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SOME REACTIONS OF 3-AMINO-*o*-CARBORANES

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SUMMARY

1. Preparative procedure for obtaining the secondary and tertiary amines of *o*-carborane [1,2-dicarbadodecaborane(12)] series by lithium aluminum hydride reduction of their acyl derivatives has been worked out.

2. *N*-Nitroso and *N*-nitro derivatives of the secondary amines of *o*-carborane series were obtained. Cleavage of 3-(acetylnitrosoamino)-*o*-carboranes was suggested to involve formation of 3-*o*-carboranyl radical.

3. An internal salt of 3-trimethylammonium 1,2-dicarbaundecaborane(13) was prepared which could be sublimed *in vacuo*.

4. The earlier unknown *o*-carboran-3-yl isocyanates were synthesized and some of their properties investigated.

5. Carborane analogues of the Schiff's bases were prepared from 3-amino-*o*-carboranes and aldehydes and their properties investigated.

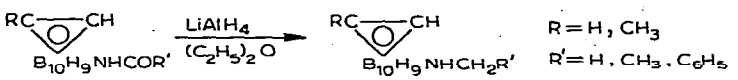
6. *o*-Carboran-3-yl isonitriles were synthesized from 3-amino-*o*-carboranes, and their possible isomerization to *o*-carboran-3-ylnitriles was discovered.

INTRODUCTION

Earlier we have reported the synthesis of 3-amino-*o*-carboranes [3-amino-1,2-dicarbadodecaboranes(12)] and studied some of their properties[1]. The present paper is concerned with investigation of the chemical behaviour of the secondary and tertiary amines of *o*-carborane [1,2-dicarbadodecaborane(12)] series, and with some novel reactions of 3-amino-*o*-carboranes.

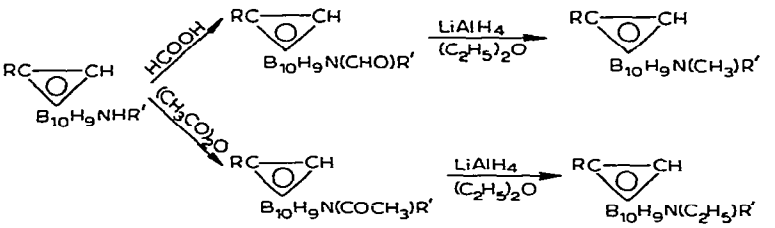
RESULTS AND DISCUSSION

We found it most convenient to obtain 3-(alkylamino)-*o*-carboranes via an almost quantitative lithium aluminum hydride reduction of 3-(acylamino)-*o*-car-



Thus, 3-(formylamino)-, (3-acetylamino)- and 3-(benzoylamino)-*o*-carboranes gave 3-(methylamino)-, 3-(ethylamino)- and 3-(benzylamino)-*o*-carboranes.

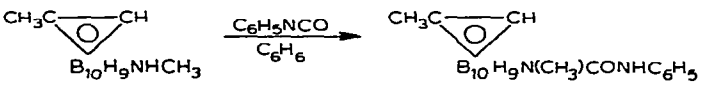
Secondary amines in turn smoothly form the acylated secondary amines of carborane series which were reduced with lithium aluminum hydride to 3-(dialkylamino)-*o*-carboranes:



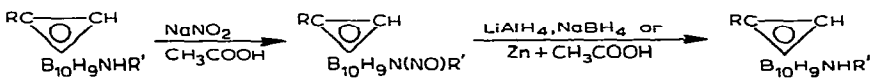
$R=H, CH_3$; $R'=CH_3, C_2H_5$

Both secondary and tertiary amines are substantially basic to give salts with acids. Thus chlorohydrates were quantitatively obtained by bubbling hydrogen chloride through a benzene solution of the corresponding amines.

