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1,2-Dicarba-*closo*-dodecaboran-1-yl Naphthalene Derivatives

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1,2-Dicarba-*closo*-dodecaboranes (*o*-carboranes) and naphthalenes have potential value as components or building blocks for supramolecular systems. We have efficiently synthesized 1-(1,2-dicarba-*closo*-dodecaboran-1-yl)naphthalene and 2-(1,2-dicarba-*closo*-dodecaboran-1-yl)naphthalene derivatives by employing three preparative methods: cyclization of the corresponding acetylenes with decaborane(14), an Ullmann-type coupling reaction of carboranes with aryl halide, and the aromatic nucleophilic substitution (S_NAr) reaction of aryl-*o*-carboranes with nitrophenyl halide. The optimum conditions of each method for synthesis of the title compounds were also investigated.

Introduction

1,2-Dicarba-*closo*-dodecaborane (*o*-carborane; **1**)[1] has unique properties and is also a useful chemical building block in the materials and biomedical sciences. For example, the high boron content and remarkable thermal and chemical stability of *o*-carborane have been utilized in the preparation of thermostable polymers[2] and carrier molecules for boron neutron capture therapy (BNCT),[3] and the delocalization of the 26 skeletal electrons in the *o*-carborane cage has been utilized in nonlinear optics.[4] We have studied the electronic properties of carboranes from the viewpoint of physical organic chemistry[5] and have taken advantage of the spherical geometry and the hydrophobic character of *o*-carborane to utilize it as a hydrophobic pharmacophore in the field of medicinal chemistry.[6] Further, the potential of *o*-carboranes as components or building blocks for supramolecular systems has been explored. Recent studies in this area include analyses of the effects of π-bonding interactions and hydrogen-bonding interactions of acidic CH in the *o*-carborane cage.[7]

Naphthalene derivatives are used in various scientific fields, such as metal complexation;[8] materials chemistry;[9] medicinal chemistry;[10] structural chemistry;[11] molecular recognition;[12] macromolecular chemistry;[13] supramolecular chemistry;[14] fluorescence chemistry;[15] and asymmetric synthesis[16] as backbones, platforms, or functional devices. Parallel substituents at the 1 and 8 positions of naphthalene show a significant steric interaction, which can provide novel

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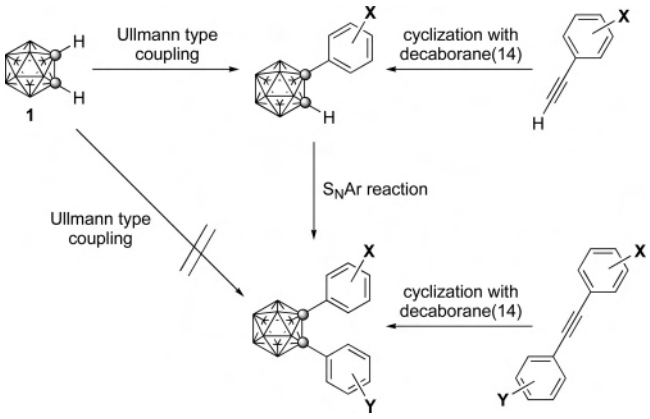

Figure 1. Synthetic route to monoaryl-*o*-carboranes and diaryl-*o*-carboranes.

properties, for example, a new type of intramolecular CT complex[17] and a stable dication with two positive rings fixed in a face-to-face conformation.[18]

Therefore, the combination of naphthalene with the *o*-carborane cage might provide a range of molecules with unprecedented features. In general, monoaryl-*o*-carborane derivatives can be synthesized by an Ullmann-type coupling reaction of the *C*-copper derivative of *o*-carborane with a variety of aryl iodides[19] or cyclization of aryl acetylenes with decaborane(14) in the presence of Lewis bases, such as acetonitrile, amines, and dialkyl sulfides.[20] The latter reaction can also be used to prepare diaryl-*o*-carborane derivatives from the corresponding diaryl acetylenes. There is a report of the preparation of 1-(*o*-carboranyl)naphthalene,[21] but details are not available.[21]

