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Synthesis of cyclopropane compounds: bicyclo[1.1.0]butanes, spiropentanes and bicyclopropanes

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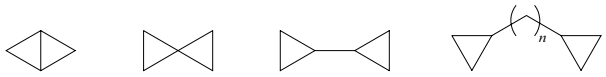
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Abstract. Data on the preparation of bicyclo[1.1.0]butanes, spiropentanes and bicyclopropanes are integrated and described systematically. The chemical reactions are classified according to the type of carbon – carbon bonds formed. The bibliography includes 244 references.

I. Introduction

In spite of the fact that polycyclopropanes are much less naturally abundant than monocylopropanes, the chemistry of polycyclopropane derivatives is an extensive and successfully developing field of research. First, it is caused by the theoretical interest of chemists in these compounds,[1,2] the existence of which was an open question even in the early 20th century. Second, the high strain of three-membered rings is responsible for the ability of polycyclopropanes to undergo a variety of synthetic transformations.[3] All polycyclopropane derivatives are classified according to the relative position of two three-membered rings, which may share a side or a corner or neither a side nor a corner. In the latter case, two cyclopropane moieties are separated by chemical bonds. Thus while designing polycyclopropane derivatives, one may be guided by the methods that have been developed for the synthesis of bicyclo[1.1.0]butane (structure **A**) and spiropentane (**B**) derivatives and 1,1′-bicyclopropanes (**C**) and that are in general similar to the methods of synthesis of cyclopropanes, though there are certain differences and restrictions. In addition, there are specific approaches to the synthesis of compounds under consideration, which will be presented below. The present review does not cover the synthesis of polycyclopropane derivatives with three-membered rings separated by carbon bridges (structure **D**) because in this case, the cyclopropane moiety has a little impact on the reaction centre formed by the second three-membered ring.



A **B** **C** **D** ($n \geqslant 1$)

Several reviews dealing with the synthesis of polycyclopropane derivatives have been published. The literature data on bicyclo[1.1.0]butanes were first generalized[4] in the mid-1960s, soon after the discovery of general method of their synthesis (see below). Carbene-based synthesis of cyclopropanes was described in 1990 in monography of O M Nefedov *et al*.[5] In 2003, the known reactions resulting in bicyclopropanes were briefly considered by J Pietruszka.[6] An extensive review of A de Meijere *et al*.[7] published in 2006 and devoted to compounds with more than one cyclopropane moiety should be particularly mentioned. In the present review, literature data on the synthesis of bicyclo[1.1.0]butanes, spiropentanes and bicyclopropanes are systematized for the first time according to the classification of chemical reactions by the types of forming carbon – carbon bonds.

II. Methods of synthesis of bicyclo[1.1.0]butanes

The first surge of the number of publications on the synthesis of bicyclo[1.1.0]butanes occurred in the 1960s. This fact is related to the preparation of bicyclo[1.1.0]butane-1-carboxylate by K Wiberg in 1959 by treating methyl 3-bromocyclobutanecarboxylate with triphenylmethylsodium (Ph_3CNa) in diethyl ether. Since the product yield in this reaction was low (20%), the subsequent studies were focused on the search for other approaches to building a bicyclobutane skeleton. The use of carbene methods based on cyclization of allylcarbenes and on cyclomethylenation of acetylenes turned out to be successful. A considerable contribution to the development of chemistry of bicyclo[1.1.0]butanes was made by Russian scientists. Pioneering

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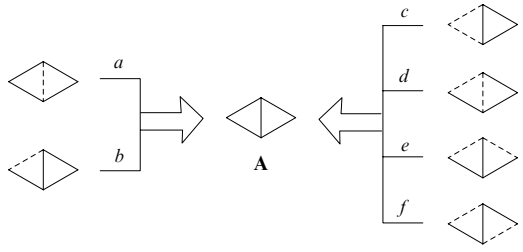
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studies of the reaction of acetylenic hydrocarbons with ethyl diazoacetate that were carried out in the 1950–1960s at the Chair of Organic Chemistry of the Leningrad State University by I A D'yakonov and his apprentice M I Komendantov should be especially noted, together with the studies of the graduate of the same chair, V V Razin. A great contribution to the solution of the problem of cyclomethylenation of acetylenes was made by O M Nefedov.

The next surge of the number of publications on this subject matter took place in the 1980s and in the early 1990s. It was related to the name of German researcher G Szeimies, who proposed a new convenient method for the synthesis of propellanes. C Manfred, A D Schlueter and P G Gassman should also be mentioned among the chemists who made a considerable contribution to the development of synthetic routes to bicyclo[1.1.0]butanes. The papers of the mentioned authors will be discussed below.

By retrosynthetic analysis of bicyclo[1.1.0]butane with the possible formation of one or two C–C bonds in one step, six possible routes of building of the target skeleton can be marked out. The first group of methods (pathways *a* and *b* in Scheme 1; from here on, dashed lines stand for the forming bonds) includes transformations giving one C–C bond as a result of 1,3-elimination, which is a classical approach to the synthesis of bicyclopropanes. Dehydrohalogenation of halocyclobutanes and dehalogenation of 1,3-dihalocyclobutanes and 1-halo-2-(halomethyl)cyclopropanes belong to this group. The intramolecular insertion into the C–H bond belongs to the same group of methods. Another group of methods combines the transformations in which two C–C bonds are formed simultaneouly in one step during the formation of bicyclo[1.1.0]butane skeleton (pathways *c*–*f*). These include cyclopropanation of cyclopropenes and acetylenes (pathway *c*), cyclization of allylcarbenes generated by various methods (pathway *d*), and photochemical isomerization of buta-1,3-dienes (pathway *f*). No examples of realization of route *e* for the preparation of bicyclo[1.1.0]butanes are known so far.

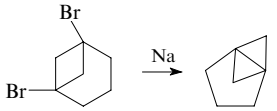
Scheme 1



1. Dehalogenation of 1,3-dihalocyclobutanes

Treatment of 1,3-dihalocyclobutanes with alkali metals is a classical method of synthesis of bicyclobutanes by pathway *a* (see Scheme 1). Thus, unsubstituted bicylo[1.1.0]-butane is formed in 94% yield from 1-bromo-3-chlorocyclobutane under the action of sodium in dioxane.[8] Similarly, 1,3-dimethylbicyclo[1.1.0]butane was obtained by the reduction of 1,3-dibromide by sodium in dioxane or in diglyme. However, when unpurified diglyme was used, 1-methyl-3-methylenecyclobutene was isolated as a side product, whereas in diglyme that had been purified from alcohol only 1,3-dimethylbicyclo[1.1.0]butane was formed in 85% yield. By varying the content of ethylene glycol in diglyme, it is possible to direct the reaction along the desired route.[9]

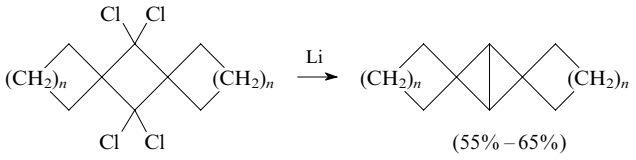
Debromination of 1,5-dibromobicyclo[3.1.1]heptane (**1**) under the action of metallic sodium led to [3.1.1]propellane (**2**), which was stable at room temperature for a fortnight.[10]



1 **2** (75%)

In the case of compounds containing functional groups sensitive to alkali metals, magnesium is used for dehalogenation. Thus bicyclo[1.1.0]butane-1-carbonitrile was obtained in a quantitative yield by treatment of 1,3-dibromocyclobutanecarbonitrile with magnesium in THF. Another approach to the synthesis of this compound consists in the thermolysis of sodium 3-chloro-1-cyanocyclobutanecarboxylate.[11] Magnesium may cause elimination of the halogen atom and the alkoxy group. For example, treating of 1-alkyl-1-chloro-3-ethoxycyclobutanes with magnesium in THF or with sodium in dioxane at 55–65 °C leads to the formation of 1-alkylbicyclo[1.1.0]butanes in relatively high yields.[12]

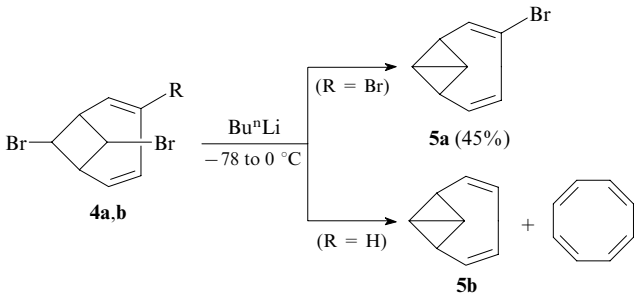
Substituted 1,1,3,3-tetrachlorocyclobutanes can be used instead of 1,3-dihalocyclobutanes. They transform into corresponding bicyclo[1.1.0]butanes under the action of alkali metals in methyl or *tert*-butyl alcohol. Under these conditions, reductive dehalogenation and closure of the carbon–carbon bridge proceed simultaneously, resulting in bicyclobutane compounds in one step and in high yields. Under the action of lithium or sodium on 5,5,10,10-tetrachlorodispiro[3.1.3.1]decane (**3a**) in methyl or *tert*-butyl alcohol, bicyclo[1.1.0]butanedi(spirocyclobutane) was formed in a 55%–65% yield.[13] Later, the authors extended this reaction to dispiro derivatives **3b**,**c**.[14]



3a–c

n = 1 (**3a**), 2 (**3b**), 3 (**3c**)

Besides alkali metals or magnesium, organolithium compounds were also used as dehalogenating agents. For example, the reaction of 1,3-dihalocyclobutane **4a** with n-butyllithium in diethyl ether at −78 °C selectively gave bromooctavalene **5a** in 45% yield as a single regioisomer. However, under similar conditions, treatment of compound

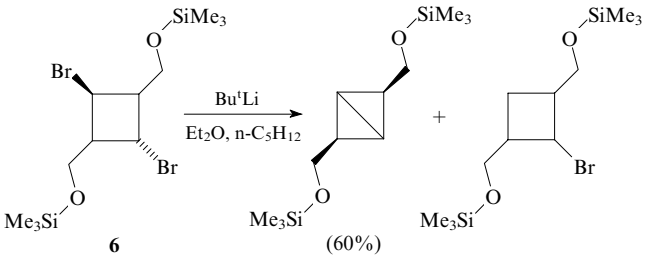


4a,**b**

R = Br (**4a**), H (**4b**)

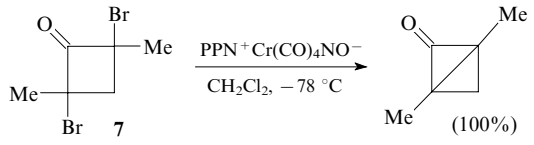
4b leads to a 3 : 1 mixture of octavalene (**5b**) and cycloocta-1,3,5,7-tetraene.[15]

An example of the use of *tert*-butyllithium for dehalogenation of 1,3-dibromocyclobutane **6** is known.[16]



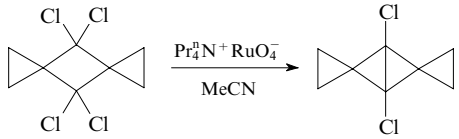
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Effective 1,3-debromination of 1,3-dibromocyclobutan-2-one **7** in the presence of $PPN^+Cr(CO)_4NO^-$ [PPN is bis(triphenylphosphine)iminium] resulting in the formation of corresponding dimethylbicyclo[1.1.0]butanone was described.[17]



7

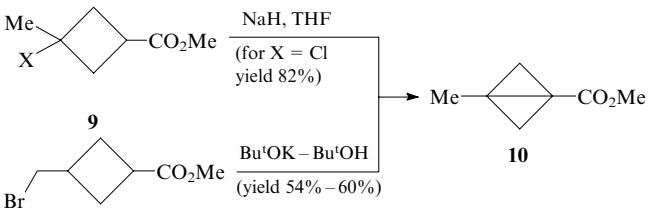
As a part of the study of the mechanism of electrochemical cleavage of carbon–halogen bond, it was discovered that 1,3-dihalocyclobutanes may be reductively carbocyclized to give bicyclo[1.1.0]butanes in good yields. 1,3-Dimethylbicyclobutane was prepared in this way from 1,3-dibromo-1,3-dimethylcyclobutane in 94% yield.[18] Electrochemical reduction of tetrachloro-substituted compound **3c** in THF resulted in 72% yield of bicyclo[1.1.0]butane derivative **8** containing four cyclopropane moieties.[19] The same compound was obtained by electrochemical reduction of di(spirocyclopropyl)tetrachlorocyclobutane **3d** ($n = 0$).[20]



3d **8** (63%)

2. Dehydrohalogenation of halocyclobutanes

As it was already mentioned, substituted bicyclo[1.1.0]butane was first obtained in 20% yield by dehydrohalogenation of methyl 3-bromocyclobutanecarboxylate under the action of Ph_3CNa.[4] If a stronger base, *e.g.*, NaH, is used in this reaction, then the yield increases to 77%. At the present time, Bu^tOK is often used as a base along with NaH. The presence of electron-withdrawing groups at the carbon atom bonded to the leaving proton promotes the reaction. Thus, dehydrohalogenation of 1-chlorocyclobutane-1,3-dicarbonitrile with the use of strong base (Bu^tOK) resulted in the corresponding substituted bicyclobutane in high yield (82%).[13] Similarly, dehydrohalogenation of chloro and bromo derivatives **9** induced by sodium hydride in THF leads to methyl 3-methylbicyclo[1.1.0]butanecarboxylate (**10**). It should be noted that product **10** may be obtained in 54%–60% yield by treatment of bromomethyl derivative **11** with potassium *tert*-butoxide in *tert*-butyl alcohol.[21]



9 **10**

11

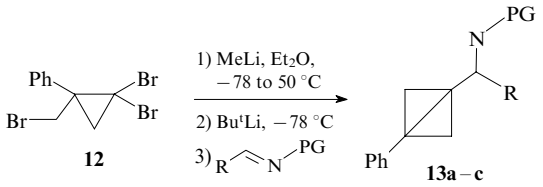
X = Cl, Br

Dehydroiodination of substituted 1-iodocyclobutane-3-carbonitriles was successfully carried out under the action of NaH in anhydrous diethyl ether.[22]

3. 1,3-Cyclization of 2-halocyclopropane derivatives

The methods of preparation of bicyclo[1.1.0]butanes that are described above are based on the cyclization of substituted cyclobutanes. Another approach to the synthesis of the mentioned bicyclic compounds consists in 1,3-cyclization of 2-halocyclopropylmethanol derivatives, which are synthesized in two steps from available allylic compounds (see pathway *b* in Scheme 1). Thus, interaction of dibromocarbene with allyl ethyl ether resulted in 1,1-dibromo-2-(ethoxymethyl)cyclopropane. This product was reduced by zinc in methanol at 0 °C to give 1-bromo-2-(ethoxymethyl)-cyclopropane, which was made to react with Mg in boiling THF to give a 4.4 : 1.5 : 1 mixture of unsubstituted bicyclo[1.1.0]butane, cyclobutene and butadiene, the total yield being 50%.[23]

Organolithium compounds are often used as reagents for 1,3-cyclization of 1-halo-2-(halomethyl)cyclopropanes. For example, consecutive treatment of *gem*-dibromocyclopropane **12** with methyllithium, *tert*-butyllithium and corresponding imine results in bicyclo[1.1.0]butanes**13a–c** in good yields.[24] Obviously, the first stage is dehalogenation with the formation of bicyclobutane moiety.

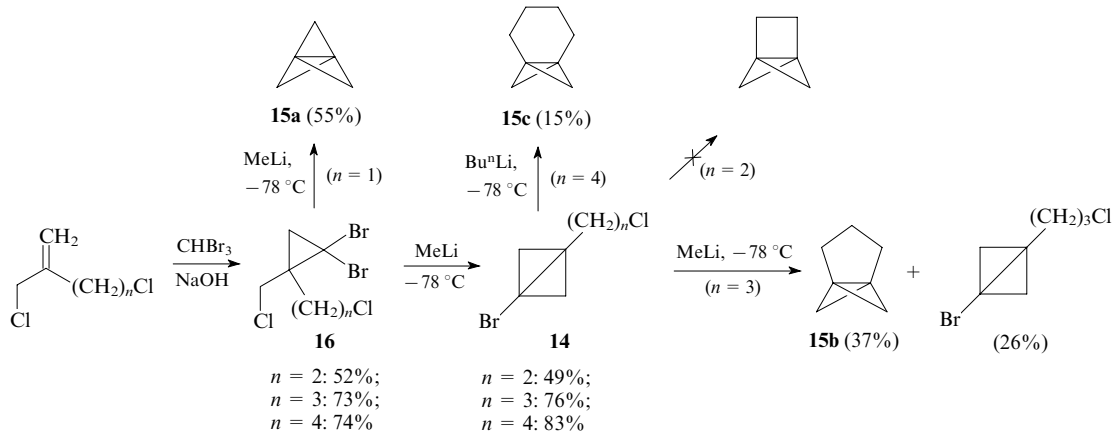


12 **13a–c**

13a: R = cyclo-C_6H_{11}, PG = Ts (75%); **13b**: R = Ph, PG = $P(O)Ph_2$ (73%); **13c**: R = Bu^t, PG = $P(O)Ph_2$ (71%); PG is protecting group

Multistage transformations are usually employed in order to obtain [*n*.1.1]propellanes, which may be regarded as bicyclobutane derivatives.[25–28] Fuchs and Szeimies[29] described a convenient method for the preparation of such compounds from halogen-substituted cyclopropanes in the presence of MeLi or Bu^nLi. Bicyclo[1.1.0]butanes **14** are intermediates in this synthesis (Scheme 2). This method was used to prepare one of the most easily accessible polycyclic compounds with small rings, namely, [1.1.1]propellane (**15a**), and also [3.1.1]- (**15b**) and [4.1.1]propellanes (**15c**).[29] Only [2.2.1]propellane has not yet been isolated in an individual state. It is supposed that this compound polymerizes at temperatures above 50 K. Interestingly, the most strained [1.1.1]propellane is, at the same time, most stable among [2.1.1]-, [2.2.1]-, [2.2.2]-, [3.2.1]-, [3.1.1]- and [4.1.1]propellanes.[30] Later, Szeimies and co-workers[31]

Scheme 2

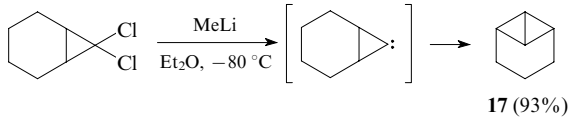


found the possibility of using alkali metals to perform dehalogenation. Thus, halogen-substituted cyclopropane **16** ($n = 1$) was reduced by a dispertion of lithium alloy containing 1% of sodium in a triglyme and n-decane mixture (4 : 1) at 73 °C in vacuum at reflux. In this case, [1.1.1]propellane (**15a**) was formed in 25% – 38% yield.

