AN EFFECTIVE APPROACH TO 1,2,3-TRIAZOLE-CONTAINING 12-VERTEX *closo*-DODECABORATES

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An efficient general synthetic approach giving a facile, rapid and inexpensive access to a wide range of novel 1,2,3-triazoles bearing *closo*-dodecaborate fragment has been developed. The method is based on the nucleophilic cleavage of oxonium dodecaborate with NaN_3 or tertiary propargylamine and subsequent Huisgen 1,3-dipolar cycloaddition ("click" methodology) of the cleavage products and organic acetylenes or azides.

Keywords: Boranes; Boron clusters; *closo*-Dodecaborate; Oxonium derivative; Azides; Terminal acetylenes; 1,3-Dipolar cycloadditions; Triazoles; Click chemistry.

Modern drug discovery requires the identification and optimization of synthetic routes to specifically acting low-molecular-weight compounds. That is why simple methods that can quickly and easily generate large libraries of compounds have become more and more utilized[1]. The "click" methodology recently introduced by Sharpless et al.[2] is one of the methods based on reactions which are of wide scope, give high yields, and use highly energetic reactants to form irreversible carbon–heteroatom bonds. The Huisgen 1,3-dipolar cycloaddition[3] perfectly illustrates this kind of reaction. It is based on the reaction of azides and terminal alkynes to give 1,2,3-triazoles. As has been recently shown[4], under copper(I) catalysis, the rate of this reaction is dramatically increased and only the corresponding 1,4-disubstituted regioisomer is obtained. 1,2,3-Triazoles are versatile compounds, which have been applied to a variety of purposes, including anticorrosive agents, dyes, agrochemicals and photographic materials[5]. Although the 1,2,3-triazole structures do not occur in nature, they occur in diverse biologically active substances, displaying anti-HIV and antimicrobial behavior as selective β_3-adrenergic receptor agonists[6].

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On the other hand, water-soluble functionalized derivatives of the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ are promising candidates for boron neutron capture therapy (BNCT)[7,8]. Synthesis of their oxonium derivatives (e.g. tetrabutylammonium (1,4-dioxan-1-ium-1-yl)-*closo*-undecahydrododecaborate (**1**)) directly from $[B_{12}H_{12}]^{2-}$ and their subsequent nucleophilic ring opening is one of the most powerful ways of the introduction of the reaction centre into the B_{12} moiety[9].

Recently we have successfully applied the "click" methodology for the preparation of functionalized aza analogs[10] of histidine as well as for efficient synthesis of novel nitrogen bisphosphonates[11] as potent drug candidates. Here we would like to disclose an advanced synthesis of a B_{12}-based azide, and of novel B_{12}-based acetylenes as well as their reactions with alkynes and azides, respectively.

EXPERIMENTAL

Materials and Equipment

Chemicals of reagent grade were used as received from standard commercial vendors. Oxonium derivative **1** was prepared by the described method[9]. The ^{1}H, ^{13}C and ^{11}B NMR spectra (δ, ppm) were recorded at 400.13, 100.61 and 128.38 MHz, respectively, on a Bruker-Avance-400 spectrometer in DMSO-d_6. The ^{1}H and ^{13}C NMR signals of novel compounds **3**, **4** and **5** were assigned by ^{1}H, ^{1}H-^{1}H-COSY and ^{13}C, ^{1}H-^{13}C-HMQC-gs spectra. Melting points were measured in open capillaries and are not corrected. IR spectra (ν, cm^{-1}) were recorded on an Infralum FT-801 FTIR spectrometer in Nujol. Elemental analysis was performed in the microanalytical laboratory of the Institute.

