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Synthesis of (*m*-Carborane-9,10-diyl)diacetic Acids and Their Derivatives

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Abstract—(*m*-Carborane-9,10-diyl)diacetic acids were obtained by oxidation of 9,10-diallyl-*m*-carborane which, in its turn, was synthesized by palladium-catalyzed cross coupling of 9,10-diiodo-*m*-carborane with allylmagnesium bromide.

(*m*-Carborane-9,10-diyl)di(alkanecarboxylic acids) in which the alkyl chain is bound by a C–B δ bond have not yet been reported. Such acids may offer interest for synthesis of previously unknown polymeric compounds containing *m*-carboranyl groups in the polymeric chain. To this end, we have prepared (*m*-caborane-9,10-diyl)diacetic acids **I** as first representatives of (*m*-carborane-9,10-diyl)di(alkanecarboxylic acids). Diacid **I** was synthesized by the following scheme from 9,10-diiodo-*m*-carborane (**II**).

$$\text{9,10-}I_2\text{-}m\text{-}C_2B_{10}H_{10} + 2CH_2{=}CH{-}CH_2MgBr^-$$

II

$$\xrightarrow{\text{Pd-cat.}} \text{9,10-}(C^cH_2{-}C^aH{=}C^bH_2)_2\text{-}m\text{-}C_2B_{10}H_{10}$$

III

$$\xrightarrow[H_2SO_4,\ \text{cat.}]{KMnO_4,\ CH_3COOH} \text{9,10-}(CH_2COOH)_2\text{-}m\text{-}C_2B_{10}H_{10}$$

I

Compound **II** [1] was brought into cross coupling with allylmagnesium bromide in a mixture of ether and tetrahydrofuran under $(Ph_3P)_2PdCl_2$ catalysis in the presence of copper iodide [2]. 9,10-Diallyl-*m*-carborane (**III**) was obtained in a high yield. Its structure was proved by ^1H and ^{11}B NMR spectroscopy. The $^{11}B\text{–}\{^1H\}$ spectra were assigned by comparing with a spectrum measured without $^{11}B\text{–}^1H$ decoupling, as well as using by analysis of off-diagonal crosspeaks in the $^{11}B\text{–}^{11}B$ COSY spectrum (see figure).

Compound **III** was oxidized with potassium permanganate in acid medium to diacid **I**. Treatment of the latter with $SOCl_2$ results in quantitative formation of dichloride **IV**.

$$\mathbf{I} + 2SOCl_2 \longrightarrow \text{9,10-}(CH_2COCl)_2\text{-}m\text{-}C_2B_{10}H_{10}.$$

IV

Dichloride **IV** was reacted with aniline to obtain dianilide **V**, and its Fridel–Crafts reaction with benzene gave 9,10-bis(bezoylmethyl)-*m*-carborane (**VI**).

$$\mathbf{IV} \xrightarrow{NH_2C_6H_5} \text{9,10-}(CH_2CO{-}NHC_6H_5)_2\text{-}m\text{-}C_2B_{10}H_{10},$$

V

$$\mathbf{IV} \xrightarrow[AlCl_3]{C_6H_6} \text{9,10-}(CH_2CO{-}C_6H_5)_2\text{-}m\text{-}C_2B_{10}H_{10}.$$

VI

Reduction of diacid **I** with lithium aluminum hydride provided 9,10-bis(2-hydroxyethyl)-*m*-carborane (**VII**).

$$\mathbf{I} \xrightarrow[\text{ether}]{LiAlH_4} \text{9,10-}(CH_2CH_2OH)_2\text{-}m\text{-}C_2B_{10}H_{10}.$$

VII

We found that (*m*-carborane-9,10-diyl)diacetic acids are stable compounds and can be used in the syntheses of other carboranyl-containing compounds, involving the B–C bond.

EXPERIMENTAL

The IR spectra were obtained in KBr on a Specord-82 instrument. The ^1H and ^{11}B NMR spectra were measured on a Bruker AMX-400 spectrometer in $CDCl_3$, internal references TMS and $(C_2H_5)_2O \cdot BF_3$, respectively.

9,10-Diiodo-*m*-carborane was prepared by the procedure in [2]. 9,10-Diallyl-*m*-carborane was oxidized by the procedure in [3].

9,10-Diallyl-*m*-carborane (III). To a stirred solution of 240 mmol of allylmagnesium bromide in ether,

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† Deceased.

