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# SYNTHESIS OF $\sigma$-(*o*-CARBORAN-9-YL)- AND $\sigma$-(*m*-CARBORAN-9-YL)-$\pi$-CYCLOPENTADIENYLDICARBONYLIRON AND THEIR REARRANGEMENT IN REACTIONS WITH BROMINE TO $\pi$-(*o*-CARBORAN-9-YL)CYCLOPENTADIENYL- AND $\pi$-(*m*-CARBORAN-9-YL)CYCLOPENTADIENYL-DICARBONYLIRON BROMIDES, RESPECTIVELY *

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## Summary

9-*o*- and 9-*m*-carboranylcarboxylic acids were used to synthesize $\sigma$-(*o*-carboran-9-yl)- and $\sigma$-(*m*-carboran-9-yl)-$\pi$-cyclopentadienyldicarbonyliron. The latter complexes, in reactions with bromine, undergo rearrangement with the cleavage of the B–Fe $\sigma$-bond, involving migration of the 9-*o*- and 9-*m*-carboranyl groups into the cyclopentadienyl ring, to give $\pi$-(*o*-carboran-9-yl)cyclopentadienyl- and $\pi$-(*m*-carboran-9-yl)cyclopentadienyl-dicarbonyliron bromides, respectively. A simple method to obtain these acids by the oxidation of 9-alkyl-*o*- and 9-alkyl-*m*-carboranes with $CrO_3$ in $CH_3COOH$ has been found.

## Results and discussion

It has been shown earlier that $\sigma$-(*o*-carboran-3-yl)-$\pi$-cyclopentadienyldicarbonyliron (I) when treated with chlorine or bromine undergoes an interesting rearrangement involving migration of the 3-*o*-carboranyl group into the Cp ring to give $\pi$-(*o*-carboran-3-yl)cyclopentadienyldicarbonyliron halide, whereas in the case of $\sigma$-(1,2-dimethyl-*o*-carboran-3-yl)-$\pi$-cyclopentadienyldicarbonyliron the rearrangement involves its migration into the CO group [1]. In contrast to this, the action of

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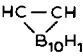
* *o*-Carborane = 1,2-dicarbaclosododecaborane(12),


$\underset{B_{10}H_{10}}{HC{-}CH}$ .

*m*-Carborane = 1,7-dicarbaclosododecaborane(12), *m*-$HCB_{10}H_{10}CH$.

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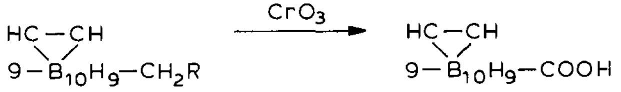
bromine on σ-(*o*-carboran-1-yl)- and σ-(*m*-carboran-1-yl)-π-cyclopentadienyldicarbonyliron results only in the bromination of the *o*- and *m*-carborane cages, the $CpFe(CO)_2$ group remaining intact [2,3].

It is known that in *o*- and *m*-carboranes the electron density on the polyhedron atoms is distributed non-uniformly [4], the corresponding carboranyl groups exhibiting different electronic effects [5]. Thus, for example, the 1-*o*-, 1-*m*- and 3-*o*-carboranyl groups possess an electron-acceptor inductive effect ($\sigma_I = +0.38$, $+0.21$ and $+0.11$, respectively) [6] whereas the 9-*o*- and 9-*m*-carboranyl groups exhibit an electron-donor inductive effect ($\sigma_I = -0.16$ and $-0.12$, respectively) [7]. Therefore it is difficult to predict the result of the reaction of halides with σ-(*o*-carboranyl)- and σ-(*m*-carboranyl)-π-cyclopentadienyldicarbonyliron containing a $CpFe(CO)_2$ group in differently positioned carborane cages. We have synthesized σ-(*o*-carboran-9-yl)- and σ-(*m*-carboran-9-yl)-π-cyclopentadienyldicarbonyliron, II and III, respectively, and have studied the action of bromine on these compounds. Compounds II and III have been synthesized from 9-*o*- and 9-*m*-carboranylcarboxylic acids, IV and V, respectively, following the procedure for the production of I from 3-*o*-carboranylcarboxylic acid [1].

Earlier, compounds IV and V were synthesized by a very complicated scheme which, apparently, does not allow their production in a form free from isomeric acid impurities [8].

