SIMPLE METHOD FOR THE PREPARATION OF 1-AMINO-o- AND 1-AMINO-m-CARBORANES

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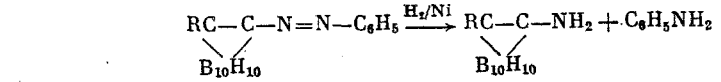
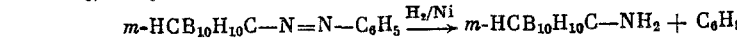
1-Amino-o- and 1-amino-m-carboranes are an interesting class of compounds, in which the amino group, in contrast to ordinary amines, is bound to a hexacoordinated carbon atom. These compounds have been obtained from the corresponding azides of carboranecarboxylic acids [1], 1-nitroso-substituted carboranes [2], and triazenes [3].

We have developed a simpler method for the preparation of 1-amino-o-, 1-amino-m-, and 1,7-bis(amino)-m-carboranes by the hydrogenation of readily available 1-benzeneazo-o-, 1-benzeneazo-m-carboranes [4], and 1,7-bis(benzeneazo)-m-carboranes.

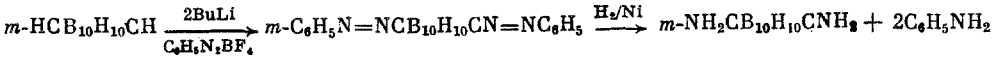


$$RC(B_{10}H_{10})C{-}N{=}N{-}C_6H_5 \xrightarrow{H_2/Ni} RC(B_{10}H_{10})C{-}NH_2 + C_6H_5NH_2$$

$R = CH_3,\ C_6H_5$



$$m\text{-}HCB_{10}H_{10}C{-}N{=}N{-}C_6H_5 \xrightarrow{H_2/Ni} m\text{-}HCB_{10}H_{10}C{-}NH_2 + C_6H_5NH_2$$



$$m\text{-}HCB_{10}H_{10}CH \xrightarrow[C_6H_5N_2BF_4]{2BuLi} m\text{-}C_6H_5N{=}NCB_{10}H_{10}CN{=}NC_6H_5 \xrightarrow{H_2/Ni} m\text{-}NH_2CB_{10}H_{10}CNH_2 + 2C_6H_5NH_2$$

The hydrogenation of 1,7-bis(benzeneazo)-m-carborane gave 1,7-bis(amino)-m-carborane, while 1,2-bis(amino)-o-carborane obtained under the same conditions from 1,2-bis(benzeneazo)-o-carborane decomposes upon separation. The presence of two amino groups at the 1,2 positions of the o-carborane system apparently leads to instability of the close structure of the o-carborane system and its decomposition, as observed for 1,2-dichloro- and 1,2-dibromo-o-carboranes [5].

EXPERIMENTAL

1-Benzeneazo-2-methyl-o-carborane, 1-benzeneazo-2-phenyl-o-carborane, and 1-benzeneazo-m-carborane were obtained according to our previous work [4].

1,2-Bis(benzeneazo)-o-carborane. A solution of 0.04 mole butyllithium in ether was added dropwise to 0.02 mole o-carborane in 20 ml abs. ether, stirred for 1 h at 0°C and, then, 0.04 mole dry phenyldiazonium tetrafluoroboride was added. The mixture was stirred for 3 h at 20°C and decomposed with water. The organic layer was dried over $CaCl_2$. The solvent was removed. The solid residue was recrystallized from hexane to give 1,2-bis(benzeneazo)-o-carborane in 65% yield, mp 110-111°C. Found, %: C 47.64, H 5.93, N 15.74. $C_{14}H_{20}B_{10}N_2$. Calculated, %: C 47.69, H 5.71, N 15.89.

Analogously, 1,7-dilithium-m-carborane gave 1,7-bis(benzeneazo)-m-carborane in 70% yield, mp 117-118°C. Found, %: C 47.73, H 5.63, N 15.80, B 30.78. $C_{14}H_{20}B_{10}N_2$. Calculated, %: C 47.69, H 5.71, N 15.89, B 30.69.

General Procedure for the Preparation of Aminocarboranes. A solution of 0.02 mole of the corresponding benzeneazocarborane derivative in 100 ml ethanol was hydrogenated over Raney nickel in an autoclave at 100°C and 75 atm hydrogen. The solution was filtered to remove the catalyst. Ethanol was evaporated off. The residue was washed with water and extracted with ether. The extract was dried over Na_2SO_4. The solvent was evaporated and the solid residue was recrystallized from hexane to give 90-95% yields of 1-methyl-2-amino-o-carborane with mp 299-301°C, 1-phenyl-2-amino-o-carborane with mp 95°C, 1-amino-m-carborane, mp 286°C, and 1,7-bis(amino)-m-carborane, mp 310-312°C [2].

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CONCLUSIONS

A simple method has been proposed for the preparation of 1-amino-o-, 1-amino-m, and 1,7-bis(amino)-m-carboranes by the hydrogenation of readily available 1-benzeneazo-o-carborane, 1-benzeneazo-m-carborane, and 1,7-bis(benzeneazo)-m-carborane over Raney nickel.

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SYNTHESIS OF S-(CARBORAN-1-YL)THIOPHOSPHATES AND S-(CARBORAN-1-YL)-THIOPHOSPHONATES

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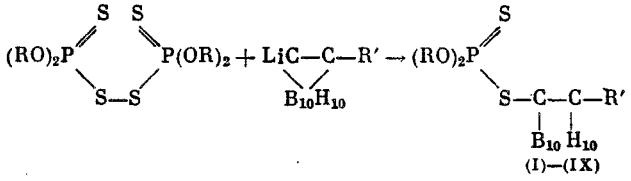
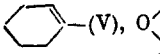
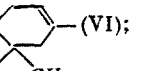
We have proposed methods for the synthesis of carboranyl esters of pentavalent phosphorus acids from phosphorus-containing propargyl esters and decaborane [1] and from the corresponding halo derivatives of pentavalent phosphorus acids and 9-mercaptocarborane [2]. In the present work, we studied the reaction of lithium carboranes with bis(thiophosphoryl)disulfides and lithium mercaptocarboranes with O-ethylmethylchlorophosphonate and thiophosphonate or O,O-diethyl-S-(β-bromoethyl)thiophosphate and the corresponding methyl thiophosphate.

The reaction of bis(dialkoxythiophosphoryl)disulfides with 1-lithium-2-substituted o-carborane in ether–benzene (in benzene for unsubstituted o- or m-lithiumcarboranes) gave the corresponding S-carboranyldithiophosphates.



(I)–(IX)

$R = C_2H_5$, $R' = o$-H (I), m-H (II), C_6H_5 (III), CH_3 (IV),  (V),  (VI);

$R = CH_3$, $R' = C_6H_5$ (VII), m-H (VIII); $R = i$-C_3H_7, $R' = C_6H_5$ (IX).

We should note that, in contrast to o-carborane, disproportionation is not found for the monolithium derivative of m-carborane with the formation of a dilithiumcarborane [3]. Thus, the reaction of equimolar amounts of the starting reagents in ether–benzene unexpectedly gave 1,2-bis(thiophosphorylmercapto)-m-carboranes (X) and (XI). In addition to (XI), the ethoxy derivative gave the corresponding trithiopyrophosphate (mp 42-44°C, δP^{31} 78.8 ppm) [4]. The formation of a similar product was confirmed spectroscopically for the methoxy derivative (δP^{31} 83.5 ppm) [4].

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