Reviews

Triangulanes

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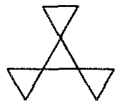
Stereochemical problems, general methods of synthesis, structures, and some properties of triangulanes, a new class of highly strained polycyclic hydrocarbons, which consist exclusively of spirocondensed cyclopropanes, are considered.

Key words: polyspirocyclopropanes; chain, branched, cyclosubstituted, and cyclic triangulanes; rotanes; heats of formation.

Introduction

Cyclopropane compounds possess a complex of unique properties and have long attracted the attention of chemists.[1–8] First, since being formally saturated, a three-membered ring manifests olefin-like properties, such as the ability to undergo reactions of Ad_E addition and conjugation with unsaturated groups.[9–11] Second, cyclopropanes are strained structures with an increased enthalpy of formation, and, hence, they are promising energy-consuming compounds.[12,13]

These peculiarities can appear to a greater extent in spirocondensed structures containing three-membered cycles. The existence of the spirocenter can primarily result in an increase in the intrinsic strain of the molecule. The question about the conjugation of cyclopropane fragments in structures of this type is also of interest. Therefore, the efforts of many organic chemists were directed at preparing aesthetically attractive and structurally unusual classes of spirocondensed structures with small cycles.[14–17] The class of [*n*]-rotanes, cyclic oligomeric cyclopropylidenes (see, *e.g.*, [3]-rotane (**1**) and [6]-rotane (**2**)),[17–19] can be mentioned as an example.



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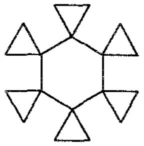

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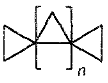

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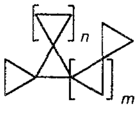

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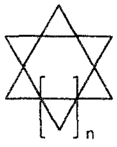

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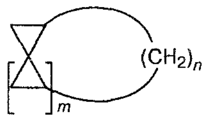
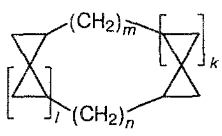


6a



6b

In 1990, *triangulanes*, compounds consisting of spirocondensed three-membered cycles (**3**—**6**), were distin-

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guished as a special class of cyclopropane hydrocarbons.[20] In other words, triangulanes are the class of compounds with oligomeric spiroannelated cyclopropane fragments. This classification is necessary, because, first, triangulanes have a large variety of structures; second, stereoisomerism of triangulanes is a complex and even a unique problem, whose solution requires methods of discrete mathematics; and, third, triangulanes possess unusual physical (for example, strain) and chemical properties, which as a whole make them especially attractive subjects for experimental study.

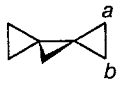
From the viewpoint of structural theory, triangulanes can be divided into several subclasses, in particular, into *chain* (CT), **3**; *branched* (BT), **4**; *cyclic* (CyT), **5**; and *cyclosubstituted* (CST), **6a** and **6b**, triangulanes. It is evident that [3]-rotane (**1**) can also be referred to the BT class.

Several words should be said about the nomenclature for triangulanes used in this work. In the standard nomenclature, the name of the compound is prefixed with the word "spiro" and the numbers of atoms in both cycles are indicated in brackets. For example, the simplest CT (**3**, $n = 0$), containing two cyclopropane rings can be called spiro[2,2]pentane. However, this nomenclature is very inconvenient for higher members of the series. Therefore, we will use the names of the [n]-triangulane type, where n is the total number of three-membered cycles in the chain, for chain triangulanes **3**. For example, compound **9** can be called chain [4]-triangulane or trispiro[2.0.0.2.1.1]nonane; this example strikingly demonstrates the advantage of the nomenclature accepted. Unfortunately, a convenient nomenclature for other types of triangulanes has not yet been developed.

Problems of stereochemistry of triangulanes

Let us consider first the stereoisomerism of *chain* triangulanes.[20] Three-membered cycles of spiropentane **7** are localized in two perpendicular planes. The molecule of this compound belongs to the point symmetry group D_{2d} and, hence, it is achiral. It can be easily seen that [3]-triangulane (**8**) is the achiral molecule as well, but it has two enantiotopic positions (*a* and *b* in the formula of **8**). This results in the fact that even [4]-triangulane (**9**) can exist as two enantiomers **9a** and **9b** due to the attachment of the fourth cyclopropane ring to [3]-triangulane **8** either to position *a* or position *b*.