We have proposed a simple method to obtain acids IV and V in a pure form. It has been found that in 9-alkyl-*o*- and 9-alkyl-*m*-carboranes that are readily formed from 9-iodo-*o*- and 9-iodo-*m*-carboranes and alkylmagnesium halides when catalyzed with palladium complexes [9] one can observe a smooth oxidation, as in the case of alkylbenzenes, of the alkyl group by $CrO_3$ in $CH_3COOH$ in the presence of $H_2SO_4$ to give acids IV and V, respectively:



(IV)

( R = H, $CH_3$ , $CH_2CH_3$ )

$$m\text{-HCB}_{10}H_9(9\text{—CH}_2R)CH \xrightarrow{CrO_3} m\text{-HCB}_{10}H_9(9\text{—COOH})CH$$

(V)

( R = H, $CH_2CH_3$ )

2-Methyl-*p*-carborane *, like 9-methyl-*o*- and 9-methyl-*m*-carboranes, is oxidized to give 2-*p*-carboranylcarboxylic acid:

$$p\text{-HCB}_{10}H_9(2\text{-CH}_3)CH \xrightarrow{CrO_3} p\text{-HCB}_{10}H_9(2\text{-COOH})CH$$

Note that 9-isopropyl-*o*- and 9-isopropyl-*m*-carboranes are also oxidized to give acids IV and V:

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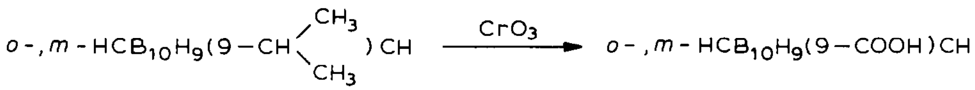
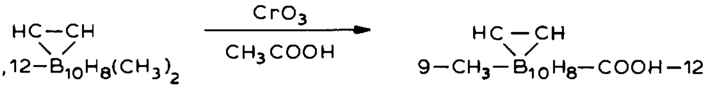
* *p*-Carborane = 1,12-dicarbaclosododecaborane(12), *p*-$HCB_{10}H_{10}CH$.



$$o\text{-},m\text{-}HCB_{10}H_9(9-CH(CH_3)_2)CH \xrightarrow{CrO_3} o\text{-},m\text{-}HCB_{10}H_9(9-COOH)CH$$

The oxidation of 9-alkyl-*o*- and 9-alkyl-*m*-carboranes is unusual in that in the system of B–C–C or B–C–H bonds the only oxidizable bonds are the C–C or the C–H bonds whereas the B–C bond is not oxidized under the reaction conditions, and the B–H bonds are more resistant to oxidation than the C–H bonds of the alkyl groups.

In the case of 9,12-dimethyl-*o*- and 9,10-dimethyl-*m*-carboranes oxidation of no more than one $CH_3$ group to the COOH group can be observed whereas the second $CH_3$ group remains unaltered under the experimental conditions:

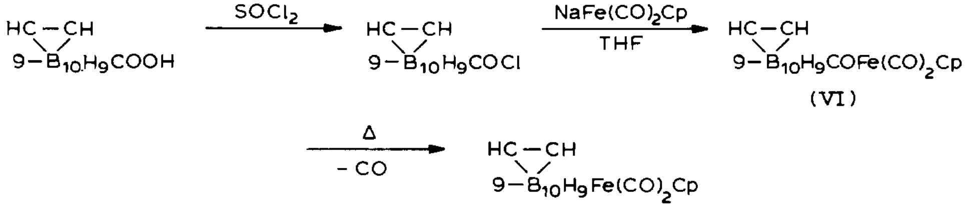


$$m\text{-}HCB_{10}H_8(9,10-CH_3)_2CH \xrightarrow[CH_3COOH,\ H_2SO_4]{CrO_3} m\text{-}HCB_{10}H_8(9-CH_3,\ 10-COOH)CH$$

The resistance of the second $CH_3$ group to oxidation appears to be due to the electronic and steric effects of the resulting COOH group. In the oxidation of 9-alkyl-*o*- and 9-alkyl-*m*-carboranes it would be optimal to have a stoichiometric amount of $CrO_3$ with a small (ca. 20%) excess. A larger excess of $CrO_3$ results in a lower yield of the carboranylcarboxylic acid due to oxidation of the carborane cage.

The earlier unknown 9-propyl-*o*-, 9-methyl-*m*-, 9-propyl-*m*-, 2-methyl-*p*-, 9,12-dimethyl-*o*- and 9,10-dimethyl-*m*-carboranes, used in the synthesis of *B*-carboranecarboxylic acids, have been obtained as described elsewhere [9].

