SYNTHESIS OF NEW CARBORANE-CONTAINING KETONES. NOVEL DEHYDROCYANATION REACTION INVOLVING BORON HYDRIDES

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Abstract

A novel dehydrocyanation reaction involving boron hydrides is described. This reaction has been applied to the synthesis of new boronated ketones: di(*o*-carboran-1-ylmethyl)ketone (**8a**) and (*o*-carboran-1-ylmethyl)benzylketone (**8b**). The stepwise alkylation of commercially-available N-(diphenylmethylene)aminoacetonitrile yielded α,α-disubstituted-[N-(diphenylmethylene)]aminoacetonitriles, **4**, which, when reacted with decaborane-acetonitrile complex, undergoes the elimination of hydrogen cyanide. The acid hydrolysis of these dehydrocyanation products, **3**, afforded the corresponding ketones, **8**.

Introduction

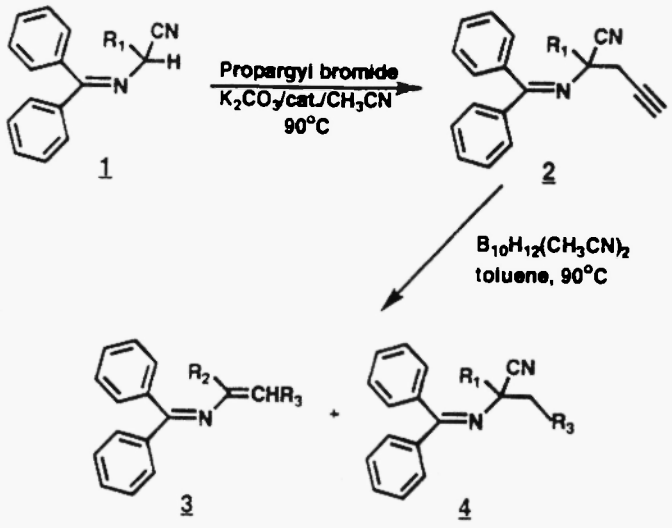
Generally, the better leaving groups in organic structures are those that are the conjugate bases of strong acids. By that criterion alone, the cyano would be considered to be a very poor leaving group (pKa of HCN is 9.22). However, there are examples of dehydrocyanation reactions involving alkylated α-aminonitriles.[1-5] Usually, these involve the use of strong bases, elevated temperatures or a combination of both, with the generation of substituted enamines.

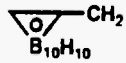
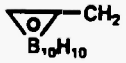
During the course of synthesizing a series of carborane-containing amino acids,[6] we observed a novel dehydrocyanation reaction that occurred in the preparation of carboranes derived from α,α-disubstituted-[N-(diphenylmethylene)]aminoacetonitriles. In this paper, we have explored the generality of this novel elimination reaction and a possible mechanism by which the cyano function has become activated and thereby has been transformed into a leaving group.

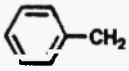
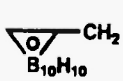
Results and Discussion

In a previous paper,[6] the synthesis of *o*-carboranylalanine is described that involved phase transfer alkylation, boronation and hydrolysis of N-(diphenylmethylene)aminoacetonitrile. The sole product in high yield was the expected amino acid. When the same procedure was applied to the synthesis of α,α-di(*o*-carboran-1-ylmethyl)glycine, a second product was obtained, in the boronation reaction, which was unexpected. Alkylation of 3-(*o*-carboranyl-1-yl)-2-[N-(diphenylmethylene)]aminopropionitrile, **1a**, with propargyl bromide yielded the desired compound **2a** (**Scheme 1**). Boronation of **2a** with bis-acetonitrile-decaborane furnished **4a** but in addition a second product **3a**. As the reaction progressed the amount of **3a** increased at the expense of **4a**. Structure determination of both products showed **3a** to be 1,3-di(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]amino-prop-1-ene and **4a** to be 2-(*o*-carboran-1-ylmethyl)-3-(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]aminopropionitrile. Therefore compound **3a** was the product of an unusual dehydrocyanation of **4a**. The same dehydrocyanation was observed for the boronation of 3-phenyl-2-(prop-1-ynyl)-2-[N-(diphenylmethylene)]-aminopropionitrile (**2b**) with decaborane-acetonitrile complex. The formation of two products: **3b** (product of boronation-dehydrocyanation) and **4b** (product of boronation) was detected and their structures were confirmed by HR MS, ^{1}H and ^{13}C NMR spectra. It is noteworthy that the extended time of boronation yielded only **3a** or **3b**. respectively.