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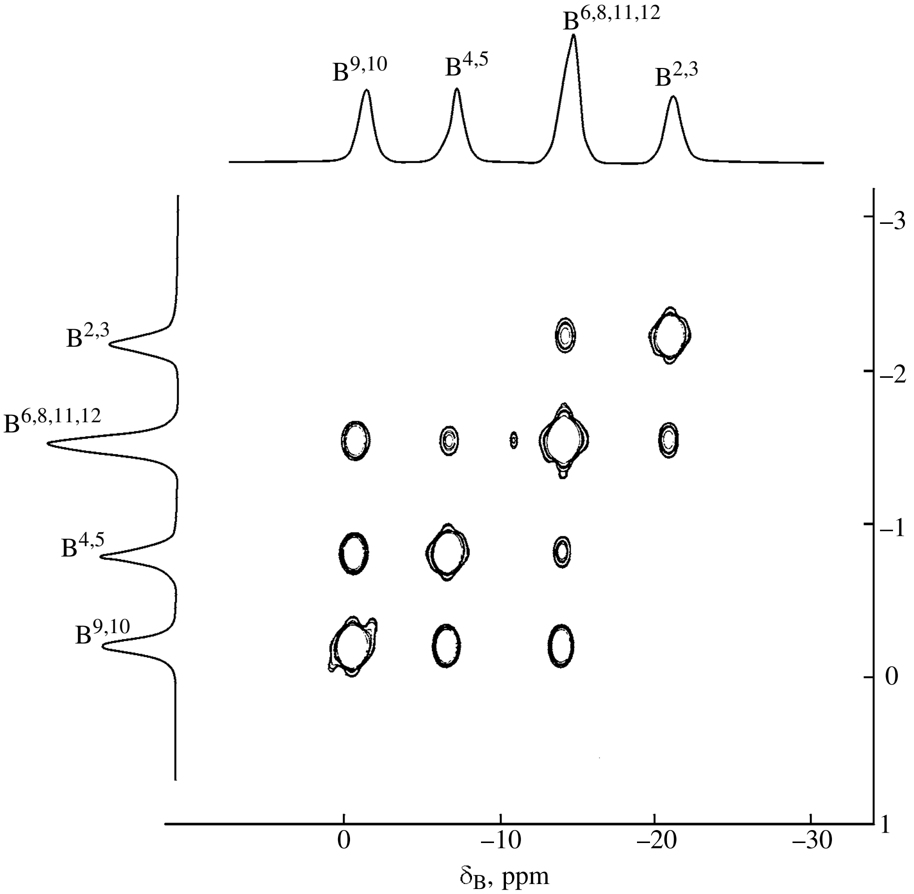

^{11}B–^{11}B COSY spectrum of 9,10-(CH_2–CH=CH_2)$_2$-*m*-$C_2B_{10}H_{10}$.

cooled with ice water, we gradually added under argon 16 g of 9,10-diiodo-*m*-carborane in 300 ml of tetrahydrofuran. After 30-min stirring, 1.12 g of $(Ph_3P)_2PdCl_2$ and 304 mg of CuI were added simultaneously. The mixture was left to stand for 12 h at room temperature and then stirred under reflux for 6 h until 9,10-diiodo-*m*-carborane was consumed completely (control by TLC on Silufol). The solvent was removed, the residue was treated with 300 ml of ether, and excess Grignard reagent was decomposed with 5% HCl with cooling. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 40 ml). The organic extracts were combined, washed with water (2 × 150 ml), and dried with $MgSO_4$. The solvent was removed in a vacuum, and the residue was subjected to column chromatography on silica gel (eluent hexane) to obtain 8.1 g (89%) of compound **III**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.88 d.d.t [1H^a, $^3J_{ac}$ 17.8, $^3J_{ab}$ 9.8, $^3J(C^aH_2)$ 7.8 Hz], 4.89 d.d.t [2H, H^c, $^3J_{ac}$ 17.8, $^2J_{bc}$ 2.2, $^4J(C^cH_2)$ 1.5 Hz], 4.83 d.d.t (2H, H^b, $^3J_{ab}$ 9.8, $^2J_{bc}$ 2.2, $^4J(C^bH_2)$ 1.0 Hz], 2.82 s (2H, carb. CH), 1.76 m (4H, CH_2). ^{11}B NMR spectrum ($CDCl_3$), δ_B, ppm: –0.41 s (2B, $B^{9,10}$), –6.51 d [2B, $B^{4,5}$, $^1J(^{11}B–^1H)$ 159 Hz], –13.84 d [4B, $B^{6,8,11,12}$, $^1J(^{11}B–^1H)$ 163 Hz], –20.61 d [2B, $B^{2,3}$, $^1J(^{11}B–^1H)$ 181 Hz].

