Synthesis of unsaturated 7,8- and 7,9-di(hydroxymethyl)decahydro-7,8- and -7,9-dicarba-*nido*-undecaborate(1−) diethers

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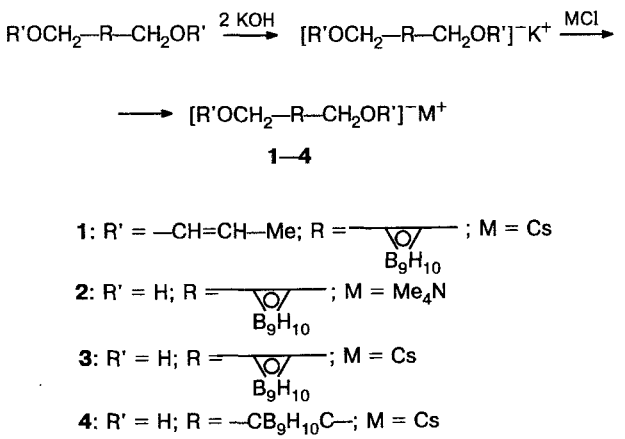
Dicarba-*nido*-undecaborate(1−) anions were obtained by treatment of 1,2-di(hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane(12) diallyl ether, 1,2-di(hydroxymethyl)-1,2-dicarba-*closo*-dodecaborane(12), and 1,7-di(hydroxymethyl)-1,7-dicarba-*closo*-dodecaborane(12) with ethanolic solutions of KOH and subsequent reaction of the products with cesium and tetramethylammonium chlorides.

Key words: *nido*-undecaborate; carborane; diallyl ether; cesium chloride, tetramethylammonium chloride; adhesive compositions; IR spectra.

Introduction of carborane fragments into various polymers is known to increase their solubilities and enhance their thermal and adhesion properties.[1,2] Unsaturated polyesters that contain carborane fragments in the acid or alcohol components are good optically transparent thermally stable adhesives.[2] To impart current-conducting properties to these materials, ionic compounds can be introduced into them. Among these compounds are dicarba-*nido*-undecaborates, whose synthesis is the subject of the present study.

Derivatives of dicarba-*nido*-undecaborates(1−) **1**—**4** were prepared by cleavage of the corresponding dicarba-*closo*-dodecaboranes(12)* with alcoholic alkali, according to Scheme 1, using the procedure described previously for unsaturated *ortho*-carborane.[3,4]

Scheme 1



* *ortho*-Carborane.

The yields of the reaction products are ~50 % for *ortho*-carboranes and exceeds 83 % in the case of *meta*-isomers. We attribute this to the fact that cleavage of the *ortho*-isomer under the experimental conditions proceeds to a greater extent (up to its complete destruction) giving salts of boric acid, and, probably, its intramolecular dehydration also occurs, giving a cyclic ester. Both processes are well known for *ortho*-carborane.[5]

The compounds **1**—**4** obtained are white powders soluble in ethanol, acetone, and THF. Their IR spectra exhibit intense absorption with a maximum at 2560 cm^{-1}, which is characteristic of the deformation vibrations of the B—H bond in undecaborate. Products **1**—**4** slowly decompose when stored in air to give boric acid, which is indicated by the fact that the IR spectra, recorded after the compounds have been exposed to air for 1 year, exhibit broad absorption bands in the regions 1300—1420 and 3200—3600 cm^{-1}. The former band corresponds to the stretching vibrations of the B—O bond, and the latter band characterizes the deformation vibrations of the associated OH groups. Analogous behavior of undecaborates has been observed previously.[6]

Compounds **5** and **6** were prepared by condensation of cesium salts of 7,8- and 7,9-di(hydroxymethyl)-7,8- and -7,9-dicarba-*nido*-undecaborates with methacryloyl chloride in THF at −15 °C in the presence of triethylamine as an acceptor of HCl (Scheme 2).