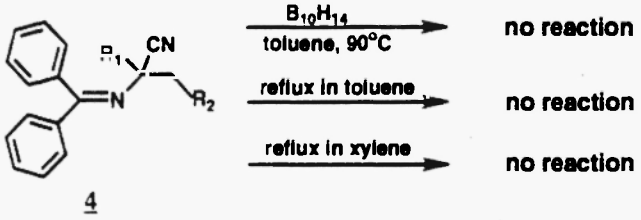
Scheme 1

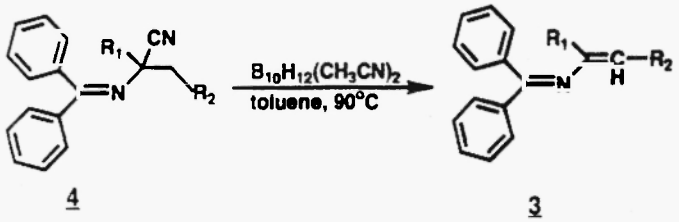


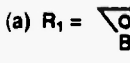
(a) R_1 =  , R_2 =  , R_3 = 

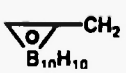
(b) R_1 =  , R_2 =  , R_3 = 

Scheme 2



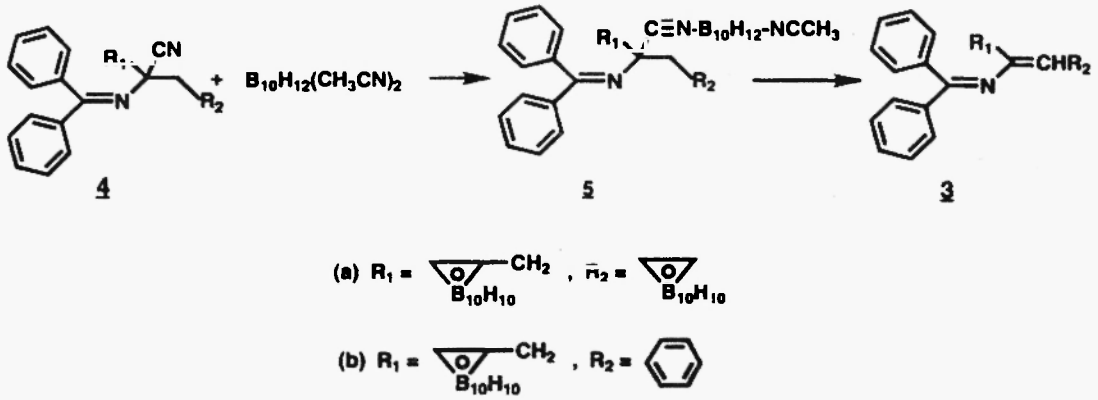


(a) R_1 =  , R_2 = 

(b) R_1 =  , R_2 = 

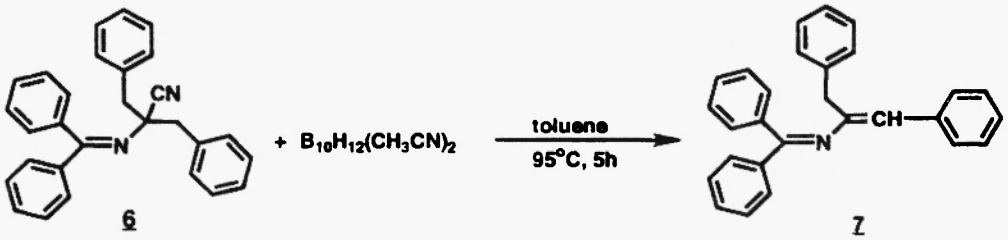
To determine what causes the elimination of hydrogen cyanide, the compounds **4a** and 4b (independently) were refluxed in either toluene, or xylene but there were no changes in **4a** or **4b**. Similarly, refluxing **4a**, and **4b**, in the presence of decaborane likewise produced no changes. However, in the presence of decaborane-acetonitrile complex dehydrocyanation occurred (**Scheme 2**). Compounds **4a** and **4b** were transformed to **3a** and **3b** (respectively).

