Mendeleev Commun., 1999, 9(3), 101–102

Reaction of 2,2-dibromotricyclo[7.1.0^{1,9}.0^{1,3}]decane with methyllithium: synthesis of bicyclo[7.1.0]decadiene-1,2 and dibromotriangulane rearrangement

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Reaction of 2,2-dibromotricyclo[7.1.0^{1,9}.0^{1,3}]decane with methyllithium gives strained cyclic allene 1 containing an ethenylidenecyclopropane unit in a nine-membered ring and dimer 6 resulting from a dibromotriangulane rearrangement.

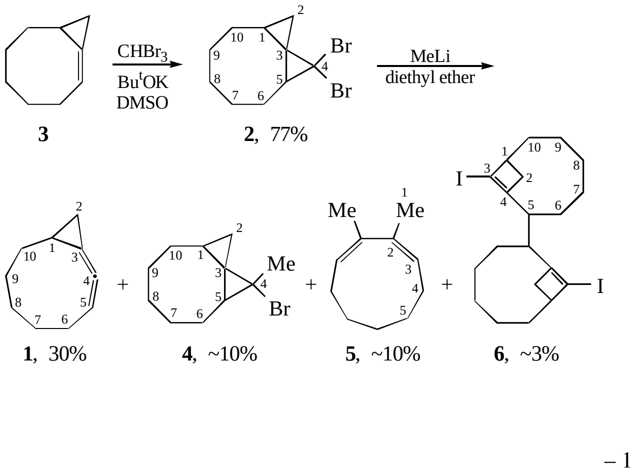
Recently we suggested a synthetic approach to highly energetic branched triangulanes,[1] which consists in the synthesis of corresponding allenes followed by cyclopropanation of the double bonds.[2] We expected that the introduction of an allene fragment into a middle-sized ring will permit us to use these cyclic allenes as starting compounds for the synthesis of peripherally cyclopropanated structures (cyclosubstituted triangulanes[2,3]). However, only few examples of allenes incorporated into a nine-membered ring are known up to now.[4] Moreover, such cyclic allenes containing a cyclopropane unit connected to a double bond are still not known. This work concerns the synthesis of bicyclo[7.1.0]deca-1,2-diene **1** which is the first example of a strained cyclic alkenylidenecyclopropane.

We used the standard synthetic procedure for generating allene fragments, which consists in [1 + 2]-cycloaddition of dibromocarbene to a corresponding olefin followed by the treatment of the obtained dibromocyclopropane with methyllithium in ether.[5] Thus, we have synthesised previously unknown dibromide **2** (77% yield) by the treatment of bicyclo[6.1.0]non-1-ene **3**[6] with bromoform and Bu^{t}OK in hexane.

The reaction of dibromide **2** with methyllithium (obtained from lithium and MeI in diethyl ether) was performed at –40 °C and 0 to –5 °C. A mixture of four products (**1**, the main product, and **4**–**6**) was obtained in both cases. The yield of allene **1** increased by 10% (up to 30%) as the temperature increased from 0 to –5 °C. Compounds **1**, **4**–**6** extracted from the reaction mixture. Allene **1** was distilled to a bulb cooled with liquid nitrogen at 2×10^{-3} Torr without heating. The residue was dissolved in ether, the solution was placed in a refrigerator (*ca.* –20 °C) and the obtained crystalline precipitate of **6** was collected on a filter. Compounds **4** and **5** were obtained from the remaining solution by preparative GLC.†

All of the obtained compounds were characterised by ^{1}H and ^{13}C NMR and mass spectrometry. Analyses of the NMR spectra and spectra–structure correlations were made by double resonance techniques and two-dimensional homonuclear (COSY H–H) and heteronuclear (COSY C–H) correlations.‡

Interpretation of the ^{1}H and ^{13}C NMR spectra of triangulanes **1**–**3** was based on the characteristic difference of the geminal coupling constants $^2J_{HH}$ (and $^1J_{CH}$ for compound **2**) of the three- and eight-membered rings. The existence of a cumulene unit in substance **1** was supported by ^{13}C NMR signals with chemical shifts typical of allenes[7] at 85.8 and 91.7 ppm for



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† *Reaction of dibromide* **2** *with MeLi*. To a magnetically stirred solution of 3.5 g (0.0119 mol) of dibromide **2** in 20 ml of dried diethyl ether under argon 13.8 ml of 1.45 M MeLi (obtained from lithium and MeI) in diethyl ether was added dropwise during 40 min at 0 to –5 °C. The reaction mixture was stirred for 2 h and then quenched with water. The organic layer was separated, washed with water and dried with MgSO$_4$. The solvent was evaporated under reduced pressure (1 Torr) into a trap cooled at –80 °C. The ‘bulb-to-bulb’ distillation of the residue at 2×10^{-2} Torr into a trap cooled with liquid N$_2$ gave ~0.4 g of allene **1** (~30%). The residue was dissolved in ether and kept at –18 °C during a week. Obtained white solid compound **6** (0.020 g, ~3%) was filtered off. GLC of the residue gave fraction I of 0.20 g (~10%) of monobromide **4** and fraction II of 0.10 g (~10%) of olefin **5**.

