Synthesis of (o-Carborane-1,2-diyl)dipropanoic Acid and Its Derivatives

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Abstract—Hydrolysis of 1,2-bis(cyanoethyl)-*o*-carborane easily available by cyanoethylation of *o*-carborane gives (*o*-carborane-1,2-diyl)dipropanoic acid. The corresponding acid dichloride, diamide, dianilide, dibenzo-phenone, and diol were prepared from it by typical procedures.

Up to now only two carborane-1,2-dicarboxylic acids have been known: o-carborane-1,2-dicarboxylic and (o-carborane-1,2-diyl)diacetic acids [1]. All attempts to prepare dicarboxylic acids with a longer chain have been unsuccessful. Kalinin *et al.* [2] have found that o-carborane is easily cyanoethylated to give 1,2-bis(cyanoethyl)-o-carborane I whose transformations had not been studied.

In the present work we effected hydrolysis of dinitrile \mathbf{I} in sulfuric acid to obtain the previously unknown (1-*o*-carborane-1,2-diyl)dipropanoic acid (\mathbf{II}) according to the following scheme.

 $\begin{array}{c} \text{CNCH}_2\text{CH}_2\text{C} & \text{-CCH}_2\text{CH}_2\text{CN}\\ \text{B}_{10}\text{H}_{10} \\ \textbf{I}\\ \hline \\ \hline \\ \underline{\text{H}}_2\text{SO}_4 + \text{H}_2\text{O}} \\ \hline \\ \hline \\ 150^{\circ}\text{C} \end{array} \xrightarrow{} \text{HOOCCH}_2\text{CH}_2\text{C} - \text{CCH}_2\text{CH}_2\text{COOH}\\ \hline \\ \\ \hline \\ \text{B}_{10}\text{H}_{10} \\ \textbf{II} \end{array}$

Acid **II** is formed in a good yield. It is a white crystalline substance, mp $244-245^{\circ}$ C. This acid can be regarded as a derivative of suberic acid, in which two *o*-carborane carbons are incorporated into the aliphatic chain of suberic acid. These two acids have different molecular weights; thus, acid **II** contains the polyhedral group $B_{10}H_{10}$ instead of four hydrogen atoms. That is why it was interesting to compare properties of derivatives of acids **II** and **III**. To this end, some reactions of the carboxy groups of acid **II** were studied. Heating of compound **II** with thionyl chloride acid gives dichloride **IV**. The reaction is similar to that with suberic acid. Dichloride **IV**, like aliphatic dichlorides, slowly hydrolyses in air.

$$\begin{array}{c} \mathbf{II} + 2\text{SOCl}_2 \longrightarrow \text{ClCOCH}_2\text{CH}_2\text{C} \\ & \\ B_{10}\text{H}_{10} \\ \mathbf{IV} \end{array}$$

Starting with dichloride **IV**, we prepared diamide **V**, dianilide **VI**, and diethylamide **VII**.



[†] Deceased.

Moreover, the dichloride easily enters the Friedel– Crafts reaction with benzene to form diketone **VIII**. These reactions proceed similar to those of suberic acid dichloride.

Reduction of compound **II** with lithium aluminumhydride in ether gives crystalline 1,2-bis(3-hydroxypropyl)-*o*-carborane (**IX**).

$$\mathbf{II} \xrightarrow{\text{LiAlH}_4} \text{HOCH}_2\text{CH}_2\text{CH}_2\text{C} \xrightarrow{\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}} \\ \xrightarrow{\text{B}_{10}\text{H}_{10}} \mathbf{IX}$$

Dinitrile I was reacted with C_6H_5MgBr in ether to obtain, after hydrolysis, diketone **VIII**. The same reaction direction is characteristic of aliphatic dinitriles.

$$\mathbf{I} + PhMgX \xrightarrow{HCl + H_2O} \mathbf{VIII}$$

Hence, it was established that dicarboxylic acid **II** and some of its derivatives behave similarly to higher dicarboxylic acids and can be used for preparing of various C-organoderivatives of *o*-carborane.

EXPERIMENTAL

The compounds obtained were characterized by the IR spectra measured on a Specord-82 instrument and by the elemental analyses.

1,2-Bis(cyanoethyl)-*o*-carborane was obtained by the procedure in [2].

(*o*-Carborane-1,2-diyl)dipropanoic acid (II). A mixture of 4 g of 1,2-bis(cyanoethyl)-*o*-carborane and 45 ml of 75% sulfuric acid was stirred at 150–155°C for 2.5 h. The reaction mixture was cooled and poured into an ice-cold water. The precipitate that formed was filtered off, washed with water (3×20 ml), and treated with 10% sodium hydroxide. The alkaline solution was extracted with ether and acidified with hydrochloric acid. The precipitate that formed on standing was filtered off and dried in a water-jet-pump vacuum to obtain 3.8 g (83%) of acid **II**, mp 244–245°C (from toluene). IR spectrum, v, cm⁻¹: 1717 (C=O), 3487 (OH). Found, %: C 33.44; H 7.01; B 37.45. C₈H₂₀B₁₀O₄. Calculated, %: C 33.33; H 6.94; B 37.45.