Scheme 3



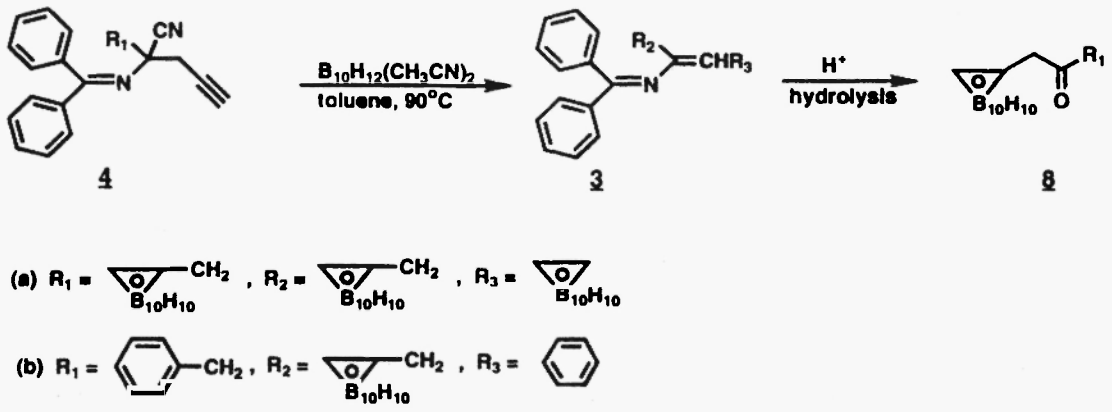
Scheme 3 describes the proposed mechanism for this unusual dehydrocyanation. Since it has been shown[7,8] that the $B_{10}H_{12}$ unit of decaborane-acetonitrile complex $[B_{10}H_{12}(CH_3CN)_2]$ can be transferred from one ligand to another, we suggest the displacement reaction between bis-acetonitrile-decaborane and compound **4** is the first step in this elimination reaction. The formation of the intermediate **5** or the intermediate, in which both acetonitrile molecules of the decaborane complex are exchanged with a molecule **4**, activates the cyano group and prompts its elimination. The loss of a β-hydrogen results in the formation of the compounds **3**. Furthermore, the possible driving force for the dehydrocyanation is provided by an increase in resonance stabilization (the conjugated system formation) and a reduction in steric strain. To determine whether this phenomenon is characteristic only for carborane-containing α,α-disubstituted-[N-(diphenylmethylene)]-aminoacetonitriles we investigated the reaction of α,α-dibenzylsubstituted derivative **6** with decaborane-acetonitrile complex. 2-Benzyl-3-phenyl-2-[N-(diphenylmethylene)]-aminopropionitrile (**6**) was prepared by the stepwise alkylation of N-(diphenylmethylene)aminoacetonitrile [**Scheme 1**: **1** (R= H)] with benzyl bromide. The reaction of **6** with $B_{10}H_{12}(CH_3CN)_2$ in refluxing toluene for 5h afforded 1,3-diphenyl-2-N-[(diphenylmethylene)]amino-prop-1-ene (**7**), the product of a dehydrocyanation reaction (**Scheme 4**).

Scheme 4



These results indicate that dehydrocyanation is a general reaction for any α,α-disubstituted-[N-(diphenylmethylene)]aminoacetonitriles having a hydrogen in the β-position that can undergo the elimination of hydrogen cyanide when the cyano group is activated by the decaborane-acetonitrile complex in boiling toluene. Furthermore, the products of dehydrocyanation are suitable substrates for the synthesis of ketones. Acid hydrolysis of compounds **3a** and **3b** afforded two novel carborane-containing ketones: di(*o*-carboran-1-ylmethyl)ketone (**8a**) and (*o*-carboran-1-ylmethyl)benzylketone (**8b**) (**Scheme 5**).

Scheme 5



In the conclusion, we have discovered a novel dehydrocyanation reaction which has been applied to the synthesis of new boronated ketones (**Scheme 5**). The stepwise alkylation of commercially-available N-(diphenylmethylene)aminoacetonitrile yielded α,α-disubstituted-[N-(diphenylmethylene)]aminoacetonitriles, **4**, which, when reacted with decaborane-acetonitrile complex, undergoes the elimination of hydrogen cyanide. The acid hydrolysis of these dehydrocyanation products, **3**, afforded the corresponding ketones, **8**.