Compounds II and III have been obtained as follows:



(VI)

(II)

$$m\text{-}HCB_{10}H_9(9-COOH)CH \xrightarrow{SOCl_2} m\text{-}HCB_{10}H_9(9-COCl)CH$$

$$\xrightarrow[THF]{NaFe(CO)_2Cp} \underset{(VII)}{m\text{-}HCB_{10}H_9[9-CO-Fe(CO)_2Cp]CH} \xrightarrow[-CO]{\Delta}$$

$$\underset{(III)}{m\text{-}HCB_{10}H_9[9-Fe(CO)_2Cp]CH}$$

When treated with $SOCl_2$, IV and V easily give acid chlorides which in reactions with $NaFe(CO)_2Cp$ in THF solution usually give σ-(*o*-carborane-9-carbonyl)- and

$\sigma$-($m$-carborane-9-carbonyl)-$\pi$-cyclopentadienyldicarbonyliron, VI and VII, respectively. The yields of these compounds exceed 50%. They are stable in air and are orange-yellow species. When heated in decane at 140°C under argon, VI and VII readily undergo decarbonylation to give II and III, respectively, in 95% yield. Complexes II and III are stable in air and yellow in colour. Note that $m$-carborane derivatives containing a B–Fe $\sigma$-bond have not previously been identified. The structures of II and III are confirmed by their IR and NMR spectra.

In the region of the stretching CO mode for compounds of the type $\pi$-$C_5H_5Fe(CO)_2R$-$\sigma$, the existence of two bands corresponding to the symmetric (the high-frequency band) and asymmetric (the low-frequency band) vibrations of two CO groups can be expected. The positions of these two bands depend on the properties of the substituent R.

TABLE 1

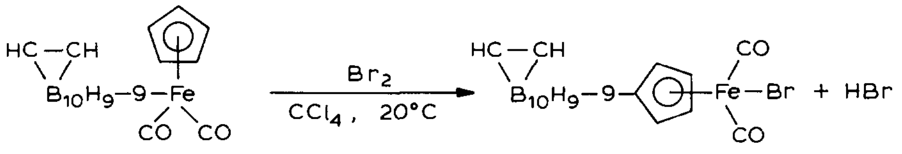
$^1$H NMR AND $^{11}$B NMR SPECTRAL DATA FOR COMPOUNDS II, III, VIII AND IX IN $C_6H_6$

| Compound | $^1$H NMR | | $^{11}$B NMR | | |
|---|---|---|---|---|---|
| | $\delta(CH_{carb})$[a] (ppm) | $\delta$(Cp) (ppm) | $\delta(^{11}B)$[b] (ppm) | $J$(B–H) (Hz) | Assignment |
| II | 2.1(1) | 4.14(5) | 9.4, s(1) | 0 | B(9) |
| | 2.3(1) | | −0.1(1) | 148 | B(12) |
| | | | −6.8(2) | 146 | B(8),B(10) |
| | | | −12.6(4) | 155 | B(4),B(5), B(7),B(11) |
| | | | −14.3(2) | ca. 125 | B(3),B(6) |
| III | 2.3(2) | 4.20(5) | −0.4, s(1) | 0 | B(9) |
| | | | −5.3(2) | 170 | B(5),B(12) |
| | | | −8.2(1) | 170 | B(10) |
| | | | ca. −12.0 (4) | ca. 161 | B(4),B(8) |
| | | | ca. −12.7 | ca. 161 | B(6),B(11) |
| | | | −16.7(1) | 179 | B(3) |
| | | | −18.6(1) | 179 | B(2) |
| VIII | 2.5(1) | 4.44(2) | 3.1, s(1) | 0 | B(9) |
| | 2.7(1) | 4.74(2) | −2.4(1) | 155 | B(12) |
| | | | −9.0(2) | 152 | B(8),B(10) |
| | | | ca. −14.0 (6) | ca. 158 | B(4),B(5),B(7) |
| | | | ca. −15.0 | ca. 160 | B(11),B(3),B(6), |
| IX | 2.3(2) | 4.49(2) | −3.9, s(1) | 0 | B(9) |
| | | 4.82(2) | −6.8(2) | 170 | B(5),B(12) |
| | | | −10.0(1) | 155 | B(10) |
| | | | ca. −13.3 (4) | ca. 167 | B(4),B(8),B(6) |
| | | | ca. −14.0 | ca. 167 | B(11) |
| | | | −17.7(1) | 179 | B(3) |
| | | | −19.6(6) | 184 | B(2) |