7



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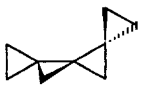
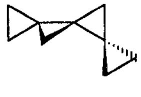
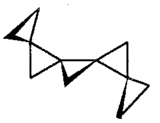


9a



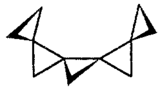
9b

In the case of [5]-triangulane (**10**), there is a possibility of the existence of diastereomers, namely: *meso*- and (±)-racemic forms.



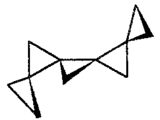
(+)

10b



meso

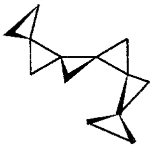
10a



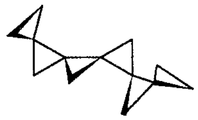
(–)

10c

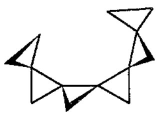
Three racemic pairs — **11a** + **11f**, **11b** + **11e**, and **11c** + **11d** — are possible for [6]-triangulane.



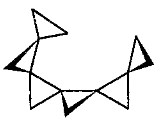
11a



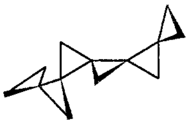
11b



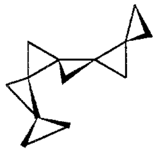
11c



11d



11e



11f

It is evident that in the case of higher CT the problem of stereoisomerism becomes very complex and needs a special mathematical consideration. Such a consideration has been performed previously.[20] The authors of Ref. 20 used the Burnside lemma for considering the stereoisomerism of chain triangulanes, which made it possible to estimate exactly the number of stereoisomers as a function of the number of three-membered cycles (Table 1).

It can be seen from the data in Table 1 that the number of possible stereoisomers increases drastically as the chain lengthens. The formation of achiral *meso*-isomers is possible only for structures with the odd number of cyclopropane rings (the only exception is the first member of this series, [2]-triangulane).

Methods for synthesis of triangulanes

Chain triangulanes (3)

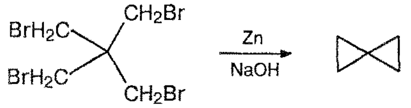
Although all general methods for synthesis of cyclopropanes should, in principle, be applicable for triangulanes as well, it is far from being so in practice.

The simplest [2]-triangulane, spiropentane, was obtained in 1896 by the reductive debromination of tetrakis(bromomethyl)methane with zinc and alkali[21] (Scheme 1).

Table 1. Possible stereoisomers of chain [*n*]-triangulanes

n	Total number of stereoisomers	Number of racemic pairs	Number of achiral isomers
2	1	0	1
3	1	0	1
4	2	1	0
5	3	1	1
6	6	3	0
7	10	4	2
8	20	10	0
9	36	16	4
10	72	36	0
11	136	64	8
12	272	136	0
13	528	256	16
14	1056	528	0
15	2080	1024	32
16	4160	2080	0
17	8258	4096	64
18	16512	8256	0
19	32896	16384	128
20	65792	32896	0

Scheme 1

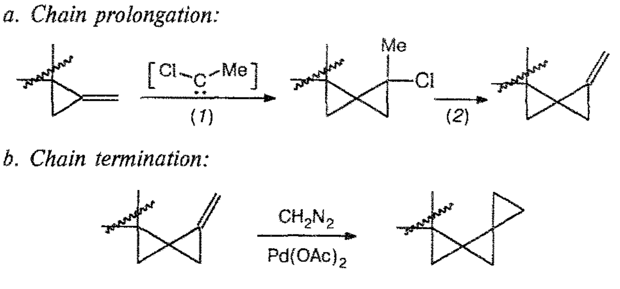


However, the formation of methylenecyclobutane and other side products decreases the synthetic potential of this reaction. Just due to the formation of rearranged compounds the methodology of reductive dehalogenation of *gem*-(dihalomethyl)cyclopropanes cannot be applied to more complex structures.[22]

The development of the chemistry of [1+2]-cycloaddition of carbenes to olefins made it possible to carry out the synthesis of [3]- and [4]-triangulanes.[16,18,23–26] Different methods for the generation of a carbenoid intermediate are used in these processes, in particular, the Simmons—Smith reaction (the use of the Zn/Cu and Zn/Ag + CH_2I_2 system for cyclopropanation) and the decomposition of diazo compounds in the presence of various catalysts. However, it is also difficult to use these methods for the synthesis of higher triangulanes, which necessitates searching the general strategy for synthesis of these compounds.

