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Cyanoethylation of *o*-Carboranes with Acrylonitrile under Conditions of Phase-Transfer Catalysis

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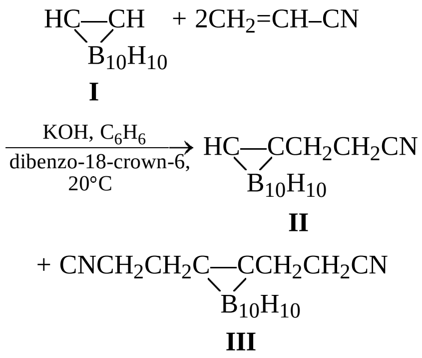
Abstract—*o*-Carboranes are cyanoethylated with acrylonitrile at the CH group of the *o*-carborane core in absolute benzene under conditions of phase-transfer catalysis.

It was briefly reported previously [1] that under conditions of catalysis with 40% aqueous Triton B *o*-carboranes are cyanoethylated at the CH group of the *o*-carborane core to form 1-(cyanoethyl)-*o*-carboranes.

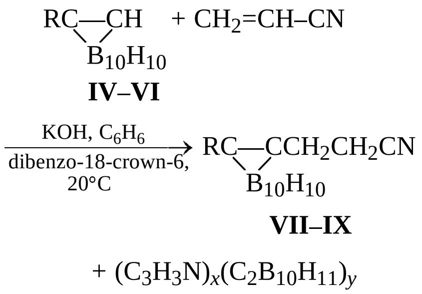
In this work we found that cyanoethylation of *o*-carborane and its 1-substituted derivatives can occur in absolute benzene under conditions of phase-transfer catalysis at room temperature. As phase-transfer catalyst we used finely divided KOH in combination with dibenzo-18-crown-6. The reaction was performed at an equimolar reactants ratio. Initially we took unsubstituted *o*-carborane **I**. The reaction occurred at 20°C by the following scheme:



$$\underset{\mathbf{I}}{\mathrm{HC{-}CH}\,(B_{10}H_{10})} + 2CH_2{=}CH{-}CN \xrightarrow[\text{dibenzo-18-crown-6, 20°C}]{\text{KOH, }C_6H_6} \underset{\mathbf{II}}{\mathrm{HC{-}CCH_2CH_2CN}\,(B_{10}H_{10})} + \underset{\mathbf{III}}{\mathrm{CNCH_2CH_2C{-}CCH_2CH_2CN}\,(B_{10}H_{10})}$$

A specific feature of this reaction, in contrast to the reaction catalyzed with Triton B, is formation of a polymeric tarry by-product containing C, H, B, and N atoms. This compound contains no free *o*-carborane, which suggests its complex structure. Despite the fact that the molar ratio of *o*-carborane and acrylonitrile was 1 : 2, a mixture of **II** and **III** was obtained. Compound **III** is formed along with **II** even at a 2 : 1 ratio of carborane **I** and acrylonitrile. Compounds **II** and **III** can be readily separated by crystallization.

Cyanoethylation under similar conditions was also performed with 1-phenyl-*o*-carborane **IV**, 1-methyl-*o*-carborane **V**, and 1-vinyl-*o*-carborane **VI**.



$$\underset{\mathbf{IV{-}VI}}{\mathrm{RC{-}CH}\,(B_{10}H_{10})} + CH_2{=}CH{-}CN \xrightarrow[\text{dibenzo-18-crown-6, 20°C}]{\text{KOH, }C_6H_6} \underset{\mathbf{VII{-}IX}}{\mathrm{RC{-}CCH_2CH_2CN}\,(B_{10}H_{10})} + (C_3H_3N)_x(C_2B_{10}H_{11})_y$$

R = C_6H_5 (**IV, VII**), CH_3 (**V, VIII**), CH=CH_2 (**VI, IX**).

In all cases, a polymeric tarry product formed, from which compounds **VII**–**IX** were separated by dissolution in benzene. The yields of **II**, **III**, and **VII**–**IX** were 55–57% based on the *o*-carborane. The products were identified by the elemental analyses and melting points.