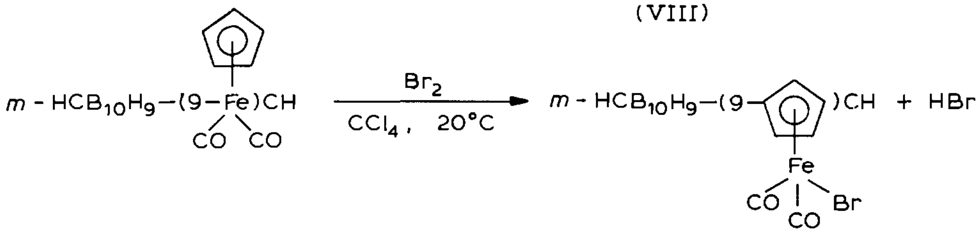
[a] $^1$H NMR data were measured relative to the internal standard tetramethylsilane. [b] $^{11}$B NMR data were measured relative to the external standard $BF_3OEt_2$. s, Singlet. The integrated signal internsity is given in parentheses.

The vibrational frequencies decrease from 1910, 1980 cm$^{-1}$ for II containing a more electron-donating 9-*o*-carboranyl group to 1930, 1990 cm$^{-1}$ for III whose 9-*m*-carboranyl group is less electron-donating. The $^1$H NMR spectra of II and III show the presence of unsubstituted Cp rings which match the singlet signals (Table 1). The spectrum of II contains two signals of non-equivalent carborane CH groups, which are due to the asymmetry of the substituent with respect to these groups. For III the carborane CH groups are equivalent and match the signal in the $^1$H NMR spectrum. The $^{11}$B NMR spectra of these compounds contain singlet signals of the B(9) atoms bound to the substituent Fe atoms. As compared with the unsubstituted *o*- and *m*-carboranes, these signals are shifted downfield by 12.5 ppm for II and by 10.6 ppm for III [10].

The action of 1 mol of bromine with 1 mol of II or III in $CCl_4$ solution at 20°C promotes smooth rearrangement of the complexes, including cleavage of the B–Fe $\sigma$-bond. This consists of migration of the 9-*o*- or 9-*m*-carboranyl group into the Cp ring and substitution of the hydrogen atom therein isolated within HBr to give $\pi$-(*o*-carboran-9-yl)cyclopentadienyl- and $\pi$-(*m*-carboran-9-yl)cyclopentadienyldicarbonyliron bromides, VIII and IX, respectively:



(VIII)



(IX)

The structures of VIII and IX are confirmed by their IR and NMR spectra. The IR spectra indicate retention of the carborane cage in the molecule (the intensive band of the B–H vibrations at 2600 cm$^{-1}$). The presence of two CO bands in the IR spectrum indicates retention of an $Fe(CO)_2$ group. The existence of a bromine atom directly at the iron atom increases the CO vibration frequencies substantially (2010 and 2060 cm$^{-1}$ for VIII, and 2015 and 2055 cm$^{-1}$ for IX).

The existence of an Fe–Br bond is confirmed by the IR spectra of these compounds at 400–700 cm$^{-1}$. Due to the fact that no absorption is observed for the carborane cage in these frequency regions, the spectra of VIII and IX are expected to be similar to that of $\pi$-$C_5H_5Fe(CO)_2Br$, which proves to be the case ($\nu$, cm$^{-1}$): VIII 447 m, 485 m, 548 vs, 570 vs, 608 vs; IX 445 m, 490 m, 548 vs, 575 vs, 608 vs; $\pi$-$C_5H_5Fe(CO)_2Br$ 440 m, 485 m, 540 vs, 570 vs, 605 vs (m designates "medium" and vs " very strong). Absorption frequencies at ca. 1250 cm$^{-1}$ for VIII and ca. 1260 cm$^{-1}$ for IX suggest the presence of a substituent in the Cp ring. These bands seem to be associated with the C–B bond vibrations. The existence of a substituted Cp ring in these compounds is confirmed by their $^1$H NMR spectra (Table 1).

It follows from these spectra that the carboranyl group is bound to the Cp ring, and the $^{11}B$ NMR spectra demonstrate the presence of a substituent at B(9) in the carborane polyhedra. The substituted Cp rings VIII and IX appear in the $^{1}H$ NMR spectra as two broad signals whose integrated intensity is 2H. The spin interaction constants of the Cp ring protons seem to be unresolved because of broadening as a result of their interaction with the quadrupole nucleus of $^{11}B$. As in the case of compounds II and III, one can observe two signals from the non-equivalent CH groups of carborane for VIII and one signal with intensity 2H for IX. In the $^{11}B$ NMR spectra, the singlet signals of B(9) bound to the substituent are shifted downfield by 6.2 ppm for VIII and by 7.1 ppm for IX, as compared with the unsubstituted structures. The doublet signals of the remaining boron atoms are shifted both downfield and upfield by ca. 1 ppm. On the other hand, the B(2) signal in the spectrum of IX is shifted upfield by 2.3 ppm (antipodal screening effect).