The general and versatile method for synthesis of chain triangulanes has been developed in the laboratory of N. S. Zefirov.[20,22] The method is based on the cycloaddition of halocarbenes to the methylenecyclopropane fragments using separate, but repeated stages of *chain prolongation* and *termination*, as shown in Scheme 2.

Scheme 2



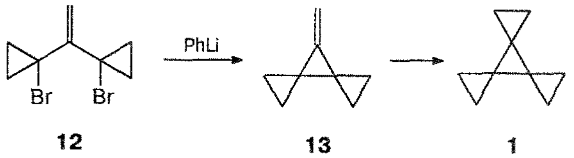
The stage of prolongation includes in turn two chemical reactions, namely: the addition of chloromethylcarbene to methylenecyclopropane (*1*) followed by the elimination to form the cyclohomologic methylenecyclopropane fragment (*2*). It has been found that the reaction between 1,1-dichloroethane and butyllithium is a convenient source of chloromethylcarbene for the [1+2]-cycloaddition to the methylenecyclopropane fragment. The dehydrohalogenation was performed by treatment with potassium *tert*-butylate in DMSO.[20,22]

The use of the diazomethane—palladium acetate system at the termination stage, *i.e.*, cyclopropanation of the last methylenecyclopropane fragment, gives the best results.[22] This method allowed the authors of Ref. 20 to synthesize [4]-, [5]-, and [6]-triangulanes as a mixture of stereoisomers.

Branched triangulanes (4)

The simplest branched triangulane **1** ([3]-rotane) has been primarily synthesized by cyclopropanation of olefin **13**, which was prepared by the reductive debromination of dibromide **12** according to Scheme 3.[16,18,27]

Scheme 3

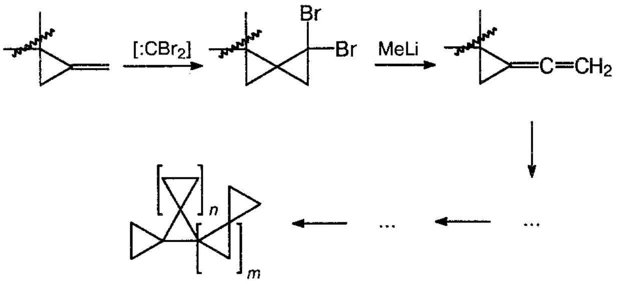


However, general and versatile methods for synthesis of the family of branched triangulanes were developed by the research groups of N. S. Zefirov[28–31] and A. de Meijere[32–35]. The first method includes the stage of formation of the vinylidenecyclopropane fragment as the basis for developing the triangulane branching.

The principal scheme of this method is the following. Initial methylenetriangulane reacts with dibromocarbene, and the dibromosubstituted derivative is transformed to the corresponding allene by reaction with methyllithium. Then both double bonds of the allene are subjected to growth of triangulane chains similar to the case of chain triangulanes (Scheme 4).

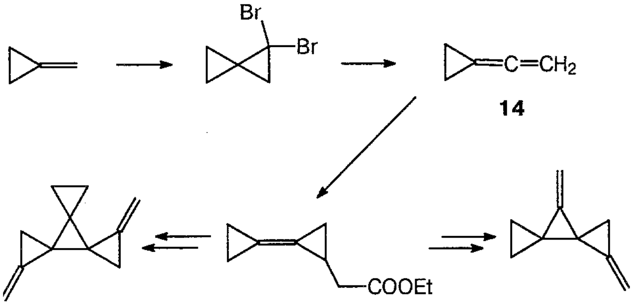
This strategy of synthesis has been realized, for example, for preparing the series of triangulanes according to Scheme 5. [28–31] Initial methylenecyclopropane is transformed into vinylidenecyclopropane **14**, the reac-

Scheme 4

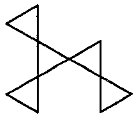


tion between which and ethyldiazoacetate results in ester **15**. Functional transformations in ester **15** followed by the addition of chloromethylcarbene allow one to obtain dienes **16** and **17**.

Scheme 5



The series of branched triangulanes **18** and **19a—c** was synthesized by the cyclopropanation of these dienes.