(*o*-Carborane-1,2-diyl)dipropanoyl chloride (IV) A solution of 3.1 g of thionyl chloride in 10 ml of dry benzene was added to 3 g of dicarboxylic acid II in 20 ml of dry benzene, and the resulting mixture was refluxed for 2 h until HCl and SO₂ no longer evolved. Excess SOCl₂ and benzene were removed in a water-

jet-pump vacuum. The solid residue was crystallized from hexane to obtain 3.1 g (92%) of compound IV, mp $87-88^{\circ}C$.

(*o*-Carborane-1,2-diyl)dipropanamide (V). Acid dichloride IV, 0.1 g, was dissolved in 8 ml of dry benzene, and dry ammonia was passed through it until complete saturation. The residue was dissolved in water and extracted with three portions of ether. The ether was removed, and the residue was crystallized from toluene, mp 161–162°C. Found, %: C 33.28; H 7.80; B 37.68; N 9.90. $C_8H_{22}B_{10}N_2O_2$. Calculated, %: C 33.56 H 7.69; B 37.76; N 9.79.

(*o*-Carborane-1,2-diyl)dipropananilide (VI). Acid dichloride IV, 0.5 g, was dissolved in 0.5 ml of dry dioxane, and the resulting solution was added to a solution of 0.57 g of freshly distilled aniline in 12 ml of dioxane. A fine precipitate formed and was treated with 10% hydrogen chloride and extracted with ether. The ethereal solution was washed with water, and the solvent was evaporated. The solid residue was recrystallized from benzene, mp 177–178°C. Found, %: C 54.26; H 6.72; B 24.77; N 6.34. C₂₀H₃₀B₁₀N₂O₂. Calculated, %: C 54.79; H 6.84; B 24.65; N 6.39.

(*o*-Carborane-1,2-diyl)di(*N*,*N*-diethylpropanamide) (VII). A solution of 0.9 ml of diethylamine in 5 ml of dioxane was added with stirring and cooling to a soluton of 1 g of acid dichloride IV in 1.5 ml of dry dioxane. The resulting mixture was left overnight. The precipitate was filtered off, treated with 10% hydrogen chloride, and extracted with three portions of ether. The ethereal solution was washed with water, and the ether was removed. The solid residue was recrystallized from hexane, mp 91–92°C. Found, %: C 48.39; H 9.98; B 27.20; N 7.09. $C_{16}H_{38}B_{10}N_2O_2$. Calculated, %: C 48.24; H 9.54; B 27.13; N 7.03.

(o-Carborane-1,2-divl)di(phenyl propanoate) (VIIIa). a. Dry benzene, 20 ml, and 1.88 g of AlCl₃ were placed in a flask equipped with a funnel, a thermometer, and a calcium chloride tube, and a solution of 2 g of acid chloride IV in 20 ml of dry benzene was added with cooling at 20°C. The resulting mixture was left overnight and then poured into an ice-cold water acidified with hydrochloric acid. The benzene layer was separated, washed with water, 2% NaOH, and dried over potassium carbonate. The solvent was removed, and the solid residue was crystallized from a toluene-hexane mixture to obtain 1.54 g (84%) of compound VIII, mp 135–136°C. IR spectrum, v, cm⁻¹: 1684 (C=O); 2605, 2573 (B-H). Found, %: C 58.89; H 6.68; B 26.04. C₂₀H₂₈B₁₀O₂. Calculated, %: C 58.82; H 6.86; B 26.47.

2,4-Dinitrophenylhydrazone, mp 165–166°C. Found, %: N 14.26. $C_{32}H_{36}B_{10}N_8O_8$. Calculated, %: N 14.58.

b. Compound I, 1 g, in 40 ml of absolute ether was gradually added to ethereal C_6H_5MgBr (obtained from 2.5 g of Mg and 12.48 g of C_6H_5Br). After 1 h, a dark precipitate formed. The mixture was stirred under reflux for 11 h, cooled, treated with 40 ml of 20% hydrochloric acid, cooled, and extracted with methylene chloride (3 × 30 ml). The solvent was removed, and the semiliquid residue was dissolved in a 9:1 heptane–benzene mixture and passed through a silica gel column which was then washed with three portions of benzene. The benzene was removed in a vacuum, and the solid tar-like residue was treated with a small amount of acetone to form a white precipitate. Recrystallization from a toluene–hexane mixture gave 0.5 g (56%) of compound **VIII**, mp 135–135°C.

2,4-Dinitrophenylhydrazone, mp 165–166°C.

1,2-(3-Hydroxypropyl)-*o*-carborane (IX). A suspension of 2 g of dicarboxylic acid II in 50 ml of dry ether was added to a suspension of 3 g of

lithium aluminum hydride in 40 ml of absolute ether. The resulting mixture was stirred for 3 h under reflux. After cooling, it was successively treated with 10 ml of 50% methanol and 20 ml of 10% sulfuric acid. For better separation of the aqueous and ethereal layers, 5 ml of hydrochloric acid was added into the separating funnel. The ethereal solution was washed with water and dried over sodium sulfate. The solvent was removed, and the residue was dissolved in benzene and precipitated with hexane. The precipitate was filtered off and washed with a 5:1 hexane–benzene mixture to obtain 1.4 g (77.7%) of compound **IX**. IR spectrum, v, cm⁻¹: 3235 (OH); 2605, 2573 (B–H). Found, %: C 36.92; H 10.03; B 40.83. C₈H₂₄B₁₀O₂. Calculated, %: C 36.92; H 9.23; B 41.53.

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