Bis(tetrabutylammonium) [2-(2-Azidoethoxy)ethoxy]undecahydro-*closo*-dodecaborate (**2**)

A mixture of 1.50 g (0.0032 mol) of **1**, 0.83 g (0.0128 mol) of NaN_3 and 1.03 g (0.0032 mol) of NBu_4Br was refluxed in 50 ml of 96% EtOH for 16 h. Then EtOH was evaporated and 10 ml of H_2O were added. A white solid was filtered off and vacuum-dried to give 2.37 g (98%) of azide **2** as a white solid, m.p. 104 °C. ^{1}H NMR: 3.56 t, 2 H (CH_2O); 3.53 m, 4 H (CH_2O); 3.35 t, 2 H (CH_2N_3); 3.16 m, 16 H ($NC\mathbf{H}_2CH_2CH_2CH_3$); 1.57 m, 16 H ($NCH_2C\mathbf{H}_2CH_2CH_3$); 1.30 m, 16 H ($NCH_2CH_2C\mathbf{H}_2CH_3$); 0.93 t, 24 H ($NCH_2CH_2CH_2C\mathbf{H}_3$); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 71.8, 69.5, 67.4 (CH_2O); 58.0 ($N\mathbf{C}H_2CH_2CH_2CH_3$); 50.6 ($CH_2N_3$); 23.4 ($NCH_2\mathbf{C}H_2CH_2CH_3$); 19.6 ($NCH_2CH_2\mathbf{C}H_2CH_3$); 14.0 ($NCH_2CH_2CH_2\mathbf{C}H_3$). ^{11}B NMR: 5.0 s, 1 B (B(1)); –17.0 d, 5 B (B(2-6)); –17.5 d, 5 B (B(7-11)); 21.5 d, 1 B (B(12)). IR (Nujol): ν(BH) 2464, ν(N_3) 2105. For $C_{36}H_{91}B_{12}N_5O_2$ (755.9) calculated: 57.21% C, 12.13% H, 9.27% N, 17.16% B; found: 57.34% C, 12.14% H, 9.51% N, 17.11% B.

Reaction of **2** with Alkynes. General Procedure

A mixture of 0.5 mmol **2**, 1.5 mmol corresponding alkyne, 0.02 mmol (5 mg) CuI and one drop of Et_3N was refluxed in 10 ml of 96% EtOH for 16 h. Then CuI was filtered off and

EtOH evaporated. The residue was dissolved in 5 ml of dry MeOH and the product was precipitated by addition of 0.1 mmol of CsF in 5 ml of MeOH. It was filtered off, washed with 5 ml of MeOH and 5 ml of CH_2Cl_2.

Dicesium {2-[2-(4-butyl-1H-1,2,3-triazol-1-yl)ethoxy]ethoxy}undecahydro-closo-dodecaborate (**3a**). Prepared from **2** and hex-1-yne. Yield 64%, m.p. 234 °C. ^{1}H NMR: 7.75 s, 1 H (CH); 4.43 t, 2 H (CH_2N); 3.79 t, 2 H (CH_2O); 3.45 m, 4 H (CH_2O); 2.58 t, 2 H (=C-CH_2-); 1.49 m, 2 H (=C-CH_2-C**H**$_2$-); 1.17 m, 2 H (C**H**$_2$-CH_3); 0.75 t, 3 H (CH_3); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 147.2 (N-**C**(CH_2)=); 124.0 (N-CH=); 71.0, 68.7, 67.5 (CH_2O); 49.9 (CH_2N); 30.8 (=C-**C**H$_2$-); 24.2 (=C-CH_2-**C**H$_2$-); 21.5 (-**C**H$_2$-CH_3); 13.1 (CH_3). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.4 d, 5 B (B(2-6)); –18.3 d, 5 B (B(7-11)); –23.2 d, 1 B (B(12)). IR (Nujol): ν(BH) 2468, ν(triazole) 1699. For $C_{10}H_{29}B_{12}Cs_2N_3O_2$ (619.0) calculated: 19.41% C, 4.72% H, 6.79% N, 20.96% B; found: 19.10% C, 4.78% H, 6.80% N, 20.52% B.