Experimental Section

FT-NMR spectra (proton and carbon) were obtained at The Ohio State University Chemical Instrument Center using a Bruker AM500 (carbon and proton) and in College of Pharmacy OSU using Bruker AC250 (proton spectra). Chemical shifts (δ) are reported in ppm downfield from an internal tetramethylsilane standard. Coupling constants (J) are reported in Hz. IR spectra were recorded on a RFX 40 FT-IR spectrometer (Laser Precision Corp.). The spectra were in accordance with the proposed structures. Melting points were determined on a Fisher-Johns melting point apparatus and are reported uncorrected. Mass spectra were obtained at The Ohio State University Chemical Instrument Center on Finnigan MAT-900 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN and Atlantic Microlab, Inc., Norcross, GA. Silica gel 60-F254 glass plates (Merck) were used for TLC. Compound visualization was achieved with UV light (254 nm), iodine, and spraying with 0.06% $PdCl_2$ / % HCl (boron) and subsequent heating at 120°C for 10-15 min. Silica gel 60 (70-230 mesh ASTM - Merck) was used for column chromathography. Reagent-grade solvents were used for reactions and chromatography. Toluene was distilled from sodium.

3-(o-Carboran-1-yl)-2-(prop-1-ynyl)-2-[N-(diphenylmethylene)]aminopropionitrile (2a). To a solution of 3.67 g of 3-(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]amino-propionitrile (**1a**) in 130 mL of dry acetonitrile were added 7.06 g of anhydrous potassium carbonate, 0.95 g of tetra-n-butytammonium bromide. A 2 mL of propargyl bromide was added dropwise to the solution refluxed (75°C) under argon for 3 h. The reaction mixture was carefully monitored by TLC (hexanes/ethyl acetate, 6:1, v/v). The reaction mixture was cooled to room temperature and filtered to remove the solid which was washed with dichloromethane. The filtrate and washings were combined and concentrated. The remaining residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v) and crystallization from hexanes/ethyl acetate (6/1, v/v) solution. **2a**: yield 3.2 g (79.2%) of colorless crystals. R_f = 0.2 (hexanes/ethyl acetate, 6:1, v/v); mp 182-183°C; MS (FAB$^+$, 3-NBA) 415 (M + H)$^+$; ^{1}H-NMR ($CDCl_3$) δ 1.5 - 3.3 (br m, 10H, B-H), 2.24 (t, 1H, HC≡C-CH_2-, $J_{1,3}$propynyl = 2.65), 2.73 (d, 2H, HC≡C-CH_2-), 3.15, 3.31 (dd, 2H, carborane-CH_2-, J = 15.3), 4.06 (br s, 1H, HC-$B_{10}H_{10}$-C-), 7.26 - 7.60 (m, 10H, aromat.); Anal. Calcd for $C_{21}H_{26}N_2B_{10}$: C, 60.84; H, 6.32; N, 6.76. Found: C, 60.89; H, 6.51; N, 6.95.

1,3-Di(o-carboran-1-yl)-2-[N-(diphenylmethylene)]amino-prop-1-ene (3a) and 2-(o-carboran-1-ylmethyl)-3-(*o*-carboran-1-yl)-2-[N-(diphenyl-methylene)]amino-propionitrile (4a). A solution of 2.8 g (6.76 mmol) quantity of 3-(o-carboran-1-yl)-2-(prop-1-ynyl)-2-[N-(diphenylmethylene)]aminopropionitrile (**2a**) and 1.51 g (7.48 mmol) of a decaborane-acetonitrile complex in 50 mL of dry toluene was heated at 90°C. The mixture became dark brown in 10 min after the addition of the complex. The progress of the reaction was checked by TLC (hexanes/ethyl acetate, 6/1, v/v). Compound **4a** has been formed during the first two hours of the reaction. Later the formation of the product **3a** was observed. It was noticeable that the amount of **4a** was decreasing while the amount of **3a** was increasing. After 4 h of heating at 90°C the toluene was evaporated and the remaining residue was purified on a silica gel column (hexanes/ethyl acetate, 6:1, v/v) and by reacrystallization from hexanes/ethyl acetate (12:1, v/v). **3a**: yield 0.97 g (28.5 %) of yellow crystals; R_f 0.38 (hexanes/ethyl acetate, 6:1, v/v); mp 189-190°C; MS (FAB$^+$, 3-NBA) 507 (M + H)$^+$; HR MS: Calc. for $C_{20}H_{35}B_{20}N$: 509. 4631. Found: 509. 4686; ^{1}H-NMR ($CDCl_3$) δ 1.5 - 2.9 (br m, 20H, B-H), 2.40 (s, 2H, -CH_2-), 3.59 (s, 1H, HC- of carborane), 4.56 (s, 1H, HC- of carborane), 5.00 (s, 1H, -C=CH-), 7.45 - 7.55 (m, 10H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 43.083 (t, -CH_2-), 58. 708, 60.315 (2d, HC- of carborane), 71.815, 72.004 (2s, -C- of carborane), 112. 986 (d, -C=CH-), 128.153, 128.996, 129.587, 131.040, 132.380 (5d, aromat.), 135.704, 137.494 (2s, aromat.), 145.005 (s, -C=CH-), 170. 094 (s, -N=C-Ph_2); **4a**: yield 0.44 g (12.2 %) of colorless crystals; R_f 0.17 (hexanes/ethyl acetate, 6:1, v/v); mp 217-218°C; MS (FAB$^+$, 3-NBA) 534 (M + H)$^+$; HR MS: Calc. for $C_{21}H_{36}N_2B_{20}$ 536.4740. Found: 536.4768; ^{1}H-NMR ($CDCl_3$) δ 1.5 - 2.9 (br, m, 20H, B-H), 2.98, 3.20 (dd, 4H, -CH_2-, J = 15.5), 3.82 (s, 2H, HC- of carborane), 7.21 - 7.62 (m, 10H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 47.611 (t, -CH2-), 59.100 (s, α-C), 60.105 (d, HC- of carborane), 69.582 (s, -C- of carborane), 116.575 (s, -CN), 127.420, 128.825, 128.946, 130.614, 132.403 (5d, aromat.), 133.375, 137.836 (2s, aromat.), 172.931 (s, -N=C-Ph_2); Anal. Calcd for $C_{21}H_{36}N_2B_{20}$: C, 47.35; H, 6.81; N, 5.26. Found: C, 47.40; H, 7.03; N, 4.90.