The suggested procedure is a simple route to (1-cyanoethyl)-*o*-carboranes.

EXPERIMENTAL

1-(Cyanoethyl)-*o*-carborane (II) and 1,2-bis(cyanoethyl)-*o*-carborane (III). A flask equipped with a stirrer, a thermometer, and a $CaCl_2$ tube was charged with 6 g of *o*-carborane in 20 ml of absolute benzene, 1 g of powdered KOH, and 0.15 g of dibenzo-18-crown-6, and 5 g of freshly distilled acrylonitrile was slowly added with stirring at 12–15°C. The mixture was stirred for an additional 20 h at 20°C, and a light orange product gradually precipitated. According to TLC, no initial *o*-carborane remained in the solution. Then 20 ml of water was added, the mixture was stirred, and the precipitate was filtered off and washed with water (2 × 5 ml) and benzene (10 ml). The precipitate was dried on the filter at 50°C in a water-jet-pump vacuum and recrystallized from

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toluene. Compound **III** was obtained; yield 3.2 g (31%), mp 225–226°C (cf. [1]). Found, %: C 38.63; H 7.75; B 43.13; N 11.26. $C_8H_{18}B_{10}N_2$. Calculated, %: C 38.40; H 7.20; B 43.20; N 11.20. The benzene layer was separated from the aqueous phase and vacuum-evaporated to dryness. The residue was recrystallized two times from hexane with separation from the oily layer by decanting. Compound **II** was obtained; yield 4 g (49%), mp 135–136°C (cf. [1]). Found, %: C 30.45; H 7.06; B 54.82; N 7.06. $C_5H_{15}B_{10}N$. Calculated, %: C 30.41; H 7.69; B 54.79; N 7.10. Composition of the polymeric tar, %: C 49.30; H 6.09; B 21.51; N 11.75.

1-Phenyl-2-(cyanoethyl)-*o*-carborane (VIII). A solution of 0.75 g of acrylonitrile in 3 ml of dry benzene was slowly added with stirring at 15°C to a solution of 3 g of **VII** in 10 ml of absolute benzene, 0.4 g of finely divided KOH, and 0.05 g of dibenzo-18-crown-6. Shortly thereafter, a light orange product started to precipitate. The mixture was stirred for an additional 20 h. After reaction completion, 10 ml of water was added, and the precipitate was filtered off, washed with absolute benzene (2 × 5 ml), and dried in air; mp 181–182°C (cf. [1]). The benzene solution was dried over $CaCl_2$. The residue after distilling off the solvent was recrystallized from toluene; mp 180–182°C. Yield of **VII** 3.7 g (71%). Found, %: C 48.46; H 6.83; B 39.83; N 5.09. $C_{11}H_{19}B_{10}N$. Calculated, %: C 48.35; H 6.95; B 39.60; N 5.13.

1-Methyl-2-(cyanoethyl)-*o*-carborane (VIII). A solution of 1.1 g of acrylonitrile in 2 ml of benzene was added with stirring at 12–15°C to a mixture of 3.2 g of **V**, 0.4 g of KOH, 0.06 g of dibenzo-18-crown-6, and 10 ml of benzene. The resulting mixture was stirred for an additional 20 h. After common workup, 2 g (46%) of **VIII** was obtained; mp 161–162°C (from toluene; cf. [1]).

1-Vinyl-2-(cyanoethyl)-*o*-carborane (IX). A solution of 1.3 g of acrylonitrile in 3 ml of benzene was added at 10–12°C to a mixture of 4.2 g of **VI**, 0.5 g of KOH, 0.06 g of dibenzo-18-crown-6, and 10 ml of benzene. After common workup, 2.6 g (47%) of **IX** was obtained; mp 128–129°C (from toluene). Found, %: C 37.72; H 7.52; B 48.39; N 6.26. $C_7H_{17}B_{10}N$. Calculated, %: C 37.66; H 7.62; B 48.34; N 6.27.

REFERENCES

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