It can be concluded from the results obtained by us and from those reported elsewhere [1] that in the case of $\sigma$-(*o*-carboranyl)- and $\sigma$-(*m*-carboranyl)-$\pi$-cyclopentadienyldicarbonyliron containing a B–Fe $\sigma$-bond in various positions of the *o*- and *m*-carborane cages the action of bromine causes rearrangement of these compounds consisting of migration of the carborane cage into the Cp ring independent of the $Fe(CO)_2Cp$ position in the former.

## Experimental

IR spectra were recorded with a UR-20 spectrometer. The samples were pressed into pellets with KBr. $^{11}B$ NMR spectra were taken with a Bruker WP-200SY instrument (operating frequency 64.2 kHz). Absolute ether and THF were obtained by distillation in a nitrogen atmosphere over $LiAlH_4$. TLC was performed on Silufol plates.

### *General method of oxidation of 9-alkyl-o-, 9-alkyl-m- and 9-alkyl-2-p-carboranes*

To a solution of 0.02 mol of 9-alkyl-*o*-, 9-alkyl-*m*- or 9-alkyl-2-*p*-carborane in 50 ml of $CH_3COOH$ and 5 ml of conc. $H_2SO_4$ was added in small portions with stirring at 10–15°C $CrO_3$ (0.02 mol). The mixture was stored at this temperature for 30 min and then heated at 50–70°C for 2–4 h. The reaction was monitored by TLC on Silufol plates; eluant, benzene/ethyl acetate (8/2). The reaction mixture was poured into 150 ml of water and subjected to extraction with ether. The ether solution was washed with water (2 × 50 ml) and then extracted with 2% NaOH solution. The alkaline solution was acidified with HCl. The precipitated acid was filtered off, washed with water, dried and recrystallized from methanol. Yield: 57–88% (Table 2).

### *9-Methyl-10-carboxy-m-carborane*

(a) A mixture of 1.38 g (8 mmol) of 9,10-dimethyl-*m*-carborane, 3.2 g (32 mmol) of $CrO_3$, 18 ml of $CH_3COOH$ and 1.8 ml of conc. $H_2SO_4$ was heated with stirring at 50–60°C for 4 h. Then the reaction mixture was poured into 200 ml of water and extracted with ether. The ether extract was dried over $Na_2SO_4$, and afterwards the ether was distilled off. The residue was subjected to fractional sublimation. At 25–30°C (1 mmHg) the sublimation gave the unreacted 9,10-dimethyl-*m*-carborane and at 150–200°C (1 mmHg) 9-methyl-10-*m*-carboranecarboxylic acid. Yield: 0.64 g

(40%), m.p. 195–196°C (ethanol). Found: C, 24.67; H, 7.03; B, 52.37. Calculated for $C_4H_{14}B_{10}O_2$: C, 23.75; H, 6.98; B, 53.45%.

(b) A mixture of 1.6 g (9.3 mmol) of 9,10-dimethyl-*m*-carborane, 8.2 g (27.9 mmol) of $K_2Cr_2O_7$, 48 ml of $CH_3COOH$ and 9.4 ml of concentrated $H_2SO_4$ was heated at 50–60°C for 4 h. The reaction mixture was treated as described above in (a). Yield: 0.8 g (42.5%).

### *9-Methyl-12-carboxy-o-carborane*

(a) To a solution of 1.38 g (8 mmol) of 9,12-dimethyl-*o*-carborane in a mixture of 18 ml of $CH_3COOH$ and 1.8 ml of concentrated $H_2SO_4$ was added in small portions with stirring at 15–20°C 3.2 g (32 mmol) of $CrO_3$. The mixture was stirred for another hour at the same temperature and then heated at 60–70°C for 4 h. Afterwards, it was poured into 300 ml of water and extracted with ether. The ether extract was dried over $Na_2SO_4$ and the ether distilled off. The unreacted 9,12-dimethyl-*o*-carborane was sublimed at 23°C (1 mmHg) and the residue recrystallized from ethanol. Yield: 0.73 g (45%), m.p. 229–231°C. Found: C, 23.73; H, 7.02; B, 53.31. $C_4H_{14}B_{10}O_2$ calcd.: C, 23.75; H, 6.98; B, 53.45%.