Here, we describe efficient syntheses of 1,2-dicarba-*closo*-dodecaboranyl naphthalenes and their 2-aryl derivatives by employing three different methods, that is, the well-known cyclization of acetylene compounds with decaborane(14) in the presence of Lewis bases, the Ullmann-type coupling reaction using an *o*-carboranyl copper derivative, and the aromatic nucleophilic substitution (S_NAr) reaction of aryl-*o*-carboranes with 4-nitrofluorobenzene (Figure 1).[22]

Experimental Section

General Considerations. Melting points were determined on a Yanaco micro melting point apparatus without correction. ^{1}H NMR, ^{13}C NMR, and ^{10}B NMR spectra were recorded with JEOL JNM-EX-270, JNM-LA-400, and JNM-LA-600 spectrometers. Chemical shifts for ^{1}H NMR spectra were referenced to tetramethylsilane (0.0 ppm) as an internal standard. Chemical shifts for ^{13}C NMR spectra were referenced to residual ^{13}C present in deuterated solvents. Chemical shift values for ^{11}B spectra were referenced relative to external BF_3·OEt (0.0 ppm with negative values upfield). Mass spectra were recorded on a JEOL JMS-DX-303 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHN analyzer.

2-(Ethynyl)naphthalene (3a). To a solution of 2-(trimethylsilylethynyl)naphthalene[23] (2.0 g, 8.9 mmol) in 25 mL of MeOH was added K_2CO_3 (1.38 g, 10 mmol), and the mixture was stirred for 14 h at room temperature. The mixture was poured into an aqueous 2 N HCl solution, and the solution was extracted with AcOEt, washed with brine, dried over $MgSO_4$, and then concentrated. The residue was purified by column chromatography on silica gel with *n*-hexane to give 1.35 g (99%) as a colorless solid: brown plates (*n*-hexane). mp 40 °C (lit.[23] mp 41 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.14 (s, 1 H), 7.46−7.54 (m, 3 H), 7.77−7.83 (m, 3 H), 8.02 (s, 1 H). MS (EI) *m*/*z*: 152 (M^+, 100%). Anal. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Found: C, 94.45; H, 5.38.

2-(Phenylethynyl)naphthalene (3b). To a solution of **2** (2.07 g, 10 mmol), ethynylbenzene (1.22 g, 12 mmol), $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol), and CuI (38 mg, 0.2 mmol) in 15 mL of THF was added diisopropylmine (2.8 mL, 20 mmol), and the mixture was refluxed for 12 h. The precipitate was removed by filtration and washed with AcOEt, and the filtrate was washed with brine, dried over $MgSO_4$, and then concentrated. The residue was purified by column chromatography on silica gel with 1:100 AcOEt/*n*-hexane to give 2.11 g (93%) of the title compound: colorless prisms (*n*-hexane). mp 118−119 °C (lit.[24] mp 114−115 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.34−7.39 (m, 3 H), 7.46−7.53 (m, 2 H), 7.56−7.60 (m, 3 H), 7.79−7.84 (m, 3 H), 8.06 (d, J = 1.1 Hz, 1 H). MS (EI) *m*/*z*: 228 (M^+, 100%). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.34; H, 5.30.

2-(1,2-Dicarba-*closo*-dodecaboran-1-yl)naphthalene (4a). Et_2S Method. A mixture of decaborane(14) (883 mg, 7.22 mmol), **3a** (1.0 g, 6.57 mmol), and Et_2S (1.63 mL, 15.16 mmol) in 30 mL of dry toluene was heated at 100 °C for 24 h. The solvent was removed under reduced pressure. The residue was purified by silica gel

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column chromatography with *n*-hexane to give 1.19 g (67%) of the title compound as a colorless solid.

CH_3CN Method. A mixture of decaborane(14) (883 mg, 7.22 mmol) and **3a** (1.0 mg, 6.57 mmol) in a mixture of 2 mL of CH_3CN and 8 mL of dry benzene was refluxed for 48 h. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with *n*-hexane to give 1.19 g (86%) of the title compound as a colorless solid: colorless cubes (*n*-hexane). mp 99−100 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.0−4.0 (m, 10 H), 4.08 (s, 1 H), 7.52−7.57 (m, 3 H), 7.78−7.85 (m, 3 H), 7.97 (d, J = 2.1 Hz, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 60.35, 76.67, 124.30, 127.34, 127.46, 127.52, 127.69, 128.35, 128.71, 130.59, 132.44, 133.28. ^{11}B NMR (192 MHz, $CDCl_3$): δ −12.89, −11.34, −10.82, −9.05, −4.48, −2.22. MS (EI) *m*/*z*: 270 (M^+, 100%). Anal. Calcd for $C_{12}H_{18}B_{10}$: C, 53.31; H, 6.71. Found: C, 53.24; H, 6.52.

