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SYNTHESIS OF 1-ISOCYANATOCARBORANES

V. N. Kalinin, A. V. Astakhin,
A. V. Kazantsev, and L. I. Zakharkin

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Isocyanates comprise one of the lesser-known classes of carboranes. Reaction of 3-amino-o-carborane with phosgene has given 3-isocyanato-o-carborane, from which have been obtained carbamates and ureas [1]. 1-Isocyanatocarborane has not been obtained in the pure state, and there has only been a report of the reaction of o-carborane-1,2-dicarbonyl chloride with LiN_3, which gave on heating 1,2-diisocyanato-o-carborane which was then converted without isolation into the methyl dicarbamate [2].

A general method for the synthesis of isocyanates is by reacting acid chlorides with Me_3SiN_3 to give the azides, which under the reaction conditions undergo the Curtius rearrangement to give the isocyanates [3]. We have used this method to prepare carborane isocyanates. It has been found that the acid chlorides of carboranecarboxylic and carboraneacetic acids react with Me_3SiN_3 in boiling toluene, dioxane, or pentane to give the carborane isocyanates:

$$o\text{-}, m\text{-}RCB_{10}H_{10}C(CH_2)_nCOCl + Me_3SiN_3 \xrightarrow[100-110^\circ]{}$$
$$\rightarrow [o\text{-}, m\text{-}RCB_{10}H_{10}C(CH_2)_nCON_3] \xrightarrow[-N_2]{} o\text{-}, m\text{-}RCB_{10}H_{10}C(CH_2)_nNCO \qquad n = 0{,}1$$

Carboranecarbonyl chlorides react with Me_3SiN_3 slowly, and completion of the reaction requires heating at 100–110°C for 30–40 h. Carboranylacetyl chloride reacts much more rapidly with Me_3SiN_3, and reaction is complete in 4–5 h.

The IR spectra of carborane isocyanates contain absorptions for NCO stretching at 2260–2280 cm^{-1}, B–H at 2600 cm^{-1}, and C–H of the carborane nucleus at 3060 cm^{-1}. In their chemical behavior, carborane isocyanates are reminiscent of aliphatic and aromatic isocyanates [4]. Reaction of the isocyanates with water gives as the principal products the carborane amines and symmetrical ureas

$$RCB_{10}H_{10}C(CH_2)_nNCO + H_2O \xrightarrow[20^\circ]{THF} RCB_{10}H_{10}C(CH_2)_nNH_2 + [RCB_{10}H_{10}C(CH_2)_nNH]_2CO$$

Carborane isocyanates react smoothly with alcohols to give carbamates in nearly quantitative yields.

$$RCB_{10}H_{10}C(CH_2)_nNCO + R'OH \xrightarrow[20^\circ]{} RCB_{10}H_{10}C(CH_2)_nNHCOOR'$$
$$R' = Me,\ CH_2C{\equiv}CH$$

Reaction of 1-isocyanato-2-phenyl-o-carborane with aniline gives the asymmetrically substituted urea

$$o\text{-}PhCB_{10}H_{10}CNCO + PhNH_2 \xrightarrow[20^\circ]{C_6H_6} o\text{-}PhCB_{10}H_{10}CNHCONHPh$$

The IR spectra of carborane carbamates and ureas contain strong CO absorption at 1720–1730 cm^{-1} in the case of carbamates, and at 1660–1670 cm^{-1} in the ureas, and NH absorption at 3260–3280 cm^{-1} in the carbamates and 3320–3340 cm^{-1} in the ureas. Propargyl carboranylcarbamates additionally show absorption for the terminal C≡CH group at 2140 and 3310 cm^{-1}.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.
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EXPERIMENTAL

The carboranecarbonyl chorides used were prepared as described in [5], and trimethylsilyl azide as described in [6]. Solvents were purified by standard methods. TLC was carried out on Silufol silica gel plates. GLC was carried out with an LKhM-8MD chromatograph with a catharometer detector, carrier gas helium, flow rate 30 ml/min, column length 2 m, diameter 3 mm, temperature 180–250°C. The stationary phase was SE–30 on Chromaton H as carrier. IR spectra were obtained on a UR–20 instrument in KBr disks.