Secondary amines of *o*-carborane series smoothly react with phenyl isocyanate in benzene to give unsymmetric urea derivatives:

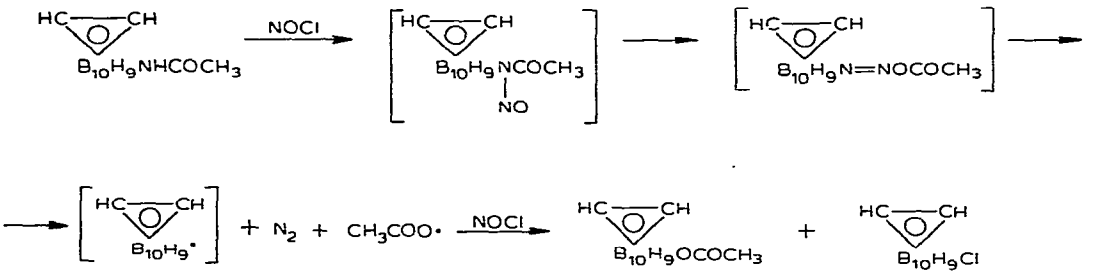


Secondary amino-*o*-carboranes may readily enter the nitrosation reaction with sodium nitrate in acetic acid affording stable *N*-nitroso derivatives. The attempts to reduce 3-(alkylnitrosoamino)-*o*-carboranes with $LiAlH_4$, $NaBH_4$, or Zn in CH_3COOH to the corresponding disubstituted hydrazines of carborane series failed because of a ready cleavage of the N–N bond leading to the initial amine:

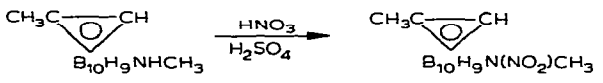


$R=H, CH_3$; $R'=CH_3, C_2H_5, CH_2C_6H_5$

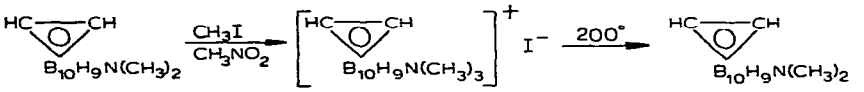
Unlike stable (alkylnitrosoamino)carboranes, (acylnitrosoamino)carboranes were shown to be unstable. On their synthesis from 3-(acylamino)carboranes in an excess of nitrosyl chloride in the mixture of acetic acid and acetic anhydride in the presence of sodium acetate they decomposed *in statu nascendi*, with the evolution of nitrogen giving 3-acetoxy- and 3-chlorocarboranes. Formation of the two latter compounds allows to suggest that (acylnitrosoamino)carboranes may probably decompose analogously to acetylarylnitrosoamines[2], with a rearrangement into diazoacetate and its radical decomposition. Decomposition product, 3-carboranyl radical, reacts with acetoxyradical to give 3-acetoxycarboranes, and in an excess of nitrosyl chloride it splits chlorine producing 3-chlorocarborane.



Secondary amino-*o*-carboranes enter the nitration reaction giving 3-(alkylnitroamino)-*o*-carboranes:

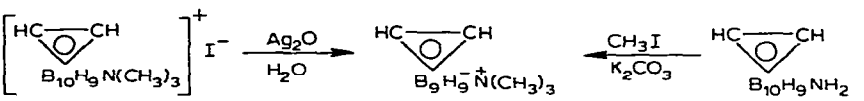


Action of methyl iodide on 3-(dimethylamino)-*o*-carborane in nitromethane results in the quarternary salt, trimethyl(*o*-carboran-3-yl)ammonium iodide. Thermal cleavage of this compound provides the starting tertiary amine alone:



Such a course of thermal cleavage of quarternary salt testifies a significant strength of the B–N bond in the salt as compared to that of C–N bond.