2-(2-Phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl)naphthalene (4b). Et_2S Method. Compound **4b** was prepared in a manner similar to that described for **4a** (65% yield).

CH_3CN Method. Compound **4b** was prepared in a manner similar to that described for **4a** (42% yield): colorless cubes (AcOEt-*n*-hexane). mp 111 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.5−3.6 (brm, 10 H), 7.05−7.18 (m, 3 H), 7.42−7.50 (m, 5 H), 7.59 (d, J = 8.9 Hz, 1H), 7.71 (m, 2 H), 7.93 (d, J = 1.7 Hz, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 85.39, 85.23, 126.52, 127.28, 127.65, 127.96, 128.24, 128.57, 128.70, 130.13, 130.55, 130.61, 131.26, 132.19, 133.33. ^{11}B NMR (192 MHz, $CDCl_3$): δ −11.46, −10.43, −9.12, −2.51. MS (EI) *m*/*z*: 346 (M^+, 100%). Anal. Calcd for $C_{18}H_{22}B_{10}$: C, 62.40; H, 6.40. Found: C, 62.23; H, 6.29.

1-(Ethynyl)naphthalene (6a).[25]A mixture of 1-(trimethylsilylethynyl)naphthalene[25] (2.0 g, 8.9 mmol) and K_2CO_3 (1.25 g, 9.0 mmol) in CH_3OH was stirred at room temperature for 5 h. The mixture was poured into water and extracted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and then concentrated. The crude mixture was purified by column chromatography on silica gel with *n*-hexane to give 1.33 g (98%) of the title compound as a brown oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.47 (s, 1 H), 7.43 (dd, J = 7.3 Hz, 8.2 Hz, 1 H), 7.56 (m, 2 H), 7.74 (d, J = 7.2 Hz, 1 H), 7.86 (d, J = 7.6 Hz, 2 H), 8.36 (d, J = 8.3 Hz, 1 H). MS (EI) *m*/*z*: 152 (M^+, 100%). HRMS Calcd for $C_{12}H_8$: 152.0626. Found: 152.0640.

1-(Phenylethynyl)naphthalene (6b).[26]To a mixture of **5** (2.07 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol), CuI (38 mg, 0.2 mmol), and ethynylbenzene (1.22 g, 12 mmol) in 15 mL of THF was added diisopropylamine (2.8 mL, 20 mmol), and the mixture was refluxed for 12 h under an argon (Ar) atmosphere. It was cooled to room temperature, the solvent was removed under reduced pressure, and the resulting residue was dissolved in AcOEt. This solution was washed with water and brine, dried over $MgSO_4$, and then evaporated. The crude product was purified by column chromatography on silica gel with 1:100 AcOEt/*n*-hexane to give 2.13 g (94%) of the title compound as a yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.2 Hz, 8.2 Hz, 1 H), 7.36−7.42 (m, 3 H), 7.53 (ddd, J = 1.7 Hz, 7.0 Hz, 7.9 Hz, 1 H), 7.60 (ddd, J = 1.7 Hz, 6.8 Hz, 7.6 Hz, 1 H), 7.62−7.67 (m, 2 H), 7.76 (dd, J = 1.2 Hz, 7.1 Hz, 1 H), 7.86 (t, J = 7.8 Hz, 2 H), 8.44 (d, J = 8.1 Hz, 1 H). MS (EI) *m*/*z*: 228 (M^+, 100%). HRMS Calcd for $C_{12}H_8$: 228.0939. Found: 228.0962.

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1-(1,2-Dicarba-*closo*-dodecaboran-1-yl)naphthalene (7a). Et_2S Method. Compound **7a** was prepared in a manner similar to that described for **4a** (30% yield).