1,3-Di(o-carboran-1-yl)-2-[N-(diphenylmethylene)]amino-prop-1-ene (3a) - Dehydrocyanation of 4a. A solution of 100 mg (0.19 mmol) quantity of 2-(*o*-carboran-1-ylmethyl)-3-(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]aminopropionitrile (**4a**) and 40.5 mg (0.2 mmol) of a decaborane-acetonitrile complex in 5 mL of dry toluene was heated at 90°C. The mixture became dark brown in 10 min after the addition of the complex. The progress of the reaction was checked by TLC (hexanes/ethyl acetate, 6/1, v/v). The reaction was completed in 2h. The toluene was evaporated and the remaining residue was purified on a silica gel column (hexanes/ethyl acetate, 6:1, v/v) and by reacrystallization from hexanes/ethyl acetate (12:1, v/v). **3a**: yield 76 mg (80 %) of yellow crystals. The analytical data of the product were the same as the sample **3a** described above.

3-Phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (1b). To a solution of 3.35 g (15.25 mmol) of N-(diphenylmethylene)aminoacetonitrile in 150 mL of dry acetonitrile were added 25.2 g (183 mmol) of anhydrous potassium carbonate, 2.95 g (3.1 mmol) of tetra-n-butylammonium bromide. A 1.9 mL (20 mmol) of benzyl bromide was added dropwise to the solution refluxed (75°C) under argon. The reaction mixture was carefully monitored by TLC (hexanes/ethyl acetate, 6/1, v/v). After 2 h the additional 1 mL of benzyl bromide was added. The reaction was completed in total 4 h and then it was cooled to room temperature and filtered to remove the solid which was washed with dichloromethane. The filtrate and washings were combined and concentrated. The remaining residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v). **1b**. yield 4.5 g (95.3 %) of yellow oil. R_f 0.42 (hexanes/ethyl acetate 6:1); HR MS: Calc. for $C_{22}H_{18}N_2$: 310.1470. Found: 310.1468; ^{1}H-NMR ($CDCl_3$) δ 3.19, 3.27 (d of ABq, 2H, -CH_2-, J_{AB} = 13.3 Hz, J_{BX} = 6.3 Hz, J_{AX} = 7.9 Hz), 4.37, 4.40 (dd, 1H, -CH-, J_{BX} = 6.4 Hz, J_{AX} = 7.8 Hz), 6.78-7.62 (m, 15H, aromat.); Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.02; Found: C, 84.91; H, 5.86; N, 8.91.