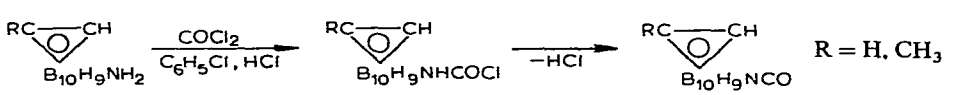
Preparation of trimethyl(*o*-carboran-3-yl)ammonium hydroxide by the treatment of trimethyl(*o*-carboran-3-yl)ammonium iodide with moist silver oxide involves fission of the carborane nucleus to 1,2-dicarbaundecaborane(13) anion with the formation of an internal salt (I). Probably, the strong electron-withdrawing effect of the trimethylammonium grouping occupying the position 3 of *o*-carborane nucleus may considerably decrease the stability of *o*-carborane nucleus towards bases. Therefore, as we have shown earlier[1] the tertiary amines of 3-carborane series are obtained in poor yield through the direct alkylation of 3-amino-*o*-carboranes with alkyl halides or dialkyl sulfates in the presence of potassium carbonate, an internal salt of 1,2-dicarbaundecaborane(13) being the major product (I):



(I)

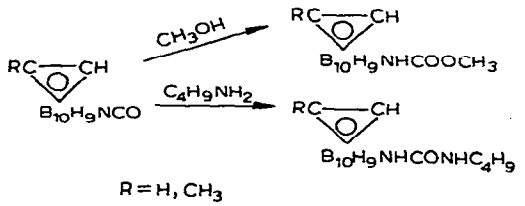
Interesting property of the internal salt of 1,2-dicarbaundecaborane(13) is its ability to sublime *in vacuo* without decomposition.

Passing carbonyl chloride through a boiling chlorobenzene solution of 3-amino-*o*-carborane gives *o*-carboran-3-yl isocyanate:

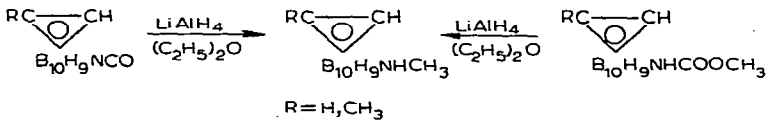


There was yet no information on the compounds with isocyanate group adjacent to the boron atom.

o-Carboran-3-yl isocyanates exhibit properties characteristic of both aliphatic and aromatic isocyanates. Thus they react readily with alcohols and amines giving respectively urethanes and unsymmetrical urea derivatives:

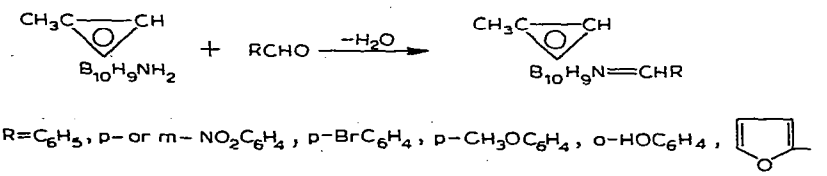


Reduction of *o*-carboran-3-yl isocyanate with lithium aluminum hydride in ether gives 3-(methylamino)-*o*-carborane, which can also be obtained by the action of lithium aluminum hydride on methyl ester of *N*-(*o*-carboran-3-yl)carbamic acid:

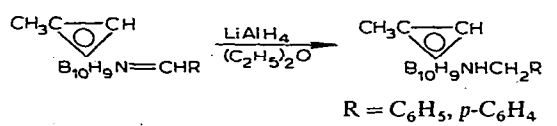


It should be noted that *o*-carboran-3-yl isocyanates do not hydrolyze even on long storage under moist atmosphere.

We found that similar to other aliphatic and aromatic amines, 3-amino-*o*-carboranes enter the condensation reactions with aromatic aldehydes giving analogues of Schiff's bases with a direct B–N bond. All the syntheses associated with the preparation of azomethines of the carborane series were conducted using 1-methyl-3-amino-*o*-carborane as example.

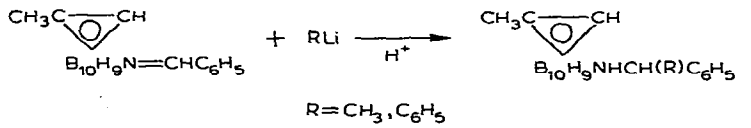


The *o*-carborane Schiff's bases obtained can easily be reduced with lithium aluminum hydride in ether to the respective (alkylamino)-*o*-carboranes.



This reaction provides a convenient route to (monoalkylamino)-*o*-carboranes.