CH_3CN Method. Compound **7a** was prepared in a manner similar to that described for **4a** (52% yield): colorless cubes (*n*-hexane). mp 137−138 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.0−4.0 (brm, 10 H), 4.63 (s, 3 H), 7.40 (t, J = 7.9 Hz, 1 H), 7.49−7.62 (m, 2 H), 7.79 (dd, J = 1.0 Hz, 7.8 Hz, 1 H), 7.89 (d, J = 9.2 Hz, 2 H), 8.70 (d, J = 9.1 Hz, 1 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 61.14, 77.37, 124.37, 124.51, 126.11, 127.19, 128.20, 128.67, 129.79, 129.88, 131.73, 134.77. ^{11}B NMR (192 MHz, $CDCl_3$): δ −13.32, −9.95, −8.90, −2.72. MS (EI) *m*/*z*: 270 (M^+, 100%). Anal. Calcd for $C_{12}H_{18}B_{10}$: C, 53.31; H, 6.71. Found: C, 53.14; H, 6.70.

1-(2-Phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl)naphthalene (7b). Et_2S Method. Compound **7b** was prepared in a manner similar to that described for **4a** (8% yield).

CH_3CN Method. Compound **7b** was prepared in a manner similar to that described for **4a** (10% yield): colorless cubes (*n*-hexane). mp 153−154 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.0−4.0 (brm, 10 H), 6.97 (t, J = 7.9 Hz, 2 H), 7.10 (t, J = 7.7 Hz, 1 H), 7.14 (t, J = 7.9 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 2 H), 7.48 (t, J = 7.7 Hz, 1 H), 7.62 (dt, J = 1.6 Hz, 7.3 Hz, 1 H), 7.72 (d, J = 8.2 Hz, 1 H), 7.77 (d, J = 8.1 Hz, 1 H), 7.90 (d, J = 7.8 Hz, 1 H), 9.05 (d, J = 9.0 Hz, 1 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 87.55, 88.89, 124.05, 124.96, 125.23, 125.74, 126.93, 128.07, 129.56, 129.95, 130.25, 130.79, 131.79, 132.59, 133.64, 134.48. ^{11}B NMR (192 MHz, $CDCl_3$): δ −10.11, −9.23, −8.86, −2.91, −1.15. MS (EI) *m*/*z*: 346 (M^+), 230 (100%). HRMS Calcd for $C_{18}H_{22}B_{10}$: 346.2725. Found: 346.2748.

Synthesis of 7a by Ullmann-type Coupling at High Concentration. To a solution of **1** (2.88 g, 20 mmol) in 30 mL of DME was added dropwise a 1.56 M solution of *n*-BuLi in *n*-hexane (27.7 mL, 44 mmol) at 0 °C under Ar. The mixture was stirred for 30 min; then, CuCl (5.15 g, 52 mmol) was added in one portion, and the mixture was stirred at room temperature for 2 h. Pyridine (12.13 mL, 150 mmol) and **5** (3.5 mL, 24 mmol) were added in one portion, and the resulting mixture was refluxed for 14 h. After cooling, insoluble materials were removed by filtration through Celite. The filtrate was washed with a 2 N HCl solution and water and brine, dried over $MgSO_4$, and then concentrated. The residue was purified by silica gel column chromatography with 1:10 AcOEt/*n*-hexane to give 4.55 g (84%) of **7a** as a colorless solid.

1-(1-Naphthyl)-2-(4-nitrophenyl)-*o*-carborane (11). To a suspension of KO^{t}Bu (136 mg, 1.2 mmol) in dry DMF was added **7a** (270 mg, 1 mmol), and then, 4-fluoronitrobenzene (0.13 mL, 1.2 mmol) was added within 1 min at 0 °C. After 40 min, the reaction was poured into an aqueous 2 N HCl solution and extracted with AcOEt. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel with 1:10 CH_2Cl_2/*n*-hexane to give 351 mg (90%) of the title compound as a pale yellow solid: pale yellow prisms (AcOEt-*n*-hexane). mp 187−188 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.0−4.0 (m, 10 H), 7.18 (t, J = 7.9 Hz, 1 H), 7.44 (d, J = 8.9 Hz, 2 H), 7.53 (t, J = 7.4 Hz, 1 H), 7.66 (ddd, J = 1.4 Hz, 8.2 Hz, 8.9 Hz, 1 H), 7.56−7.83 (m, 2 H), 7.82 (d, J = 9.1 Hz, 2 H), 7.91 (d, J = 7.9 Hz, 1 H), 9.01 (d, J = 9.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 85.96, 88.06, 123.08, 124.14, 124.60, 124.67, 126.12, 127.38, 129.82, 131.31, 131.62, 133.24, 133.68, 134.54, 137.15, 148.36. ^{11}B NMR (192 MHz, $CDCl_3$): δ −10.51, −9.52, −8.49, −1.90, −0.99. MS (EI) *m*/*z*: 391 (M^+, 100%). Anal. Calcd for $C_{18}H_{21}B_{10}NO_2$: C, 55.23; H, 5.41; N, 3.58. Found: C, 55.01; H, 5.36; N, 3.72.