3-Phenyl-2-(prop-1-ynyl)-2-[N-(diphenylmethylene)]aminopropionitrile (2b). To a solution of 4.5 g (14.5 mmol) of 3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (**1b**) in 150 mL of dry acetonitrile were added 24 g (174 mmol) of anhydrous potassium carbonate, 2.8 g (8.7 mmol) of tetra-n-butylammonium bromide. A 6 mL (67.3 mmol) of propargyl bromide was added dropwise to the solution refluxed (75°C) under argon for 24 h. The reaction mixture was carefully monitored by TLC (hexanes/ethyl acetate, 6/1, v/v). The reaction mixture was cooled to room temperature and filtered to remove the solid which was washed with dichloromethane. The filtrate and washings were combined and concentrated. The remaining residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v) and recrystallization from hexanes/ethyl acetate (10/1, v/v) solution. **2b**: yield 3.4 g (79.2%) of colorless crystals; mp 111-112 C; R_f 0.39 (hexanes/ethyl acetate, 6/1, v/v); HR MS: Calc. for $C_{25}H_{20}N_2$: 348.1626. Found: 348.1607; ^{1}H-NMR ($CDCl_3$) δ 2.21 (t, 1H, -C≡CH, $J_{1,3propynyl}$ = 2.6), 2.90, 2.95 (dd, 2H, -CH_2-C≡CH, J = 16.4, $J_{1,3propynyl}$ = 2.6), 3.29, 3.35 (dd, 2H, J = 13.1, -CH_2-Ph), 7.24-7.81 (m, 15H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 33.310 (t, -$\underline{C}H_2$-Ph), 46.910 (t, -$\underline{C}H_2$-C≡CH), 62.787 (s, a-$\underline{C}$), 72.771 (d, -C≡$\underline{C}$H), 78.369 (s, -$\underline{C}$≡CH), 118.168 (s, -CN), 127.567-139.538 (ds and ss, aromat.), 169.137 (s, -N=$\underline{C}$-Ph_2); Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.18; H, 5.79; N, 8.04; Found: C, 85.97; H, 5.75; N, 7.98.

3-(*o*-Carboran-1-yl)-1-phenyl-2-[N-(diphenylmethylene)]amino-prop-1-ene (3b) and 2-(*o*-carboran-1-ylmethyl)-3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (4b). A solution of 3.25 g (9.33 mmol) quantity of 3-phenyl-2-(prop-1-ynyl)-2-[N-(diphenylmethylene)]aminopropionitrile (**2b**) and 2.1g (10.38 mmol) of a decaborane-acetonitrile complex in 50 mL of dry toluene was heated at 90°C. The mixture became dark brown in 10 min after the addition of the complex. The progress of the reaction was checked by TLC (hexanes/ethyl acetate, 6/1, v/v). Compound **4b** has been formed during the first two hours of the reaction. Later the formation of the product **3b** was observed. It was noticeable that the amount of **4b** was decreasing while the amount of **3b** was increasing. After 3 h of heating at 90°C the solution was cooled to room temperature, the toluene was evaporated and the remaining residue was purified on a silica gel column (hexanes/ethyl acetate, 6:1, v/v) and by reacrystallization from hexanes/ethyl acetate (12:1, v/v). **3b**: yield 0.28 g (7 %) of yellow crystals; R_f 0.58 (hexanes/ethyl acetate, 6:1, v/v); mp 200-201 C; HR MS: Calc. for $C_{24}H_{29}NB_{10}$: 441.3231. Found: 441.3271; ^{1}H-NMR ($CDCl_3$) δ 1.6 - 2.9 (br m, 10H, B-H), 2.80 (s, 2H, -CH_2-), 4.25 (s, 1H, H$\underline{C}$- of carborane), 5.65 (s, 1H, -C=C$\underline{H}$-), 6.97-7.71 (m, 15H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 46.206 (t, -CH_2-), 60.771 (d, H$\underline{C}$- of carborane), 73.170 (s, -$\underline{C}$- of carborane), 117.381 (d, -C=$\underline{C}$H-), 126.739, 127.482, 128.431, 128.586, 128.843, 129.340, 129.646, 131.588 (8d, aromat.), 136.010, 137.872 (2s, aromat.), 141.820 (s, -$\underline{C}$=CH-), 168.204 (s, -N=$\underline{C}$-Ph_2); **4b**: yield 0.92 g (21 %) of colorless

