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Mendeleev Commun., 1993, **3(3)**, 91–92
Mendeleev Communications

Subsequent Peripheral Cyclopropanation as a Synthetic Approach to Cyclic and Cyclo-substituted Triangulanes

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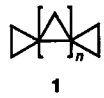
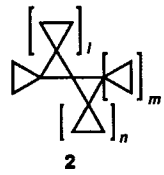
A general scheme for cyclo-substituted triangulane synthesis has been developed, based on subsequent cyclopropanation of olefinic structures of type **5** and **6**.

Recently we have defined the *triangulanes* as a unique class of highly strained polycyclic hydrocarbons whose skeleton is constructed from spiroannulated three-membered rings.[1–5] In the course of systematic studies on these compounds we developed general approaches for preparation of both the *linear* **1**,[1,2] and *branched* triangulanes **2**.[3–5] However, it is possible to imagine one more sub-class of triangulanes, namely *cyclic* triangulanes **3 (CT)**. Obviously, the synthesis of cyclic triangulanes may present an intriguing problem.



1

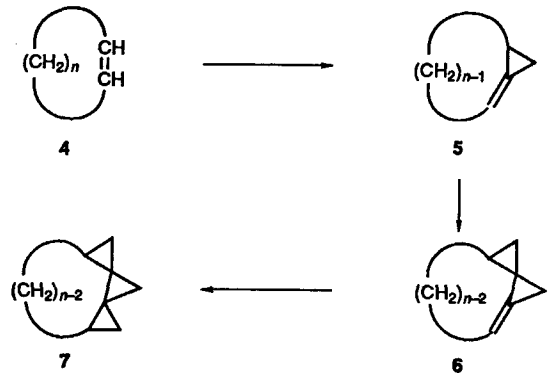


2

3

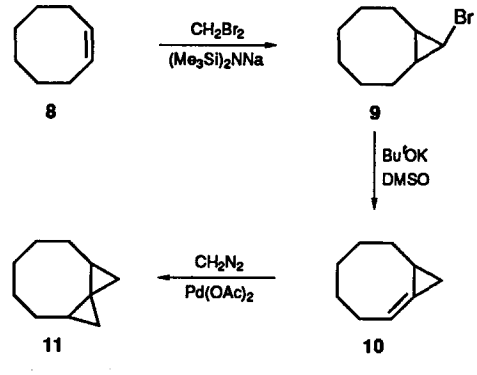
The present paper describes our first attempt to develop general methodology to the synthesis of cyclic triangulanes. The idea of the approach is the following: the corresponding cycloolefin **4** must be transformed into a cyclo-substituted cyclopropane with an external double bond, **5**. Application

of the same procedure to the olefin **5** should give olefin **6**, whose cyclopropanation completes the process to give cyclo-substituted triangulane **7**. Repetition of these reaction sequences is equivalent to the peripheral cyclopropanation of the corresponding cyclopolyallene and may probably lead to formation of the corresponding [n+2]-cyclotriangulane, Scheme 1.



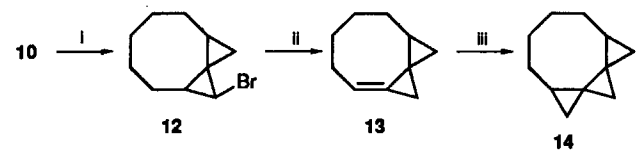
Scheme 1

Cyclooctene **8** was selected as the starting material for development of this synthetic protocol. Bromocyclopropanation of olefin **8**[6] gave bromide **9** (35–40%; 20:1 mixture of *cis–trans* isomers). Dehydrobromination of **9**[7] gave olefin **10**. Final cyclopropanation of **10** with CH_2N_2 in the presence of $Pd(OAc)_2$ gave tricyclo[7.1.0.0^{7,9}]decane **11** (two isomers, 9:1),† Scheme 2.



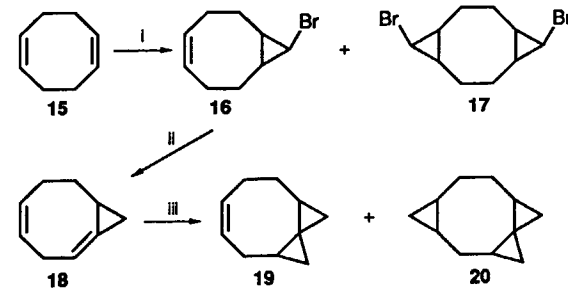
Scheme 2

Repetition of the same reaction sequence with olefin **10** gave bromide **12** (30%), then the olefin **13** (its formation was fixed by GLC and the olefin was used without purification) and finally tetracyclo[8.1.0.0^{6,8}.0^{8,10}]undecane **14** which was isolated and purified by preparative GLC,† Scheme 3.



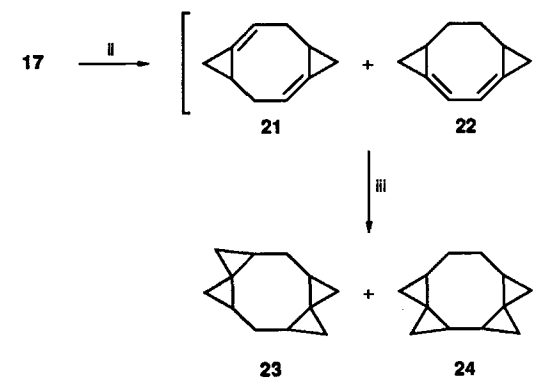
Scheme 3 *Reagents*: i, $CH_2Br_2/(Me_3Si)_2NNa$; ii, Bu^{t}OK/DMSO; iii, $CH_2N_2/Pd(OAc)_2$

Bromocyclopropanation of cycloocta-1,5-diene **15** gave a mixture of monobromide **16** (35%) and dibromide **17** (5%). Dehydrobromination of **16** smoothly gave diene **18** (^{1}H NMR) and its cyclopropanation with an excess of diazomethan gave a mixture of mono (**19**) and bis (**20**) adducts, separated by preparative GLC,† Scheme 4.



Scheme 4 *Reagents*: i, $CH_2Br_2/(Me_3Si)_2NNa$; ii, Bu^{t}OK/DMSO; iii, $CH_2N_2Pd(OAc)_2$

Finally, dehydrobromination of the dibromide **17** gave a mixture of diolefins **21** and **22** which was treated with diazomethane without purification. The isolated products (preparative GLC) were the cyclo-substituted triangulanes **23** and **24**,† Scheme 5.



Scheme 5 *Reagents*: ii, Bu^{t}OK/DMSO; iii, $CH_2N_2/Pd(OAc)_2$

In conclusion, we have demonstrated that our methodology can be successfully applied to the synthesis of cyclo-substituted triangulanes. The study of scope and limitation of the suggested methodology for synthesis of cyclo-substituted and cyclic triangulanes is actively underway.

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† All compounds obtained have satisfactory analytical and spectroscopic data (indicating the mixture of diastereomers).

Received: Moscow, 25th December 1992
Cambridge, 26th January 1993; Com. 2/06896F