General Method for the Preparation of Carborane Isocyanates. The carborane-carbonyl chloride (0.05 mole) and 0.07 mole of Me_3SiN_3 were boiled in 50 ml of dry toluene (or heptane or dioxane) until evolution of nitrogen had ceased completely (followed by GLC). The solvent was distilled off, and the residue distilled in vacuo or recrystallized from hexane to give 40% of 1-isocyanato-o-carborane, mp 168–170°C. Found; N 8.12% $C_3H_{11}B_{10}NO$. Calculated; N 7.56%; 1-isocyanato-2-methyl-o-carborane (52%, mp 121–122°C). Found; N 7.47% $C_4H_{13}B_{10}NO$. Calculated; N 7.03%; 1-isocyanato-2-phenyl-o-carborane (70%, mp 41–41.5°C), Found; B 41.47; N 5.02%. $C_9H_{15}B_{10}NO$. Calculated; B 41.38; N 5.36%; 1-isocyanato-2-isopropenyl-o-carborane (35%, bp 128–130°C/1 mm), Found; C 31.92; H 6.52%. $C_6H_{15}B_{10}NO$. Calculated; C 31.97; H 6.71%; 1-isocyanatomethyl-o-carborane (78%, mp 39–39.5°C), Found; C 24.41; H 6.98; N 7.02%. $C_4H_{13}B_{10}NO$. Calculated; C 24.10; H 6.57; N 7.03%; 1-isocyanato-m-carborane (51%, mp 148–150°C), Found; C 19.44; H 6.23; N 7.52%. $C_3H_{11}B_{10}NO$. Calculated; C 19.44; H 5.98; N 7.56%.

Hydrolysis of Isocyanates. To 0.01 mole of the carborane isocyanate in 20 ml of THF was added 5 ml of water at 15–20°C, and after 1 h the mixture was poured into 200 ml of water, 40 ml of ether added, and the ether layer dried over $MgSO_4$. The products were separated on a silica column, eluant benzene–hexane (1 : 1). Hydrolysis afforded: from 1-isocyanato-o-carborane, 1-amino-o-carborane, mp 299–301°C [7] and N,N'-di-(o-carboranyl)urea, mp 272°C. Found: C 17.79; H 6.70; N 7.99%. $C_5H_{24}B_{20}N_2O$. Calculated: C 17.41; H 7.02; N 8.14%: from 1-isocyanato-2-phenyl-o-carborane, 1-amino-2-phenyl-o-carborane, mp 90–91°C [7]; from 1-isocyanato-2- isopropenyl-o-carborane, N,N'-di-(isopropenyl-o-carboranyl)urea, mp 176-177°C. Found: C 31.51; H 7.77; N 6.74%. $C_{11}H_{32}B_{20}N_2O$. Calculated: C 31.19; H 7.62; N 6.62%: from 1-isocyanatomethyl-o-carborane, N,N'-di-(o-carboranylmethyl)urea, mp 226–227°C. Found: C 23.22; H 7.40; N 7.54%. $C_7H_{28}B_{20}N_2O$. Calculated: C 22.58; H 7.58; N 7.53%.

General Method for the Preparation of Carbamates. To 0.01 mole of the carborane isocyanate in 20 ml of dry THF was added at 15–20°C 0.02 mole of the alcohol, and the mixture kept for 2 h. The solvent was distilled off, and the residue crystallized from heptane or a mixture of heptane and toluene, to give methyl phenyl-o-carboranylcarbamate, mp 167°C in 90% yield. Found: C 41.26; H 6.55; B 35.74%. $C_{10}H_{19}B_{10}NO_2$. Calculated: C 40.93; H 6.53; B 36.87%. Methyl methyl-o-carboranylcarbamate, mp 121°C, yield 94%. Found: N 6.47%. $C_5H_{17}B_{10}NO_2$. Calculated: N 6.07%. Methyl-o-carboranylmethylcarbamate, mp 218–220°C, yield 90%. Found: N 6.85%. $C_5H_{17}B_{10}NO_2$. Calculated: N 6.07%. Propargyl o-carboranylcarbamate, mp 106–107°C, yield 91%. Found: C 29.91; H 5.90%. $C_6H_{15}B_{10}NO_2$. Calculated: C 29.87; H 6.27%. Propargyl phenyl-o-carboranylcarbamate, mp 131–132°C, yield 92%. Found: C 45.57; H 6.58%. $C_{12}H_{19}B_{10}NO_2$. Calculated: C 45.53; H 6.04%.