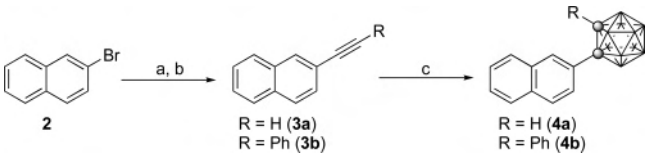
Table 1. *o*-Carborane Construction by the Reaction of 2-(Ethynyl)naphthalenes (**3**) with Decaborane(14)

entry	R	Lewis base	solvent	time (h)	temp (°C)	product	yield (%)
1	H (**3a**)	CH_3CN	benzene	48	reflux	**4a**	86
2	H (**3a**)	Et_2S	toluene	48	80	**4a**	67
3	Ph (**3b**)	CH_3CN	benzene	48	reflux	**4b**	42
4	Ph (**3b**)	Et_2S	toluene	48	80	**4b**	65

Table 2. *o*-Carborane Construction by the Reaction of 1-(Ethynyl)naphthalenes (**6**) with Decaborane(14)

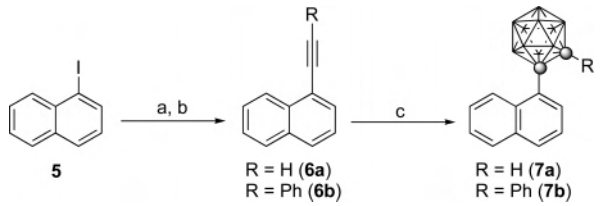
entry	R	Lewis base	solvent	time (h)	temp (°C)	product	yield (%)
1	H (**6a**)	CH_3CN	benzene	48	reflux	**7a**	52
2	H (**6a**)	Et_2S	toluene	48	80	**7a**	30
3	Ph (**6b**)	CH_3CN	benzene	48	reflux	**7b**	10
4	Ph (**6b**)	Et_2S	toluene	48	80	**7b**	8

Scheme 1. Synthesis of 2-(*o*-Carboranyl)naphthalene Derivatives (**4**)



(a) Ethynylbenzene or ethynyltrimethylsilane, $PdCl_2(PPh_3)_2$, CuI, diisopropylamine, THF. (b) K_2CO_3, MeOH. (c) Decarborane(14), Lewis base.

Scheme 2. Synthesis of 1-(*o*-Carboranyl)naphthalene Derivatives (**7**)



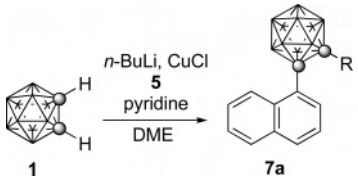
(a) Ethynylbenzene or ethynyltrimethylsilane, $PdCl_2(PPh_3)_2$, CuI, diisopropylamine, THF. (b) K_2CO_3, MeOH. (c) Decarborane(14), Lewis base.

Results and Discussion

First, we attempted to prepare 2-(*o*-carboranyl)naphthalene derivatives **4** by the cyclization of acetylenes **3** with decaborane(14) in the presence of a Lewis base (Scheme 1). The acetylene derivatives **3** were prepared by a palladium-catalyzed Sonogashira reaction with the corresponding acetylene units derived from 2-bromonaphthalene **2**.[23] The trimethylsilyl group in the precursor of **3a** was removed with potassium carbonate in methanol.[27] Compounds **3** were converted into 2-(*o*-carboranyl)naphthalene derivatives **4** by cyclization with decaborane(14) in the presence of a Lewis base in moderate yields, in a manner similar to that used for the *o*-carboranyl benzene derivatives (Table 1).[20] We examined the effect of the Lewis base in this cyclization. It is already known that the use of diethyl sulfide as a Lewis base generates *o*-carborane derivatives more efficiently as compared to acetonitrile.[28] We found that acetonitrile is a better Lewis base than diethyl sulfide in the cyclization of 2-(ethynyl)naphthalene **3a** with decaborane(14) and that 2-(phenylethynyl)naphthalene **3b** reacts efficiently with decaborane(14) in the presence of diethyl sulfide as a Lewis base to give the desired product **4b** in better yield.