We were not able to obtain pure dimethylacrylate derivatives of 7,8- and 7,9-di(hydroxymethyl)-7,8- and -7,9-dicarba-*nido*-undecaborates(1−), since they readily polymerize in the course of isolation. The formation of a product having the desired dicarbaundecaborate composition is confirmed by the IR spectra of the reaction solution, which exhibit absorption bands typical of dicarbaundecaborate, C=O, and C=C bonds (2540, 1720,

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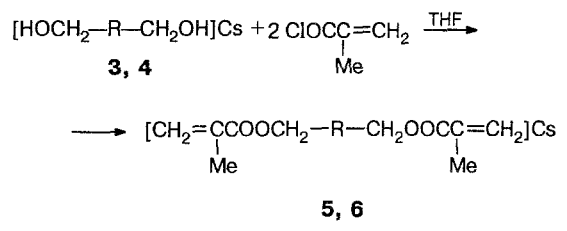
Scheme 2



and 1650 cm^{-1}, respectively). The virtually quantitative yields of triethylammonium chloride (83 % and more) and the content of boron found by elemental analysis for the 7,8-isomer also serve as evidence of the formation of the desired undecaborate. The addition of inhibitors does not result in the stabilization of dimethacrylate derivatives of 7,8- and 7,9-dicarba-*nido*-undecaborates(1−) even at low temperatures. The ability of the compounds formed to easily polymerize can apparently be explained by the presence of dicarbaundecaborate groups, since the dimethacrylate derivative of 1,2-di(hydroxymethyl)-*o*-carborane (see Ref. 7) undergoes copolymerization with cyanoacrylates only in the presence of initiators.

The possibility of developing current-conducting optically transparent adhesive compositions based on the compounds with dicarbaundecaborate groups prepared by us was shown for a test composition consisting of ethyl-α-cyanoacrylate and 10 % tetramethylammonium-7,8-di(hydroxymethyl)-7,9-dicarba-*nido*-undecaborate, whose average electric resistance (R_{av}) was $4.5 \cdot 10^6$ Ohm and the average volume resistivity (ρV_{av}) was $7.8 \cdot 10^8$ Ohm cm^{-1}.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer in the 400—4000 cm^{-1} range with solid samples (pellets with KBr) or THF solutions.

Cesium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate diallyl ether (1). Anhydrous methanol (150 mL) and KOH (1.12 g, 20.0 mmol) were placed in a flask equipped with a reflux condenser, a stirrer, and an argon inlet tube. 1,2-Di(hydroxymethyl)-*o*-carborane diallyl ether (3 g, 10.5 mmol) prepared by a previously described procedure[8] was added. The solution was stirred for 1.5 h at ~20 °C and then heated with refluxing for 4 h. Anhydrous methanol (30 mL) was added to the cooled reaction mixture, and the solution was saturated with dry CO_2 in order to remove excess KOH as potassium carbonate. The precipitate was filtered off and washed 3—4 times with small quantities of methanol, the filtrates were combined, and the solvent was evaporated to dryness under a water-jet-pump vacuum. The solid residue was dissolved in 120 mL of distilled water. An aqueous solution of cesium chloride (1.8 g, 10.6 mmol) was added to the resulting aqueous solution of potassium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate diallyl ether (**7**).* The precipitate was filtered off, washed with distilled water, and dried at 60—80 °C (2 Torr) until its weight was constant giving 1.92 g (47.7 %) of compound **1** (white powder), m.p. 150—152 °C. Found (%): C, 29.02; H, 5.86; B, 24.65; Cs, 32.93. $C_{10}H_{24}B_9O_2Cs$. Calculated (%): C, 29.50; H, 5.94; B, 24.05; Cs, 32.63.