Dicesium {2-[2-(4-hexyl-1H-1,2,3-triazol-1-yl)ethoxy]ethoxy}undecahydro-closo-dodecaborate (**3b**). Prepared from **2** and oct-1-yne. Yield 68%, m.p. 242 °C. ^{1}H NMR: 7.89 s, 1 H (CH); 4.44 t, 2 H (CH_2N); 3.73 t, 2 H (CH_2O); 3.39 m, 4 H (CH_2O); 2.59 t, 2 H (=C-CH_2-); 1.58 m, 2 H (=C-CH_2-C**H**$_2$-); 1.28 m, 6 H ((C**H**$_2$)$_3$-CH_3); 0.86 t, 3 H (CH_3); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 148.4 (N-**C**(CH_2)=); 123.1 (N-CH=); 72.5, 69.1, 67.7 (CH_2O); 49.9 (CH_2N); 31.5 (=C-**C**H$_2$-); 29.5, 28.8, 25.5, 22.5 (-(**C**H$_2$)$_4$-CH_3); 14.4 (CH_3). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.4 d, 5 B (B(2-6)); –18.3 d, 5 B (B(7-11)); –23.2 d, 1 B (B(12)). IR (Nujol): ν(BH) 2465, ν(triazole) 1691. For $C_{12}H_{33}B_{12}Cs_2N_3O_2$ (646.9) calculated: 22.28% C, 5.14% H, 6.50% N, 20.05% B; found: 22.11% C, 5.19% H, 6.72% N, 19.95% B.

Dicesium {2-[2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethoxy]ethoxy}undecahydro-closo-dodecaborate (**3c**). Prepared from **2** and phenylacetylene. Yield 69%, m.p. 290 °C. ^{1}H NMR: 8.31 s, 1 H (CH); 7.77 d, 2 H (*o*-CH); 7.43 t, 2 H (*m*-CH); 7.35 t, 1 H (*p*-CH); 4.57 t, 2 H (CH_2N); 3.90 t, 2 H (CH_2O); 3.64 m, 4 H (CH_2O); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 146.6 (N-**C**(Ph)=); 129.5, 129.1, 128.7, 125.8 (Ph); 123.0 (N-CH=); 71.0, 68.6, 67.5 (CH_2O); 50.2 (CH_2N). ^{11}B NMR: 6.3 s, 1 B (B(1)); –16.3 d, 5 B (B(2-6)); –18.1 d, 5 B (B(7-11)); –23.5 d, 1 B (B(12)). IR (Nujol): ν (BH) 2464, ν(triazole) 1697. For $C_{13}H_{27}B_{12}Cs_2N_3O_3$ (638.9) calculated: 22.56% C, 3.94% H, 6.58% N, 20.30% B; found: 22.41% C, 3.96% H, 6.62% N, 20.12% B.

Dicesium {2-[2-(4-(2-hydroxymethyl)-1H-1,2,3-triazol-1-yl)ethoxy]ethoxy}undecahydro-closo-dodecaborate (**3d**). Prepared from **2** and prop-2-yn-1-ol. Yield 72%, m.p. 256 °C. ^{1}H NMR: 4.60 t, 2 H (CH_2N); 4.47 s, 2 H (CH_2OH); 3.81 t, 2 H (CH_2O); 3.45 m, 4 H (CH_2O); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 147.4 (N-**C**(CH_2)=); 125.0 (N-CH=); 71.0, 68.5, 67.4 (CH_2O); 50.0 (CH_2OH); 48.8 (CH_2N). ^{11}B NMR: 6.6 s, 1 B (B(1)); –16.7 d, 5 B (B(2-6)); –18.0 d, 5 B (B(7-11)); –22.0 d, 1 B (B(12)). IR (Nujol): ν(OH) 3237, ν(BH) 2466, ν(triazole) 1695. For $C_7H_{23}B_{12}Cs_2N_3O_3$ (592.8) calculated: 14.18% C, 3.91% H, 7.09% N, 21.88% B; found: 14.05% C, 3.94% H, 7.15% N, 21.72% B.

Dicesium {2-[2-(4-(2-hydroxyethyl)-1H-1,2,3-triazol-1-yl)ethoxy]ethoxy}undecahydro-closo-dodecaborate (**3e**). Prepared from **2** and but-3-yn-1-ol. Yield 65%, m.p. 250 °C. ^{1}H NMR: 7.82 s, 1 H (CH); 4.45 t, 2 H (CH_2N); 3.81 t, 2 H (CH_2OH); 3.74 t, 2 H (CH_2O); 3.46 m, 4 H (CH_2O); 2.82 t, 2 H (C-CH_2); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 145.2 (N-**C**(CH_2)=); 124.6 (N-CH=); 71.0, 68.6, 67.5 (CH_2O); 60.7 (CH_2OH); 49.9 (CH_2N); 27.8 (C-**C**H$_2$). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.9 d, 5 B (B(2-6)); –17.8 d, 5 B (B(7-11)); –22.3 d, 1 B (B(12)). IR (Nujol): ν(OH) 3231, ν(BH) 2465, ν(triazole) 1692. For $C_8H_{25}B_{12}Cs_2N_3O_3$ (606.8) calculated: 15.83% C, 4.15% H, 6.28% N, 21.38% B; found: 15.42% C, 4.18 H, 6.30% N, 21.9% B.