Next, 1-(*o*-carboranyl)naphthalene derivatives **7** were synthesized by means of a procedure similar to that used for the preparation of 2-(*o*-carboranyl)naphthalene derivatives **4** (Scheme 2). We performed the Sonogashira reaction of commercially available 1-iodonaphthalene **5** with ethynyltrimethylsilane or ethynylbenzene, followed by deprotection of the trimethylsilyl group. The cyclization of 1-(ethynyl)-naphthalene **6a** with decaborane(14) in the presence of acetonitrile or diethyl sulfide gave 1-(*o*-carboranyl)naphthalene **7a** in 52% or 30% yield, respectively (Table 2; entries 1 and 2). However, the yield of 1-(2-phenyl-*o*-carboranyl)-naphthalene **7b** was markedly reduced to less than 10%, regardless of the kind of Lewis base used in the cyclization. Moreover, the yield when acetonitrile was used as a Lewis base was greater than that in the case of diethyl sulfide (Table 2; entries 3 and 4). There are significant structural disadvantages for the cyclization of 1-(phenylethynyl)naphthalene **6b** with decaborane(14), because 1-(2-phenyl-*o*-carboranyl)-naphthalene **7b** has greater steric hindrance due to the hydrogen at the 8 position in the naphthalene ring and the two aromatic rings bound to the two carbon atoms in *o*-carborane than does 2-(2-phenyl-*o*-carboranyl)naphthalene **4b**.

Table 3. Synthesis of 1-(*o*-Carboranyl)naphthalene (**7a**) by Ullmann-Type Coupling



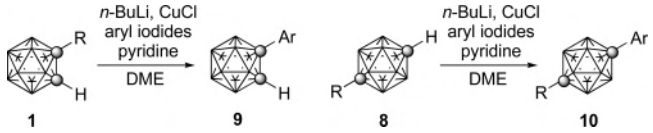
entry	*n*-BuLi (eq)	CuCl (eq)	concentration (M)	time (h)	yield (%)
1	2.2	2.6	0.1	48	41
2	2.2	2.6	0.3	5	84

The features of the cyclization of acetylenes and decaborane(14) in the presence of Lewis bases can be summarized as follows: (1) Diethyl sulfide is an effective Lewis base for the cyclization of *endo*-acetylene derivatives. (2) Acetonitrile is an effective Lewis base for the cyclization of *exo*-acetylene derivatives. (3) Diethyl sulfide is less influenced by steric effects as compared to acetonitrile. We have previously reported the synthesis and structure of 1,2-bis-(*o*-carboranyl)benzene, which has a distorted benzene ring due to the enormous steric hindrance arising from two neighboring *o*-carboranes.[29] The procedure using acetonitrile

(27) Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1965**, *4*, 217−228.

(28) Teplyakov, M. M.; Khotina, I. A.; Gelashvili, T. L.; Kovshak, V. V. *Dokl. Akad. Nauk. SSSR* **1980**, *271*, 874−877. (b) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 3056−3058.

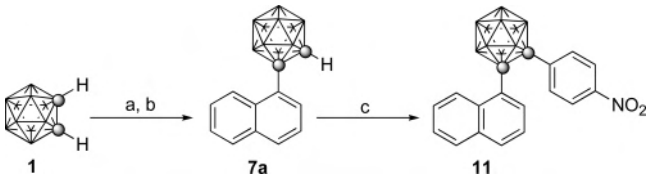
Table 4. Synthesis of Various Aryl Carboranes by Ullmann-Type Reaction at High Concentration



substrate	carboranes	R	Ar	time (h)[a]	product	yield (%)[a]
1	*o*-carborane	H	3-NO_2−Ph	8 (42)	**9**	70 (37)
8a	*p*-carborane	H	Ph	8 (20)	**10a**	64 (52)
8b	*p*-carborane	-CH_2OTBS	3-CN−Ph	4 (24)	**10b**	70 (19)