Tetramethylammonium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate (2). This compound was prepared similarly to compound **1**. The reaction of 1,2-di(hydroxymethyl)-*o*-carborane (13.2 g, 64.5 mmol) with KOH (7.46 g, 132.9 mmol) and tetrabutylammonium chloride (9.78 g, 33.05 mmol) gave 4.9 g (50.1 %) of compound **2** (white powder), m.p. 91—92 °C. Found (%): C, 56.45; H, 11.95; B, 22.30; N, 3.54. $C_{20}H_{52}B_9NO_2$. Calculated (%): C, 55.60; H, 12.02; B, 22.33; N, 3.21.

Cesium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate (3). 1,2-Di(hydroxymethyl)-*o*-carborane (13.2 g, 64.5 mmol) was added to a solution of KOH (7.46 g, 132.9 mmol) in anhydrous ether (400 mL). The subsequent procedure was similar to that described in the synthesis of compound **1** up to the formation of an aqueous solution of the corresponding potassium salt. Then cesium chloride (5.06 g, 29.8 mmol) was added to the transparent aqueous solution containing potassium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate (7 g, 30.0 mmol), and the resulting aqueous solution was concentrated under an oil-pump vacuum at 60 °C. The solid residue was extracted with acetone, and the solution was dried with $CaCl_2$. Evaporation of the acetone afforded 4.8 g (42.97 %) of compound **3** (white powder; when heated in a capillary to 300 °C it turns dark without melting). Found (%): C, 15.17; H, 4.94; B, 30.67; Cs, 40.0. $C_4H_{16}B_9O_2Cs$. Calculated (%): C, 14.79; H, 4.95; B, 29.77; Cs, 40.75.

Cesium 7,9-di(hydroxymethyl)-7,9-dicarba-*nido*-undecaborate (4) was synthesized and isolated similarly to compound **3**. The reaction of 1,7-di(hydroxymethyl)-*m*-carborane (13.2 g, 64.5 mmol) with KOH (7.46 g, 132.9 mmol) and cesium chloride (10.87 g, 64.5 mmol) gave 17.6 g (83.8 %) of compound **4** (white powder; when heated in a capillary to 300 °C, it does not melt and produces a light color). Found (%): C, 15.06; H, 4.85; B, 30.15; Cs, 39.90. $C_4H_{16}B_9O_2Cs$. Calculated (%): C, 14.79; H, 4.95; B, 29.77; Cs, 40.75.

Cesium 7,9-di(hydroxymethyl)-7,9-dicarba-*nido*-undecaborate dimethacrylate (5). Triethylamine (3.2 g, 30.5 mmol) was added dropwise to a solution of compound **4** (5 g, 15.3 mmol) in anhydrous THF (25 mL). The reaction mixture was stirred for 1 h at ~20 °C and then cooled to −15 °C. A solution of methacryloyl chloride (3.2 g, 30.5 mmol) in THF (10 mL) was added, and the mixture was stirred for 2 h at −15 °C. After that, the temperature of the reaction mixture was brought to ambient temperature. The precipitate of triethylammonium chloride (3.5 g, 83.3 %) was filtered off. The IR spectrum of the transparent solution exhibited absorption bands at 2540, 1720, and 1650 cm^{-1} corresponding to dicarbaundecaborate

* The quantity of ester **7** was determined from the difference between the weights of the solid residue obtained after evaporation of methanol and the solid residue that did not dissolve in water.

groups, and C=O and C=C bonds, respectively. The transparent filtrate was concentrated under a water-jet-pump vacuum at ~20 °C and then at 30—35 °C in the presence of an inhibitor. After evaporation of the solvent, the absorption band corresponding to C=C vibrations (1650 cm^{-1}) in the IR spectrum of the compound was weak.

Cesium 7,8-di(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate dimethacrylate (6) was synthesized, isolated, and purified similarly to compound **5**. In the reaction of compound **3** (5 g, 15.3 mmol) with triethylamine (3.2 g, 30.5 mmol) and methacryloyl chloride (3.2 g, 30.5 mmol), 4.0 g (95.6 %) of triethylammonium chloride was produced. After evaporation of the solvent, the absorption corresponding to the vibrations of the C=C bonds was virtually missing from the IR spectrum.

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