Tetrabutylammonium (2-{2-[dimethyl(prop-2-yn-1-yl)ammonium]ethoxy}ethoxy)undecahydro-closo-dodecaborate (**4a**). A mixture of 0.9 g (2 mmol) of **1**, 0.32 g (4 mmol) of *N*,*N*-dimethyl-

prop-2-yn-1-amine and 10 ml of 96% EtOH was refluxed for 40 h. The precipitate was filtered off, washed with 3–4 ml of ethanol and air-dried to give 0.65 g (61%) of **4a**, m.p. 216 °C. ^{1}H NMR: 4.38 d, 2 H ($CH_2C\equiv$); 3.95 t, 1 H (≡CH); 3.85 t, 2 H (CH_2O); 3.62 t, 2 H (CH_2O); 3.53 m, 4 H (OCH_2CH_2N); 3.14 m, 8 H ($NCH_2CH_2CH_2CH_3$); 3.10 s, 6 H (CH_3); 1.52 m, 8 H ($NCH_2CH_2CH_2CH_3$); 1.27 m, 8 H ($NCH_2CH_2CH_2CH_3$); 0.89 t, 12 H ($NCH_2CH_2CH_2CH_3$); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 83.6 (-C≡); 73.3, 72.1, 68.3 (CH_2O); 64.6, 63.4 (CH_2N); 58.0 ($NCH_2CH_2CH_2CH_3$); 55.0 (NCH_3); 51.4 (HC≡); 23.5 ($NCH_2CH_2CH_2CH_3$); 19.6 ($NCH_2CH_2CH_2CH_3$); 13.9 ($NCH_2CH_2CH_2CH_3$). ^{11}B NMR: 6.7 s, 1 B (B(1)); –16.8 d, 5 B (B(2-6)); –18.1 d, 5 B (B(7-11)); –22.7 d, 1 B (B(12)). IR (Nujol): ν(BH) 2468, ν(C≡C) 2123. For $C_{25}H_{64}B_{12}N_2O_2$ (554.5) calculated: 54.15% C, 11.63% H, 5.05% N, 23.39% B; found: 54.09% C, 11.62% H, 5.08% N, 23.42% B.

Tetrabutylammonium (2-{2-[diethyl(prop-2-yn-1-yl)ammonium]ethoxy}ethoxy)undecahydro-closo-dodecaborate (**4b**). Prepared in the same way as **4a** from 1 g (0.0021 mol) of **1** and 0.47 g (0.0042 mol) of *N*,*N*-dimethylprop-2-yn-1-amine. Yield 0.77 g (62%), m.p. 236 °C. ^{1}H NMR: 4.35 d, 2 H ($CH_2C\equiv$); 3.94 t, 1 H (≡CH); 3.83 t, 2 H (CH_2O); 3.6–3.4 m, 10 H (2 × OCH_2 and 3 × CH_2N); 3.12 m, 8 H ($NCH_2CH_2CH_2CH_3$); 1.53 m, 8 H ($NCH_2CH_2CH_2CH_3$); 1.30 t, 6 H (NCH_2CH_3); 1.27 m, 8 H ($NCH_2CH_2CH_2CH_3$); 0.89 t, 12 H ($NCH_2CH_2CH_2CH_3$); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 82.7 (-C≡); 73.0, 72.0, 68.4 (CH_2O); 64.3, 60.9 (CH_2N); 58.0 ($NCH_2CH_2CH_2CH_3$); 55.0 (NCH_2CH_3); 49.3 (HC≡); 23.5 ($NCH_2CH_2CH_2CH_3$); 19.6 ($NCH_2CH_2CH_2CH_3$); 13.9 ($NCH_2CH_2CH_2CH_3$); 8.1 (NCH_2CH_3). ^{11}B NMR: 6.7 s, 1 B (B(1)); –16.8 d, 5 B (B(2-6)); –18.2 d, 5 B (B(7-11)); –22.7 d, 1 B (B(12)). IR (Nujol): ν(BH) 2466, ν(C≡C) 2129. For $C_{27}H_{68}B_{12}N_2O_2$ (582.6) calculated: 55.67% C, 11.77% H, 4.81% N, 22.27% B; found: 55.47% C, 11.79% H, 4.76% N, 22.13% B.

