-[α -carboranyl]anilinium ions. These data were obtained at 25.0° in 40% methanol-60% water (by volume) solutions of sulfuric acid using the procedure of Hammett as described by Roberts and co-workers.¹⁵ A least-squares treatment of the data produced a ρ value of 2.91. The σ constants obtained for the *m*- and *p*-[α -carboranyl] substituents were $+0.478 \pm 0.025$ and $+0.519 \pm 0.025$, respectively.

The synthesis of the *m*- and *p*-[α -carboranyl]benzoic acids was accomplished as shown in Chart I.

Chart I


The *m*- and *p*-[α -carboranyl]bromobenzenes were prepared from the corresponding acetylenes using B₁₀H₁₂(CH₃CN)₂ as the other reactant. Initial attempts to prepare *m*- and *p*-[α -carboranyl]phenyllithium using 1 or 2 molar equiv. of *n*-butyllithium resulted in the formation of [α -carboranyl]benzene, a result which suggested that the transmetalation reactions proceeded more rapidly than proton abstraction from the C-H bonds. This problem was circumvented by prior removal of the C-H protons with methylmagnesium iodide followed by transmetalation with *n*-butyllithium at low temperatures. Carbonation of the resulting dianions followed by the selective removal of the carboxyl group directly attached to the α -carborane unit resulted in the desired products. Table II reports the apparent pK_a values obtained by the method of Roberts¹⁶ for a series of *meta*- and *para*-substituted

(14) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1495 (1962).

(15) J. D. Roberts, R. Armstrong, and E. A. McElhill, *ibid.*, **71**, 2923 (1949).

(16) J. D. Roberts, R. L. Webb, and E. A. McElhill, *ibid.*, **72**, 408 (1950).

benzoic acids, including the *m*- and *p*-[α -carboranyl]-benzoic acids, at 25.0° in 25% water–75% ethanol (by volume). Least-squares treatment of the data produced a ρ value¹⁷ of 1.52 from which σ constants of the *m*- and *p*-[α -carboranyl] substituents were shown to be $+0.473 \pm 0.025$ and $+0.460 \pm 0.025$, respectively.

Table II. Ionization Constants for Substituted Benzoic Acids

| Substituent | Apparent ^{a,b} pK _a |
|-----------------------------------|--|
| H | 6.58 |
| <i>p</i> -Cl | 6.13 |
| <i>m</i> -Br | 6.05 |
| <i>p</i> -NO ₂ | 5.36 |
| <i>m</i> -[α -Carboranyl] | 5.84 |
| <i>p</i> -[α -Carboranyl] | 5.86 |

^a Measured at 25.0° in 75% ethanol–25% H₂O. ^b Calculated assuming unit activities and reading of pH meter scale equal to logarithm of reciprocal of hydrogen ion concentration.

The *m*- and *p*-[α -carboranyl]fluorobenzenes were prepared from the corresponding acetylenes by reaction with B₁₀H₁₂(CH₃CN)₂. The *m*- and *p*-[β -carboranyl]-fluorobenzenes were prepared from the corresponding α -carboranyl species by heating in an evacuated bomb at 415° for 36 hr. Table III reports the observed ¹⁹F chemical shifts relative to fluorobenzene for the *m*- and *p*-[α - and β -carboranyl]fluorobenzenes. These data were obtained at 25° in cyclohexane using fluorobenzene as an internal standard. A concentration study showed no concentration dependence of chemical shifts. Treatment of these data by the method of Taft¹³ gave σ_I values of $+0.375 \pm 0.010$ and $+0.194 \pm 0.010$, and σ_{R^0} values of $+0.003 \pm 0.005$ and -0.039 ± 0.005 for the α - and β -carboranyl groups, respectively.

Table III. ¹⁹F Chemical Shifts for Substituted Fluorobenzenes

| Substituent | Internal std. | Chemical shift ^a |
|-----------------------------------|---|-----------------------------|
| <i>m</i> -[α -Carboranyl] | Fluorobenzene | -2.06 ± 0.06 |
| <i>p</i> -[α -Carboranyl] | Fluorobenzene | -2.14 ± 0.06 |
| <i>m</i> -[β -Carboranyl] | Fluorobenzene | -0.78 ± 0.08 |
| <i>p</i> -[β -Carboranyl] | <i>m</i> -[α -Carboranyl]- fluorobenzene | $+0.32 \pm 0.06$ |

^a Relative to C₆H₅F in p.p.m.; measured at 25° in cyclohexane.