(*m*-Carborane-9,10-diyl)diacetic acids I. To a stirred mixture of 6 g of compound **III**, 200 ml of CH_2Cl_2, 200 ml of water, 30 ml of 50% H_2SO_4, 4 ml of acetic acid, and 2.4 g of $PhCH_2(C_2H_5)_3NBr$, cooled to 0°C, we gradually added 25 g of $KMnO_4$. The resulting mixture was kept for 40 min at that temperature and then allowed to warm to 20°C. The residue was filtered off and washed with 100 ml of CH_2Cl_2 and 100 ml of water, transferred into a flask, and shaken twice with 100 ml of 10% KOH. The alkaline extracts were combined, acidified with dilute HCl, the white precipitate that formed was filtered off, washed with water to neutral, and dried in a water-jet-pump vacuum at 60°C to obtain 4.5 g (65%) of compound **I**, mp 200–201°C (toluene). IR spectrum, ν, cm^{-1}: 1683 (C=O), 3060–2881 (COOH). Found, %: C 28.43; H 6.34; B 41.35. $C_6H_{16}B_{10}O_4$. Calculated, %: C 27.69; H 6.15; B 41.53.

(*m*-Carboranyl-9,10-diyl)di(acetyl chlorides)

IV. To a solution of 2.5 g of diacid **I** in 25 ml of dry benzene we added 2.9 g of $SOCl_2$ at 20°C. The reaction mixture was heated for 2 h until HCl and SO_2 no longer evolved, cooled, and the solvent and excess $SOCl_2$ were removed in a vacuum to obtain 2.77 g (98%) of a solid dichloride.

(*m*-Carborane-9,10-diyl)diacetanilides V. Dichloride **IV** (3 g) in 10 ml of dry dioxane was slowly added to a solution of 0.56 g of freshly distilled aniline in 4 ml of dry dioxane. The precipitate that formed was transferred together with the solvent to a dropping funnel, treated with 10% HCl, and extracted twice with ether. The ether solution was washed with water, and the ether was removed in a vacuum to obtain 0.3 g (73%) of compound **V**, mp 225–226°C (toluene–hexane). IR spectrum, ν, cm^{-1}: 1658 (CO), 3191, 3132 (NH). Found N, %: 7.04. $C_{18}H_{26}B_{10}N_2O_2$. Calculated N, %: 6.82.

9,10-Bis(benzoylmethyl)-*m*-carborane (VI). To 1 g of $AlCl_3$ in 10 ml of dry benzene at 20°C we added 1 g of dichloride **IV** in 10 ml of dry benzene, and the mixture was stirred for 5 h at room temperature. The reaction mixture was poured into 5% HCl, the benzene layer was separated, and the aqueous layer was extracted with benzene. The organic extracts were combined, washed with 2% NaOH and water, and dried with K_2CO_3. The benzene was removed, the residue was dissolved in a little benzene, the solution was refluxed, the benzene was decanted from the oily residue, and treated with hexane to precipitate 0.8 g (50%) of compound **VI**, mp 97–98°C. Found, %: C 56.92; H 6.99. $C_{18}H_{24}B_{10}O_2$. Calculated, %: C 56.84; H 6.31. 2,4-Dinitrophenylhydrazone, mp 270–271°C (benzene–hexane). Found N, %: 14.55. $C_{30}H_{32}B_{10}N_8O_8$. Calculated N, %: 15.13.

9,10-Bis(2-hydroxyethyl)-*m*-carborane (VII). To 1 g of diacid **I** in 30 ml of dry ether we added 1.2 g of $LiAlH_4$ in 25 ml of dry ether. The suspension was heated under reflux for 10 h. After cooling, the reaction mixture was decomposed with caution with 10% H_2SO_4, the organic layer was separated, and the aqueous layer was extracted with ether. The ether extracts were washed with water, dried with Na_2SO_4, and the ether was removed to obtain 0.75 g (85%) of diol **VII**, mp 113–114°C (ethanol–benzene). IR spectrum, ν, cm^{-1}: 3276 (OH). Found,%: C 31.24; H 8.20; B 46.94. $C_6H_{20}B_{10}O_2$. Calculated,%: C 31.03; H 8.62; B 46.55.

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