The *o*-carborane Schiff bases react readily with the organolithium compounds at the nitrogen–carbon double bond (affording adducts). On subsequent hydrolysis the latter are converted to 3-(alkylamino)-*o*-carboranes:

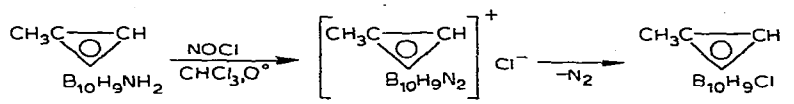


This procedure can readily give [(diphenylmethyl)amino]-*o*-carborane derivative.

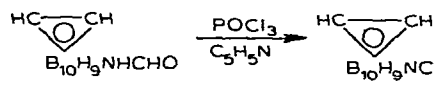
The *o*-carborane Schiff bases easily cleave to the starting 3-amino-*o*-carborane and aldehyde during chromatography on alumina which in general was found to be an effective catalyst of azomethine hydrolysis[3].

Nitrosyl chloride readily reacts with the carborane Schiff bases in inert media producing the salt, *o*-carboran-3-yldiazonium chloride unstable at 0°, decomposing to 3-chloro-*o*-carborane with the evolution of nitrogen.

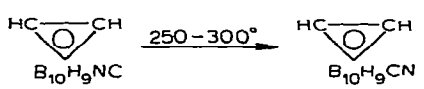
It should be pointed out that 3-amino-*o*-carboranes themselves easily react with nitrosyl chloride leading to 3-chloro-*o*-carboranes:



Analogously to other aliphatic and aromatic amines the 3-amino-*o*-carborane *N*-formyl derivatives react with phosphonyl chloride producing *o*-carboran-3-ylisonitriles.



At 250–300° *o*-carboran-3-ylisonitriles rearrange to the respective *o*-carboran-3-ylnitriles:



The last reaction is the first example of a carboranyl group migration with transition from B–N to to B–C bond. This reaction may provide possible route to synthesize various 3-substituted *o*-carboranes from readily available 3-amino-*o*-carboranes. All the compounds obtained in this work are listed in Tables 1–3.

EXPERIMENTAL

General procedure for the preparation of 3-(alkylamino)- and 3-(dialkylamino)-o-carboranes

A solution of 0.01 mole of 3-(acylamino)- or 3-(alkylacylamino)-*o*-carborane in ether was added with stirring at 20° to 0.012 *M* of $LiAlH_4$ in ether. The mixture was stirred and refluxed for 1 h and finally decomposed with water. The ethereal layer was dried over $MgSO_4$. The residue obtained (after evaporation) of ether was crystallized from pentane. Liquid secondary amines were distilled *in vacuo*. (Alkylamino)carboranes obtained are listed in Table 1 along with 3-(alkylacylamino)-*o*-carboranes and chlorohydrates of the secondary and tertiary *o*-carborane amines.