The magnitude of σ_{R^0} measured for the β -carboranyl group (-0.039) is approximately of the same magnitude, but of opposite sign, as the $\Delta\sigma$ *para* between the acid and anilinium equilibria measured for the α -carboranyl group. The $\Delta\sigma$ *para* corresponds to a deviation of 0.09 pK_a unit for the acid equilibria and is probably not significant when compared to the inherent experimental error present in pK_a determinations. However, the σ_{R^0} value of the β -carboranyl group corresponds to a chemical shift deviation of 1.10 p.p.m. which is significant when compared to the inherent experimental error (0.1 p.p.m.).

(17) The ρ value previously reported [W. L. Bright and H. T. Briscoe, *J. Phys. Chem.*, **37**, 787 (1933)] for 70% ethanol–30% water (by volume) was 1.738. The ρ value obtained for 50% ethanol–50% water (by volume) by these workers was 0.178 unit greater than normally observed for this solvent [see H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953)].

The magnitude of σ_{meta} and σ_I for the α -carboranyl substituent shows that this group is very strongly electron withdrawing by an inductive mechanism and its $-I$ effect is of the same order of magnitude as that of the halogens. The magnitude of the σ_I constant for the β -carboranyl substituent shows that this group is far less effective as a $-I$ substituent than the α -carboranyl group. The source of the electron-withdrawing power of both carboranyl groups is most likely the localized electron deficiency in the region of the carbon atoms in the icosahedral surface. Separation of the carbon atoms in the β -carboranyl group would be expected to effectively lower this localized electron deficiency, as is observed. This relief of localized electron deficiency may provide the driving force for the thermal rearrangement of the α -carborane system to the β -carborane system. It is interesting to note that the results of molecular orbital calculations¹⁸ place twice as much positive charge on each carbon atom in α -carborane than upon the carbon atoms of β -carborane.

The approximate equality of the Hammett σ constants obtained for both the benzoic acid and anilinium ion equilibria and the value of σ_{R^0} obtained from the ¹⁹F data for the α -carboranyl unit conclusively show that no large ground-state extension of electron delocalization by interaction of the aryl group with the highly delocalized α -carboranyl group exists. The value of σ_{R^0} obtained from the ¹⁹F data for the β -carboranyl unit suggests a weak ground-state extension of electron delocalization through electron donation from the β -carboranyl group to the aryl group. The source of the inhibition of an analogous ground-state electron delocalization effect in the α -carboranyl derivatives could conceivably be the result of the strongly localized electron deficiency discussed above.

The isomer ratios observed in the mixed acid nitration of [α -carboranyl]benzene suggest the possible extension of electron delocalization in the electron-deficient transition state since the transition state for aromatic nitration is normally assumed to resemble the σ complex intermediate to a greater extent than the initial reactant.¹¹ It is not inconceivable that the electron demand of the transition state could overcome the coulombic inhibition of electron delocalization mentioned above.

A theoretical treatment of the B₁₂H₁₂²⁻ ion by Longuet-Higgins¹⁹ suggested that the highest-filled molecular orbitals of the icosahedron were composed solely of 2p atomic orbitals tangential to the icosahedral surface. The existence of similar molecular orbitals in the isoelectronic α - and β -carboranyl groups would provide a source for the observed π -donating power of the α - and β -carboranyl groups. No evidence for the extension of electron delocalization through electron donation by the aryl groups to either carboranyl group was detected in this investigation. Such back-bonding by π substituents on the isoelectronic B₁₂H₁₂²⁻ ion has been previously postulated^{18,20} and should perhaps be reconsidered in light of this investigation.

(18) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(19) H. E. Longuet-Higgins and M. D. Roberts, *Proc. Roy. Soc. (London)*, **A230**, 110 (1955).