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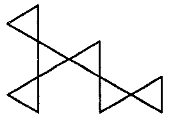
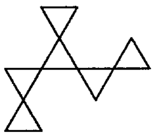
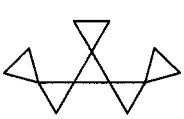


19a



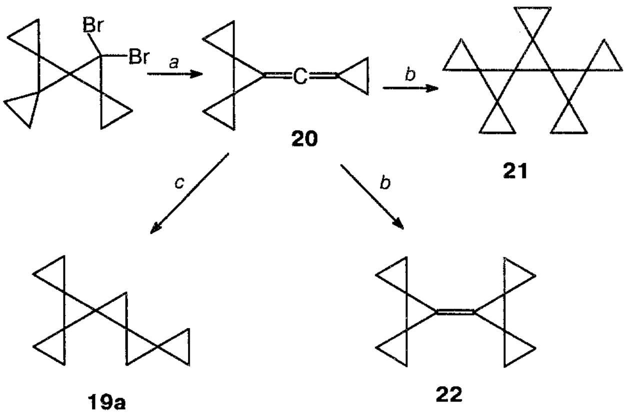
19b



19c

Another example of using the "allene" methodology in synthesis of branched triangulanes[33] is the preparation of triangulanes **19a** and **21** based on allene **20** according to Scheme 6.

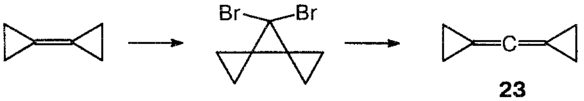
Scheme 6



Reagents: *a*, MeLi; *b*, $\triangleright{=}N_2$; *c*, $CH_2N_2/Pd(OAc)_2$.

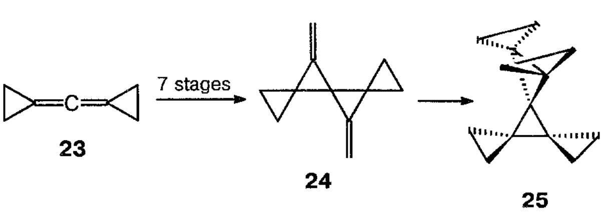
Allene **23** prepared according to Scheme 7 turned out to be very useful for synthesis of branched triangulanes.[16,31]

Scheme 7



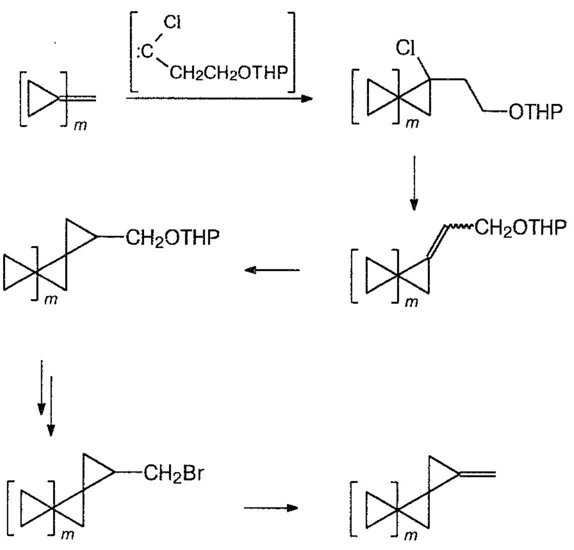
In particular, several transformations allowed one to transform allene **23** to diene **24** and then to triangulane **25** (Scheme 8) with a very interesting propeller-type structure with D_{2h} symmetry (the data of the X-ray diffraction analysis of triangulane **25** were published in Refs. 36 and 37).

Scheme 8



Another general strategy for synthesis of branched triangulanes developed by the combined efforts of the research groups of N. S. Zefirov and A. de Meijere[33] is based on the cycloaddition of *functionally substituted* chloroethylcarbenes to methylenecyclopropanes. Scheme 9 shows the sequence of the stages, which result in the formation of olefin **26**, the direct precursor of branched triangulanes.

Scheme 9



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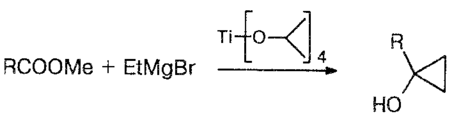
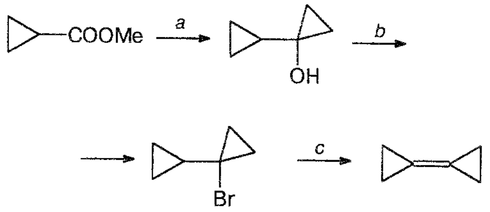
Scheme 10