In 1988, staffane was isolated as a product of spontaneous polymerization of [1.1.1]propellane (**15a**). The composition of the polymer is $+C(CH_2)_3C+_n$. Staffanes may act as 'rigid rods' for the design of various nanostructures.[32]

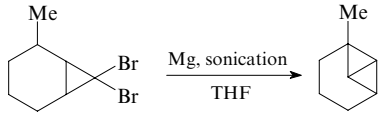
4. Insertion of carbenes at the C – H bond

Another method of formation of bicyclobutane structure according to pathway *b* (see Scheme 1) is based on the intramolecular insertion of cyclopropylidene at C – H bond (the Doering – Moore – Skattebøl reaction). Thus, upon the reaction of 7,7-dichlorobicyclo[4.1.0]heptane with MeLi in diethyl ether at −80 °C, a hydrocarbon fraction was isolated in 40% yield; its subsequent separation afforded three isomers.[33] Hydrocarbon **17** was the major product (yield 93%).



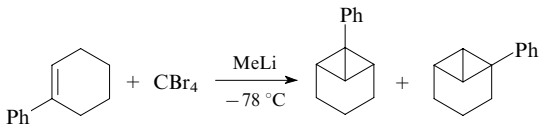
17 (93%)

However, the Doering – Moore – Skattebøl method is also a convenient and general route to substituted allenes. Thus, the formation of allene is often accompanied by the formation of bicyclobutane skeleton. This competition between the two routes of the reaction depends on the character of substituents that may favour conformational transformations and may affect the steric strain in the molecule being formed.[34] The most favourable situation for the preparation of bicyclo[1.1.0]butanes is observed in the case of norcarane structures.[35] Thus the ultrasound-assisted reaction of *gem*-dibromocyclopropane **18** with metals (Li, Mg or Na) results solely in substituted bicyclobutane **19**. The reaction is completed in 15 min and gives the product in a moderate yield.[36]



18 **19** (55%)

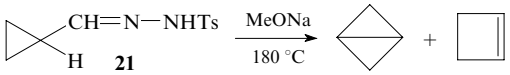
The efficiency of the discussed approach regarding the synthesis of bicyclobutane derivatives has been demonstrated by the preparation of phenyl derivatives of tricyclo[4.1.0.0^{2,7}]heptane **20a**,**b** in one step from 1-phenylcyclohexene and tetrabromomethane in the presence of methyllithium.[37] The total yield of the products was 79%, isomer **20a** significantly predominating in the mixture (93%).



20a **20b**

5. Carbocationic rearrangements

In the case of rearrangements that involve carbocations or carbanions, the bicyclo[1.1.0]butane system may be formed both by pathway *a* and by pathway *b* (see Scheme 1). Intramolecular reactions of cyclopropylmethyl, cyclobutyl and allylmethyl cations lead to bicyclobutane derivatives and are usually accompanied by side formation of cyclobutene, methylenecyclopropane and butadiene, the product ratio depending on the solvent and the particular substrate. For example, heating of cyclopropanecarboxaldehyde *p*-toluenesulfonylhydrazone (**21**) with MeONa in triglyme produced a mixture of bicyclo[1.1.0]butane and cyclobutene (ratio 4 : 1, total yield 27%).[38, 39] The authors supposed that cyclopropylcarbene had been formed as an intermediate, but later the ionic mechanism of this reaction involving cyclopropylmethyl cation was proposed.[38, 39]



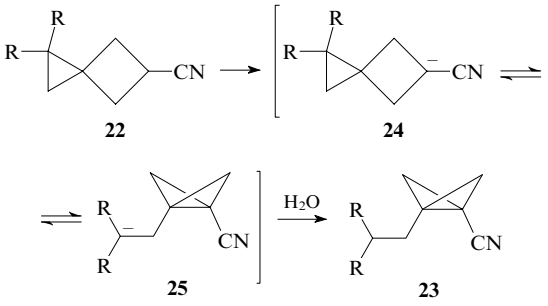
21

Thermal decomposition of the sodium salt of cyclobutanone *p*-tosylhydrazone in ethylene glycol proceeded similarly, yielding 52% of bicyclo[1.1.0]butane.[40] However, the highest selectivity with respect to bicyclo[1.1.0]butane (79% – 97%) was observed in the reaction of cyclopropylmethyl- or cyclobutylamine with amyl nitrite and acetic acid in chloroform, the yield of the product being 30% – 50%.

6. Carbanionic rearrangements

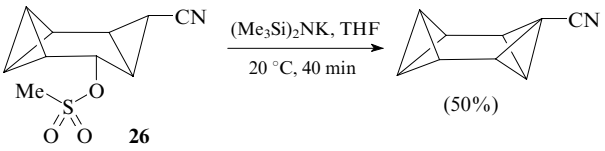
It is known that activated cyclopropanes containing a substituent with a CH-acidic group undergo base-induced prototropic isomerization to give a new ring instead of the

opening three-membered ring. For example, isomerization of spiro[2.3]hexanes **22** proceeds rapidly at room temperature to afford the corresponding substituted bicylobutanes **23** in high yields. The observed prototropic isomerization **22** → **23** is especially interesting because the equilibrium is irreversibly shifted to the formation of bicyclobutane compounds in spite of the higher strain energy of the bicyclobutane skeleton (63.9 kcal mol^{-1}) in comparison with the spirohexane one (56.7 kcal mol^{-1}).[41] Since the reaction was carried out in aprotic medium using a strong base, the direction of isomerization under these conditions was determined by equilibrium between carbanionic intermediates **24** and **25**.

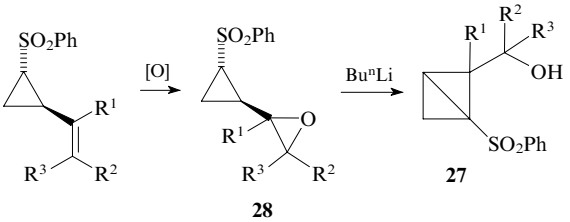


R = CO_2Me (75%), CO_2Et (71%), CN (72%)

The intramolecular nucleophilic substitution proceeds easily if mesylate or tosylate anion is the leaving group, as, for example, in the case of cyclization of compound **26**.[42]

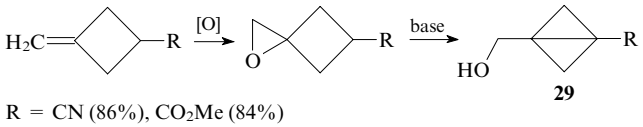


Epoxy sulfones, epoxy ketones, epoxy esters and epoxy nitriles of suitable structure transform into corresponding substituted bicyclobutylmethanols under the action of bases. Gaoni[43] used this principle for the creation of three-carbon rings in the synthesis of functionally substituted bicyclobutylmethanols **27** from corresponding vinylcyclopropanes. This transformation proceeds *via* the intermediate formation of epoxides **28**.



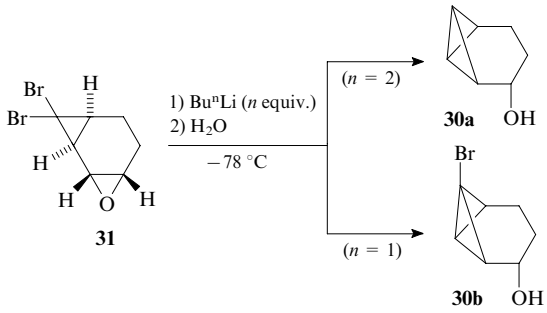
R^1	R^2	R^3	Yield (%)	
			28	**27**
Me	H	H	12	64
H	Me	Me	66	82
$(CH_2)_3$		H	70	95

A similar approach was used in the synthesis of substituted bicyclobutylmethanols **29** from substituted methylenecyclobutanes.[44] Unlike the scheme proposed by Gaoni, this reaction results in a closure of the central rather than side bicyclobutane C−C bond, and the hydroxymethyl group occurs in the bridgehead position of the bicyclobutane moiety.

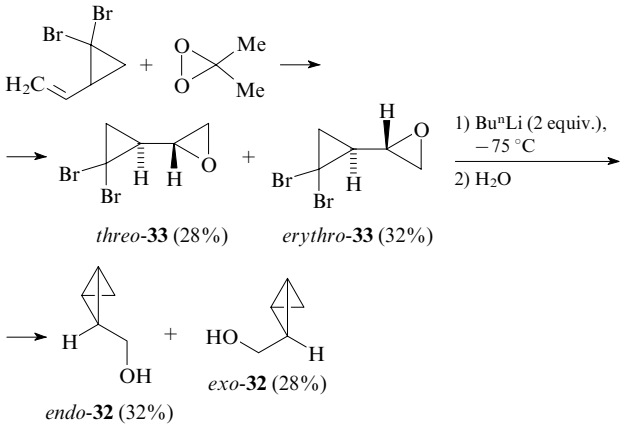


R = CN (86%), CO_2Me (84%)

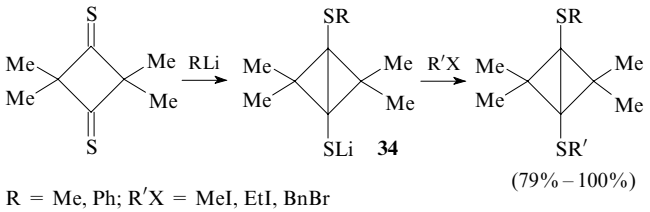
Tricyclo[4.1.0.$0^{2,7}$]heptan-3-oles **30a**,**b** were synthesized by treatment of *gem*-dibromocyclopropylepoxide **31** with n-butyllithium.[45] The structure of the product depended on the amount of butyllithium brought into reaction.



A similar strategy has been used for the preparation of bicyclo[1.1.0]but-2-ylmethylmethanol **32** *via* the formation of epoxides **33**.[45]



The addition of alkyllithium to C=S double bonds of 2,2,4,4-tetramethylcyclobutane-1,3-dithione was accompanied by generation of a carbanion, which then rearranged to give bicyclobutane **34**. This product was able to react with alkyl halide.[46] 2,2,4,4-Tetramethylcyclobutan-1-one-3-thione reacts similarly.[47]



R = Me, Ph; R′X = MeI, EtI, BnBr

7. Cyclopropanation of acetylenes

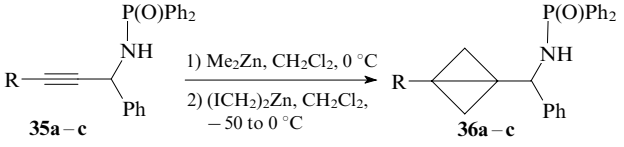
Cyclopropanation of acetylenes by carbenoids is one of the most effective and popular methods for building the bicyclobutane skeleton (see pathway *c* in Scheme 1). Indeed, the $CuCl_2$-catalyzed addition of diazomethane and ethyl diazoacetate to disubstituted acetylenes leading to corresponding

bicyclobutanes and butadienes was carried out back in the 1960s. 1,3-Dimethylbicyclo[1.1.0]butane and 2,3-dimethylbuta-2,3-diene were prepared from but-2-yne and diazomethane in 13% and 3% yields, respectively. The reaction proceeds *via* intermediate formation of cyclopropenes. The authors have noted the importance of the use of organotin compound (Bu^n_3SnCl), because otherwise no bicyclobutanes were formed.[48,49]

However, the formation of substituted bicyclo[1.1.0]butane in 14% yield upon cyclopropanation of 1-phenylpropyne by ethyl diazoacetate in the presence of copper catalyst ($CuSO_4$) alone has been reported.[50] Bis(trifluoromethyl)-acetylene reacted with difluorocarbene in the gas phase at 100 °C to give 1,3-dimethylbicyclobutane (yield 25%).[51] Perfluorobutadiene was isolated as a side product.

The researchers were able to prevent the side formation of dienes in the direct catalytic cyclomethylenation of alkyl(trimethylsilyl)acetylenes by diazomethane, resulting in a mixture of corresponding cyclopropenes and bicyclobutanes in good yields (~75%) (ratio ~1 : 1). The experiments were carried out at temperatures ranging from −10 to 0 °C by slow addition of diazomethane in a diethyl ether solution or by passing it with inert gas flow into the solution of freshly distilled acetylene in CH_2Cl_2 in the presence of 2 mol.% – 3 mol.% of CuCl.[52] Interestingly, if CuCl is replaced by catalytic amounts of $Pd(acac)_2$, $Fe(acac)_3$, $CoCl_2$ or $(cod)_2RhCl$ (acac is acetylacetonate, cod is cycloocta-1,5-diene), acetylenes do not react with diazomethane under the same conditions, in spite of the fact that diazomethane itself easily decomposes with the formation of volatile products.[53] Cyclopropanation of phenylacetylene under the action of ethyl diazoacetate catalyzed by $[Os(TTP)]_2$ [TTP is 5,10,15,20-tetrakis(*p*-tolyl)porphyrin] with a 46% product yield was reported.[54]

Zinc carbenoids have been used along with copper carbenoids for cyclopropanation of acetylenes. For example, interaction of phosphonylamides **35a–c** with Me_2Zn followed by addition of di(iodomethyl)zinc at −50 °C resulted in bicyclobutanes **36a–c**.[24]

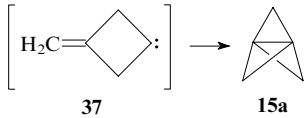


R = 4-$MeO_2CC_6H_4$ (**a**, 42%), 4-NCC_6H_4 (**b**, 35%), 3-Py (**c**, 40%); Py is pyridyl

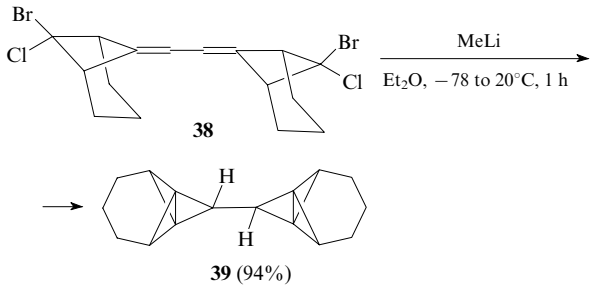
8. Cyclization of allylcarbenes

The cyclization reaction of allylcarbenes has found the widest application in the synthesis of bicyclo[1.1.0]butanes (see Scheme 1, pathway *d*). There are many modifications of this reaction, which are reduced to generation of allylcarbenes from either *gem*-dihalides or diazo compounds. In the latter case, the reaction has been implemented as a catalytic, photochemical and thermal versions.

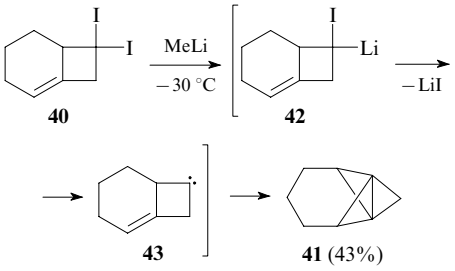
The cyclization of cyclic allylcarbenes of type **37** opens up a new effective synthetic route to propellane **15a** derivatives.



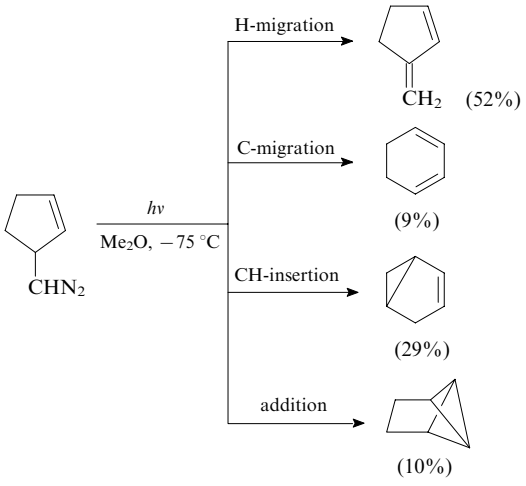
For example, the reaction of *gem*-dihalides **38** with 2.1 equiv. of MeLi in diethyl ether resulted in dipropellane **39** in high yield.[55]



Similarly, treatment of *gem*-diiodide **40** with methyllithium in diethyl ether at −30 °C resulted in propellane **41** in 43% yield. Probably, carbenoid **42** and carbene **43** are the intermediates of intramolecular cyclization reaction.[56]

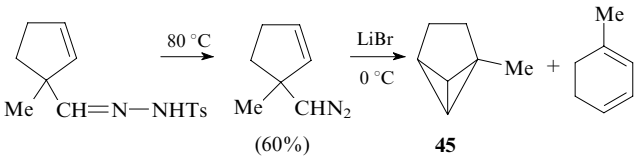


The synthesis of propellane **41** *via* generation of allylcarbene from diazo compounds represents a more traditional approach. Thus, photolysis of 5% solution of allyldiazomethane in heptane at −78 °C affords a 1 : 5 mixture of bicyclo[1.1.0]butane and butadiene.[57] A series of tricyclic hydrocarbons containing bicyclobutane moiety were obtained by thermal and photochemical decomposition of corresponding diazo compounds. The formed allylcarbene is converted along several pathways, resulting in not only the product of addition of the carbene to the double bond but also in H-migration and CH-insertion products. For example, upon the photolysis, the conversion of cyclopentyldiazomethane **44** is 65%, the product of proton migration being predominantly formed.[58]

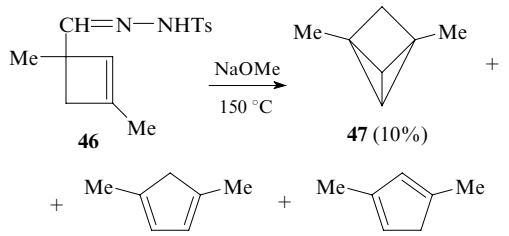


It should be noted that generation of corresponding diazo compound from 1-methylcyclopent-2-enecarboxaldehyde tosylhydrazone in the presence of LiBr in diethyl ether

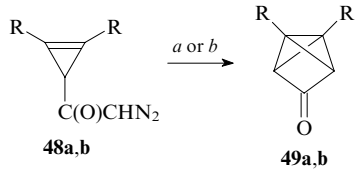
at 0 °C leads to tricyclo[2.1.1.0^{5,6}]hexane **45** with rather low selectivity of and in relatively low yield.[59] An equimolar amount of 1-methylcyclohexa-1,3-diene is formed as a side product.