Reaction of **4** with Azides; Synthesis of Triazoles **5a**–**5c**. General Procedure

A mixture of 0.27 mmol of **4**, 0.27 mmol of azide, 0.002 ml (0.02 mmol) of Et_3N and 0.004 g (0.02 mmol) of CuI was refluxed in 5 ml of 96% EtOH (**5a**, **5c**) or CH_3CN (**5b**) for 24 h. Then CuI was filtered off and the solvent was evaporated. Products **5b** and **5c** were then suspended in dry THF, filtered and air-dried. In the case of **5a**, the residue after evaporation was dissolved in 5 ml of MeOH, and 0.041 g (0.27 mmol) of CsF in 0.5 ml of MeOH were added to precipitate the product. It was filtered off and air-dried.

Cesium [2-(2-{dimethyl[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]ammonium}ethoxy)ethoxy]-undecahydro-closo-dodecaborate (**5a**). Prepared from **4a** and phenyl azide. Yield 82%, m.p. 289 °C (dec). ^{1}H NMR: 9.02 s, 1 H (CH); 7.93 d, 2 H (*o*-Ph); 7.59 t, 2 H (*m*-Ph); 7.49 t, 1 H (*p*-Ph); 4.81 s, 2 H (Ar-CH_2-N); 3.93 t, 2 H (CH_2O); 3.67 t, 2 H (CH_2O); 3.58 t, 2 H (CH_2O); 3.53 m, 2 H (CH_2N); 3.12 s, 6 H (CH_3N); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 145.1 (C-triazole); 136.9 (CH-triazole); 130.0, 129.4, 127.6, 120.9 (Ph); 72.2, 68.3, 64.7 (CH_2O); 63.6, 58.5 (CH_2N); 51.4 (CH_3N). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.9 d, 5 B (B(2-6)); –17.8 d, 5 B (B(7-11)); –22.3 d, 1 B (B(12)). IR (Nujol): ν(BH) 2464, ν(triazole) 1698. For $C_{15}H_{33}B_{12}CsN_4O_2$ (564.1) calculated: 31.94% C, 5.90% H, 9.93% N, 23.00% B; found: 31.81% C, 5.95% H, 9.85% N, 23.07% B.

Tetrabutylammonium [2-(2-{diethyl[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]ammonium}ethoxy)-ethoxy]undecahydro-closo-dodecaborate (**5b**). Prepared from **4b** and benzenetriazole. Yield 79%, m.p. 146 °C. ^{1}H NMR: 8.98 s, 1 H (CH); 7.91 d, 2 H (*o*-Ph); 7.57 t, 2 H (*m*-Ph); 4.47 d, 1 H (*p*-Ph); 4.73 s, 2 H (Ar-CH_2-N); 3.91 t, 2 H (CH_2O); 3.74 t, 2 H (CH_2O); 3.62 t, 2 H (CH_2O); 3.41 m, 2 H (CH_2N); 3.33 q, 4 H (NCH_2CH_3); 3.11 m, 8 H ($NCH_2CH_2CH_2CH_3$); 1.52 m, 8 H