(b) To a solution of 2.8 g (0.016 mmol) of 9,12-dimethyl-*o*-carborane in a mixture of 84 ml of $CH_3COOH$ and 16.4 ml of concentrated $H_2SO_4$ was added in small portions with stirring at 23°C 14.1 g (48 mmol) of $K_2Cr_2O_7$. The mixture was stored at 23°C for 16 h and then heated at 50–60°C for 4 h. The reaction was followed by TLC. The acid was isolated as described above in (a). Yield: 1.45 g (45%).

### *9-m-Carboranecarboxylic acid chloride*

To 1.17 g (6.2 mmol) of 9-*m*-carboranecarboxylic acid was added 7 ml of thionyl chloride. The mixture was refluxed for 2 h and excess $SOCl_2$ was distilled off in vacuo. To remove traces of thionyl chloride, the residue was stored in vacuo (1 mmHg) at 40–50°C for 1 h. Yield: 1.18 g (92%).

### *9-o-Carboranecarboxylic acid chloride*

A similar procedure to that described in the previous subsection was used to obtain the title compound from 1 g (5.3 mmol) of 9-*o*-carboranecarboxylic acid and 7 ml of $SOCl_2$. Yield: 0.9 g (90%).

### *σ-(o-Carborane-9-carbonyl)- and σ-(m-carborane-9-carbonyl)-π-cyclopentadienyldicarbonyliron, VI and VII, respectively*

To a solution of $CpFe(CO)_2Na$ obtained under nitrogen from 0.85 g (2.4 mmol) of $[CpFe(CO)_2]_2$ and sodium amalgam (0.4 g of sodium and 7 ml of mercury) in 30 ml of absolute THF was added dropwise with stirring at −70°C a solution of 1.0 g (4.8 mmol) of 9-*o*- or 9-*m*-carboranecarboxylic acid chloride in 5 ml of absolute THF. The mixture was gradually heated to 23°C and stored for 16 h. The reaction product was isolated in air. THF was distilled off in vacuo and the residue was chromatographed on a 20 × 1.5 cm column of silica gel L 40–100 μm; eluant benzene. The benzene was distilled off in vacuo. Constants, yields, elemental analyses and IR spectra are listed in Table 3.

### *σ-9-o- and σ-9-m-Carboranyl-π-cyclopentadienyldicarbonyliron, II and III, respectively*

1 g (2.8 mmol) of VI or VII was heated in a nitrogen atmosphere in 15 ml of

(Continued on p. 90)

TABLE 2

DATA ON THE OXIDATION OF *B*-ALKYLCARBORANES TO *B*-CARBORANECARBOXYLIC ACIDS TOGETHER WITH YIELDS, CONSTANTS AND ELEMENTAL ANALYSES OF THE RESULTING ACIDS

| Compound | Amount of $C_2B_{10}H_{11}R$ (mmol) (R) | Time of reaction (h)/ Temperature (°C)) | Amount of $CrO_3$ (mmol) | Acid obtained | Yield (%) | M.p. (°C) | Analyses (Found (calcd.) (%)) | | | General formula |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | B | |
| 9-R-1,2-$C_2B_{10}H_{11}$ | 38($CH_3$) | 3(60–70) | 91 | 9-COOH-1,2-$C_2B_{10}H_{11}$ | 57 | 239–240 [a] (methanol, dec.) | 19.32 (19.14) | 6.35 (6.43) | 57.78 (57.43) | $C_3H_{12}B_{10}O_2$ |
| | 3.2($C_2H_5$) | 2(60–65) | 14 | | 87 | | | | | |
| | 2.7(n-$C_3H_7$) | 2(70) | 16 | | 68 | | | | | |
| | 20(i-$C_3H_7$) | 2(70) | 120 | | 87 | | | | | |
| 9-R-1,7-$C_2B_{10}H_{11}$ | 46($CH_3$) | 4(65–70) | 110 | 9-COOH-1,7-$C_2B_{10}H_{11}$ | 66 | 220–222 [b] (methanol) | 19.52 (19.14) | 6.62 (6.43) | 57.08 (57.43) | $C_3H_{12}B_{10}O_2$ |
| | 5.4(n-$C_3H_7$) | 1(75) | 40 | | 88 | | | | | |
| | 20(i-$C_3H_7$) | 2(75) | 120 | | 85 | | | | | |
| 2-R-1,12-$C_2B_{10}H_{11}$ | 1.4($CH_3$) | 4(65–70) | 3.1 | 2-COOH-1,12-$C_2B_{10}H_{11}$ | 61 | 130–131 [c] (methanol) | – | – | – | $C_3H_{12}B_{10}O_2$ |

[a] M.p. 210–212°C [8]. [b] M.p. 214–216°C [8]. [c] M.p. 126–128°C [11].