Tosylhydrazone **46** was converted to tricyclopentane **47** under more severe conditions.[59] The yield of the target product was rather low, the mixture of dimethylcyclopentadienes being mainly isolated (90%).

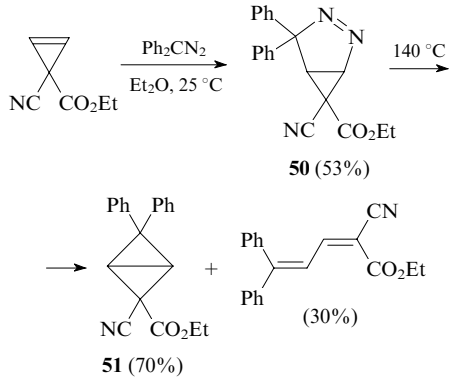


Photolysis and pyrolysis of cyclopropene-substituted α-ketocarbenoids **48a**,**b** lead to tricyclic ketones **49a**,**b**.[60, 61] The yield of compound **49a** is not specified in the original article, and dimethyl-substituted derivative **49b** has been obtained in 1% yield.

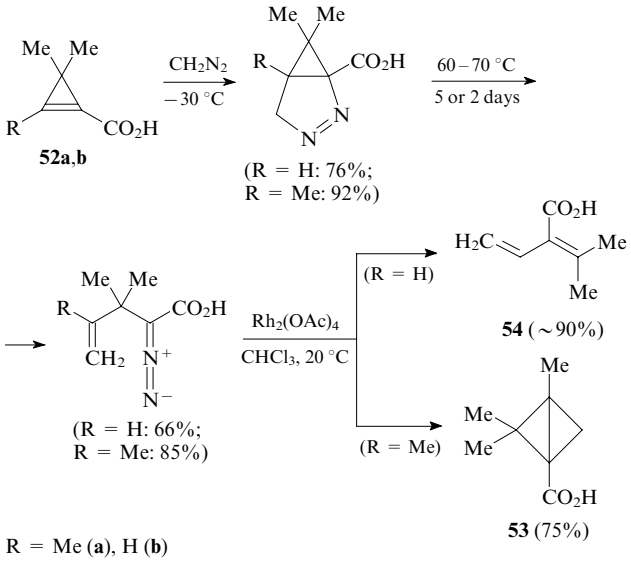


(*a*) *hv*, THF, 20 °C, R = Ph (**a**); (*b*) Cu, hexane, Δ, R = Me (**b**)

Another approach consists in generation of allylcarbenes from pyrazolines, which are in turn easily formed upon the reaction of diazoco mpounds with unsaturated substrates. For example, pyrolysis of pyrazoline **50** at 140 °C leads to bicyclobutane **51** in 70% yield.[62]

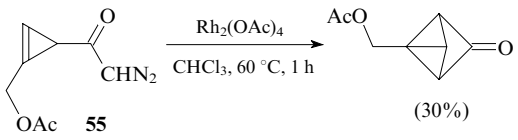


The catalytic decomposition of diazo compounds proceeds under milder conditions. Rhodium acetate is commonly used as a catalyst of such transformations.[63] The nature of the substituent in pyrazoline has an influence on the reaction route, which is either intramolecular cyclization or 1,2-vinyl shift. In the case of compound **52a**, bicyclobutane **53** is exclusively formed, while in the case of R = H, only the product of 1,2-vinyl shift **54** is isolated. The authors suggested that this difference was caused by conformational effects.

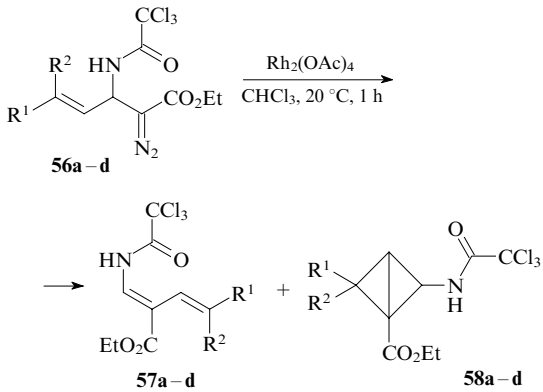


R = Me (**a**), H (**b**)

In the case of ketone **55**, a similar reaction gives the corresponding bicyclobutane in moderate yield.[64]

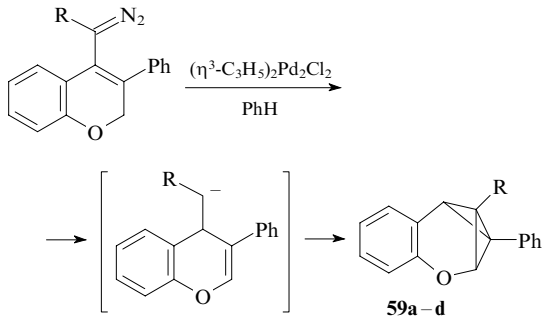


The influence of the substituents at the double bond in compounds **56a**–**d** on occurrence of the reaction as either 1,2-migration (product **57**) or intramolecular cyclopropanation (product **58**) has been investigated.[65] The presence of bulky phenyl substituent at the double bond prevents the formation of bicyclobutane structure. In the case of either alkyl substituents or terminal double bond, the ratio of products of both transformations is ~1 : 1.



Compounds **56**–**59**	R^1	R^2	Total yield (%)	Ratio **57** : **58**
a	Ph	H	84	100 : 0
b	H	Ph	98	100 : 0
c	Me	H	100	56 : 44
d	H	H	97	52 : 48

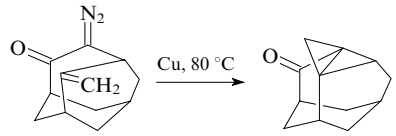
Apart from rhodium acetate, palladium salts or metallic copper are also used as catalysts of decomposition of diazo compounds. Thus intramolecular [2 + 1]-cycloaddition of carbenes with the formation of fused systems **59a – d** containing bicyclobutane moieties has been described.[66] The catalysis of the reaction is realized by palladium π-allyl complex.



59a – d

R = P(O)(OMe)$_2$ (**a**, 91%), P(O)(OMe)Ph (**b**, 94%), P(O)Ph$_2$ (**c**, 71%), CO_2Me (**d**, 47%)

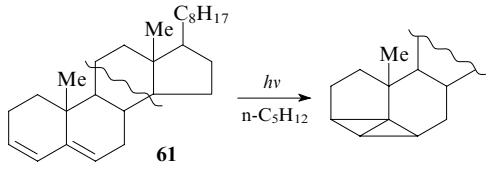
[4.1.1]Propellanone derivative **60** was obtained by intramolecular cyclization of corresponding diazo compounds during its catalytic decomposition in the presence of metallic copper at 80 °C.[67]



60 (95%)

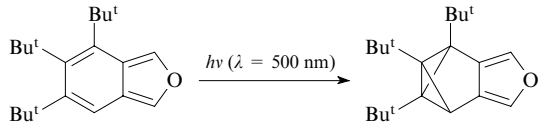
9. Photochemical reactions and isomerization

Photochemical isomerization of 1,3-diene systems is a rather unusual and elegant method for the preparation of bicyclobutanes (see Scheme 1, pathway *f*). Photolysis of a 1% solution of buta-1,3-diene in diethyl ether in the presence of $CuCl_2$ leads to bicyclo[1.1.0]butane in only a 5% – 6% yield. The major product formed in the reaction is cyclobutene (yield 30%).[68] However, in some cases, photochemical isomerization gives high yields of the product and high selecticity. For example, in the case of photochemical reaction, the conversion of cholesta-3,5-diene (**61**) is 98%.[69]



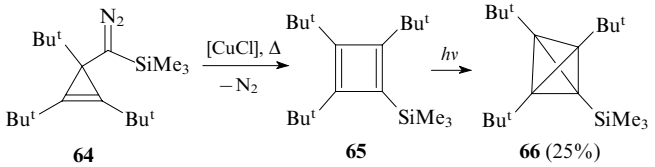
61

Isobenzofuran and its derivatives are important synthons in organic chemistry. Miki and co-workers[70] converted 3,4,5-tri-*tert*-butylisobenzofuran (**62**) to annulated bicyclobutane **63** in high yield. The quantum yield (φ) of the reaction is 0.02. Photolysis of tetracene-5,12-dione proceeds similarly.[71]



62 **63** (86%)

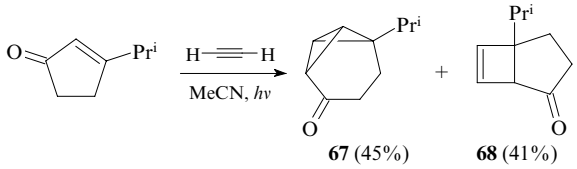
The photochemical isomerization of substituted cyclobutadienes is a unique method for the synthesis of tetrahedranes. Thus, CuCl-catalyzed thermolysis of silyl diazo compound **64** resulted in cyclobutadiene **65**, which isomerized under irradiation to give substituted tetrahedrane **66**.[72]



64 **65** **66** (25%)

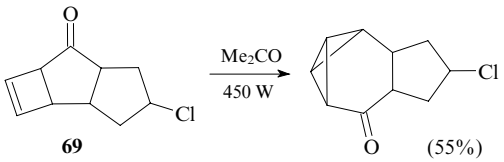
At the same time, photoisomerization of tetrakis(trimethylsilyl)cyclobutadiene leads mainly to its decomposition into bis(trimethylsilyl)acetylene. Only carrying out the reaction in pentane at −100 °C for 70 h, did afford tetrakis(trimethylsilyl)tetrahedrane in 50% yield.[73]

Irradiation of a mixture of acetylene and 3-isopropylcyclopent-2-enone in acetonitrile results in a mixture of products containing, in particular, bicyclobutane **67**, which is apparently formed upon isomerization of the [2 + 2]-cycloaddition product **68**.[74]



67 (45%) **68** (41%)

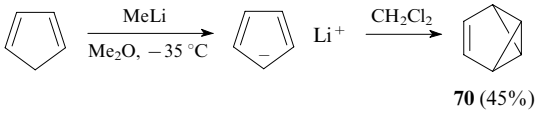
This assumption is supported by the fact that photochemical isomerization of compound **69** results in the corresponding bicyclobutane formed in 1 h in a moderate yield.[75]



69 (55%)

10. Miscellaneous reactions

Benzvalene **70** was obtained in 1999 from cyclopentadienyllithium and dichloromethane.[76] This method turned out to be convenient for practical purposes and made benzvalene an available precursor for the synthesis of its various derivatives.



70 (45%)

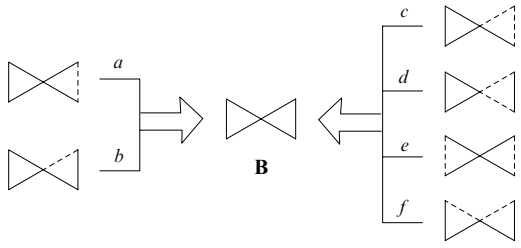
III. Methods of synthesis of spiropentanes

In 1887, G Gustavson obtained spiropentane (**B**) for the first time by treatment of tetrabromoneopentane with zinc powder. By mistake, this compound was identified as vinylcyclopropane. This mistake was corrected 25 years later by Russian chemist N D Zelinsky. However, for a long time, until 1970s, no due attention was paid to the problem of synthesis of spiropentanes. In the 1960s – 1970s, a series of papers on cyclopropanation of allenes by the Simmons –

Smith reagent† and dihalocarbenes appeared. In the first place, the studies of the French chemist J-M Conia should be noted among them. Since the 1970s, the number of papers devoted to the synthesis of spiropentane systems has begun to grow and peaked in 1980. A great contribution to the development of methods for the synthesis of spiropentanes and triangulanes was made by N S Zefirov's scientific school (Chair of Organic Chemistry of the Department of Chemistry, Moscow State University). The dihalocarbene method has been systematically studied at the Leningrad University by R R Kostikov and A P Molchanov. For cyclopropanation of α-allenic alcohols, M Laytens and P H M Delanghe used for the first time samarium carbenoids. Extensive studies performed by O M Nefedov and his followers should be specially noted. They worked out a convenient method for the preparation of spiropentanes using *N*-nitroso-*N*-cyclopropylurea.

Retrosynthetic analysis of the spiropentane structure with regard to the formation of one or two carbon–carbon bonds in one step distinguishes six possible pathways of building of the required skeleton (Scheme 3). Pathways *a* and *b* represent a classical approach to the synthesis of cyclopropanes by 1,3-dehalogenation of halocyclopropanes. However, currently, more widely used are carbene methods of spiropentanes synthesis, such as cyclopropanation of methylenecyclopropanes and allenes by carbene reagents, and also cyclopropanation of alkenes by cyclopropylidenes (pathways *c* and *d*). The last two of the possible ways of building of the spiropentane skeleton (pathways *e* and *f*) still remain theoretical; there are still no examples of their implementation.

Scheme 3

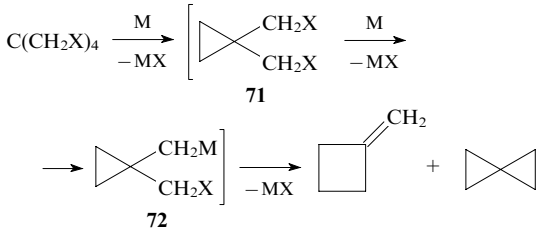


1. 1,3-Dehalogenation

Reductive cyclization of 1,3-dihalides (see Scheme 3, pathways *a* and *b*) has been known since 1887, and is still widely used for the synthesis of cyclopropanes and spiropentanes. As it was already mentioned above, Gustavson and coworkers [77, 78] obtained a hydrocarbon of composition C_5H_8, which was originally identified as vinylcyclopropane. However, 20 years later H Fecht [79] came to a conclusion that the obtained hydrocarbon comprised two cyclopropane rings, one of the carbon atoms belonging to both rings. In 1913, N D Zelinsky [80] synthesized a hydrocarbon by treatment of 1,1-di(bromomethyl)cyclopropane with zinc powder. The physical properties of this hydrocarbon were consistent with the properties of the compound earlier obtained by Gustavson. Zelinsky experimentally proved its structure to be $(CH_2)_2C(CH_2)_2$.

† The Simmons–Smith reaction is the transformation of alkenes into cyclopropanes under the action of methyl iodide and the Zn–Cu pair. It is assumed that iodomethylzinc iodide (ICH_2ZnI), also known as the Simmons–Smith reagent, is the active species in this reaction.

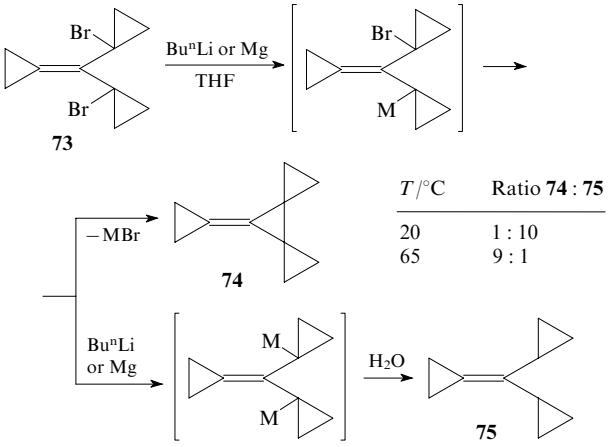
The addition of sodium ethylenediamintetraacetare to the reaction mixture of tetrabromoneopentane with zinc in n-heptane, D Applequist *et al.*[81] found out that the yield of spiropentane reached 81%. The authors suggested that binding of Zn^{2+} ions had prevented the formation of carbocations and, therefore, the formation of the methylenecyclobutane molecule. Subsequently, such cyclization was carried out under the action of magnesium, zinc, alkali metals under various conditions, and also by electrochemical method.[82] In a study of the mechanism of the reaction of tetrabromoneopentane with Zn, Mg, Li and Na in different solvents, it has been suggested that the Gustavson rearrangement, *i.e.*, the formation of methylenecyclobutane along with the expected spiropentane, involved intermediate 1,1-bis(halomethyl)cyclopropane **71** and γ-halogenated organometallic compound **72**.