(20) A. Kaczmarczyk and G. B. Kolski, *Inorg. Chem.*, **4**, 665 (1965).

Experimental Section

The substituted anilines and benzoic acids employed in the ionization constant methods for comparison and controls were purified commercial products. The phenylacetylene and substituted acetophenones used in the synthesis of carboranyl derivatives were commercial products. The procedure of Allen and Cook²¹ was employed in the synthesis of all substituted phenylacetylenes. All new carborane derivatives were characterized by their infrared and ¹H n.m.r. spectra and elemental analysis.

p-[α -Carboranyl]bromobenzene. To a refluxing solution of 13.4 g. (0.110 mole) of sublimed decaborane and 7.0 g. (0.13 mole) of acetonitrile in 200 ml. of reagent grade benzene was added slowly, over several hours, a solution of 18.1 g. (0.100 mole) of *p*-bromophenylacetylene in 75 ml. of reagent grade benzene. The resultant solution was heated under reflux for 30 hr. After removal of solvent under reduced pressure, the residual oil was extracted three times with 300-ml. portions of a 50% *n*-pentane–50% diethyl ether solution. The combined extracts were washed three times with 500-ml. portions of a \sim 1.0 *M* sodium hydroxide solution, twice washed with 500-ml. portions of water, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, repeated recrystallizations of the resultant solid from cyclohexane afforded 21.0 g. (70.3% of theory) of a white solid (m.p. 135–136°).

Anal. Calcd. for B₁₀C₈H₁₅Br: B, 36.13; C, 32.11; H, 5.05; Br, 26.71. Found: B, 36.08; C, 32.11; H, 5.14; Br, 26.68.

m-[α -Carboranyl]bromobenzene. Eighteen grams (0.100 mole) of *m*-bromophenylacetylene was converted to 22.5 g. (75.3% of theory) of *m*-[α -carboranyl]bromobenzene (m.p. 107–108°) by the procedure described for its *para* isomer.

Anal. Calcd. for B₁₀C₈H₁₅Br: B, 36.13; C, 32.11; H, 5.05; Br, 26.71. Found: B, 36.10; C, 32.13; H, 5.16; Br, 26.61.

[α -Carboranyl]benzene. Ten grams (0.100 mole) of phenylacetylene was converted to 16.7 g. (76.1% of theory) of [α -carboranyl]benzene (m.p. 69–70°) by the procedure described above for *p*-[α -carboranyl]bromobenzene with the exception that methanol instead of cyclohexane was used for recrystallization.

p-[α -Carboranyl]fluorobenzene. Twelve grams (0.100 mole) of *p*-fluorophenylacetylene was converted to *p*-[α -carboranyl]fluorobenzene by the procedure described above for *p*-[α -carboranyl]bromobenzene. The crude product was chromatographed on silica gel (8% water) using cyclohexane as the eluent and recrystallized from 85% ethanol to afford 15.9 g. (66.8% of theory) of a white solid (m.p. 138–139°).

Anal. Calcd. for B₁₀C₈H₁₅F: B, 45.38; C, 40.34; H, 6.30; F, 7.98. Found: B, 45.43; C, 40.48; H, 6.52; F, 7.57.

m-[α -Carboranyl]fluorobenzene. Twelve grams (0.100 mole) of *m*-fluorophenylacetylene was converted to *m*-[α -carboranyl]fluorobenzene by the procedure described above for *p*-[α -carboranyl]fluorobenzene. The crude product was chromatographed on silica gel (8%

water) using hexane as the eluent and crystallized from *n*-pentane at –78° to afford 25.5 g. (75.7% of theory) of a white solid (m.p. 68–68.5°).

Anal. Calcd. for B₁₀C₈H₁₅F: B, 45.38; C, 40.34; H, 6.30; F, 7.98. Found: B, 45.56; C, 40.24; H, 6.36; F, 7.84.

p-[β -Carboranyl]fluorobenzene. Five grams of *p*-[α -carboranyl]fluorobenzene was heated in a stainless steel bomb at 415° for 36 hr. The resultant crude product was chromatographed on silica gel (8% water) using hexane as the eluent and crystallized from *n*-pentane at –78° to afford 2.8 g. (56.0% of theory) of a white solid (m.p. 61–62°).