N-Phenyl-N'-(phenyl-o-carboranyl)urea. To a solution of 1.7 g of 1-isocyanato-2-phenyl-o-carborane in 10 ml of dry benzene was added 1 g of aniline, the mixture kept for 1 h, 50 ml of ether added, and the organic layer washed with dil. HCl and dried over $MgSO_4$. Removal of the solvent gave 2 g (87%) of N-phenyl-N'-(phenyl-o-carboranyl)urea, mp 203–204°C (heptane–toluene). Found: N 7.89%. $C_{15}H_{22}B_{10}N_2O$. Calculated: N 7.90%.

CONCLUSIONS

1. A preparative method has been developed for the synthesis of 1-isocyanato-carboranes, by reaction of carboranecarbonyl chlorides with trimethylsilyl azide.

2. 1-Isocyanatocarboranes display properties characteristic of aliphatic and aromatic isocyanates.

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CYCLOPALLADATION OF CARBORANE TERTIARY AMINES

V. N. Kalinin, A. V. Usatov, and L. I. Zakharkin

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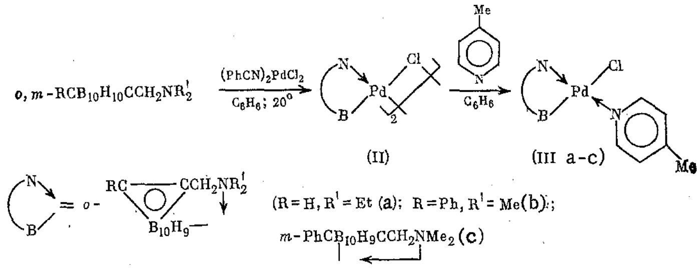
The cyclopalladation of tertiary amines has been used extensively both for the preparation of compounds with C–Pd bonds, and in organic syntheses [1]. We have examined the cyclopalladation of carborane amines for the purpose of synthesizing compounds containing σ B–Pd bonds.

It has been found that the reaction of carborane amines o, m-$RCB_{10}H_{10}CCH_2NR_2'$ (I) with $(PhCN)_2PdCl_2$ in benzene readily affords the cyclopalladized complexes (II), characterized as the monomeric compounds (III), obtained by cleaving the chlorine bridges in (II) with 4-methylpyridine



Compounds (IIIa-c) contain a five-membered chelate metallocycle with the N—C—C—B—Pd system of bonds. Since the palladium atom has the square planar configuration, the most favorable conformation for the five-membered ring is the "envelope" [2], as shown in Fig. 1.

When the metallocycle is formed, the protons of the methylene group and the methyl and ethyl groups at the nitrogen atom become diastereoisomeric (since the molecule has no elements of symmetry), as shown by the PMR spectra of these compounds (Table 1). The strong coordination of N with the Pd atom results in a shift of the Me and CH_2 (present in the ring) protons to lower field in (IIIa-c) as compared with the signals for the original amines. Such shifts are characteristic of complexes with intramolecular N→ Pd coordination [1]. Study of molecular models of (IIIa) shows that in the ethyl group on nitrogen, present in the endo-position with respect to the metallocycle (Fig. 1), rotation around the C–N bond is hindered by interactions with the bulky carborane moiety, resulting in the nonequivalence of the CH_2 protons. The PMR spectrum of (IIIa) shows two triplets for the methyl protons of the ethyl groups. These signals were assigned by homonuclear double resonance (Fig. 2, b and c). The methyl group with a signal at 1.39 ppm bonded to a CH_2 group corresponds to the multiplet at 3.6 ppm (Fig. 2b). The Me group (δ 1.55 ppm) is bonded to CH_2, which corresponds to two multiplets of nonequivalent protons. Suppression of interactions with the protons of this methyl group (Fig. 2c) enables the chemical shifts and the spin-spin coupling constant of the CH_2 protons to be measured (Table 1).

Compounds (IIIa-c) are colorless crystalline solids which are stable in air, and which decompose on heating without melting. The B–Pd bond is readily cleaved by acids.

Complexes (II) and (III) form products in which two diphenylacetylene molecules are inserted at the B–Pd bond. From (IIa) and (IIIa) are formed the derivative (IVa), which contains a five-membered metallocycle in which the Pd atom and the double bond of the butadiene moiety are intramolecularly coordinated.

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