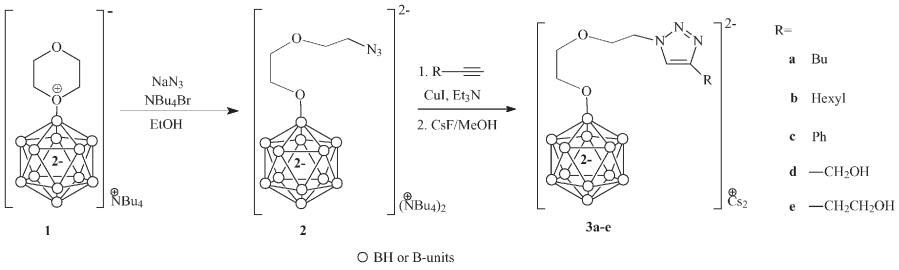
($NCH_2C\mathbf{H}_2CH_2CH_3$); 1.34 t, 6 H ($NCH_2C\mathbf{H}_3$); 1.25 m, 8 H ($NCH_2CH_2C\mathbf{H}_2CH_3$); 0.88 t, 12 H ($NCH_2CH_2CH_2C\mathbf{H}_3$); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 144.7 (C-triazole); 137.1 (CH-triazole); 130.4, 129.1, 127.3, 120.7 (Ph); 72.5, 68.4, 65.0 (CH_2O); 63.6, 58.2 (CH_2N); 58.0 ($NCH_2CH_2CH_2CH_3$); 55.3 (NCH_2CH_3); 23.5 ($NCH_2CH_2CH_2CH_3$); 19.6 ($NCH_2CH_2CH_2CH_3$); 13.9 ($NCH_2CH_2CH_2CH_3$); 8.0 (NCH_2CH_3). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.9 d, 5 B (B(2-6)); –17.8 d, 5 B (B(7-11)); –22.3 d, 1 B (B(12)). IR (Nujol): ν(BH) 2461, ν(triazole) 1695. For $C_{33}H_{73}B_{12}N_5O_2$ (701.7) calculated: 56.49% C, 10.49% H, 9.98% N, 18.49% B; found: 56.38% C, 10.57% H, 9.85% N, 18.61% B.

Tetrabutylammonium (2-{2-[dimethyl({1-[2-(perfluorooctyl)ethyl]-1H-1,2,3-triazol-4-yl}methyl)-ammonium]ethoxy}ethoxy)undecahydro-closo-dodecaborate (**5c**). Prepared from **4a** and *n*-$C_8F_{17}CH_2CH_2N_3$. Yield 77%, m.p. 176 °C. ^{1}H NMR: 8.57 s, 1 H (CH(Ar)); 4.80 t, 2 H ($NC\mathbf{H}_2CH_2C_8F_{17}$); 4.74 s, 2 H (Ar-$CH_2$-N); 3.93 t, 2 H ($CH_2O$); 3.66 t, 2 H ($CH_2O$); 3.59 t, 2 H ($CH_2O$); 3.47 m, 2 H ($CH_2N$); 3.16 m, 8 H ($NC\mathbf{H}_2CH_2CH_2CH_3$); 3.08 s, 6 H ($NCH_3$); 3.01 m, 2 H ($NCH_2C\mathbf{H}_2C_8F_{17}$); 1.57 m, 8 H ($NCH_2C\mathbf{H}_2CH_2CH_3$); 1.30 m, 8 H ($NCH_2CH_2C\mathbf{H}_2CH_3$); 0.93 t, 12 H ($NCH_2CH_2CH_2C\mathbf{H}_3$); 2.0–0.4 broad m, 11 H (BH). ^{13}C NMR: 146.0 (C-triazole); 136.1 (CH-triazole); 129.8–108.4 (CF, group of multiplets); 72.3, 68.2, 64.7 (CH_2O); 63.0, 58.7 (CH_2N); 58.0 ($NCH_2CH_2CH_2CH_3$); 51.1 (NCH_3); 30.7 (t, CH_2CF_2); 23.6 ($NCH_2CH_2CH_2CH_3$); 19.7 ($NCH_2CH_2CH_2CH_3$); 13.9 ($NCH_2CH_2CH_2CH_3$). ^{11}B NMR: 6.5 s, 1 B (B(1)); –16.9 d, 5 B (B(2-6)); –17.8 d, 5 B (B(7-11)); –22.3 d, 1 B (B(12)). IR (Nujol): ν(BH) 2469, ν(triazole) 1692. For $C_{35}H_{68}B_{12}F_{17}N_5O_2$ (1043.7) calculated: 40.28% C, 6.57% H, 6.71% N, 12.43% B; found: 40.12% C, 6.62% H, 6.83% N, 12.34% B.