TABLE 1

N-SUBSTITUTED 3-AMINO-*o*-CARBORANES

Compound	M.p. (°C)	Brutto formula	Analysis found (calcd.) (%)			
			C	H	B	N
3-(Methylamino)-*o*-carborane	36–37	$C_3H_{15}B_{10}N$	20.84 (20.78)	8.77 (8.70)	62.41 (62.40)	8.12 (8.08)
1-Methyl-3-(methylamino)-*o*-carborane	39–40	$C_4H_{17}B_{10}N$	25.43 (25.65)	9.00 (9.14)	57.86 (57.75)	7.55 (7.47)
3-(Ethylamino)-*o*-carborane[a]		$C_4H_{17}B_{10}N$	25.91 (25.65)	9.12 (9.14)	57.79 (57.75)	8.08 (7.47)
1-Methyl-3-(ethylamino)-*o*-carborane[b]		$C_5H_{19}B_{10}N$	29.73 (29.83)	9.45 (9.49)	53.80 (53.72)	6.95 (6.95)
3-(Benzylamino)-*o*-carborane	49–50	$C_9H_{19}B_{10}N$	43.31 (43.30)	7.67 (7.67)	43.51 (43.34)	5.45 (5.61)
1-Methyl-3-[(*p*-bromobenzyl) amino]-*o*-carborane[c]	77–79	$C_{10}H_{20}B_{10}NBr$	34.95 (35.03)	5.84 (5.86)		
1-Methyl-3-[(α-ethylphenyl)amino]-*o*-carborane	61–63	$C_{11}H_{23}B_{10}N$	46.95 (47.63)	8.92 (8.36)	39.05 (39.00)	
1-Methyl-3-[diphenylmethyl)-amino]-*o*-carborane	72–73	$C_{16}H_{25}B_{10}N$	56.71 (56.72)	7.48 (7.42)	32.13 (31.93)	4.00 (4.14)
3-(Methylformylamino)-*o*-carborane	80–81	$C_4H_{15}B_{10}NO$	24.23 (23.89)	7.54 (7.51)	54.25 (53.79)	6.52 (6.97)
1-Methyl-3-(methylformylamino)-*o*-carborane	77.5–78.5	$C_5H_{17}B_{10}NO$	28.09 (27.92)	7.92 (7.97)	50.40 (50.04)	6.41 (6.51)
3-(Ethylacetylamino)-*o*-carborane	119.5–120	$C_6H_{19}B_{10}NO$	31.66 (31.42)	7.81 (8.35)	46.88 (47.21)	6.29 (6.12)
1-Methyl-3-(ethylamino)-*o*-carborane chlorohydrate[d]	228–231	$C_5H_{20}B_{10}NCl$				6.08 (5.89)
3-(Benzylamino)-*o*-carborane chlorohydrate	232–235	$C_9H_{20}B_{10}NCl$				5.33 (4.91)
1-Methyl-3-[(α-ethylphenyl)-amino]-*o*-carborane chlorohydrate[e]	229–231	$C_{11}H_{24}B_{10}NCl$				4.19 (4.46)
3-(Dimethylamino)-*o*-carborane chlorohydrate[f]	199–201	$C_6H_{22}B_{10}NCl$				5.68 (5.56)
3-(Methylnitrosoamino)-*o*-carborane	81–82	$C_3H_{14}B_{10}N_2O$	17.74 (17.83)	6.80 (6.97)	53.59 (53.46)	14.04 (13.86)
1-Methyl-3-(methylnitrosoamino)-*o*-carborane	53–54	$C_4H_{16}B_{10}N_2O$	22.37 (22.25)	7.48 (7.44)	49.83 (49.99)	12.74 (12.95)
3-(Ethylnitrosoamino)-*o*-carborane	82–83	$C_4H_{16}B_{10}N_2O$	22.30 (22.25)	7.36 (7.44)	49.73 (49.99)	12.95 (12.95)
1-Methyl-3-(ethylnitrosoamino)-*o*-carborane	63–64	$C_5H_{18}B_{10}N_2O$	26.08 (26.08)	7.89 (7.87)	47.04 (46.92)	12.50 (12.14)
3-(Benzylnitrosoamino)-*o*-carborane	96–97	$C_9H_{18}B_{10}N_2O$	38.76 (38.80)	6.42 (6.51)	38.59 (38.83)	10.09 (10.01)

TABLE 1 (*continued*)

Compound	M.p. (°C)	Brutto formula	Analysis found (calcd.) (%)			
			C	H	B	N
1-Methyl-3-(benzylnitroso-amino)-*o*-carborane	97–98	$C_{10}H_{20}B_{10}N_2O$			37.01 (36.99)	9.58 (9.59)
1-Methyl-3-(benzylamino)-*o*-carborane	41–42	$C_{10}H_{21}B_{10}N$	46.66 (46.02)	8.43 (8.03)	41.22 (41.01)	5.42 (5.32)

[a] B.p. 128–130 (2 mm), n_D^{20} 1.5558. [b] B.p. 136–138 (2 mm), n_D^{20} 1.5459. [c] Found: Br, 23.01; calcd.: Br, 23.30%. [d] Found: Cl, 15.48; calcd.: Cl, 14.96%. [e] Found: Cl, 11.41; calcd.: Cl, 11.30%. [f] Found: Cl, 14.13; calcd.: Cl, 14.07%.