X = Cl, Br; M = Li, Na, Zn/2, Mg/2

The use of electron-donating solvents (dioxane, THF) instead of n-heptane was found to increase the yield of spiropentane. Similar results were obtained by interaction of tetrabromoneopentane with Bu^nLi and with EtMgBr in THF.[83] The use of zinc powder in a 3%–10% solution of KOH (80 °C, 30 min) led to the formation of mixture of compounds (total yield 70%–80%). Along with 1,1-dimethylcyclopropane and 2-methylbut-1-ene, this mixture contained up to 90% of spiropentane and also trace amounts of methylenecyclobutane. Thus, the reaction of tetrabromoneopentane with metallic zinc described above may proceed by two pathways depending on the medium.[84]

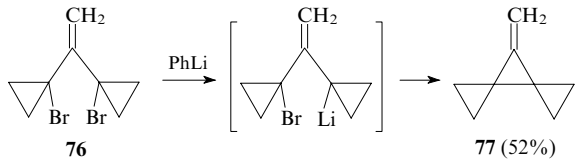
Another approach to the preparation of spiropentanes consists in 1,3-dehalogenation of 1-halo-1-(2-haloethyl)cyclopropanes. Thus dibromo derivative **73** easily reacts with magnesium in THF giving 4-cyclopropylidenedispiro[2.0.2.1]heptane (**74**), the amount of the latter increasing with the increase in the reaction temperature.[85]



Probably, on treatment of compound **73** with magnesium (or n-butyllithium), first one bromine atom is replaced by a

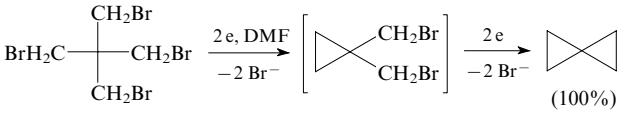
metal (M = Mg or Li) to give the corresponding organometallic compound. Then the reaction may follow two pathways, (i) intramolecular cyclization with elimination of magnesium (or lithium) bromide leading to hydrocarbon **74**; (ii) replacement of the second bromine atom. In the latter case, hydrocarbon **75** is formed upon treatment of the reaction mixture with water.

Treatment of 1,1-bis(1-bromocyclopropyl)ethene (**76**) with phenyllithium led to tricyclane **77**.[86]



76 **77** (52%)

Electrochemical reduction of 1,1-bis(halomethyl)cyclopropanes in aprotic solvents furnishes spiropentane. The yields of spiropentane in this transformation are highest compared with the yields obtained using other methods.[87,88]

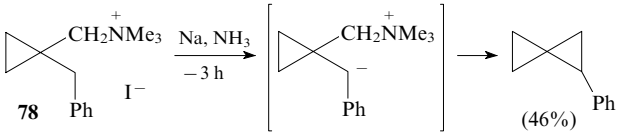


(100%)

However, the introduction of vinyl substituent into the 1,1-bis(bromomethyl)cyclopropane molecule significantly changes the electrochemical reduction pathway. Under these conditions, products of three-membered ring cleavage are mainly formed from 1,1-bis(bromomethyl)-2-vinylcyclopropane.[89] The maximum yield of vinylspiropentane that was possible to obtain was only 20%.

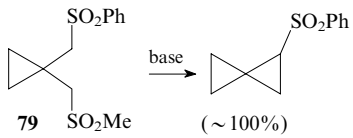
2. Carbanionic cyclization

The two methods of formation of spiropentane skeleton by pathway *a* (see Scheme 3) that are discussed below are less widely used, but they demonstrate two different approaches to the formation of carbon–carbon bond, *i.e.*, the formation by ionic and by radical mechanisms. Treatment of quartenary ammonium salt **78** with sodium amide in liquid ammonia results in phenylspiropentane in moderate yield. Meanwhile, the products of isomerization or rearrangement of the intermediate zwitter-ion were not observed.[90]



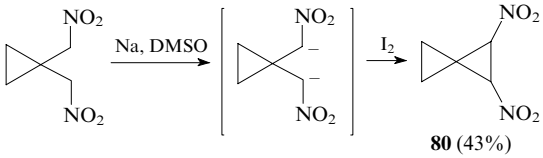
78 (46%)

Similarly, cyclization of 1-methylsulfonylmethyl-1-phenylsulfonylmethylcyclopropane **79** proceeds *via* the formation of stable sulfonylmethyl-substituted carbanion.[91]



79 (~100%)

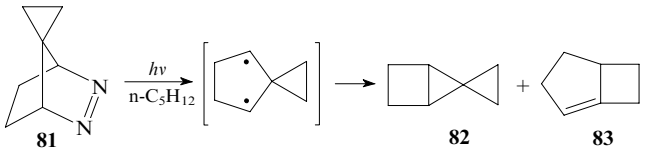
The dianion that is formed on treatment of 1,1-bis(nitromethyl)cyclopropane with sodium methylsulfinylmethylide [$NaCH_2S(O)Me$] is cyclized to afford crystalline 1,2-dinitrospiropentane **80**.[92]



80 (43%)

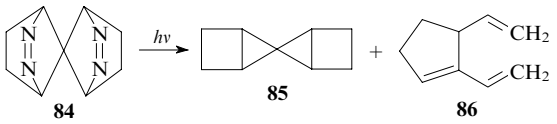
3. Photolysis of diazoalkanes

Photochemical transformations of polycyclic compounds with diazo groups also proceed by pathway *a* (see Scheme 3). For example, photochemical denitrogenation of cyclopropyl-containing diazabicyclo[2.2.1]hept-2-ene **81** results in tricyclic spiropentane **82** and bicyclo[3.2.0]hept-1-ene (**83**).[93] Photodecomposition of spiro derivative **84** with two diazo groups proceeds similarly.[94] In both cases, in the absence of photosensitizers, singlet biradicals are formed and, hence, cyclization products **82** (ratio *exo* : *endo* = 2.3) and **85**, respectively are obtained. Meanwhile, the generation of triplet biradical under benzophenone sensitization mainly leads to the products of 1,2-allyl shift, namely, alkenes **83** and **86**.



81 **82** **83**

Photosensitizer	Yield (%)	
	82	**83**
Benzophenone	9	91
–	92	8

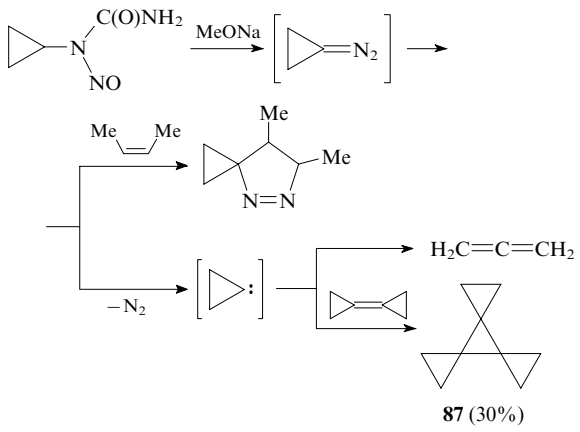


84 **85** **86**

Photosensitizer	Yield (%)	
	85	**86**
Benzophenone	2	85
–	87	10

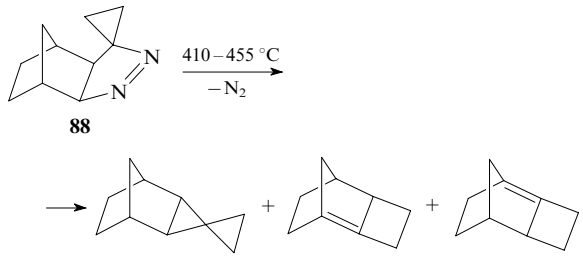
4. Transformations of *N*-nitroso-*N*-cyclopropylurea

Chemical transformations of *N*-nitroso-*N*-cyclopropylurea have been studied for more than 70 years. Currently, this compound is the most convenient source for generation of some highly reactive intermediates, specifically such as diazocyclopropane and cyclopropyldiazonium ion. 1,3-Dipolar cycloaddition of diazocyclopropane generated *in situ* to unsaturated compounds[95–99] is one of the most convenient and general methods for the preparation of 1- or 2-pyrazolines containing spiro-linked cyclopropane moiety (see pathway *b* in Scheme 3). In the absence of suitable traps, diazocyclopropane undergoes spontaneous dediazotization, resulting in generation of unstable cyclopropylidene, which is capable of cyclopropanation of the double bond in bicyclopropylidene (pathway *d*) with the formation of spiropentane **87**.[100] Another example of formation of this compound from cyclopropylidene intermediate will be considered in Section III.13.



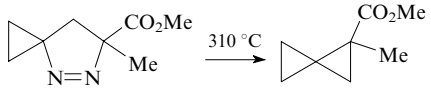
87 (30%)

1-Pyrazolines **88** obtained by 1,3-dipolar cycloaddition of diazocyclopropane to norbornene or deltacyclene[101] at 410–455 °C are dediazotized to give a mixture of strained polycyclic hydrocarbons in 30%–70% total yield.[98]



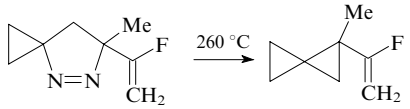
88

Among all the studied examples of pyrolysis of pyrazolines, the transformation of functionally sybstituted pyrazoline **89** proceeds most smoothly and selectively. At 300–310 °C, its conversion was 95%, the yield of 1-methyl-1-methoxycarbonylspiropentane (**90**) being 90%.[102]



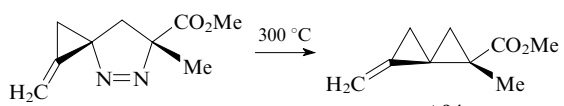
89 **90** (90%)

In the case of substituted pyrazoline **91** with terminal double bond, thermolysis proceeds with high conversion, but dediazotization is accompanied by considerable resinification of the reaction mixture. Nevertheless, 1-methyl-1-(1-fluorovinyl)spiropentane (**92**) was isolated as the major reaction product.[103]

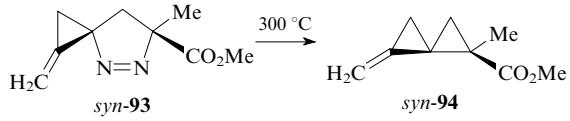


91 **92** (51%)

Thermal dediazotization of a mixture of *syn*- and *anti*-isomeric pyrazolines **93** containing vinyl group is highly selective, resulting in isomeric 1-methyl-4-methylenespiropentancarboxylates **94** (total yield 71%).[104]



anti-**93** *anti*-**94**

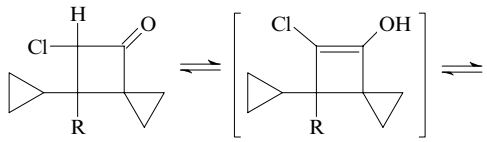


syn-**93** *syn*-**94**

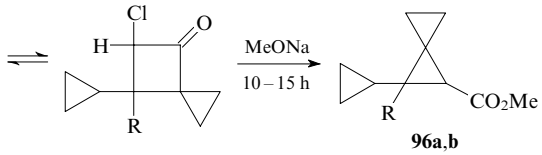
Note that the use of Cs_2CO_3 as a base in the preparation of pyrazolines from N-substituted maleimides and *N*-nitroso-*N*-cyclopropylurea reduces the reaction time 5–6-fold and has practically no impact on the yields of the corresponding heterocycles.[105]

5. The quasi-Favorskii rearrangement

The skeletal rearrangement of α-halo ketones (see pathway *b* in Scheme 3) has been used for ring contraction in substituted 5-chlorospiro[2.3]hexan-4-ones **95**. Treatment of chloroketones **95a**,**b** with a 8-fold excess of MeONa gives esters of spiropentancarboxylic acid **96a**,**b** in high yields. The rearrangement is non-stereospecific, probably due to enolization of the starting ketone.[106]



95a,**b**



96a,**b**

R = Me (**a**, 84%), cyclo-C_3H_5 (**b**, 95%)

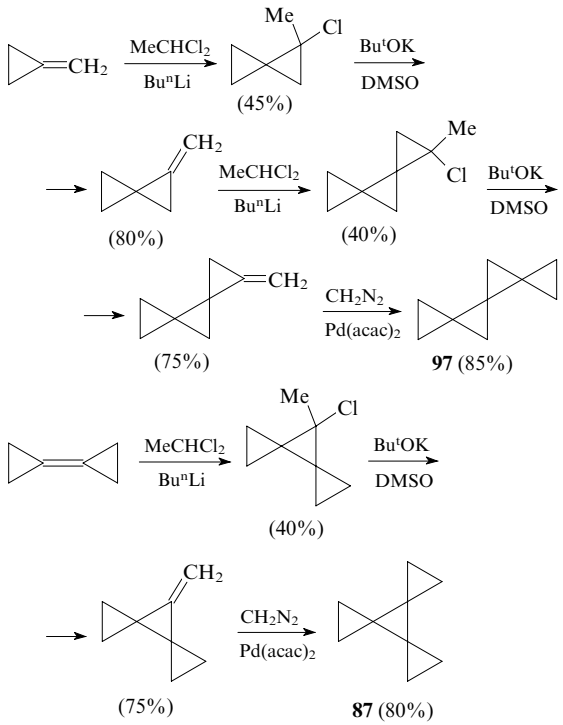
6. Cyclopropanation of methylenecyclopropanes by diazomethane

As mentioned above, spiropentane was obtained for the first time by debromination of tetrabromoneopentane. However, currently, cyclopropanation of methylenecyclopropanes or allenes is used more often for its synthesis. Diazomethane, dihalocarbenes or the Simmons–Smith reagent are used as reagents. The next six sections of the present review, which are devoted to cyclopropanation, correspond to pathway *c* in Scheme 3.

Thus, it is possible to obtain methyl spiropentancarboxylate in good yield by the treatment of methyl methylenecyclopropanecarboxylate with CH_2N_2 in pentane in the presence of CuCl.[3] Cyclopropanation of methyl ethylidenecyclopropanecarboxylate with ethyl diazoacetate or diazomethane proceeds non-stereospecifically and leads to a mixture of diastereomers. In the case of diazomethane, the configuration of substituents is retained. Thermocatalytic decomposition of ethyl diazoacetate in the presence of Cu(II) salts at 80 °C was reported.[107] A solution of diazomethane in diethyl ether and $Pd(OAc)_2$ catalyst are now used most often for cyclopropanation of methylenecyclopropanes.[108]

This approach has been used by N S Zefirov and coworkers[109,110] to prepare triangulanes, *i.e.*, compounds consisting of spiro-linked three-membered rings. An unusual combination of high strain energy, unique geometry and stereochemistry and also the possibility of interaction between the three-membered rings make these compounds promising for theoretical and experimental studies. Compound **87** is the simplest [2]-triangulane (it is

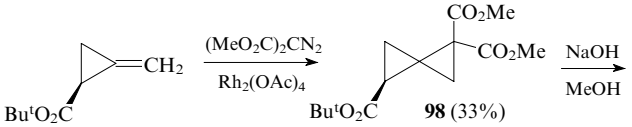
also called [3]-rotane). In recent years, a general approach to the synthesis of triangulanes **87** and **97** has been developed. It consists in successive generation of methylenecyclopropane moieties with subsequent cyclopropanation by diazomethane in the presence of palladium acetylacetonate.[104, 111]

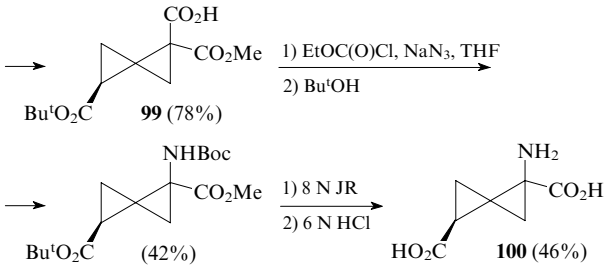


Cyclopropanation by the $CH_2N_2-Pd(acac)_2$ system was also used in the final stage of synthesis of alicyclic spiropentanes based on cycloocta-1,5-diene.[112–114]

Cyclopropanation of bicyclopropylidene (cyclopropylidencyclopropane) by diazomethane in the presence of CuCl results in dispiro[2.0.2.1]heptane in a yield not higher than 60%; this necessitates the use of preparative GLC for the isolation of the product.[3] At the same time, in the presence of $Pd(acac)_2$, cyclopropanation proceeds non-selectively to give a mixture of hydrocarbons, which is attributable to the insertion of three or four $:CH_2$ equivalents into the alkene molecule (this process was called oligomethylenation by N S Zefirov[115]). Vinylidenecyclopropane reacts with $CH_2N_2-Pd(acac)_2$ system in a similar way. Along with the expected dispiroheptane (formed in 9% yield), a complex mixture of hydrocarbons is produced.[116] However, the use of rhodium acetate instead of palladium acetate as a catalyst resulted in selective cyclopropanation of bicyclopropylidene by ethyl diazoacetate (yield 77%).[117]

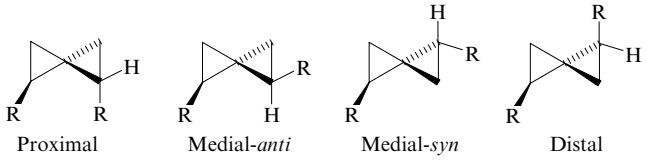
Dimethyl diazomalonate in the presence of rhodium catalyst was used as the cyclopropanating agent to transform *tert*-butyl 2-methylenecyclopropanecarboxylate.[118] The resulting spiropentatricarboxylate **98** was subjected to selective hydrolysis, and using the Curtius rearrangement, compound **99** was converted to 1-aminospiropentane-1,4-dicarboxylic acid (**100**).