[a] Yield and time using the original procedure of Ullmann-type coupling in parentheses.[19]

Scheme 3. Efficient Synthesis of 1-[(4-Nitrophenyl)-*o*-carboranyl]naphthalene Derivatives (**11**)



(a) *n*-BuLi, CuCl, 1-iodonaphthalene, pyridine, DME. (b) KO^{t}Bu, 4-fluoronitrobenzene, DMF.

as a Lewis base worked effectively in the preparation of 1,2-bis(*o*-carboranyl)benzene, whereas the desired product was not obtained in the presence of diethyl sulfide as a Lewis base. Acetonitrile is a more effective Lewis base for the cyclization with decaborane(14) in the cases of *exo*-acetylenes and sterically hindered acetylenes.

We also attempted a direct synthesis of 1-(*o*-carboranyl)-naphthalene **7a** by means of the Ullmann-type coupling reaction of 1-iodonaphthalene **5** with an *o*-carboranyl copper derivative (Table 3). Under the conditions of the original procedure for Ullmann-type coupling,[19] compound **7a** was obtained in low yield (41%), after prolonged reaction. However, when the reaction was conducted at a high concentration, such as 0.3 M, it proceeded smoothly within 5 h to afford the desired compound, **7a**, in excellent yield (84%), which was much better than that of the cyclization of 1-(ethynyl)naphthalene **6a** with decaborane(14). Various aryliodides were examined in the Ullmann-type coupling reaction at high concentrations (Table 4). This approach resulted in marked improvements of the reaction rate and the yield with all of the substrates examined, affording the corresponding arylated carboranes **9**, **10a**, and **10b** in high yields. The concentration of the reaction solution is likely to be an extremely important factor in controlling the reaction rate and yield of this coupling reaction.

We have recently reported a novel synthetic method of 1,2-diaryl-*o*-carboranes via an S_NAr reaction.[22] This reaction proceeds smoothly under mild conditions and is a powerful tool for the synthesis of 1,2-diaryl-*o*-carboranes from monoaryl-*o*-carboranes. To obtain 1-[2-(4-nitrophenyl)-*o*-carboranyl]-naphthalene **11** bearing a nitro group, which could readily be transformed into various substituents, we applied the S_N-Ar reaction to 1-(*o*-carboranyl)naphthalene **7a**. The reaction of 1-(*o*-carboranyl)naphthalene **7a** with 4-nitrofluorobenzene in the presence of KO^{t}Bu in DMF at 0 °C proceeded smoothly to give 1-[2-(4-nitrophenyl)-*o*-carboranyl]naphthalene **11** within 40 min in 90% yield (Scheme 3).

Conclusion

In conclusion, we have efficiently synthesized 2-(*o*-carboranyl)naphthalene derivatives **4** and 1-(*o*-carboranyl)-naphthalene derivatives **7** by employing three methods. 2-(*o*-Carboranyl)naphthalene derivatives **4** are effectively synthesized by employing cyclization of 2-ethynylnaphthalenes, even if a second aryl substituent exists on the acetylene group. However, the synthesis of 1-(*o*-carboranyl)naphthalene derivatives **7** has some difficulties. Although unsubstituted 1-(*o*-carboranyl)naphthalene **7a** could be prepared by cyclization of 1-(ethynyl)naphthalene in moderate yield, it was better to use the Ullmann-type coupling reaction. In the case of synthesis of sterically hindered 1-(2-phenyl-*o*-carboranyl)-naphthalene **7b**, the cyclization of 1-(phenylethynyl)naphthalene **6b** with decaborane(14) afforded a poor result. The combination of an Ullmann-type coupling reaction followed by an S_NAr reaction seems to be more suitable for the preparation of 1-(2-aryl-*o*-carboranyl)naphthalene. Thus, a variety of molecules in which naphthalene is linked with the *o*-carborane cage can be easily prepared. The results described here should provide a basis for synthesizing a variety of sterically hindered molecules and supramolecules on the basis of host−guest interactions involving the combination of naphthalene and *o*-carborane.

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