N-Phenyl-N'-methyl-N'-(1-methyl-o-carboran-3-yl) urea

1.9 g of 1-methyl-3-(methylamino)-*o*-carborane was refluxed for 6 h with 1.2 g of phenyl isocyanate in 20 ml of benzene. After evaporation of benzene, 2.1 g (68%) of *N*-phenyl-*N'*-methyl-*N'*-(1-methyl-*o*-carboran-3-yl)urea was obtained. M.p. 137–138° (heptane). (Found: C, 43.15; H, 7.18; B, 35.15; N, 9.58. $C_{11}H_{22}B_{10}N_2O$ calcd.: C, 43.20; H, 7.22; B, 35.32; N, 9.15%.)

General procedure for the preparation of 3-(alkylnitrosoamino)-o-carboranes

0.012 mole of $NaNO_2$ in 2 ml of water was added at 10° to a solution of 0.01 mole of 3-(alkylamino)-*o*-carborane in 20 ml of acetic acid. The mixture was stirred for 1 h at 20°, poured in water and extracted with ether. The ethereal extracts were washed with bicarbonate solution, water and dried over $MgSO_4$. After evaporation of the solvent the residue was crystallized from pentane. (Alkylnitrosoamino)-*o*-carboranes prepared are listed in Table 1. 3-(Nitrosoalkylamino)-*o*-carboranes show characteristic absorption within 1400–1430 cm^{-1} assigned to the N–NO stretching band.

3-(Methylnitroamino)-1-methyl-o-carborane

3 ml of nitric acid (d = 1.51) was slowly added at 10° to 0.5 g of 1-methyl-3-(methylamino)-*o*-carborane in 20 ml of sulfuric acid. The mixture was stirred for 5 h at 20° and poured on ice. Aqueous layer was extracted with benzene and the extracts dried over $MgSO_4$. After evaporation of the solvent 0.18 g of 1-methyl-3-(methylnitroamino)-*o*-carborane was obtained, m.p. 49–50° (pentane). (Found: N, 12.07. $C_4H_{16}B_{10}N_2O_2$ calcd.: N, 12.04%.)

Reaction of 3-(N-acylamino)-o-carboranes with nitrosyl chloride

1 g of nitrosyl chloride in 3 ml of acetic anhydride was added at 0° to 2 g of 3-(acetylamino)-*o*-carborane in a mixture of 25 ml of acetic acid, 10 ml of acetic anhydride, 1 g of sodium acetate and 0.1 g of phosphorus pentoxide. The mixture was stirred for 1 h at 20°, poured in water and extracted with benzene. The benzene extracts were washed with bicarbonate solution, water and dried over $MgSO_4$. After evaporation of the solvent, 3-acetoxy-*o*-carborane (57%) and 3-chloro-*o*-carborane (43%) were identified in the residue by GLC analysis.

Trimethyl(o-carboran-3-yl)ammonium iodide

5 ml of methyl iodide was added to a solution of 1.9 g of 3-(dimethylamino)-*o*-carborane in 20 ml of nitromethane and the mixture was refluxed for 2 h. 1.85 g (56°) of trimethyl(*o*-carboran-3-yl)ammonium iodide was obtained. M.p. 170.5–171.5° (ether/methanol). (Found: C, 18.08; H, 6.22; B, 32.61; N, 4.31. $C_5H_{20}B_{10}NI$ calcd.: C, 18.24; H, 6.12; B, 32.88; N, 4.26%.)

Internal salt of trimethylammonium 1,2-dicarbaundecaborane(13)

To a solution of 3.3 g of trimethyl(*o*-carboran-3-yl)ammonium iodide in 20 ml of methanol a suspension of Ag_2O in water was added. After stirring for 2 h at 20° the residue was filtered off and the filtrate evaporated. 1.13 g (59%) of internal salt of trimethylammonium 1,2-dicarbaundecaborane(13) was obtained. M.p. 306–309° (ether/methanol). (Found: C, 31.06; H, 10.41; B, 50.43; N, 7.55. $C_5H_{20}B_9N$ calcd.: C, 31.39; H, 10.52; B, 50.80; N, 7.32%.)