‡ The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian VXR-400 spectrometer in CDCl$_3$, TMS as a standard. Mass spectra were obtained on Varian MAT 311A and 1321A spectrometers. GLC analyses and separations were performed using silicon E-301 (15% on Inerton AW).

Bicyclo[7.1.0]deca-1,2-diene **1**. ^{1}H NMR, δ: 0.85 (m, 1H), 1.17 (m, 1H), 1.31 (ddd, 1H, 2-H, ^2J 7.1 Hz, ^5J 3.2 Hz, ^3J 4.8 Hz), 1.52–1.74 (m, 5H), 1.57 (m, 1H, 2′-H), 1.90 (m, 1H, 6-H, ^2J 16.0 Hz), 1.93 (m, 1H), 2.07 (m, 1H, 1-H), 2.29 (m, 1H, 6′-H, ^2J 16.0 Hz), 5.21 (m, 1H, 5-H). ^{13}C NMR, δ: 12.75 (C-2), 19.68 (C-1), 24.19, 26.56, 26.80 and 27.19 (C-7 through C-10), 30.67 (C-6), 85.79 (C-3), 91.66 (C-5), 193.15 (C-4). MS, *m/z* (%): 134 (3) [M]$^+$, 133 (3) [M – 1]$^+$, 119 (16), 105 (33), 106 (16), 93 (19), 92 (26), 91 (100), 79 (38), 78 (30), 77 (45), 67 (17), 66 (10), 65 (22), 51 (18), 41 (29). IR, ν/cm^{-1}: 1950 (C=C=C).

2,2-Dibromotricyclo[7.1.0.0^{4,3}]decane **2**. ^{1}H NMR, δ: 0.95 (dd, 1H, 2′-H, ^2J 4.8 Hz, ^3J 6.0 Hz), 1.02 (m, 1H, 7-H), 1.19 (dd, 1H, 2-H, ^2J 4.8 Hz, ^3J 8.8 Hz), 1.30 (m, 1H, 8-H), 1.32 (m, 1H, 9-H), 1.43 (m, 1H, 7′-H), 1.56 (m, 1H, 8′-H), 1.59 (m, 1H, 10-H), 1.60 (m, 1H, 9′-H), 1.63 (m, 1H, 1-H), 1.71 (m, 1H, 6-H, ^2J 14.6 Hz, ^3J 8.0 Hz), 1.86 (m, 1H, 6′-H), 2.08 (m, 1H, 10′-H), 2.08 (m, 1H, 5-H). ^{13}C NMR, δ: 15.69 (C-2, *J* 163 Hz), 19.75 (C-7, *J* 125 Hz), 22.82 (C-1, *J* 163 Hz), 23.26 (C-9, *J* 127 Hz), 27.47 (C-6, *J* 128 Hz), 28.38 (C-10, *J* 128 Hz), 30.70 (C-8, *J* 127 Hz), 33.48 (C-3), 35.46 (C-5, *J* 162 Hz), 40.72 (C-4). Found (%): C, 40.85; H, 4.80. Calc. for C$_{10}$H$_{14}$Br$_2$ (%): C, 41.39; H, 5.32.

2-Methyl-2-bromotricyclo[7.1.0.0^{1,3}]decane **4**. ^{1}H NMR, δ: 0.63 (dd, 1H, 2′-H, ^2J 4.3 Hz, ^3J 5.4 Hz), 1.00 (dd, 1H, 2-H, ^1J 4.3 Hz, ^3J 8.6 Hz), 1.31 (m, 1H, 1-H), 1.33 (m, 1H), 1.40–1.75 (m, 7H), 1.88 (dm, 1H), 1.75 (s, 3H, Me), 2.03 (m, 1H, 6-H). ^{13}C NMR, δ: 9.77 (C-2), 18.78 (C-1), 19.26 (C-7), 23.60 (C-9), 26.65 (C-6), 27.94 (C-8), 29.85 (C-10), 27.73 (Me), 28.66 (C-3), 28.80 (C-5), 44.79 (C-4). MS, *m/z* (%): 149 (39) [M – Br]$^+$, 135 (4), 133 (8), 121 (12), 119 (11), 107 (47), 105 (30), 95 (46), 93 (42), 91 (62), 67 (70), 55 (35), 53 (32), 41 (42), 39 (29).