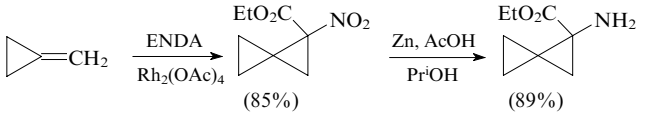


JR is the Jones reagent ($CrO_3-H_2SO_4-H_2O$)

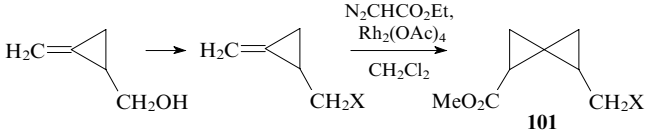
Acid **100** may exist as four diastereomers. In 1970, Gajewsky and Burka[119] proposed stereochemical nomenclature for the description of disubstituted spiropentanes. It was based on remoteness of one substituent from another in space and on the relative orientation of substituents to the plane of one of the rings. If the priority rules of substituents are used, then it is possible to apply this nomenclature to spiropentanes with more substituents. The names of isomers of disubstituted spiropentane are given below:



Another approach to the synthesis of α-aminospiro[2.2]-pentanecarboxylic acids consists in the reaction of methylenecyclopropane with ethyl nitrodiazoacetate (ENDA) in the presence of catalytic amounts of rhodium acetate with the subsequent reduction of the nitro group.[120] The products of cyclopropanation of polycyclic methylenecyclopropanes were obtained in a similar way.[3]



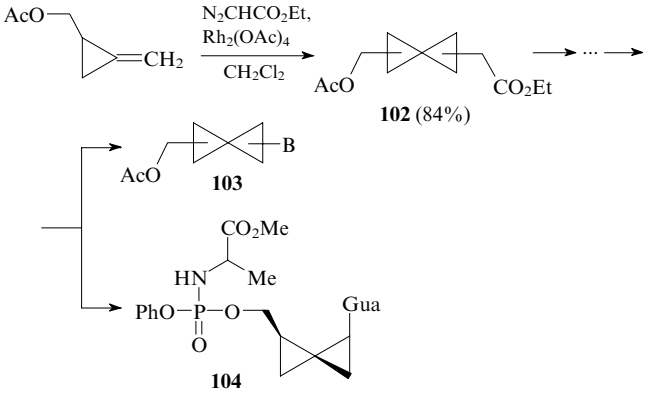
In the case of 2-methylenecyclopropylmethanol, the alcohol group was protected and then the reaction mixture was treated with ethyl diazoacetate in the presence of a catalyst, namely, $Rh_2(OAc)_4$.[121] The yield of substituted spiropentane **101** increased if the trimethylsilyl protecting group was used. The authors did not indicate the stereochemistry of the cyclopropanation products, which were further converted to spiropentylglycines. It should be noted that methylenecyclopropanecarboxaldehyde diethylacetal is inactive in the cyclopropanation reaction.



X	Total yield (%)	Diastereomer ratio
OTHP	10	3 : 2 : 1.5 : 1
OTMS	49	3.5 : 3 : 2 : 1

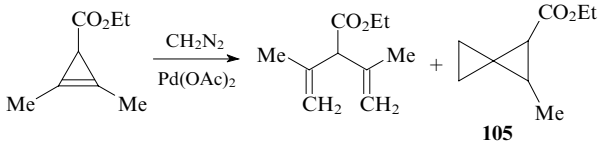
THP is tetrahydropyran-2-yl; TMS is trimethylsilyl

The reaction of ethyl diazoacetate with (2-methylcyclopropyl)methylacetate catalyzed by rhodium salts gave [122] a mixture of all four possible isomeric spiropentanes **102**, which were partially separated by column chromatography (yield of proximal and medial-*syn* isomers was 44%, that of distal and medial-*anti* isomers was 36%). Spiropentanes **102** were used to prepare spirocyclic analogues of 2′-deoxyadenosine and 2′-deoxyguanosine **103**, which showed antiviral activity against human cytomegalovirus (HCMV) and Epstein–Barr virus (EBV). Spirocyclic phosphoryl alaninate **104** is active against herpes simplex virus type 1 (HSV-1), varicella zoster virus (VZV), human immunodeficiency virus (HIV-1) and hepatitis B (HBV).[122]



B is adenine, Gua is guanidine

Highly strained cyclopropenes are known to undergo various transformations in the presence of transition metals salts. Evidently, the formation of spiropentane **105** in the reaction of ethyl 2,3-dimethylcycloprop-2-enecarboxylate with diazomethane may be explained by isomerization of cyclopropene into corresponding methylenecyclopropane and by subsequent cyclopropanation.[123] The yield of a mixture of compound **105** and the corresponding diene is 15%.

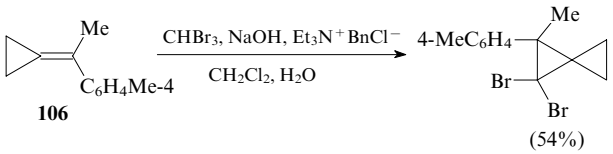


7. Cyclopropanation of methylenecyclopropanes by dihalocarbenes

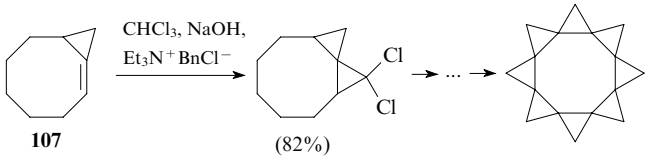
A general approach to the synthesis of cyclopropane derivatives consists in cycloaddition of carbenes generated from polyhalomethanes to alkenes. Examples of its use for the synthesis of triangulanes have already been given above. The versatility of this approach lies in the possibility of successive building-up of methylenecyclopropane moieties. In combination with a convenient method of cyclopropanation of double bond in methylenecyclopropanes, this opens up the way for the preparation of various hydrocarbons with spiro-connected three-membered rings.[109, 111, 124]

The yield of the products of the Doering–Hoffmann [1 + 2]-cycloaddition of dibromocarbene to substituted methylenecyclopropanes depends little on the substitution pattern.[125] The addition of dichloro and dibromo carbenes to 2-substituted methylenecyclopropanes is stereospecific. The double bond is attacked from the less sterically hindered side, and it results in the formation of spiropentanes with *anti*-arrangement of the halogen atoms and the substituent. The activating influence of substituents decreases in the series $SiMe_3$ > Alk > CO_2Me.

However, 2,2-bis(trimethylsilyl)methylenecyclopropane does not react with dichlorocarbene under conditions of phase transfer catalysis, which is evidently caused by steric hindrance of the carbene attack on the double bond. The lower reactivity (by a factor of 6.7) of 2,2-dicyclopropylmethylenecyclopropane in comparison with non-1-ene is explained in the same way.[126] Nevertheless, the reactivity of the exocyclic double bond in 2-substituted methylenecyclopropanes is higher than that of the double bond in monosubstituted alkenes. Moreover, the reactivity of cyclopropyl-substituted methylenecyclopropanes towards dichlorocarbenes is significantly higher than that of 1,1-dicyclopropylethene, the substituents in the methylenecyclopropane moiety having rather a spatial than electronic influence.[127–129] Thereby, the presence of bulky substituents at double bond does not prevent the reaction. Thus aryl-substituted ethylidenecyclopropane **106** is converted to the corresponding spiropentane in 54% yield.[130]



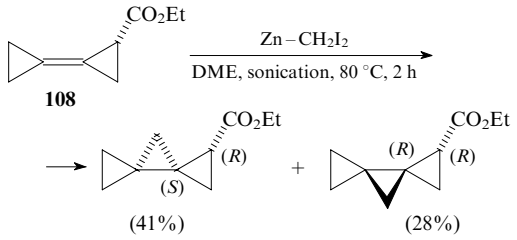
The cyclopropanation of 1-chloro-2-methylenecyclopropane by dichlorocarbene generated in the system $CHCl_3$–NaOH–Bu^n_3N proceeds with a high yield.[131] The cyclopropanation of cyclooctene **107** and cycloocta-1,5-diene derivatives was used in the synthesis of [8]-cyclotriangulanes.[132, 133]



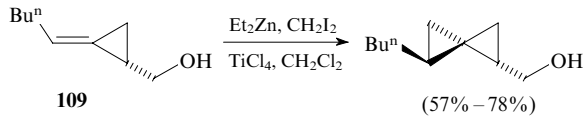
8. The Simmons–Smith cyclopropanation of methylenecyclopropanes

The Simmons–Smith reaction is the most popular laboratory method for direct cyclopropanation of alkenes and their derivatives.[134] (However, in the case of methylenecyclopropanes, catalytic decomposition of diazo compounds is used more often.) Of the few examples of the use of zinc carbenoids, cyclopropanation of methylenespiran in the presence of 2,3-dimethylbutadiene [135] and preparation of [3]-rotane **87** from 7-methylenedispiro[2.0.2.1]heptane in 86% yield [136] should be noted. In the latter case, a zinc–silver pair is used instead of zinc–copper.

Bicyclopropylidene reacts with the Simmons–Smith reagent very slowly, but under the action of ultrasound, cyclopropanation of substituted bicyclopropylidene **108** is completed within 2 hours.[137]



Cyclopropanation of pentylidenecyclopropane **109** by Furukawa's reagent ($CH_2I_2-Et_2Zn$) was performed using 15 mol.% $TiCl_4$ (relative to the amount of substituted methylenecyclopropane) as the catalyst.[138]



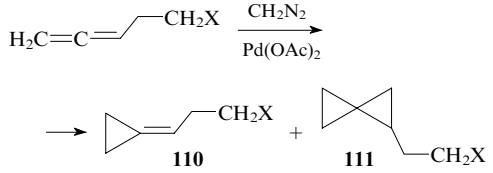
9. Cyclopropanation of allenes by diazomethane

The reaction of substituted allenes with diazomethane in the presence of palladium(II) compounds involves the less substituted double bond and gives the corresponding methylenecyclopropanes.

The introduction of palladium diacetate or dibenzonitrile palladium dichloride into a diethyl ether solution of butylallene and diazomethane causes vigorous decomposition of the latter.[139] The reaction mixture thus formed contains methylcyclopropane and spiropentane in 67 : 25 ratio along with the starting allene (~8%). Repeated treatment of the reaction mixture by diazomethane leads to spiropentane **87** in >90% yield.

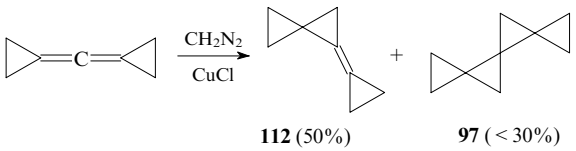
Vinylidenecyclobutane is cyclopropanated by diazomethane in the presence of palladium catalyst to give selectively the product of monocyclopropanation (yield 92%). However, the palladium-catalyzed reaction of vinylidenecyclopropane with diazomethane is non-selective giving a mixture of unsaturated hydrocarbons. This is attributable to unusual insertion of three or four methylene groups into the allene molecule.[140] At the same time, cyclonona-1,2-diene reacts with diazomethane in the presence of $Pd(OAc)_2$ with the formation of bicyclo[7.1.0]dec-1-ene in 85% yield. Repeated treatment with diazomethane results in dicyclopropane derivative, but the yield of the latter does not exceed 15%.[139]

N S Zefirov *et al.*[141] studied the reaction of functionally substituted allenes with diazomethane in diethyl ether in the presence of dibenzonitrile palladium dichloride and palladium acetate. The use of the former only led to compound **110** with one cyclopropane moiety, whereas the preferential formation of spiropentane **111** derivatives was observed if palladium acetate was used.



111: X = OH (60%), Br (30%), OAc (56%)

Copper salts have also been used as catalysts of allene cyclopropanation. However, the reaction of biallenyl with diazomethane in the presence of CuCl proceeds non-selectively, the product of complete cyclopropanation being formed in ~12% yield.[142] Under similar conditions, dicyclopropylidenemethane transforms into a mixture of spiropentane **112** and trispiro[2.0.0.2.1.1]nonane **97**.[143]

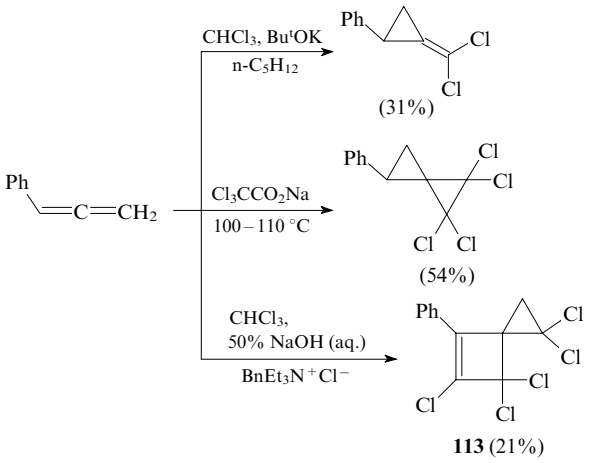


10. Cyclopropanation of allenes by dihalocarbenes

The reactions of allenes with dihalocarbene generated under phase transfer catalysis conditions result in the formation of the mono- and bisaddition products, depending on the structure of reactants. Unsubstituted allene reacts with chloroform in the presence of NaOH to give a mixture of chloro-substituted methylenecyclopropane and spiropentane.[144] At the same time, under these conditions, pentyl-substituted allene preferentially gives monoadduct (yield 16%).[145]

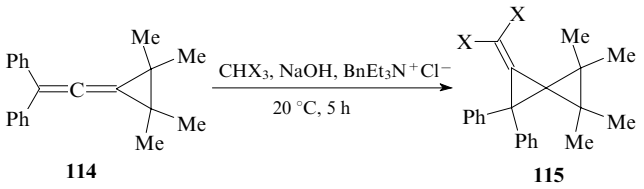
The addition of dichlorocarbene to allenes with aliphatic and aromatic substituents involves the most substituted double bond, which is promoted by spatial shielding of the neighbouring, less substituted double bond. In allenes, as in alkenes, the reactivity of double bond depends on the character of substituents and increases with the increase in the degree of substitution. Conjugated double bond in allene does not have a significant impact on the activity of the reacting bond.[146] Thus, monocyclopropanation of 1,1-dicyclopropylallene[126] and 1-methyl-1-cyclopropylallene[147] procceds in 80% and 31% yields respectively.

The composition of the addition products of dichlorocarbene to phenylallene depends on the method of carbene generation. It is possible to obtain mono- and bisaddition products by varying the reagents.



Thus, under the conditions of phase-transfer catalysis, cyclopropanation of phenylallene by chloroform in aqeous alkali leads to a complex mixture of products from which spiro[2.3]hex-4-ene derivative **113** was isolated. This product formed upon the rearrangement of the monoadduct formed intially. The presence of aromatic group at the three-membered ring markedly accelerates the isomerization of *gem*-dihalocyclopropanes.

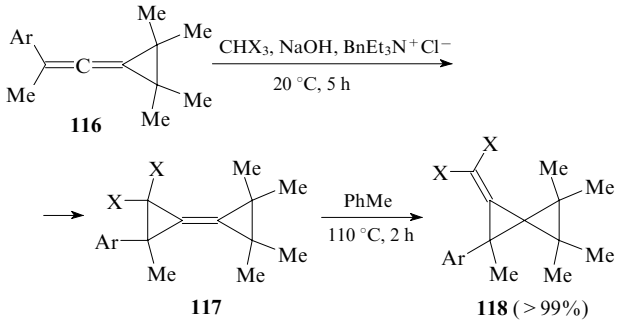
Higher yields of target spiropentanes have been obtained in the case of tetrasubstituted allenes containing a cyclopropane moiety. For example, diphenyl-substituted allene **114** gives spiropentane **115** in 73% yield.[148]



114 **115**

X = Br (73%), Cl (99%)

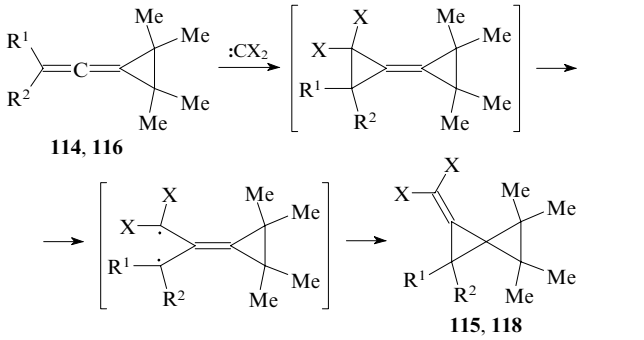
Under similar conditions, the reaction with methyl(naphtyl)-substituted allene **116** results in the selective formation of cyclopropylidenecyclopropane **117**, which quantitatively transforms into spiropentane **118** within 2 hours of refluxing in toluene.[148]



116 **117** **118** (> 99%)

Ar = 1-Naph; X = Br (68%), Cl (79%); Naph is naphthyl

Consideratiing the obtained results, a possible mechanism of formation of compounds **115** and **118** was proposed.[148]



114, **116** **115**, **118**

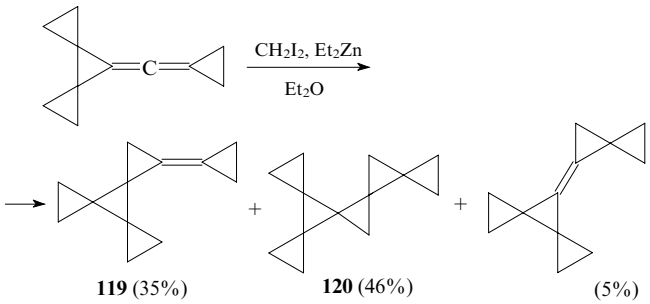
$R^1 = R^2$ = Ph (**114**, **115**); R^1 = 1-Naph, R^2 = Me (**116**, **118**); X = Br, Cl

Under the indicated conditions, tetrasubstituted allenes containing alkyl substituents do not undergo such rearrangement. For example, ultrasonic activation of a mixture of tetramethylallene and bromoform in the presence of solid sodium hydroxide results in the formation of a mixture of addition products of one and two equivalents of dibromocarbene.[149]

11. The Simmons–Smith cyclopropanation of allenes

Under the conditions of the Simmons–Smith reaction, allenes form methylenecyclopropanes and spiropentanes.[3] In the case of alkyl-substituted allenes, an excess of cyclopropanating agent results in spiropentanes being formed as the major products, the conversion of allenes being < 10%. The reaction with an equimolar amount of Zn and CH_2I_2 yields all of the three possible products of cyclopropanation in equal proportions. However, under these conditions, tetramethylallene undergoes only the monoaddition giving 1-isopropylidene-2,2-dimethylcyclopropane in 83% yield. On refluxing in Et_2O for 48 h in the presence of the Simmons–Smith reagent, vinylidenecyclopropane is cyclopropanated only at the terminal double bond giving bicyclopropylidene (yield 15%).[150, 151] With ultrasonic activation, the transformation of vinylidenecyclopropane under the action of CH_2I_2 and Zn–Cu in diethyl ether results in a mixture of bicyclopropylidene (30%–40%) and triangulane (10%–15%).[152]