General procedure for preparation of o-carboran-3-yl isocyanates

A solution of 0.01 mole of 3 amino-*o*-carborane in 50 ml of chlorobenzene was saturated with dry gaseous HCl at 70°. Then at boiling temperature phosgene was passed until the formation of a transparent solution. After evaporation of chlorobenzene the residue was crystallized from hexane. *o*-Carboran-3-yl isocyanates obtained are listed in Table 2. *o*-Carboran-3-yl isocyanates show characteristic absorption within the region 2310–2325 cm^{-1} assigned to the NCO stretching vibrations.

TABLE 2

DERIVATIVES OF 3-AMINO-*o*-CARBORANES

Compound	M.p. (°C)	Brutto formula	Analysis found (calcd)(%)			
			C	H	B	N
o-Carboran-3-yl isocyanate	114.5–115.5	$C_3H_{11}B_{10}NO$	19.83 (19.45)	6.08 (5.98)	58.54 (58.43)	7.55 (7.56)
(1-Methyl-*o*-carboran-3-yl) isocyanate	95–97	$C_4H_{13}B_{10}NO$	28.84 (24.19)	6.74 (6.58)	53.85 (54.25)	7.16 (7.03)
Methyl ester of *o*-carboran-3-ylcarbamic acid	117–118	$C_4H_{15}B_{10}NO_2$				6.20 (6.44)
Methyl ester of (1-methyl-*o*-carboran-3-yl)carbamic acid	113–114	$C_5H_{17}B_{10}NO_2$				5.82 (6.06)
N-Butyl-*N'*-(*o*-carboran-3-yl)urea	183–184	$C_7H_{22}B_{10}N_2O$				10.57 (10.82)
N-Butyl-*N'*-(1-methyl-*o*-carboran-3-yl)-urea	185–186	$C_8H_{24}B_{10}N_2O$	36.03 (35.25)	9.29 (8.88)	39.71 (39.71)	10.31 (10.06)

General procedure for preparation of methyl esters of N-(o-carboran-3-yl)carbamic acid

5 ml of methanol was added to a solution of 0.01 mole of *o*-carboran-3-yl isocyanate in 20 ml of benzene and the mixture was heated for 2 h. After evaporation of benzene the residue was crystallized from hexane. Methyl esters of *N*-(*o*-carboran-3-yl)carbamic acid obtained are listed in Table 2.

General procedure for preparation of N-butyl-N'-(o-carboran-3-yl)urea

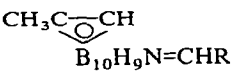
0.01 mole of butylamine in 5 ml of benzene was added to a solution of 0.01 mole of *o*-carboran-3-yl isocyanate in 20 ml of benzene and the mixture kept for 2 h. After evaporation of benzene the residue was crystallized from heptane/chlorobenzene. *N*-Butyl-*N'*-(*o*-carboran-3-yl)ureas obtained are listed in Table 2.

General procedure for preparation of Schiff's bases from 1-methyl-3-amino-o-carborane and aromatic aldehydes

A solution of 0.012 mole of a respective aromatic aldehyde in 10 ml of methylene chloride was added to 0.01 mole of 1-methyl-3-amino-*o*-carborane in 20 ml of methylene chloride. The solution was left for 2 h at 20°. After evaporation of methylene chloride the residue was crystallized from hexane. The *o*-carborane analogues of the Schiff bases obtained are shown in Table 3. The Schiff bases show absorption bands within 1630–1665 cm^{-1} assigned to the C=N stretching vibrations.