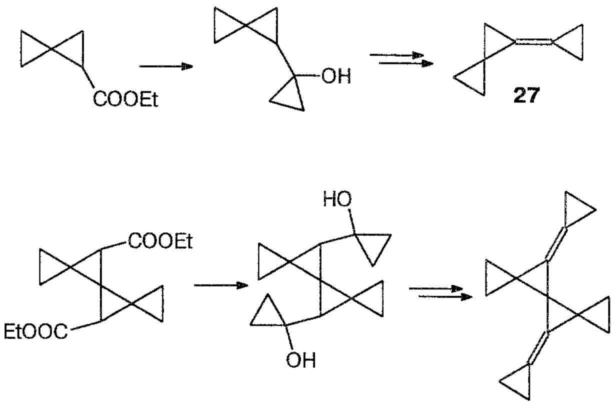


Scheme 11



Reagents: *a*, EtMgBr, $Ti(OPr^i)_4$, Et_2O (yield 99 %); *b*, Ph_3PBr_2, Py, CH_2Cl_2 (yield 78 %); *c*, $Bu^tOK/DMSO$ (yield 81 %).

Scheme 12



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The key point for developing this method is the selection of conditions for the generation and cycloaddition of the corresponding functionally substituted carbene from precursors, 1,1-dichloro-3-alkoxypropanes.[33] The method is successful when the bis(trimethylsilyl)amide anion is used as a base; the use of butyllithium results either in the formation of products of opening of the three-membered cycle or in the isomerization of the multiple bond. This general approach was used for synthesizing triangulanes **19a—c** and **25**.

The next general method for synthesis of branched triangulanes is based on the Kulinkovich reaction.[38,39] It has been shown previously[38—40] that the reaction between esters and ethylmagnesium bromide in the presence of titanium tetraisopropylate results in the formation of cyclopropanols according to Scheme 10.

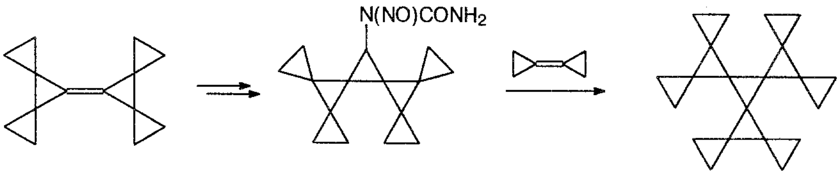
It can formally be assumed that the dianionic intermediate [$^-CH_2—CH_2^-$] participates in the formation of the small cycle.[41] It is evident that this reaction provides wide possibilities for synthesis of triangulanes. First, one of the key initial compounds, dicyclopropylidene, becomes available due to this reaction[34] (Scheme 11).

Moreover, the general method for synthesis of various higher bicyclopropylidenes, for example, compounds **27** and **28** (Scheme 12), was developed on the basis of this reaction.[34]

In particular, it is the cycloaddition to bicyclopropylidene that is the main stage in the synthesis of pericyclopropanated [3]-rotane, hydrocarbon **29** (Scheme 13).[35]

[3]-Rotane (**1**) has the D_{3h} symmetry. [10]-Triangulane **29** also has D_{3h} symmetry, and, thus, it is the

Scheme 13



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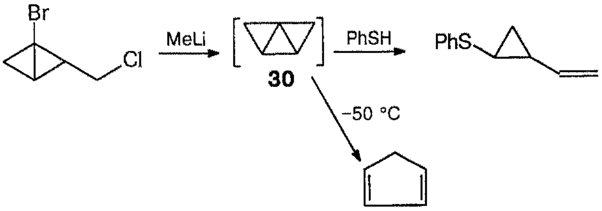
second member (after [3]-rotane) of the family of star-like structures (an interesting consideration of hypothetical structures of this type is presented in Ref. 35).

Cyclosubstituted (6a,b) and cyclic (5) triangulanes

Cyclic triangulanes (CyT) **5** are the most strained structures in the family of triangulanes. First members of this hydrocarbon series with $n = 0$ to 2 possess so strain energies that the possibility of their syntheses has yet been highly conjectural.[42] Only 8-CyT ($n = 3$) is considered to be a relatively real structure for synthesis.[42,43] The introduction of methylene bridges in molecules of cyclic triangulanes decreases their intrinsic strain, and cyclosubstituted triangulanes (CST) **6a,b** formed are relatively available synthetic objects. As a whole, the preparation of compounds with the cyclic or cyclosubstituted triangulane framework is considered as a basically important theoretical and synthetic problem.[42]