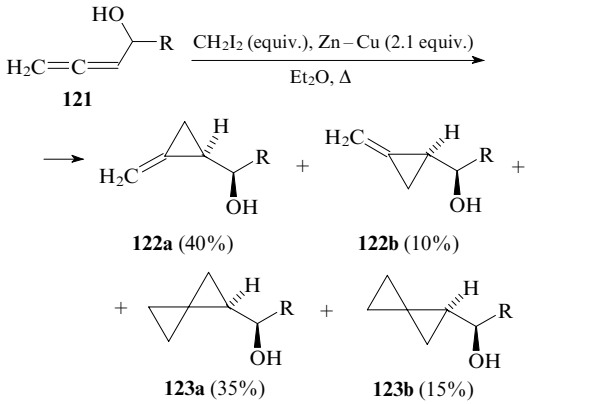
The cyclopropanation of triangulane-substituted allene preferably occurs at the double bond that contains a bulkier substituent, with the predominant formation of compound **119** and the product of double cyclopropanation **120**.[153]



119 (35%) **120** (46%) (5%)

It should be noted that aryl-substituted allenes are not cyclopropanated on treatment with the Simmons–Smith reagent.[154]

The reaction of allenic alcohols **121** with the Simmons–Smith reagent results in an equimolar mixture of diastereomeric methylenecyclopropanes **122** and spiropentanes **123**.[155] Thus, cyclopropanation of the double bond in allenic alcohols under traditional Simmons—Smith conditions or with the use of other zinc-based reagents, *e.g.*, the Furukawa reagent, proceeds non-selectively.[156]



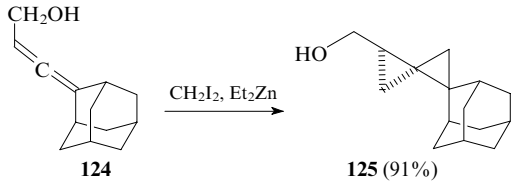
121

122a (40%) **122b** (10%)

123a (35%) **123b** (15%)

R = Alk

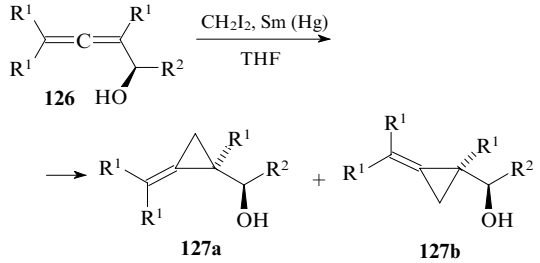
However, in the cyclopropanation of allenic alcohol **124** containing adamantane moiety with the CH_2I_2–Et_2Zn system, the yield of target spiropentane **125** reaches 91%.[157]



124 **125** (91%)

Lautens and Delanghe[156, 158] have reported on the regioselective cyclopropanation of α-allenic alcohols **126** with the use of samarium carbenoid. As a result, various methylene- and alkylidenecyclopropyl alcohols **127** were obtained. The diastereoselectivity of cyclopropanation of unsubstituted and terminally substituted allenic alcohols

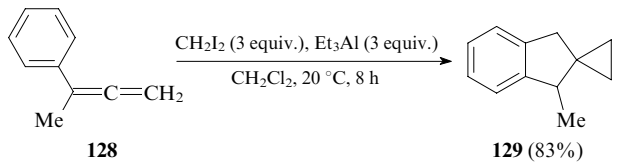
depends on the steric bulk of the substituent at the carbon atom bearing the hydroxy group and on the degree of substitution of the allene. The ratio of diastereomers **127a** : **127b** varies from 1 : 2 to 50 : 1.[156] It should be noted that the use of CH_2X_2-Sm (X = I, Br) reagent is essential for the optimization of cyclopropanation regioselectivity of α-allenic alcohols and minimizes the formation of spiropentylmethanol, whereas using the Simmons–Smith reagent leads to the formation of spiropentanes along with alkylidenecylopropanes.



R^1	R^2	Total yield (%)	Ratio **127a** : **127b**
H	Pr^i	67	4 : 1
H	Bu^t	57	50 : 1
H	cyclo-C_6H_{11}	64	9 : 1
H	n-C_7H_{15}	73	1 : 2
Pr^n	cyclo-C_6H_{11}	43	1.7 : 1

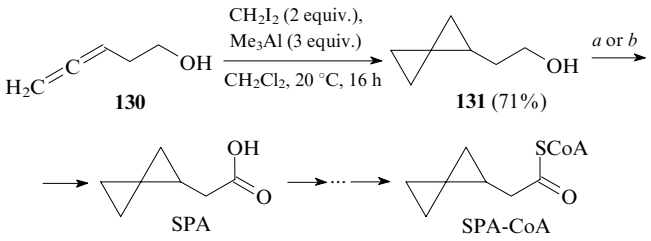
Unlike the Simmons–Smith reagent, aluminium carbenoid Et_2AlCH_2I obtained from Et_3Al and CH_2I_2 reacts with cyclonona-1,2-diene and cyclotrideca-1,2-diene giving the corresponding spiropentanes in high yields (80%–90%). Unlike zinc carbenoids, Et_2AlCH_2I also reacts with phenylallene giving phenylspiropropane in 73% yield.[159] At the same time, the reaction of phenylallene with CH_2N_2 in the presence of $Pd(acac)_2$ catalyst results solely in the product of monocyclopropanation, *i.e.*, benzylidenecyclopropane (yield 49%). As mentioned above, exhaustive cyclopropanation of cyclonona-1,2-diene by diazomethane results in spirocyclic product in only 15% yield.

The reaction of α-methylphenylallene **128** with three equivalents of CH_2I_2 and Et_3Al in CH_2Cl_2 led to the formation of 1′-methylspiro(cyclopropane-1,2′-indane) (**129**) in a high yield.[159]



Under the action of aluminium carbenoid generated in the $CH_2I_2-Me_3Al$ system, selective cyclopropanation of homoallenic alcohol **130** was successfully carried out, resulting in the formation of (2-hydroxyethyl)spiropentane (**131**).[160] The authors emphasized the importance of using Me_3Al, since aluminium carbenoids, which were prepared from Et_3Al and Bu^i_3Al, decomposed under the reaction conditions. However, this conclusion may be a consequence of the procedure according to which tricycloalkane was slowly added to a mixture of homoallenic alcohol and CH_2I_2. Cyclopropanation of compound **130** by the Simmons–Smith reagent had an unsatisfactory result.

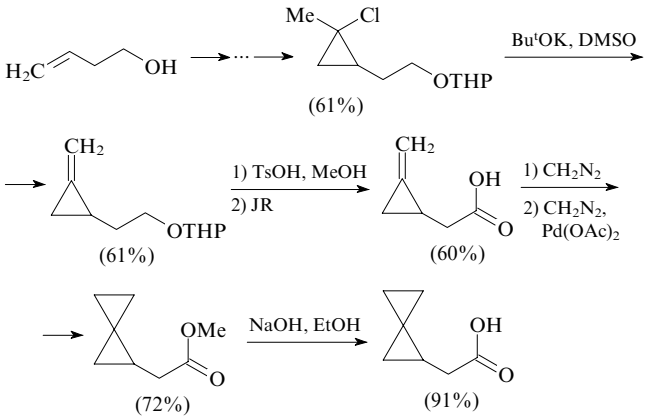
(2-Hydroxyethyl)spiropentane (**131**) was used in the synthesis of spiropentaneacetic acid (SPA) (in 50% or 60% yields depending on the oxidant) and spiropentylacetyl-CoA (SPA-CoA), which could be used as model compounds for the investigation of genetic diseases caused by deficiency of medium-chain acyl-coenzyme A-dehydrogenase.[160]



(*a*) JR (yield 71%), (*b*) TEMPO, HOCl, KBr, pH 9 (yield 92%); TEMPO is 2,2,6,6-tetramethylpiperidine 1-oxide

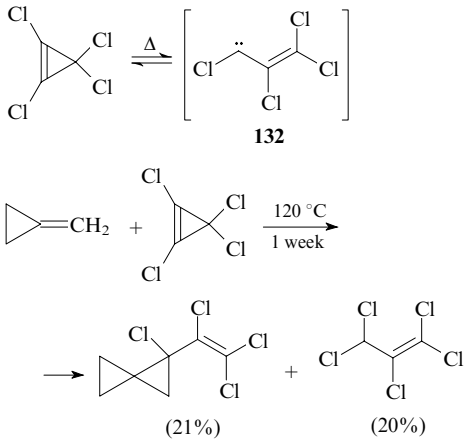
Note that the use of the $^{13}CH_2I_2-Me_3Al$ system proved to be a convenient method for the introduction of a ^{13}C-isotope label into the spiropentane structure.

It is interesting that formerly spiropentylacetic acid was prepared form but-3-enol in only 20% total yield by the route given below.[161]



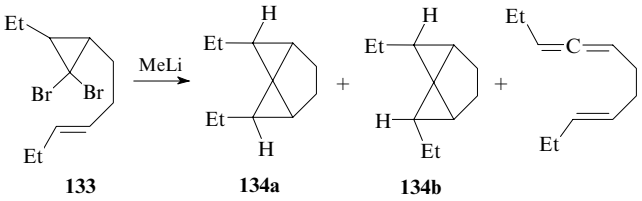
12. Cyclopropanation of methylenecyclopropane by perchlorovinylcarbene

Tetracyclopropene undergoes ring opening above 150 °C to give perchlorovinylcarbene **132**, which is capable of intramolecular cyclopropanation of alkenes, *e.g.*, methylenecyclopropane.[162]



13. Cyclopropanation under the action of cyclopropylidene

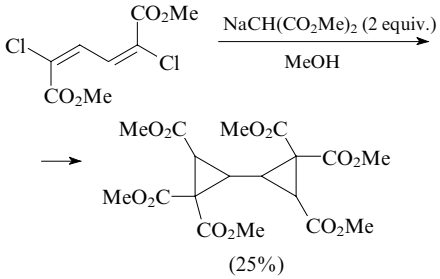
While considering the transformations of *N*-nitroso-*N*-cyclopropylurea, it has already been noted that the reaction of cyclopropylidene with bicyclopropylidene also results in the formation of spiropentanes (see Scheme 3, pathway *d*). In spite of good prospects of this approach, it remains little developed, apparently, because of easy isomerization of cyclopropylidene intermediates into allenic compounds. The reaction of dibromocyclopropane with MeLi **133** at −78 °C in diethyl ether results in a 12 : 1 mixture of tricyclic hydrocarbons **134a**,**b** in 40% total yield.[163] The intramolecular addition of carbene competes with opening of the three-membered ring.



133 **134a** **134b**

IV. Methods of synthesis of bicyclopropanes

The primary interest in bicyclopropanes has aroused in connection with attempts to synthesize prismane (an alternative formula of benzene proposed by Ladenburg) and its precursors. For the first time, a bicyclopropane derivative was obtained in 1923 by the reaction of dimethyl *trans*,-*trans*-2,5-dichloromuconoate with sodium dimethyl malonate by E H Farmer.[164]

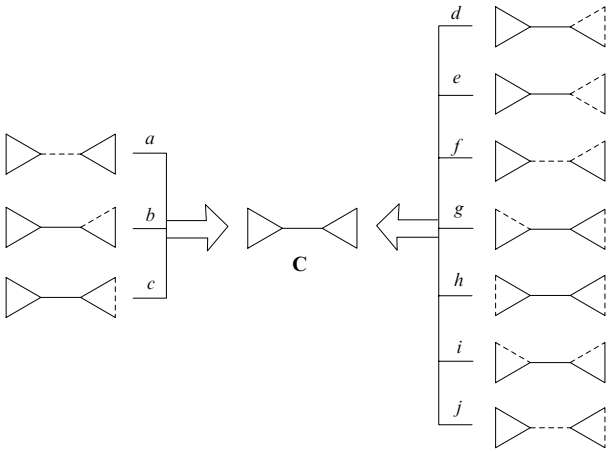


Subsequently, E Müller and O Roser,[165] who studied the reaction of butadiene with ethyl diazoacetate, isolated 1,1′-bicyclopropane-2,2′-dicarboxylic acid in a low yield upon decomposition of bipyrazoline. In the early 1950s, hydrocarbons with a bicyclopropane moiety, including bicyclopropane, were synthesized for the first time.[166, 167]

Further advances of bicyclopropane chemistry are unseparably linked with carbene methods. O M Nefedov, N S Zefirov and A G M Barrett have made a crucial contribution to their development. In addition, note pioneering studies of A De Meijere on the investigation of non-carbene methods of synthesis of bicyclopropanes performed in the 1970s. In the 1990s, heightened interest in the synthesis of cyclopropane systems was caused by isolation of nucleoside FR-900848 from the culture medium of *Streptoverticillium fervens* bacteria. This nucleoside shows potent, selective activity against filamentous fungi such as *Aspergillus niger*, *Mucor rouxianus*, *Aureobasidium pullulans*, and it is inactive against non-filamentous fungi such as *Candida albicans* and Gram −positive and gram-negative bacteria.[168, 169] In 1995, a structurally similar polycyclopropane, U-106305, was isolated from the *Streptomyces* sp. UC-11136 bacteria.[170]

Retrosynthetic analysis of the structure of bicyclopropanes with possible formation of one or two C−C bonds in one step distinguishes ten possible pathways for building of the bicyclopropane skeleton (Scheme 4).

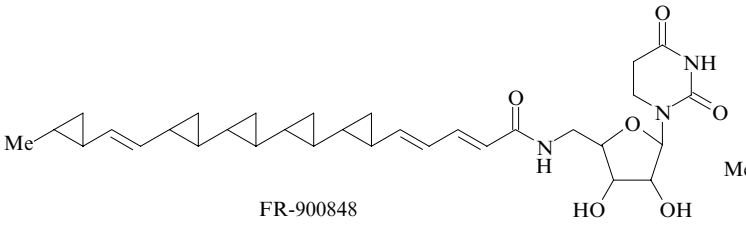
Scheme 4



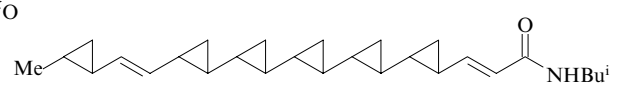
The first group of methods (pathways *a*–*c*) combines transformations yielding one C−C bond. These are reactions of coupling of cyclopropane compounds, oligomerization of cyclopropenes (pathway *a*), decomposition of cyclopropane-containing pyrazolines, the homoallyl–cyclopropylmethyl rearrangement, preparation of bicyclopropanes by the Kulinkovich reaction (pathway *b*), the Wideqvist reaction and 1,3-debromination of 1,1-bis(bromomethyl)methylcyclopropanes (pathway *c*). Another group of methods combines transformations yielding two C−C bonds in one step (pathway *d*–*j*). These are the reactions of cyclopropanation of 1,3-dienes and alkenylcyclopropanes by various carbene reagents (pathway *d*) and also cyclopropanation of alkenes by cyclopropylcarbene and cyclopropyl-containing carbene chromium complex (pathway *e*). Examples of preparation of bicyclopropanes by pathways *f*–*j* are yet unknown.

1. The coupling reactions

The examples given below illustrate the building of bicyclopropane skeleton *via* pathway *a* (see Scheme 4). The simplest representitave of bicyclic hydrocarbons, *i.e.*, 1,1′-bicyclopropane, was obtained by V A Slabey in 1952 by the reaction of chlorocyclopropane with lithium in diethyl ether (yield 12%).[166] Cyclopropane was the major product of this reaction. In spite of the fact that the Würtz



FR-900848

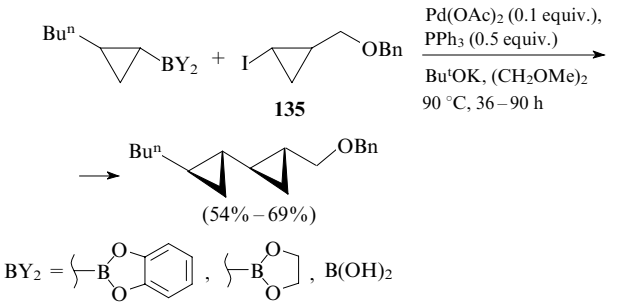


U-106305

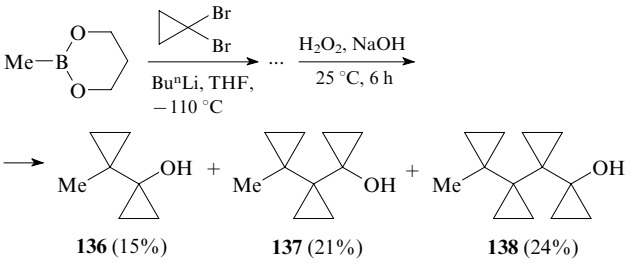
reaction is often used in the synthesis of bicyclobutanes, in the case of bicyclopropane, the approaches based on cross-coupling of organoboron and organotin compounds proved to be more effective.

The Suzuki cross-coupling reaction between 2-hydroxymethyl-1-iodocyclopropane or its *O*-benzyl-protected derivative **135** and 2-n-butylcyclopropylboronate esters gave satisfactory results only in the case of the use of Bu^tOK as a base and dimethoxyethane as a solvent (Scheme 5).[171] In the presence of K_2CO_3 and Bu^n_4NCl in aqueous DMF, iodocyclopropanes decomposed.