Anal. Calcd. for B₁₀C₈H₁₅F: B, 45.38; C, 40.34; H, 6.30; F, 7.98. Found: B, 45.31; C, 40.30; H, 6.74; F, 7.65.

m-[β -Carboranyl]fluorobenzene. Five grams of *m*-[α -carboranyl]fluorobenzene was converted to *m*-[β -carboranyl]fluorobenzene by the procedure described above for its *para* isomer to afford 3.3 g. (66.0% of theory) of a white solid (m.p. 45–46°).

Anal. Calcd. for B₁₀C₈H₁₅F: B, 45.38; C, 40.34; H, 6.30; F, 7.98. Found: B, 45.14; C, 40.30; H, 6.54; F, 8.02.

p-[α -Carboranyl]benzoic Acid. To a stirred solution of 20.0 g. (0.067 mole) of *p*-[α -carboranyl]bromobenzene in 300 ml. of dry tetrahydrofuran at 0° was added 45.0 ml. of 1.67 *M* methylmagnesium iodide in diethyl ether. The resultant solution was stirred for 4 hr. and then cooled to Dry Ice–acetone temperature. At this time 45 ml. of 1.61 *M* butyllithium in hexane was added and stirring was continued for an additional hour. After pouring the resultant solution onto an excess of crushed Dry Ice and warming slowly to room temperature, 500 ml. of \sim 1 *M* aqueous hydrochloric acid solution was added. After separation of the organic phase, the aqueous phase was extracted three times with 200-ml. portions of diethyl ether. The ether extracts were combined with the original organic phase and washed twice with 200-ml. portions of water. The oily residue obtained after removal of solvent was refluxed in 200 ml. of 60% aqueous ethanol for 4 hr. with evolution of carbon dioxide. After addition of 200 ml. of water, the aqueous solution was extracted three times with diethyl ether. The combined ether extracts were washed twice with 200-ml. portions of water and dried over anhydrous sodium sulfate; the solvent was removed at reduced pressure. Recrystallization from 75% aqueous ethanol afforded 14.5 g. (81.8% of theory) of a white solid (m.p. 224–225°).

Anal. Calcd. for B₁₀C₉H₁₆O₂: B, 40.91; C, 40.91; H, 6.06. Found: B, 40.59; C, 40.94; H, 6.13.

m-[α -Carboranyl]benzoic Acid. Twenty grams (0.067 mole) of *m*-[α -carboranyl]bromobenzene was converted to *m*-[α -carboranyl]benzoic acid by the procedure described above for its *para* isomer to afford 15.2 g. (86.3% of theory) of a white solid (m.p. 280–281°).

Anal. Calcd. for B₁₀C₉H₁₆O₂: B, 40.91; C, 40.91; H, 6.06. Found: B, 41.03; C, 40.83; H, 6.32.

Nitration of [α -Carboranyl]benzene. To a stirred solution of 100 ml. of 15% concentrated HNO₃–85% concentrated H₂SO₄ (by volume) at room temperature

(21) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1085 (1963).

was added a solution of 5.0 g. (0.0227 mole) of [α -carboranyl]benzene in 100 ml. of methylene chloride. Stirring was continued for 18 hr. Vapor phase chromatography of the methylene chloride phase on a Carbowax column at 215° with a flow rate of 40 ml./min. of argon showed that the final reaction mixture contained 4% *o*-, 26% *m*- and 70% *p*-[α -carboranyl]nitrobenzene. No dinitration products were detected. After separation of the methylene chloride phase from the concentrated acids phase, it was washed twice with water and dried over anhydrous sodium sulfate; the solvent was removed at reduced pressure. Two recrystallizations from carbon tetrachloride afforded 3.1 g. (50.2% of theory) of a white solid (m.p. 167–168°). The proton n.m.r. spectra of this compound showed an A_2B_2 pattern in the aromatic region confirming that it was *p*-[α -carboranyl]nitrobenzene.

Anal. Calcd. for $B_{10}C_8H_{15}NO_2$: B, 40.75; C, 36.22; H, 5.66; N, 5.28. Found: B, 40.84; C, 36.16; H, 5.89; N, 5.30.