TABLE 3

CONSTANTS, YIELDS, ELEMENTAL ANALYSES AND IR SPECTRAL DATA OF σ-(*o*-CARBORANE-9-CARBONYL)-, σ-(*m*-CARBORANE-9-CARBONYL)- AND σ-9-*o*- AND σ-9-*m*-CARBORANYL-π-CYCLOPENTADIENYLDICARBONYLIRON

| Compound | Yield (%) | M.p. (°C) | Analyses (Found (calc.) (%)) | | | | General formula | IR spectra (ν, cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | B | Fe | | |
| R-9-COFe(CO)$_2$C$_5$H$_5$ (VI)[a] | 50 | 132–133 (heptane, dec.) | 34.38 (34.49) | 4.98 (4.63) | 31.12 (31.05) | 15.90 (16.03) | $C_{10}H_{16}B_{10}FeO_3$ | 3070 (CH of carborane C$_5$H$_5$); 2580–2640 (BH); 1940, 1990 (CO); 1600 (acyl CO) |
| R′-9-COFe(CO)$_2$C$_5$H$_5$ (VII)[b] | 53 | 114–115 (heptane, dec.) | 34.19 (34.49) | 4.69 (4.63) | 31.26 (31.05) | – | $C_{10}H_{15}B_{10}FeO_3$ | 3070 (C$_5$H$_5$); 3050 (CH of carborane); 2570–2670 (BH); 1950, 2010 (CO); 1600 (acyl CO) |
| R-9-Fe(CO)$_2$C$_5$H$_5$ (II) | 95 | 109–110 (hexane) | 33.98 (33.76) | 4.98 (5.04) | – | 16.95 (17.44) | $C_9H_{16}B_{10}FeO_2$ | 3090(C$_5$H$_5$); 3060 (CH of carborane); 2520–2650 (BH); 1910, 1980 (CO) |
| R′-9-Fe(CO)$_2$C$_5$H$_5$ (III) | 94 | 70–72 (hexane) | 33.85 (33.76) | 4.87 (5.04) | 33.66 (33.76) | – | $C_9H_{16}B_{10}FeO_2$ | 3090(C$_5$H$_5$); 3065 (CH of carborane); 2550–2260 (BH); 1930, 1990 (CO) |

[a] R = *o*-$C_2H_2B_{10}H_9$. [b] R′ = *m*-$C_2H_2B_{10}H_9$.

decane at 140°C and stirred for 3 h. The solvent was distilled off in vacuo and the residue was recrystallized from hexane. Constants, yields, elemental analyses and IR spectra are listed in Table 3.

### *π-(o-Carboran-9-yl)cyclopentadienyldicarbonyliron bromide (VIII)*

To a solution of 0.43 g (1.3 mmol) of II in 20 ml of $CCl_4$ was added 0.21 g (1.3 mmol) of $Br_2$ in 1 ml of $CCl_4$. The mixture was stirred at 23°C for 2 h. $CCl_4$ was distilled off in vacuo and the residue was chromatographed on a 15 × 1.5 cm column of silica gel L 40–100 μm; eluant benzene. Yield: 0.43 g (82%), m.p. 111–112°C (benzene/heptane, dec.). Found: C, 27.57; H, 3.86; B, 27.10; Fe, 14.91. $C_9H_{15}B_{10}BrFeO_2$ calcd.: C, 27.08; H, 3.79; B, 27.08; Fe, 14.74%.

### *π-(m-Carboran-9-yl)cyclopentadienyldicarbonyliron bromide (IX)*

The reaction was carried out as described in the previous subsection. 0.35 g (1.1 mmol) of III and 0.18 g (1.1 mmol) of $Br_2$ in 1 ml of $CCl_4$ gave 0.4 g (91%) of the title compound, m.p. 128–129°C (benzene/heptane, dec.). Found: C, 27.12; H, 3.99; B, 27.19. $C_9H_{15}B_{10}BrFeO_2$ calcd.: C, 27.08; H, 3.79; B, 27.08%.