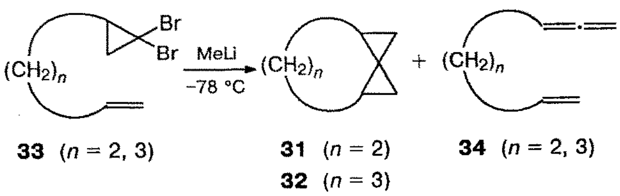
Tricyclo[2.1.0.0^{1,3}]pentane (**30**) is the first member of the CST series of the **6a** type ($n = 0$, $m = 1$). It is evident that it is one of the most strained hydrocarbons of this type. It was synthesized by the reaction between 1-bromo-2-chloromethylbicyclobutane and methyllithium at −78 °C [44,45] and was detected by low-temperature ^{13}C NMR spectroscopy. The product of its reaction with thiophenol was isolated as well. When thiophenol is absent, complete isomerization of hydrocarbon **30** to cyclopentadiene[44] occurs at −50 °C (Scheme 14).

Scheme 14



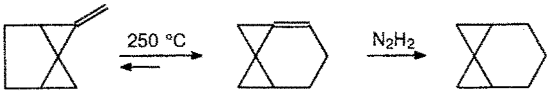
Less strained tricyclic hydrocarbons containing the spiropentane fragment in combination with five- and six-membered cycles (of the **6a** type, $n = 2$ and 3, $m = 1$), **31** and **32**, were obtained by the intramolecular reaction of [1+2]-cycloaddition[46] in the series of alkenylcyclopropylidenes **33** (Scheme 15).

Scheme 15



However, this synthetic approach has serious disadvantages and restrictions. For example, the reaction is accompanied by the cyclopropylidene-allene rearrangement, and even at −78 °C the corresponding allenes of the **34** type are formed in considerable amounts. They are the only products of such reactions at higher temperatures.[46] In addition, the intramolecular [1+2]-reaction of cyclopropylidenes **33** is very sensitive to the number of methylene units between two reaction centers. Only tricycloheptane **31** and its several derivatives[46—52] were obtained by this method in appropriate yields. The homolog of hydrocarbon **31**, tricyclo[5.1.0.0^{1,3}]octane (**32**) was isolated in a very low yield in a similar way.[46] It is mentioned in the literature[53] that hydrocarbon **32** is not formed from cyclopropylidene **33** ($n = 3$) at all, and the reaction with methyllithium at −78 °C results in the formation of allene **34** ($n = 3$) and 2-vinylbicyclo[3.1.0]hexane. Tricyclooctane **32** has recently been synthesized by another method (Scheme 16) from methylenetricycloheptane.[54]

Scheme 16



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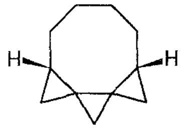
It is clear that such a nontrivial approach has a particular character and cannot be used for preparing other polycyclic compounds.

The subsequent peripheral cyclopropanation of cycloolefins was suggested by N. S. Zefirov and coworkers as a general and versatile method for synthesis of cyclosubstituted triangulanes of the **6a,b** type.[42,43,55] The first stage of the synthesis includes the transformation of the cycloolefin to the compound containing the methylenecyclopropane fragment, as shown in Scheme 17. The second stage, *homologization of the methylenecyclopropane fragment*, is based on the same sequence of reactions (peripheral cyclopropanation of the base polygon). This synthetic sequence is completed by the formation of cyclosubstituted triangulane according to Scheme 17.

This synthetic scheme was successfully realized for cyclooctene,[42,43,55] which served as a basis for the subsequent preparation of cyclosubstituted triangulanes **35—38**.

In principle, the peripheral cyclopropanation can be performed in two directions, choosing cyclic dienes as initial compounds. For example, cyclosubstituted triangulanes **39—41** were obtained[42,43] on the basis of cyclodiene-1,5 (Scheme 18).

The most interesting question about the possibility of synthesizing cyclic triangulanes of type **5** by this method remains unsolved.



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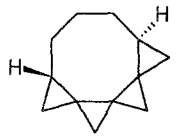

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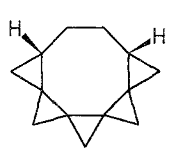

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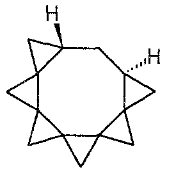

