Synthesis of Cyclo-substituted Triangulanes with Four and Five Spiroannulated Three-membered Rings by Sequential Peripheral Cyclopropanation of Cyclooctene

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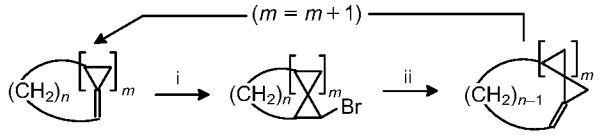
Synthesis of pentacyclo[9.1.0.0^{1,3}.0^{3,5}.0^{5,7}]dodecane **4** and hexacyclo[10.1.0.0^{1,3}.0^{3,5}.0^{5,7}.0^{7,9}]tridecane **5** has been performed, based on sequential bromocyclopropanation of the C=C bond and elimination to give a repeating endomethylenecyclopropane framework, with termination of the sequence by cyclopropanation.

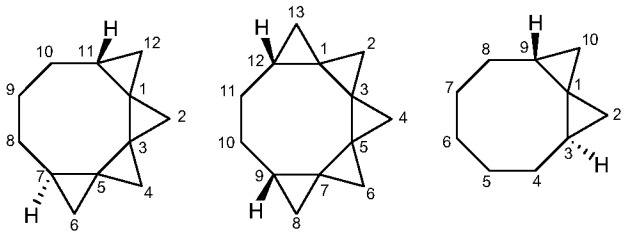
Triangulanes are a class of highly strained polycyclic hydrocarbons in which the skeleton is constructed from spiroannulated three-membered rings.[1–5] We have already elaborated general approaches to the synthesis of *chain* triangulanes.[1,3] Recently, we have proposed[3–5] (as have De Meijere and co-workers[5,6]) general strategies for the synthesis of *branched* triangulanes.

More recently we have suggested a synthetic protocol for synthesis of *cyclo-substituted* triangulanes (CST) containing an eight-membered ring,[7] based on the sequential introduction of an endomethylenecyclopropane framework (Scheme 1).



Scheme 1 *Reagents*: i, $CH_2Br_2/(Me_3Si)_2NNa$; ii, Bu^tOK/DMSO.

The goal of the present paper was the application of this protocol in the synthesis of polyspirocyclopropanated CST **4** and **5**.



Bromocyclopropanation of olefine **1** ($m = 2$, $n = 4$)[7] provides bromide **2** ($m = 2$, $n = 4$), dehydrobromination of which gives the olefin **3** ($m = 2$, $n = 4$). Final cyclopropanation of this olefin with CH_2N_2 in the presence of $Pd(OAc)_2$[1] gave pentacyclo[9.1.0.0^{1,3}.0^{3,5}.0^{5,7}]dodecane **4** (yield 78%).†

The ^{13}C NMR spectrum of **4**† reveals only seven signals, expected for the isomer having C_2 symmetry. Analogous data were observed for tricyclo[7.1.0.0^{1,3}]decane **6**, the simplest cyclo-substituted triangulane, containing an eight-membered ring:[7] ^{13}C NMR of **6** reveals six signals expected for the structure with C_2 symmetry.

Repetition of the same reaction sequence (Scheme 1) with olefin **3** ($m = 2$, $n = 4$) gave the corresponding bromide **2** ($m = 3$, $n = 3$), olefin **3** ($m = 3$, $n = 3$) and finally hexacyclo[10.1.0.0^{1,3}.0^{3,5}.0^{5,7}.0^{7,9}]tridecane **5**, which was isolated by preparative GLC as a mixture of two isomers (4:1) with total yield 80%.

The ^1H and ^{13}C NMR spectra of the major isomer of **5**† reveal C_s symmetry. Thus, methylene protons of C^9 and C^{12} have a *cis*-configuration and we obtained one of the two possible *cis*-isomers of **5**.

In the ^1H NMR spectrum of the minor isomer **5a**† there are *three* isolated AX-systems corresponding to methylene protons of C^2, C^4 and C^6 (*cf.* with *two* corresponding resonances in the *cis*-isomer, **5**) and four different complex resonances for $C^{10}H_2$–$C^{11}H_2$ protons, which allows us to suggest a *trans*-configuration for **5a**.

This work was supported by the Russian Foundation for Fundamental Researches (grant no. 93-03-5222).

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† For **4**: ^1H NMR (400 MHz, $CDCl_3$) δ 0.28 (t, 2H, $J = 3.6$ Hz), 0.61–0.73 (m, 2H), 0.93 (dd, 2H, $J_1 = 7.5$, $J_2 = 3.8$ Hz), 0.99–1.07 (m, 2H), 1.12 (d, 2H, $J = 4.12$ Hz), 1.36 (d, 2H, $J = 4.12$ Hz), 1.42–1.53 (m, 2H), 2.01 (dq, 2H, $J_1 = 14.0$, $J_2 = 3.1$ Hz); ^{13}C NMR (CD_2Cl_2) δ 11.93 (C^2, C^4), 13.47 (C^6, C^{12}), 17.75 (C^7, C^{11}), 19.13 (C^1, C^5), 20.07 (C^3), 26.55 (C^9), 31.81 (C^8, C^{10}).

For the major isomer of **5**: ^1H NMR (500 MHz, CD_2Cl_2) δ 0.065 (dt, 2H, $J_1 = 13.5$, $J_2 = 11.5$ Hz), 0.391 (t, 2H, $J = 4.0$ Hz), 0.941 (d, 1H, $J = 3.8$ Hz), 1.153 (d, 1H, $J = 3.8$ Hz), 1.254 (dd, 2H, $J_1 = 8.0$, $J_2 = 4.0$ Hz), 1.308 (d, 2H, $J = 3.8$ Hz), 1.345–1.40 (m, 2H), 1.375 (d, 2H, $J = 3.8$ Hz), 2.42 (dt, 2H, $J_1 = 13.5$, $J_2 = 2.5$ Hz); ^{13}C NMR (CD_2Cl_2) δ 13.01 (C^4), 13.47 (C^1, C^7), 15.56 (C^8, C^{13}), 19.27 (C^3, C^5), 19.50 (C^9, C^{12}), 20.37 (C^2, C^6), 27.78 (C^{10}, C^{11}).

For minor isomer **5a**: ^1H NMR (500 MHz, CD_2Cl_2) δ −0.15 to −0.10 (m, 1H), 0.18 (t, $J = 4.5$ Hz, 1H), 0.23 (dd, $J_1 = 5.0$ Hz, $J_2 = 6.5$ Hz, 1H), 0.615 (t, $J = 4.5$ Hz, 1H), 0.63–0.84 (m, 3H), 0.76 (d, $J = 4.8$ Hz, 1H), 0.86 (d, $J = 4.8$ Hz, 1H), 0.99 (d, $J = 4.0$ Hz, 1H), 1.20 (d, $J = 4.0$ Hz, 1H), 1.35 (d, $J = 4.0$ Hz, 1H), 1.54 (d, $J = 4.0$ Hz, 1H), 1.66–1.76 (m, 2H), 1.98–2.12 (m, 1H).

Received: Moscow, 20th May 1994
Cambridge, 4th August 1994; Com. 4/03122I