RESULTS AND DISCUSSION

Preparation of azide derivatives of *closo*-dodecaborates via cleavage of its oxonium derivatives was reported previously[12]. In this work we have simplified the described method for preparation of azide **2** (Scheme 1). We have prepared pure **2** by the reaction of **1** with NBu_4N_3 generated in situ. Azide **2** was obtained in quantitative yield as a white solid (m.p. 104 °C), not a colorless oil[12].

Azide **2** undergoes Cu(I) "click" reactions with a series of terminal acetylenes giving novel B_{12}-substituted 1,2,3-triazoles **3a**–**3e** (Scheme 1). The reactions were monitored by ^{1}H NMR. After work-up and isolation the yields of triazoles **3a**–**3e** were obtained in high yields (60–70%). Attempts to react

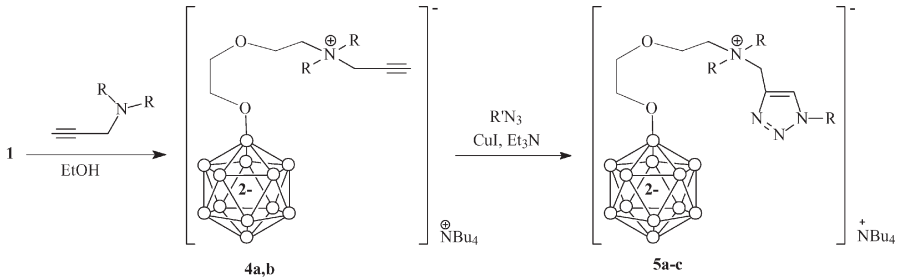


SCHEME 1

non-terminal acetylenes with azide **2** in boiling EtOH or DMF resulted in recovery of starting materials. Compounds **3a**–**3e** were characterized by IR and NMR spectra and microanalysis. In the IR spectra of **3a**–**3e** the absorption bands of BH (2470 cm^{-1}) and 1,2,3-triazole (1700 cm^{-1}) were observed. In the ^1H NMR spectra of the obtained compounds, the characteristic signal of triazole CH (ca. 7.5–8.5 ppm) was detected. The other signals were of the spacer chain, R of triazole and a broad multiplet of BH protons. In the ^{11}B NMR spectra of **3a**–**3e** the signal of B–O (B(1)) was observed as expected at δ 6.3–6.7 ppm.

In our previous work we have found that amines cleave B_{12}-oxonium derivatives to give corresponding ammonium derivatives[13]. Using these reactions, we have found that **1** reacts with propargylamines giving novel ammonium derivatives **4a**, **4b** with terminal acetylene group (Scheme 2). The structure of **4a**, **4b** was confirmed by NMR and IR spectra. In the ^{11}B NMR spectra of ammonium salts **4** the signal of the substituted boron atom is shifted ca. 2 ppm downfield compared with the starting materials **1** [9]. This is typical of the transformation of the BO^+R_2 grouping to B–OR. In the ^1H NMR spectra of **4** the signals of CH of the triple bond was detected at about 3.9 ppm. In the IR spectra of **4** absorption of the C≡C bond was found at 2120 cm^{-1}.

Finally, we have reacted boronated acetylenes **4a**, **4b** with azides in "click" reactions. These reactions afforded novel 1,2,3-triazoles **5a**–**5c** (Scheme 2). ^1H NMR monitoring of the reactions has shown 100% yields in 24 h. Triazoles **5a** and **5b**, **5c** were isolated as Cs and NBu_4 salts, respectively. The yields of the novel compounds were high (about 80%). The structure of triazoles **5a**–**5c** was proved by NMR, IR spectra and microanalysis.



SCHEME 2

CONCLUSION

We have developed an efficient general synthetic approach giving facile, rapid and inexpensive access to a wide range of novel 1,2,3-triazoles bearing *closo*-dodecaborate moiety, based on nucleophilic cleavage of oxonium dodecaborate with NaN_3 or a tertiary propargylamine and the Huisgen 1,3-dipolar cycloaddition ("click" methodology) of corresponding cleavage products and organic acetylenes or azides. The method allows the incorporation of additional functional groups into the dodecaborate molecule and could be useful in search of new potential agents for boron neutron capture therapy of cancer.

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