TABLE 3

o-CARBORAN-3-YL ANALOGUES OF SCHIFF'S BASES



R	M.p. (°C)	Brutto formula	Analysis found (calcd.) (%)			
			C	H	B	N
C_6H_5	91–92	$C_{10}H_{19}B_{10}N$	45.73 (46.30)	7.37 (7.34)	41.21 (41.40)	5.32 (5.37)
p-$NO_2C_6H_4$	192–194	$C_{10}H_{18}B_{10}N_2O$	39.61 (39.92)	5.86 (5.92)	34.69 (35.35)	8.93 (9.15)
m-$NO_2C_6H_4$	104–105	$C_{10}H_{18}B_{10}N_2O$	39.77 (39.92)	6.05 (5.92)	35.04 (35.35)	9.04 (9.15)
p-BrC_6H_4[a]	75–76.5	$C_{10}H_{18}B_{10}NBr$	35.65 (35.30)	5.96 (5.34)		4.11 (4.11)
o-HOC_6H_4	142–143	$C_{10}H_{19}B_{10}NO$	43.96 (43.60)	7.02 (6.90)	39.30 (39.00)	5.08 (5.06)
p-$CH_3OC_6H_4$	70.5–72	$C_{11}H_{21}B_{10}NO$	45.06 (45.50)	7.23 (7.25)	37.35 (37.20)	4.63 (4.82)
	92–93.5	$C_8H_{17}B_{10}NO$	38.34 (38.39)	6.64 (6.82)	43.14 (43.20)	5.76 (5.59)

[a] Found: Br, 23.50; calcd.: Br, 23.42%.

Interaction of 1-methyl-3-(benzylideneamino)-o-carborane with organolithium compounds

A four-fold excess of organolithium compound in ether was added to a solution of 0.01 mole of 1-methyl-3-(benzylideneamino)-*o*-carborane in 30 ml of ether at 20°. The mixture was refluxed for 1 h. After decomposing with water the ethereal layer was dried over $MgSO_4$. After evaporation of the solvent the residue was crystallized from hexane; 3-(alkylamino)-*o*-carboranes obtained are listed in Table 1.

Reaction of 1-methyl-3-(benzylideneamino)-o-carborane with nitrosyl chloride

A solution of 1 g of nitrosyl chloride in 5 ml of ether was added at 0° to 2.6 g

of 1-methyl-3-(benzylideneamino)-*o*-carborane in 30 ml of ether. The mixture was stirred at 20° for 1 h, poured in water and the ethereal layer dried over $MgSO_4$. After evaporation of the solvent 0.56 g (29%) of 1-methyl-3-chloro-*o*-carborane was obtained.

Reaction of 1-methyl-3-amino-o-carborane with nitrosyl chloride

A solution of 1.5 g of nitrosyl chloride in 5 ml of chloroform was added at 0° to 1.7 g of 1-methyl-3-amino-*o*-carborane in 30 ml of chloroform. The mixture was stirred at 20° for 1 h, poured in water and the organic layer dried over $MgSO_4$. After evaporation of the solvent 1.7 g (88%) of 1-methyl-3-chloro-*o*-carborane was obtained.

3-Isocyano-o-carborane

A solution of 1.6 g of freshly distilled phosphonyl chloride in 10 ml of chloroform was added at 5° to 1.9 g of 3-(formylamino)-*o*-carborane in 25 ml of pyridine. The mixture was stirred at 40° for 2 h, poured in water and the chloroform layer acidified with aqueous hydrochloric acid solution and then treated with a solution of phosphoric acid and dried over $MgSO_4$. After the evaporation of chloroform, 0.78 g (46%) of 3-isocyano-*o*-carborane was obtained. M.p. 140° (decompn.)(hexane). (Found: C, 21.67; H, 6.40; B, 63.74; N, 8.33. $C_3H_{11}B_{10}N$ calcd.: C, 21.30; H, 6.56; B, 64.05; N, 8.28%.) ν(NC) 2140 cm^{-1}.

3-Cyano-o-carborane

1.7 g of 3-isocyano-*o*-carborane was heated in a sealed ampule at 250–300° for 3 h. The reaction mixture was sublimed *in vacuo*. 0.66 g (39%) of 3-cyano-*o*-carborane was obtained, m.p. 221–222.5° (heptane). (Found: C, 21.34; H, 6.57; B, 63.82; N, 8.50. $C_3H_{10}B_{10}N$ calcd.: C, 21.30; H, 6.56; B, 64.05; N, 8.28%.)

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