crystals; R_f 0.3 (hexanes/ethyl acetate, 6/1, v/v); mp 212-213°C; HR MS: Calc. for $C_{25}H_{30}N_2B_{10}$: 468.3340. Found: 468.3389; ^{1}H-NMR ($CDCl_3$) δ 1.3 - 3.0 (br m, 10H, B-H), 2.81, 3.22 (dd, 2H, -CH_2-, J = 15.3 Hz), 3.085, 3.18 (dd, 2H, -CH_2-, J = 13.4 Hz), 3.92 (br s, 1H, HC- of carborane), 6.75-7.58 (m, 15H, aromat.); ^{13}C-NMR ($CDCl_3$) d 49.008 (t, -CH_2-), 49.057 (t, -CH_2-), 59.139 (d, HC- of carborane), 61.003 (s, α-C), 71.218 (s, -C- of carborane), 117.710 (s, -CN), 128.068, 128.263, 128.489, 128.761, 129.787, 131.275, 131.389, (7d, aromat.), 132.684, 133.863, 138.814 (3s, aromat.), 170.326 (s, -N=C-Ph_2).

2-(*o*-Carboran-1-ylmethyl)-3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (4b). To a solution of 130 mg (0.35 mmol) of 3-(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]aminopropionitrile (**1a**) in 10 mL of dry acetonitrile were added 285.5 mg of (2.1 mmol) anhydrous potassium carbonate, 33.4 mg (0.1 mmol) of tetra-n-butylammonium bromide. A 82 mL (0.7 mmol) of benzyl bromide was added dropwise to the solution refluxed under argon. The reaction was completed in 5 h and the reaction mixture was carefully monitored by TLC (hexanes/ethyl acetate, 6/1, v/v). The reaction mixture was cooled to room temperature and filtered to remove the solid which was washed with dichloromethane. The filtrate and washings were combined and concentrated. The remaining residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v) and crystallization from hexanes/ethyl acetate (10/1, v/v) solution. **4b**: yield 100 mg (62%) of colorless crystals; The analytical data of the product were the same as the sample **4b** described above.

3-(*o*-Carboran-1-yl)-1-phenyl-2-[N-(diphenylmethylene)]amino-prop-1-ene (3b) - Dehydrocyanation of 4b. A solution of 100 mg (0.21 mmol) quantity of 2-(*o*-carboran-1-ylmethyl)-3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (**4b**) and 42.5 mg (0.21 mmol) of a decaborane-acetonitrile complex in 5 mL of dry toluene was heated at 90°C. The mixture became dark brown in 10 min after the addition of the complex. The progress of the reaction was checked by TLC (hexanes/ethyl acetate, 6/1, v/v). The reaction was completed in 2h. The toluene was evaporated and the remaining residue was purified on a silica gel column (hexanes/ethyl acetate, 6:1, v/v) and by reacrystallization from hexanes/ethyl acetate (12:1, v/v). **3b**: yield 80 mg (85 %) of yellow crystals. The analytical data of the product were the same as the sample **3b** described above.

2-Benzyl-3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (6). To a solution of 1.78 g (5.7 mmol) of 3-phenyl-2-[N-(diphenylmethylene)]aminopropionitrile (**1b**) in 40 mL of dry acetonitrile were added 4.76 g (34.4 mmol) of anhydrous potassium carbonate, 0.56 g (1.74 mmol) of tetra-n-butylammonium bromide. A 1.3 mL (11.5 mmol) of benzyl bromide was added dropwise to the solution refluxed under argon. The reaction mixture was carefully monitored by TLC (hexanes/ethyl acetate, 6/1, v/v) that showed only spot with Rf characteristic for the substrate. After 24 h of stirring under reflux the reaction mixture was cooled to room temperature and filtered to remove the solid which was washed with dichloromethane. The filtrate and washings were combined and concentrated. The remaining yellow oil was analyzed by ^{1}H NMR which showed that residue contains only crude product which was precipitated out from acetone solution and recrystallized from hexanes/ethyl acetate (6/1, v/v). **6**: yield 1.344 g (58.5 %) of colorless crystals; mp 171°C; R_f 0.44 (hexanes/ethyl acetate, 6/1, v/v); HR MS: Calc. for $C_{29}H_{24}N_2$: 400.1939. Found: 400.1923; ^{1}H-NMR ($CDCl_3$) δ 3.27, 3.47 (dd, 2H, -CH_2-, J = 13.0 Hz), 5.61, 6.95-7.54 (m, 10H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 48.833 (t, -CH_2-), 65.349 (s, α-C), 118.578 (s, -CN), 127.070, 127.254, 127.881, 128.056, 128.344, 128.657, 130.322, 131.145 (8d, aromat.), 134.520, 135.080, 139.222 (3s, aromat.), 167.623 (s, -N=C-Ph_2); Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.97; H, 6.04; N, 6.99; Found: C, 86.76; H, 6.05; N, 6.92.