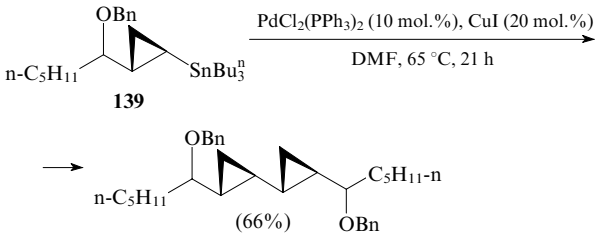
Scheme 5



Recently an original approach to the synthesis of polycyclopropane compounds using the Matteson homologation has been developed. Treatment of a 2-methyl-1,3-dioxaborinane solution with 1,1-dibromocyclopropane and Bu^nLi and -110 °C four times followed by oxidation resulted in a mixture of polycyclopropyl-containing alcohols **136**–**138** in 60% total yield.[172]

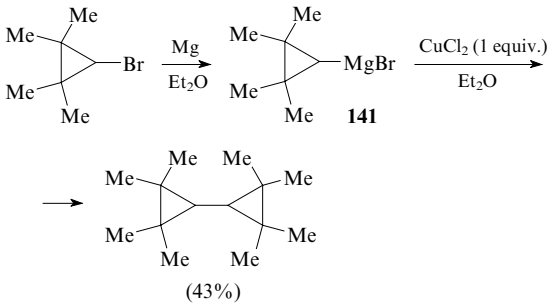


Dimerization of tributylstannylcyclopropane **139** in the presence of catalytic amounts of palladium compounds or copper compounds proceeds with a relatively high yield, the configuration of the cyclopropane moiety being retained.[173]

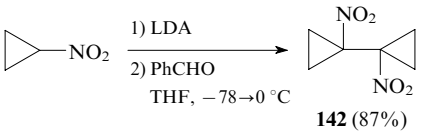


Another method of dimerization of tri-n-butylstannylcyclopropane comprises transmetallation of cyclopropylstannanes (replacement of tin by lithium). Under the action of Bu^sLi, this process proceeds stereoselectively to give the corresponding lithium-substituted cyclopropane with retention of the configuration. Treatment of the latter by the cuprate complex with the subsequent oxidation by O_2 results in the formation of *syn-trans*-bicyclopropane **140** in a high yield.[174, 175] This technique has been used for the synthesis of the natural cyclopropane FR-900848 (total yield 2.7%) (Scheme 6).

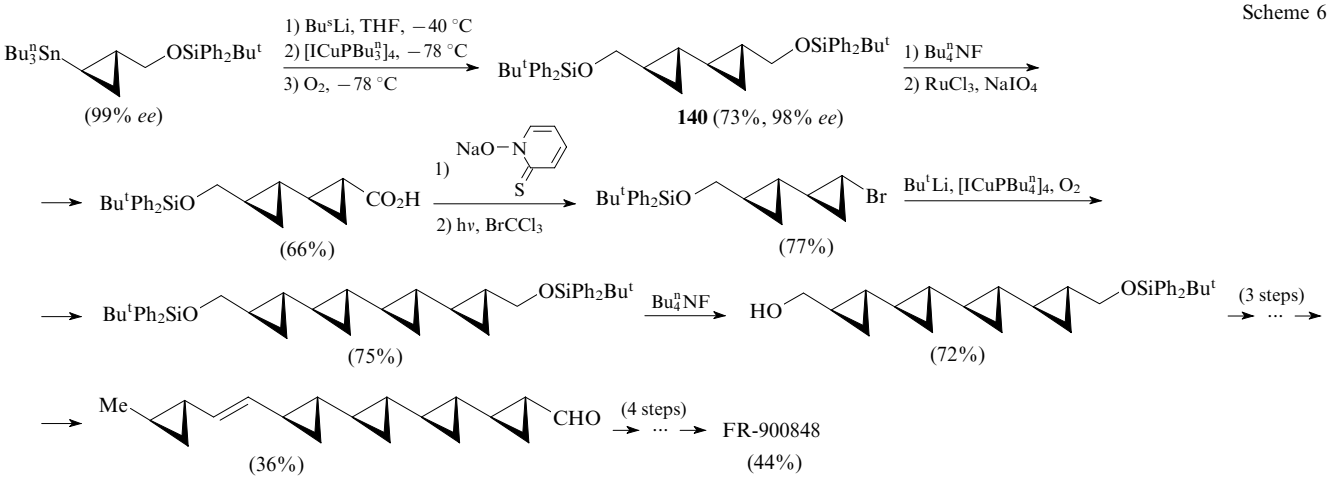
Octamethyl-substituted bicyclopropane was obtained in a moderate yield by oxidative dimerization of cyclopropylmagnesium compound **141** under the action of $CuCl_2$.[176]



Consecutive treatment of nitrocyclopropane by lithium diisopropylamide and benzaldehyde at -78 °C leads to the 1-nitrocyclopropyl anion, which is converted to a substituted bicyclopropane **142** under these conditions.[177, 178]

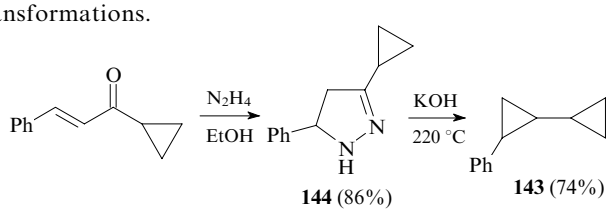


Scheme 6



2. Decomposition of pyrazolines

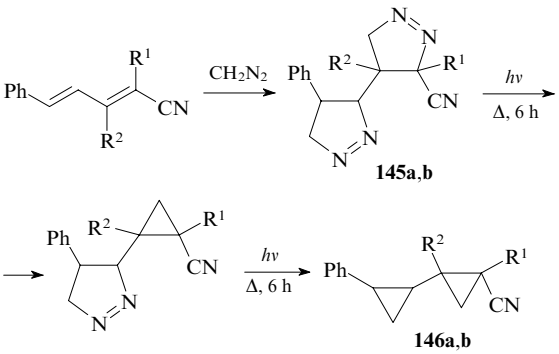
The first bicyclopropane-containing hydrocarbon, 2-phenyl-1,1′-bicyclopropane (**143**), was obtained in 1951 by L I Smith and E R Roger[167] by decomposition of 2-pyrazoline **144** (see pathway *b* in Scheme 4). The attempts of the authors to synthesize unsubstituted or alkyl-substituted bicyclopropane had no success, as the corresponding alkenyl cyclopropyl ketones either were not formed at all or their yields were too low for their use in subsequent transformations.



144 (86%) **143** (74%)

Instead of the expected monoadduct, the reaction of buta-1,3-diene with phenyldiazomethane gave a mixture of three bisadducts. Their thermal and photochemical decomposition resulted in a mixture of stereoisomers of 2,2′-diphenyl-1,1′-bicyclopropane in a quantitative yield.[179]

However, in the case of phenyl-substituted 1,3-dienes the formation of bipyrazolines **145a**,**b** is regioselective. Decomposition of compounds **145a**,**b** produces functionally substituted bicyclopropanes **146a**,**b**.[180]

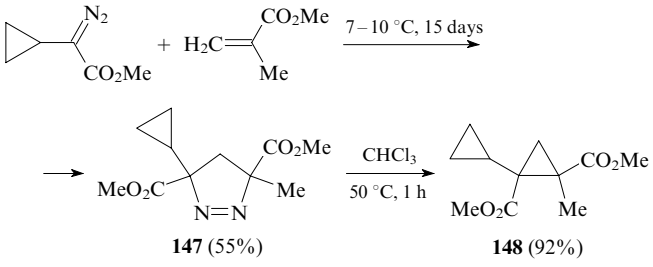


145a,**b**

146a,**b**

R^1 = CO_2Me, R^2 = Ph (**a**); R^1 = CN, R^2 = Bn (**b**)

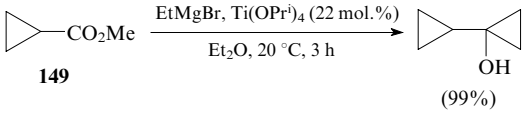
1-Pyrazoline **147** obtained from methyl 2-diazo-2-cyclopropylcarboxylate and methyl methacrylate easily decomposes upon gentle heating (50 °C) within 1 h with the release of nitrogen and formation of dimethyl-1-cyclopropylcyclopropane-1,2-dicarboxylate **148**.[181] At the same time, the reaction of the starting diazo ester with methyl acrylate and acrylonitrile results in thermally stable 2-pyrazolines.



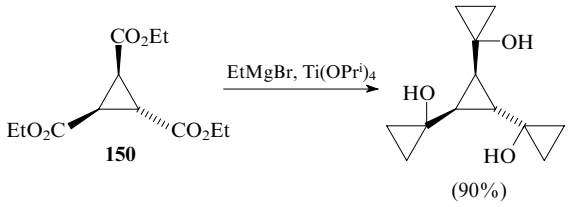
147 (55%) **148** (92%)

3. The Kulinkovich reaction

Cyclopropanols have beeb prepared by $Ti(OPr^i)_4$-catalyzed reaction of esters with the Grignard reagent containing a β-hydrogen atom (see Scheme 4, pathway *b*). According to the Kulinkovich reaction, alkyl cyclopropanecarboxylates (**149**) and alkyl cyclopropanetricarboxylates (**150**) can be converted to cyclopropyl-substituted cyclopropanols.[117,182]

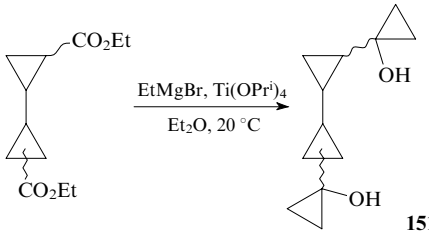


149 (99%)



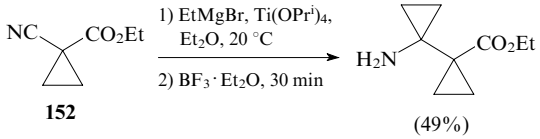
150 (90%)

A similar approach has been used for the preparation of tetracyclopropane **151**.[183]



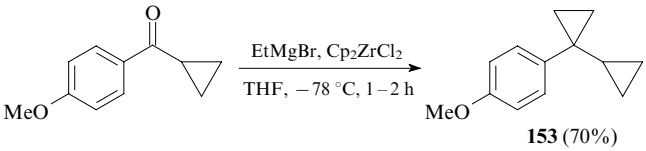
151 (99%)

In order to transform ethyl 1-cyanocyclopropanecarboxylate **152** into substituted bicyclopropane, subsequent treatment of the reaction mixture with a Lewis acid is required, only the nitrile group taking part in the reaction.[184]



152 (49%)

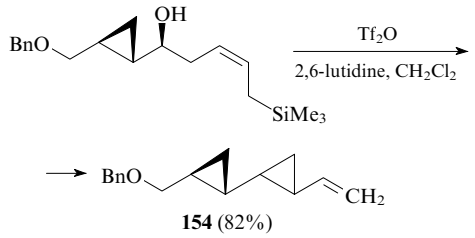
While discussing the Kulinkovich reaction, it is necessary to mention an interesting transformation of saturated, unsaturated and aromatic aldehydes and ketones under the action of EtMgBr and Cp_2ZrCl_2 (Cp is cyclopentadienyl) to give 1,1-substituted cyclopropanes, *e.g.*, compound **153**.[185]



153 (70%)

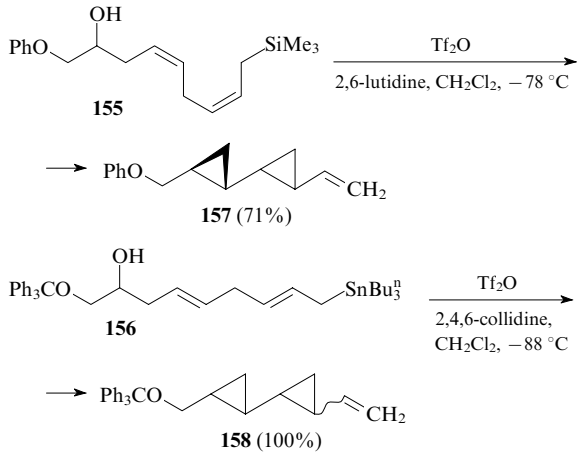
4. Homoallyl – cyclopropylmethyl rearrangement

Homoallyl alcohols and epoxides rearrange to three-membered rings (see pathway *b* in Scheme 4) under the action of the Lewis acids or trifluoromethanesulfonic anhydride (Tf_2O).[186,187] The cyclopropylmethyl carbocation being formed is stabilized either by reacting with nucleophile or by elimination. This transformation was used to prepare *trans*,*syn*,*trans*- and *trans*,*anti*,*trans*-bicyclopropanes **154**.[188] The reaction is non-stereospecific, resulting in the formation of 1 : 1 mixtures of diastereomers. Epoxidation with subsequent iteration of the procedure provides an effective route to polycyclopropanes.



154 (82%)

The yield of the products significantly increases if allylstannanes are used instead of allylsilanes. However, the higher reactivity of allylstannanes leads to the loss of selectivity of the process and, as a result, *cis*-substituted cyclopropanes are additionally formed.[189, 190] The use of homoallyl–cyclopropylmethyl rearrangement in the cascade cyclization of diene systems **155** and **156** should be mentioned.[189] In the former case, *trans*-substituted cyclopropanes **157** (*syn*- to *anti*-diastereomers ratio being 1 : 1) are formed, while in the latter case, the reaction gives diastereomeric *trans*- and *cis*-cyclopropanes **158**.



155

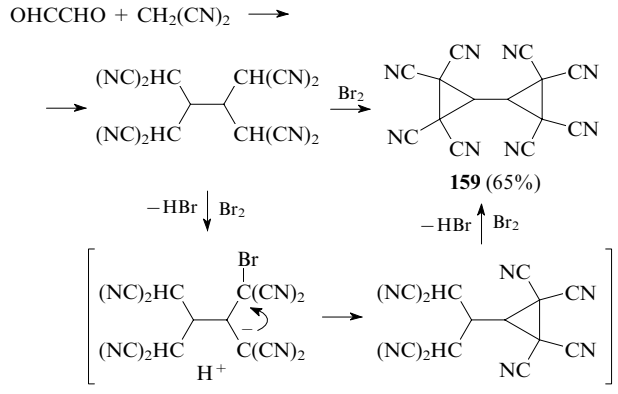
157 (71%)

156

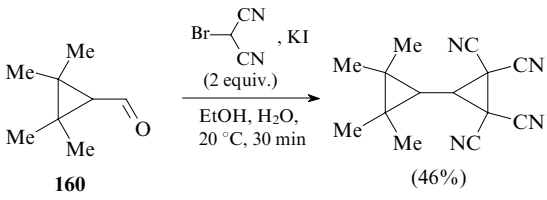
158 (100%)

5. The Wideqvist reaction

An interesting approach to the synthesis of cyclopropane compounds has been implemented with the use of alkylidenebis(malononitriles) (the Wideqvist reaction, see Scheme 4, pathway *c*).[191] In the presence of catalytic amounts of β-alanine, the reaction of glyoxal and malononitrile with the subsequent bromination led to the formation of bicyclopropane octacarbonitrile **159**.[176]



Tetramethylcyclopropanecarboxaldehyde (**160**) has been used instead of glyoxal in one of the modifications of this method.[176]



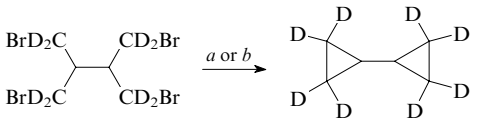
160

(46%)

It should be noted that the replacement of cyclopropylcarboxaldehyde by acrolein also results in bicyclopropane. In this case, the Michael addition of bromomalononitrile to acrolein affords dinitrile-substituted cyclopropanecarboxaldehyde, namely, 2-formyl-1,1-cyclopropanedicarbonitrile, which subsequently transforms into hexanitrile-substituted bicyclopropane *via* the Wideqvist reaction.[176]

6. 1,3-Debromination

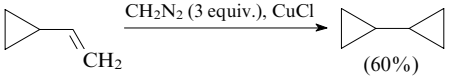
1,3-Debromination of 1,1,2,2-tetrakis(bromodideuteriomethyl)ethane induced by zinc powder results in deuterated bicyclopropane in 37% yield (see pathway *c* in Scheme 4). A higher yield of the product has been obtained by the reduction of starting tetrabromide by the chromium complex with ethylenediamine. In the latter case, no side formation of other hydrocarbons was observed.[176]



(*a*) Zn (yield 37%); (*b*) Cr^{II}, $(CH_2NH_2)_2$, DMF, H_2O (yield 70%)

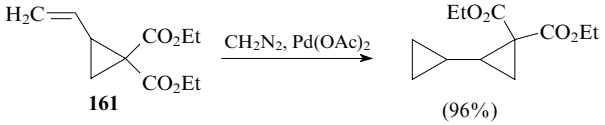
7. Cyclopropanation of alkenylcyclopropanes and 1,3-dienes by diazomethane

The methods of cyclopropanation under the action of different reagents listed below correspond to the formation of bicylopropane skeleton *via* pathway *d* (see Scheme 4). The presence of cyclopropane moiety at the double bond does not prevent the interaction of vinylcyclopropane with diazomethane catalyzed by copper(I) salts.[192] This reaction proceeds selectively in good yield.



(60%)

A similar transformation has been carried out for the substituted vinylcyclopropane **161** in the presence of palladium acetate.[192]

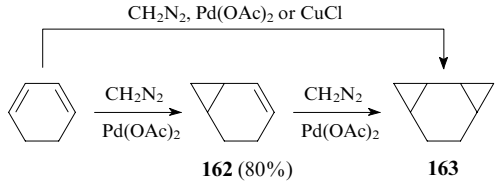


161

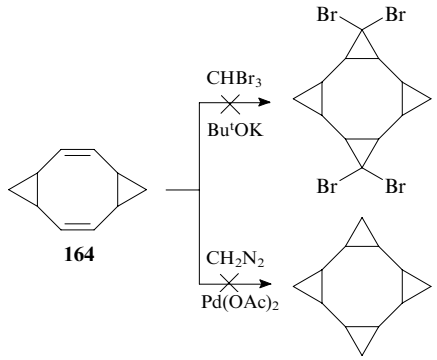
(96%)

Moreover, the introduction of a three-membered ring or a conjugated double bond into the cycloalkene molecule activates the double bond towards CH_2N_2 in the presence of catalytic amounts of $Pd(OAc)_2$.[193] Indeed, diazomethane does not cyclopropanate cyclohexene in the presene of palladium catalyst, but easily forms mono- (**162**) and bis- (**163**) addition products with hexa-1,3-diene. Cyclopropanation of hexa-1,3-diene by diazomethane in the presence of $Pd(OAc)_2$ ensures stereospecificity of the process, > 90% of *trans*-isomer **163** being formed. At the same time, the use of

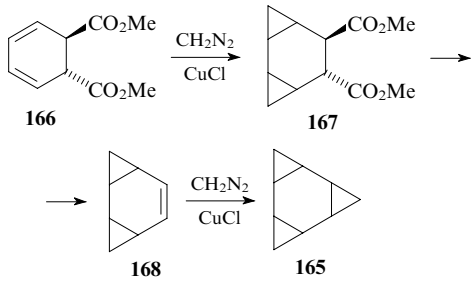
CuCl as a catalyst results in low stereoselectivity of the reaction,[194] leading to the mixture of *trans*- (54%) and *cis*-isomers (32%).