### *General method for the production of 9-alkyl-o-, 9-alkyl-m- and 9-alkyl-2-p-carboranes*

A mixture of 10 mmol of 9-iodo-*o*-, 9-iodo-*m*- or 2-iodo-*p*-carborane, 20–40 mmol of alkylmagnesium halide and 0.2 mmol of $[(C_6H_5)_3P]_2PdCl_2$ in 50 ml of absolute ether was refluxed for 5–15 h under nitrogen until the iodocarborane completely disappeared. The reaction was monitored by TLC. The mixture was decomposed with water, washed with dilute HCl and then with water, and dried over $Na_2SO_4$. The resulting *B*-alkylcarboranes were chromatographed on a column of silica gel L 40–100 μm, eluant petroleum ether (b.p. 40–70°C), for the *m*- and *p*-carborane derivatives, and a mixture of benzene and petroleum ether (2/8) for the *o*-carborane derivatives. Afterwards, the liquid products were distilled off in vacuo (1 mmHg). The solid products were sublimed at 30–60°C in vacuo (1 mmHg) and recrystallized from pentane. Constants, yields and elemental analyses are listed in Table 4.

TABLE 4

CONSTANTS, YIELDS AND ELEMENTAL ANALYSES FOR *B*-ALKYLCARBORANES $RC_2B_{10}H_{11}$ AND $R_2C_2B_{10}H_{10}$

| Compound | M.p. (b.p.) °C) | Yield (%) | Analyses (Found (calc.) (%)) | | | General formula |
|---|---|---|---|---|---|---|
| | | | C | H | B | |
| 9-n-$C_3H_7$-1,2-$C_2B_{10}H_{11}$ | 42–43<br>(pentane) | 75 | 32.95<br>(32.23) | 9.73<br>(9.74) | 57.83<br>(68.03) | $C_5H_{18}B_{10}$ |
| 9-n-$C_3H_7$-1,7-$C_2B_{10}H_{11}$ | 65–66<br>(at 1 mmHg) | 55 | 32.93<br>(32.23) | 9.89<br>(9.74) | 57.67<br>(58.03) | $C_5H_{18}B_{10}$ |
| 9-$CH_3$-1,7-$C_2B_{10}H_{11}$ | 145–146<br>(pentane) | 90 | 22.82<br>(22.77) | 9.05<br>(8.92) | 68.43<br>(68.31) | $C_3H_{14}B_{10}$ |
| 2-$CH_3$-1,12-$C_2B_{10}H_{11}$ | 139–140<br>(pentane) | 63 | 22.72<br>(22.77) | 8.84<br>(8.92) | - | $C_3H_{14}B_{10}$ |
| 9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ | 186–187<br>(pentane) | 95 | 28.02<br>(27.89) | 9.32<br>(9.36) | 65.58<br>(62.75) | $C_4H_{16}B_{10}$ |
| 9,10-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ | 139–140<br>(pentane) | 90 | 27.61<br>(27.89) | 9.25<br>(9.36) | 62.77<br>(62.75) | $C_4H_{16}B_{10}$ |

## References

1 L.I. Zakharkin, L.V. Orlova, B.V. Lokshin and L.A. Fedorov, J. Organomet. Chem., 40 (1972) 15.
2 L.I. Zakharkin, L.V. Orlova and L.I. Denisovich, Zh. Obshch. Khim., 42 (1972) 2217.
3 A.I. Kovredov, M.G. Meiramov, A.V. Kazantsev and L.I. Zakharkin, Zh. Obshch. Khim., 51 (1981) 854.
4 R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36 (1962) 3489.
5 L.I. Zakharkin, V.N. Kalinin and I.P. Shepilov, Dokl. Akad. Nauk SSSR, 174 (1967) 607.
6 L.I. Zakharkin, V.N. Kalinin, A.P. Snyakin and B.A. Kvasov, J. Organomet. Chem., 18 (1969) 19.
7 L.I. Zakharkin, A.I. Kovredov and V.A. Olshevskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2159.
8 V.F. Mironov, S.Ya. Pechurina and V.I. Grigos, Dokl. Akad. Nauk SSSR, 230 (1976) 865.
9 L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya and Zh.S. Shaugumbekova, J. Organomet. Chem., 226 (1982) 217.
10 A.R. Garber, G.M. Bodner, L.J. Todd and A.R. Siedle, J. Magn. Reson., 28 (1977) 383.
11 V.N. Kalinin, N.I. Kobelkova and L.I. Zakharkin, Zh. Obshch. Khim., 50 (1980) 910.