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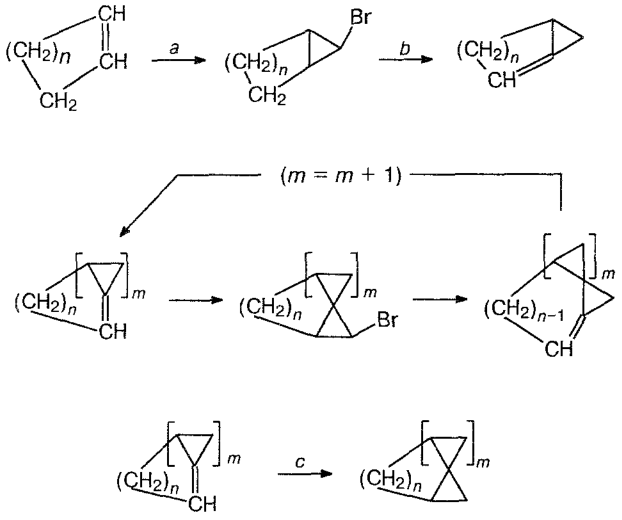
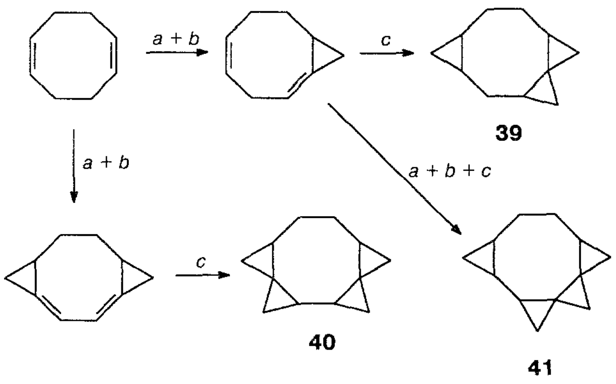
Scheme 17



Reagents: *a*, $CH_2Br_2/(Me_3Si)_2NNa$;
b, $Bu^tOK/DMSO$;
c, $CH_2N_2/Pd(OAc)_2$.

Scheme 18



Reagents: *a*, $CH_2Br_2/(Me_3Si)_2NNa$;
b, $Bu^tOK/DMSO$;
c, $CH_2N_2/Pd(OAc)_2$.

Properties of triangulanes

Spectral properties and geometric structure

Results of studying structures of triangulanes and their derivatives by X-ray diffraction analysis are presented in several works.[36,37,56] The following peculiarities of deformation of three-membered cycles in these molecules are mentioned: (1) lengthening of C—C bonds, which lie opposite to spiro atoms, and shortening of vicinal bonds in terminal three-membered cycles; (2) considerable shortening of C—C bonds with two neighboring spiro atoms; and (3) shortening of all C—C bonds in trispirosubstituted cyclopropanes.

To determine correlations between the structure and chemical shifts in ^{13}C NMR spectra, several triangulanes were analyzed.[57] The additive scheme of chemical shifts for establishing and predicting structural assignments in triangulanes was suggested.

Strain and thermochemical data

Starting from the work by von Bayer,[58] who introduced the term "strain" into the chemical lexicon, there is much data in the literature referring both to refinement of this notion[1,11,12] and to experimental and computational methods for determining heats of formation of organic compounds, which allow one to estimate the energy of strain.[59,60]

Available data on heats of formation of spirocondensed cyclopropanes with five- and six-membered cycles revealed no excessive strain. In other words, the energy of strain in these cases is equal to the sum of strains of the cyclopropane ring and the larger cycle.[11]

Thermochemical data on the enthalpy of formation of spiropentane[61,62] show that its strain is equal to 265.8 kJ mol^{-1} (see Ref. 11), which is approximately 31.1 kJ mol^{-1} higher than the sum of strains of two cyclopropane rings. Such an increase in the strain is quite understandable, because there is an additional angular distortion for sp^3-orbitals of the spiro atom in the triangulane structure.

Enthalpies of formation of four triangulane hydrocarbons[63] were determined experimentally; these data along with literature data for spiropentane **7** are presented in Table 2.

Table 2. Heats of formation of some triangulanes

Triangulane	Δ_fH° /kJ mol^{-1}	$\Delta_fH(C^{3,3}_{4spiro})$ /kJ mol^{-1}
7	185	114
8	303	107
9	429	107.8
10	544	105
1	424	105.7

In terms of the additive scheme, the data in Table 2 make it possible to calculate the contribution of the quaternary spiro atom to the heat of formation ($\Delta_f H$ ($C^{3,3}_{4spiro}$)): its mean value is 106.4 kJ mol^{-1}. It is noteworthy that this value is 65 kJ mol^{-1} greater than the contribution of the quaternary C atom in alkyl-substituted cyclopropanes. Thus, triangulane molecules have an excessive strain, and the results obtained testify that it is additively accumulated as the number of spiro atoms increases.[63]

If it is assumed that the strain of [10]-BT **29** is at least not lower than the tenfold strain of the cyclopropane ring, this value can be estimated as $\geq$1130 kJ mol^{-1}, and, thus, [10]-BT **29** is more strained than cubane.[64] At the same time, this compound is rather stable (m.p. 200—201 °C), and its thermal decomposition begins only at temperatures >250 °C.[35] It is known that cubane is sometimes considered the "structure of the XXI century".[65] The comparison presented above proves convincingly that the class of triangulanes is promising for future technologies.