1,3-Diphenyl-2-[N-(diphenylmethylene)]amino-prop-1-ene (7). A solution of 250 mg (0.6 mmol) quantity of 2-benzyl-3-phenyi-2-[N-(diphenylmethylene)]amino-propionitrile (**6**) and 139 mg (0.7 mmol) of a decaborane-acetonitrile complex in 5 mL of dry toluene was heated at 90 °C.

The mixture became dark brown in 10 min after the addition of the complex. The progress of the reaction was checked by TLC (hexanes/ethyl acetate, 10/1, v/v). Formation of the new compound with R_f 0.67 was observed. The reaction was completed in 5h. Toluene was evaporated and the remaining residue was purified on a silica gel column (hexanes/ethyl acetate, 10:1, v/v). Y. yield 78 mg (33.5 %) of yellow oil; Rf 0.67 (hexanes/ethyl acetate, 10:1, v/v); FAB$^+$ MS: 373 (M); HR MS: Calc. for $C_{28}H_{23}N$: 373.1831. Found: 373.1845; ^{1}H-NMR ($CDCl_3$) δ 3.26 (s, 2H, -CH_2-), 5.42 (s, 1H, -C=C<u>H</u>-), 7.0-7.8 (m, 20H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 42.872 (t, -CH_2-), 112.707 (d, -C=<u>C</u>H-), 138.208-125.354 (d and s, aromat.), 148.586 (s, -<u>C</u>=CH-), 166.334 (s, -N=<u>C</u>-Ph_2).

Di(o-carboran-1-ylmethyl)ketone (8a) - Hydrolysis of (3a). A 150 mg (0.3 mmol) quantity of 1,3-di(*o*-carboran-1-yl)-2-[N-(diphenylmethylene)]amino-prop-1-ene (**3a**) was reacted with 10 mL of 70% H2SO4 at 95°C for 5 days. The mixture was cooled (ice-bath). The organic residue was washed with water and dried under vaccum. The resulting brown oily residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v) and crystallization from hexanes/ethyl acetate (10/1, v/v). **8a**: yield 63 mg (62 %); mp 215°C; R_f 0.31 (hexanes/ethyl acetate, 6:1, v/v); HR MS: Calc. for $C_7H_{26}B_{20}O$: 346.3845. Found: 346.3810; ^{1}H-NMR ($CDCl_3$) δ 1.5 - 2.9 (br m, 20H, B-H), 3.34 (s, 4H, -CH_2-), 4.45 (s, 2H, <u>H</u>C- of carborane); ^{13}C-NMR ($CDCl_3$) δ 48.001 (t, -CH_2-), 58.361 (d, H<u>C</u>- of carborane), 67.013 (s, -<u>C</u>- of carborane), 197.716 (s, C=O).

(o-Carboran-1-ylmethyl)benzylketone (8b) - Hydrolysis of 3b. A 160 mg (0.36 mmol) quantity of 3-(*o*-carboran-1-yl)-1-phenyl-2-[N-(diphenylmethylene)]amino-prop-1-ene (**3b**) was reacted with 10 mL of 70% H2SO4 at 95°C for 5 days. The mixture was cooled (ice-bath). The organic residue was washed with water and dried under vaccum. The resulting brown oily residue was purified by column chromatography (hexanes/ethyl acetate, 6/1, v/v) and crystallization from hexanes/ethyl acetate (10/1, v/v). **8b**: yield 83 mg (82.5 %); R_f 0.36 (hexanes/ethyl acetate, 6:1, v/v); mp 67-69°C; HR MS: Calc. for $C_{11}H_{20}OB_{10}$: 278.2445. Found: 278.2451; ^{1}H-NMR ($CDCl_3$) δ 1.5 - 2.8 (br m, 10H, B-H), 3.34 (s, 2H, -CH_2-), 3.68 (s, 2H, -CH_2-), 4.64 (br s, 1H, <u>H</u>C- of carborane), 7.14-7.38 (m, 5H, aromat.); ^{13}C-NMR ($CDCl_3$) δ 45.703 (t, -CH_2-), 51.118 (t, -CH_2-), 58.187 (d, H<u>C</u>- of carborane), 68.383 (s, -<u>C</u>- of carborane), 128.032, 129.181, 129.403 (3d, aromat.), 131.911 (s, aromat.), 201.741 (s, C=O).

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