After removal of the solvent from the first carbon tetrachloride supernatant from above, the residue was crystallized twice from glacial acetic acid to afford 0.30 g. (5.0% of theory) of a yellow-white product (m.p. 140–141°). The aromatic portion of the proton n.m.r. spectrum was very similar to that observed for the known *meta*-substituted carboranylbenzenes reported above.

Anal. Calcd. for $B_{10}C_8H_{15}NO_2$: B, 40.75; C, 36.22; H, 5.66; N, 5.28. Found: B, 40.72; C, 36.43; H, 5.86; N, 5.03.

The small peak (4%) observed to come first off the v.p.c. column was never isolated and was tentatively identified as *o*-[α -carboranyl]nitrobenzene.

p-[α -Carboranyl]aniline. One gram of *p*-[α -carboranyl]nitrobenzene was reduced to *p*-[α -carboranyl]aniline over a platinum chloride–sodium borohydride catalyst as reported by Brown and Brown¹⁴ to afford 0.80 g. (90.2% of theory) of a white solid (m.p. 104–105°).

Anal. Calcd. for $B_{10}C_8H_{17}N$: B, 46.00; C, 40.81;

H, 7.24; N, 5.95. Found: B, 45.84; C, 40.88; H, 7.42; N, 6.22.

m-[α -Carboranyl]aniline. One gram of *m*-[α -carboranyl]nitrobenzene was converted to *m*-[α -carboranyl]aniline by the same procedure as described above for its *para* isomer to afford 0.81 g. (91.4% of theory) of a white solid (m.p. 81–82°).

Anal. Calcd. for $B_{10}C_8H_{17}N$: B, 46.00; C, 40.81; H, 7.24; N, 5.95. Found: B, 45.74; C, 41.02; H, 7.22; N, 5.81.

Ionization Constants of Benzoic Acids. Apparent ionization constants of the substituted benzoic acids were obtained at 25.0° in 25% water–75% ethyl alcohol (by volume) as described by Roberts and co-workers¹⁶ using a Leeds and Northrop pH meter. The data are presented in Table I.

Ionization Constants of Anilinium Ions. Ionization constants (pK_a) of substituted anilinium ions were measured at room temperature in 40% methyl alcohol–60% water sulfuric acid solutions by the procedure of Hammett, as modified by Roberts and co-workers.¹⁵ A Cary Model 14 recording spectrophotometer was used to measure the spectra. The standard employed was *m*-chloroaniline. The data are given in Table I.

Determination of ^{19}F Chemical Shifts of Fluorobenzenes. The ^{19}F chemical shifts relative to fluorobenzene were obtained in cyclohexane solution at room temperature at concentrations of 0.15, 0.10, and 0.05 mole % using fluorobenzene as an internal standard. A Varian HR-60 n.m.r. spectrophotometer was employed in these measurements. The normal side-band technique was employed to determine the chemical shifts in c.p.s. No concentration dependence was observed. The internal standard employed for *p*-[β -carboranyl]fluorobenzene was *m*-[α -carboranyl]fluorobenzene.

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Dimethylselenium Dihalides and Their Adducts with Boron Trihalides

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To test the possible coordinate bond-forming ability of the unshared electron pair associated with the central atom of a trigonal bipyramidal molecule, 1:1 adducts of dimethylselenium dihalides and boron trihalides have been prepared and the infrared spectra of these adducts examined. These data indicate that the electron pair is not involved in a classical Lewis acid–base sense, but that halide transfer occurs leading to monohalogenodimethylselenium(IV) tetrahaloborate ionic substances.

Introduction

Structural investigation of those chalcogen tetrahalides, and alkyl and aryl derivatives of these tetrahalides, existing in molecular form has revealed in each case a trigonal bipyramidal structure having an unshared electron pair in the trigonal plane.¹ As with

(1) A few references to typical molecules in this category are: (a) $TeCl_4(g)$, D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **62**, 1267 (1940); (b) $SeF_4(l)$, J. A. Rolfe, L. A. Woodward, and D. A. Long,