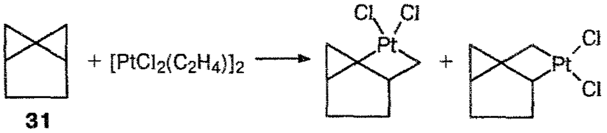
Chemical properties of triangulanes

The chemistry of triangulanes is almost unstudied. Only data on the reactivity of the simplest triangulane, spiropentane, are given in the literature.[66—73] The reaction of free-radical chlorination has been studied for spiropentane by analogy with cyclopropane. This reaction occurs under conditions of photoinitiation to form a mixture of substitution products and chlorides, which are formed due to opening of the small cycle.[66] The reaction of thermal isomerization of spiropentane and its ethoxycarbonyl derivative has been studied,[67—69] and it has been established that heating at 300 to 400 °C in both cases results smoothly in spiropentane-methylenecyclobutane rearrangement to form methylenecyclobutanes.

There were attempts to study the solvolysis of spiropentylhalides and tosyloxymethylspiropentane[70,71] in the context of studying nonclassical stabilization of carbonium ions. Transformations of functional groups were studied for most available derivatives of spiropentane, such as spiropentyl chloride and ethoxycarbonylspiropentane (see, *e.g.*, Refs. 70—73).

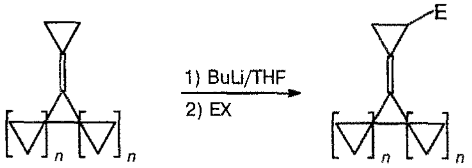
The study of chemistry of triangulanes has been starting very recently. The effect of the considerable intrinsic strain in cyclosubstituted triangulanes on chemical properties are pronounced in the reaction between tricycloheptane **31** and the Zeise salt,[74] which occurs with the cleavage of one of external cyclopropane C—C bonds followed by the insertion of platinum (Scheme 19).

Scheme 19



The direct functionalization of triangular hydrocarbons is a sufficiently complex problem due to the low mobility of hydrogen atoms. However, the exocyclic double bond activates neighboring C—H bonds in the three-membered cycle. The procedure for deprotonation of olefins of the triangulane series, dicyclopropylidenes, by butyllithium in THF is developed, and reactions between lithium derivatives formed and various electrophilic reagents are described[75] (Scheme 20).

Scheme 20

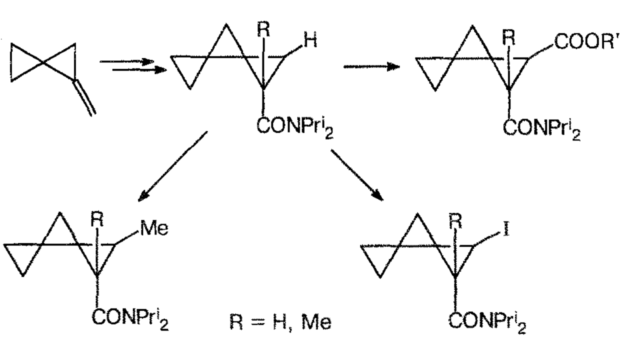


EX = Me_3SiX, PhSSPh, CCl_3CCl_3, CH_2BrCH_2Br, CO_2, MeCOMe
n = 0, 1

Thus, the series of functionally substituted triangulane olefins, whose cyclopropanation is a reliable method for synthesizing various triangulanes, has been obtained.

Another method for activation of C—H bonds in triangulanes has been suggested recently.[76] It has been shown that the *N*,*N*-diisopropylcarbamide group introduced into one of cyclopropane rings (Scheme 21) activates neighboring C—H bonds to make the stereospecific functionalization of triangulanes possible.

Scheme 21



The reactions of carboxylation followed by esterification, substitution of the α-H atom by iodine, and methylation have been performed. The carbamido-directed activation of C—H bonds is a promising synthetic method for functionalization of triangulanes and, in principle, can be used in synthesis of precursors of cyclic triangulanes.

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