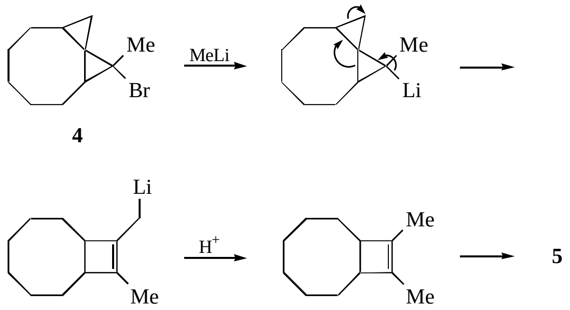
2,3-Dimethylnona-1,3-diene **5**. ^{1}H NMR, δ: 1.40 (br. m, 4H, 5-H), 1.56 (m, 2H, 6-H), 1.75 (d, 6H, 1-H, ^4J 1.5 Hz), 1.98 (m, 4H, 4-H), 5.31 (tq, 2H, 3-H, ^3J 8.5 Hz, ^4J 1.5 Hz). ^{13}C NMR, δ: 21.57 (C-1), 27.07 and 29.59 (C-4 and C-5), 29.90 (C-6), 125.90 (C-3), 138.00 (C-2). MS, *m/z* (%): 150 (49) [M]$^+$, 135 (38), 121 (28), 107 (77), 93 (100), 91 (63), 79 (91), 77 (48), 67 (77), 55 (45), 53 (46), 51 (27), 41 (96), 39 (92), 29 (38), 27 (67).

9,9′-Diiodo-2,2′-bis(bicyclo[6.1.1]dec-9-ene) **6**. ^{1}H NMR, δ: 0.96–1.21 (m, 6H), 1.50–1.86 (m, 12H), 1.93 (m, 2H), 2.02 (m, 2H), 2.57 (d, 2H, 2-H, ^2J 11.0 Hz), 2.70 (dd, 2H, 2′-H, ^2J 11.0 Hz, ^3J 4.4 Hz), 3.16 (br. t, 2H, 1-H, ^3J 4.4 Hz, ^3J 4.5 Hz). ^{13}C NMR, δ: 27.09, 27.74, 29.15, 29.99, 33.82 (C-6 through C-10), 37.42 (C-2), 45.13 (C-1), 46.91 (C-5), 92.16 (C-3), 157.90 (C-4).

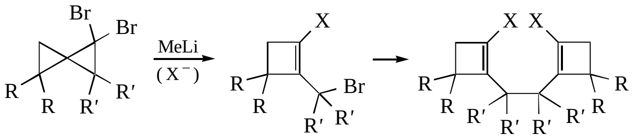
edge carbon atoms and 193.1 ppm for the central atom. The long-range coupling between the terminal allene proton and one of the methylene protons ($^5J_{HH}$ 3.2 Hz) point at the direct connection of this unit with the three-membered ring. The structure of the diene unit of compound **5** (the adjacent position of the two methyl groups at inner carbon atoms of the diene unit) was based on the spin–spin coupling data. The structure of dimer **6** was unequivocally established by X-ray crystal structure analysis.[§]

The obtained results are remarkable. First, we have synthesised strained cyclic allene **1** having cyclopropane unit directly connected to an allene unit. Second, the isolation of by-products **4**, **5** and, especially, **6** is important for a general understanding of the process.

The intermediate formation of monobromolithium species in the reaction of dibromocyclopropanes with methyllithium is well documented.[4] However, the formation of by-products of the type **4** and **5** was not observed and hence was unexpected. It seems that the formation of monobromide **4** resulted from the methylation of a lithiumcarbenoid intermediate in the presence of methyl bromide or methyl iodide in the reaction mixture.[4(*e*)] A reasonable mechanism for the formation of olefin **5** is the sequence of bromine–lithium exchange on **4** followed by a ring-opening rearrangement, subsequent protonation and electrocyclic ring opening of the ring-annelated cyclobutene.[8]



The isolation of the dimeric diiodide is especially remarkable. Previously we have described the unique rearrangement[7] of triangulane dibromides **7** in the presence of methyllithium to give corresponding cyclobutene dibromides **8** as primary products in accordance with the scheme



7 **8** **9a** X = Br
9b X = I

While the isomeric dibromides can be isolated, they undergo further transformation in the presence of an excess of MeLi to give dimeric products **9** in the case of R′ = H. It is of interest that the presence of iodide anions in the reaction mixture (from the reaction of MeI with Li) leads to formation of iodides **9b**. However, the detailed mechanism of this rearrangement still remains speculative.

This work was supported by the Russian Foundation for Basic Research (grant no. 98-03-32876a).

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Received: 24th November 1998; Com. 98/1405 (8/09468C)

[§] Crystal data for **6** were obtained by Dr. A. E. Lysov and Dr. K. A. Potekhin (Vladimir, Russian Federation); the detailed results will be published elsewhere.