On the other hand, it has been reported[195] that the double bonds of cyclic diene **164** are inert towards diazomethane and dibromocarbene.

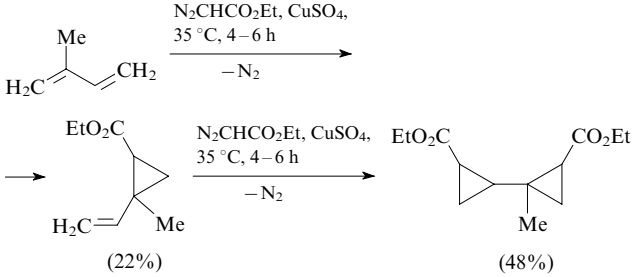


The diazomethane method of catalytic cyclopropanation of double bonds in aliphatic rings has been successfully used for targeted synthesis of trishomobenzene **165** from dimethyl *trans*-dihydrophthalate **166**.[196] Compound **165** could not be obtained by direct cyclopropanation of benzene due to easy isomerization of primarily formed norcaradiene. With that end in view, cyclohexadiene **166** has been transformed on treatment with an excess of CH_2N_2 in the presence of CuCl into the corresponding double cyclopropanation product **167**. Then the ester groups were removed and the resulting substituted *trans*-cyclooctene **168** was cyclopropanated by diazomethane once more. The yields of products were not specified in the original article.



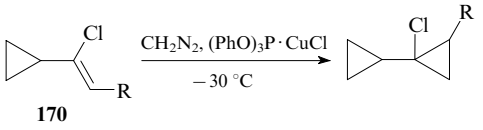
The reaction of *cis*-hexatriene with CH_2N_2 in the presence of CuCl results in the formation of all possible products of methylene group addition to the double bonds of the starting triene.[197] Cyclic hydrocarbons have been detected in the reaction mixture in minor quantities. The authors supposed that they had been formed as a result of rearrangement of 1,2-divinylcyclopropane into cyclohepta-1,4-diene and subsequent cyclopropanation. In spite of the excess of CH_2N_2, they failed to achieve complete conversion of hexatriene. Cyclopropanation of *cis*- and *trans*-penta-1,3-dienes also proceeded non-selectively.[198]

However, the $CuSO_4$-catalyzed reaction of ethyl diazoacetate with isoprene was selective, the more substituted double bond being more reactive.[199] The repeated treatment of the obtained substituted vinylcyclopropene with ethyl diazoacetate resulted in corresponding bicyclopropane.



The use of palladium catalyst in the cyclopropanation of 1-methoxybuta-1,3-diene favoured high regioselectivity of the formation of monoadduct **169**, which contrasted with the results obtained by using the copper catalyst.[200] What is more, the configuration of substituents at the double bond is retained after cyclopropanation in the case of palladium catalysis (Scheme 7).

Less satisfactory results have been obtained in the cyclopropanation of cyclopropyl-substituted alkenyl halides. Unlike the reaction with unsaturated hydrocarbons, the copper salt-catalyzed interaction of diazomethane with alkenyl halides gave the desired products in low yields. The use of the complex $(PhO)_3P \cdot CuCl$ as a catalyst slightly increased the yield of products of methylenation of compound **170**.[201]

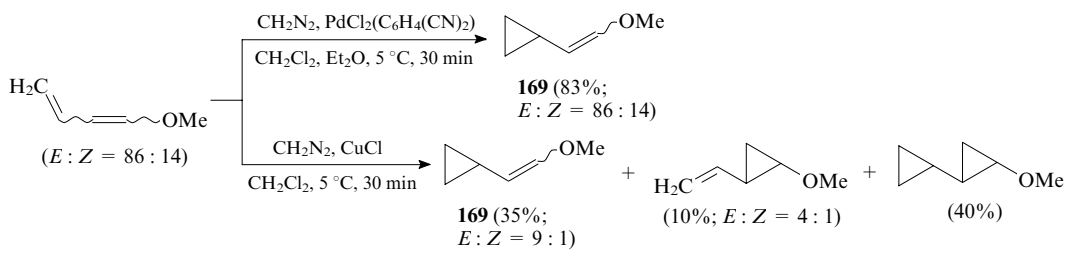


R = H (35%), CH(cyclo-C_3H_5)Me (24%), CH_2CH_2Cl (19%)

8. Cyclopropanation by dihalocarbenes

L Skattebol[202] has carried out detailed investigation of the reaction of dibromocarbene with dienes with various structures. If equimolar quantities of 1,3-diene and bromoform

Scheme 7

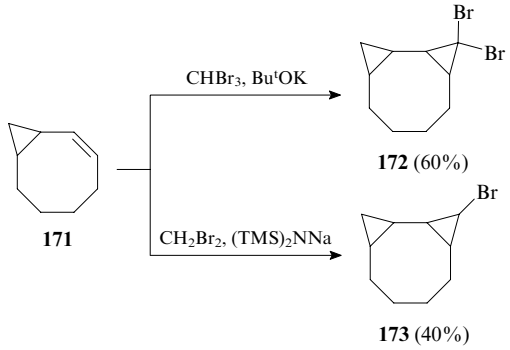


were used, then monoaddition mainly occurred with the formation of monoadduct in good yields. However if an excess of bromoform was taken, then 2,5-dimethylhexa-2,4-diene was converted only to the bisadduct in 92% yield, the reaction with other dienes resulting in mixtures of the products of mono- and bisaddition. The yield of bicyclopropane derivative increased with the growth of the degree of substitution of 1,3-diene, which was attributed to the rise of reactivity in the series of substituted alkenes (1-substituted < 1,2-disubstituted < 1,1-disubstituted < 1,1,2-trisubstituted). The same series determines the regioselectivity of monocycloaddition.

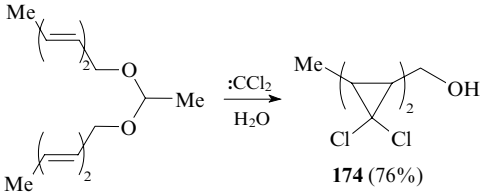
In 1969 Makosza (cited by Ref. 203) proposed a new method of cyclopropanation with dihalocarbenes in aqueous medium. It greatly widened the scope of applicability of reactions with carbenes, because earlier it had been considered that such transformations had strictly required water-free conditions. Thus, it was possible to obtain bisadduct in 39% yield from butadiene using 2.2 equiv. of $CHCl_3$, the yield of the product of monocycloaddition being only 12%.[203]

The reaction of buta-1,3-diene with the Seyferth reagent ($PhHgCCl_2Br$) is more selective, resulting in the formation of 1-vinyl-2,2-dichlorocyclopropane and 2,2,2′,2′-tetrachlorobicyclopropane as a minor component. On using of the excess of the reagent, the yield of tetrachlorinated bicyclopropane increases up to 91%.[204]

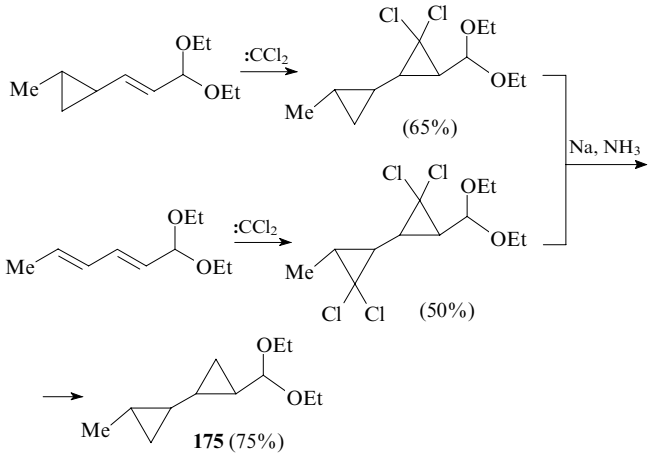
The difference in reactivities of cyclic compounds, namely, diene **164** and cycloalkene **171**, towards dibromocarbene is noteworthy. Despite the structural similarity, the former is inactive in the cyclopropanation reaction, while the latter is converted to dibromide **172** in 60% yield.[195] Monobromo derivative **173** has been obtained from cycloalkene **171** under the action of sodium bis(trimethylsilyl)amide and dibromomethane.[195]



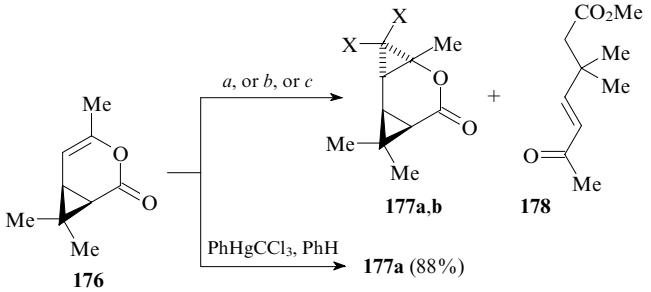
Allylic alcohols react with dichlorocarbene to give a complex mixture of products, but by using acetal protection, it has been possible to synthesize hydroxymethyl-substituted bicyclopropane **174** from sorbic alcohol.[205]



Bicyclopropane acetal **175** has been obtained in a similar way using unsaturated aldehyde as the starting compound. The attempts at synthesizing a tricyclopropane acetal by addition of bicyclopropane acetal **175** to vinyl ether, *etc.*, according to the given scheme, ended in the opening of the three-membered ring remote from the acetal group.[206]

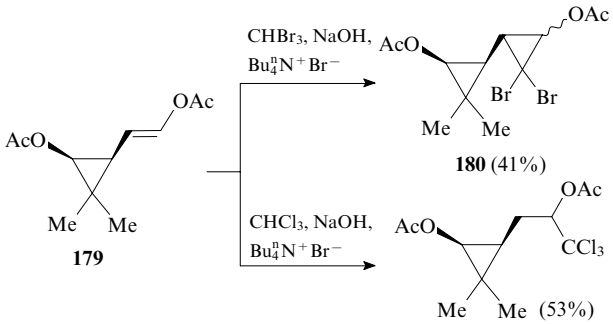


The yields of the products of reaction of unsaturated lactone **176** depend on the character of dihalocarbene and on the carbene generation method. The cyclopropanation with dichlorocarbene generated from $PhHgCCl_3$ (Ref. 207) or under the Makosza reaction conditions (in $CHCl_3 - NaOH - BnEt_3N^+Cl^-$ system) gave product **177a** in a rather high yield. However, the yield of dibromo derivative **177b** in the cyclopropanation of compound **176** by dibromocarbene generated under the same conditions ($CHBr_3 - NaOH - BnEt_3N^+Cl^-$) did not exceed 55%.[208] It has been established that at the temperatue of $>30\ ^\circ C$, along with the products **177a**,**b**, a significant amount (up to 65%) of methyl 3,3-dimethyl-6-oxohept-4*E*-enoate (**178**) is formed.[209] The generation of dihalocarbene by the reaction of K_2CO_3 with haloforms resulted only in compound **177a**,**b** in high yields (83% – 85%).



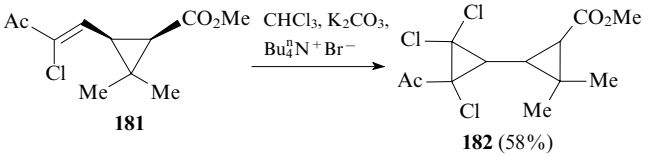
X = Cl (**a**), Br (**b**); (*a*) CHX_3, NaOH, $BnEt_3N^+Br^-$, CH_2Cl_2, MeOH;
(*b*) $CHCl_3$, K_2CO_3, $Bu^n_4N^+Br^-$, Cl_3CCO_2Na;
(*c*) $CHCl_3$, K_2CO_3, $Bu^n_4N^+Br^-$

Due to activation of the double bond by cyclopropane moiety, compound **179** can be brought into the reaction



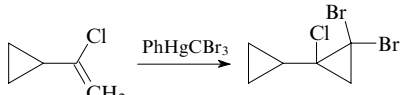
with dibromocarbene, thus giving the cycloaddition product **180**. Such activation is insufficient for dichlorocarbene, so the reacting species is the anion CCl_3^- (Ref. 210).

However, in the case of cyclopropanation of the double bond at the chlorine atom in vinylcyclopropane **181**, the reaction gives a satisfactory yield of product **182** even if chloroform is used as the source of dichlorocarbene. A mixture of *syn*- and *anti*-isomers with a slight dominance of the *syn*-isomer is formed, which is typical of cyclopropanation of vinylcyclopropanes with electron-deficient double bond.[211] Note that in the cyclopropanation of compound **181** by the ylide generated from $Me_3S^+(O)I^-$, the ratio of *syn*- and *anti*-diastereomers was 4 : 1.[211]



181 **182** (58%)

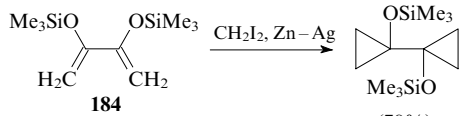
The application of the Seyferth reagent for the cyclopropanation of vinyl chlorides also proved to be successful. In its presence, 1-chloro-1-cyclopropylethylene transforms into trihalo-substituted bicylopropane **183** in a good yield.[173]



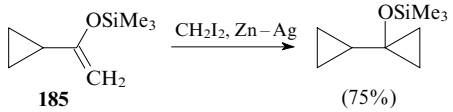
183 (65%)

9. The Simmons – Smith cyclopropanation

In 1963, Overberger and Halek[212] first observed the formation of bicyclopropane as a side product (yield 7% – 23%) in the Simmons – Smith preparation of vinylcyclopropane from buta-1,3-diene. Subsequently, this reaction was used for the preparation of 1,1-dicyclopropylcyclopropane from 1,1-dicyclopropylethylene.[213] J M Conia and co-workers[214] proposed an improved technique of the Simmons – Smith reaction consisting in the use of zinc – silver pair (instead of zinc – copper) and pyridine for the treatment of the reaction mixture. This is essential for organosilicon enols **184** and **185**, which may form cyclopropanols and ring opening products upon usual treatment.[215, 216]



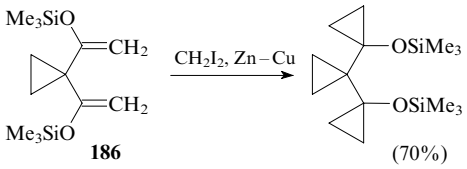
184 (78%)



185 (75%)

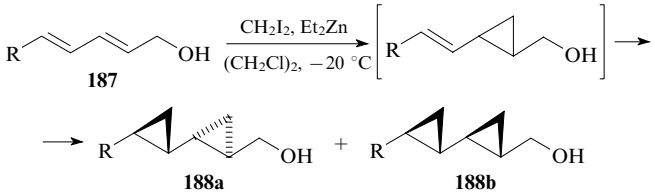
It has been discovered[214] that the zinc – silver pair has a higher reactivity than zinc – copper with respect to diiodomethane. Its use gave better yields in the reactions with alkenes, and also it required only a little excess of the reagent and the time of the reaction was significantly reduced. It should be noted that in the presence of the zinc – copper pair, on similar treatment with pyridine, the yield of bisadduct decreased insignificantly.

Later, N S Zefirov *et al.*[217] successfully carried out cyclopropanation of the organosilicon dienol **186** by the Simmons – Smith reagent, though the details of the subsequent treatment and isolation of the product were not given in the article.



186 (70%)

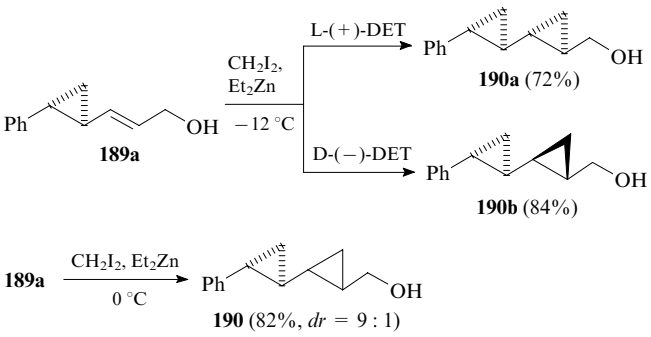
The Furukawa reagent has found extensive synthetic application. It has been successfully used for the cyclopropanation of 2,4-dienols in the synthesis of the antifungal agent FR-900848 and cholesteryl ester transfer protein inhibitor U-106305. It has been demonstrated that 2,4-dienols **187** react with the $CH_2I_2 - Et_2Zn$ system in dichloroethane at −20 °C to give racemic mixtures of bicyclopropanes **188a**,**b** in good yields (68% – 80%) and good diastereoselectivity [ratio of diastereomers (*dr*) varied from 5 : 1 to 95 : 5] with respect to *anti*-isomer **188a**.[218] The double bond located in the allyl position relative to the hydroxy group is the first to be cyclopropanated. The stereochemistry of the second three-membered ring is determined by the influence of the first one and by the character of the substituent at the terminal double bond.[219]



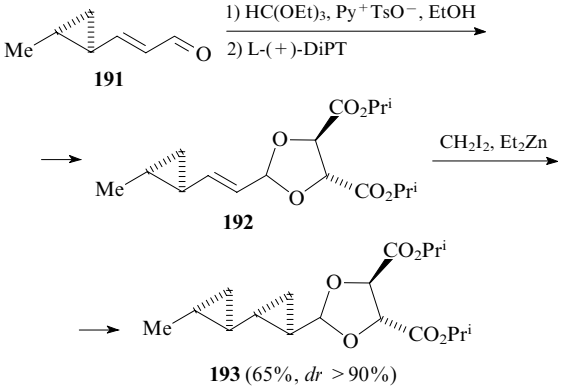
187 **188a** **188b**

R	Yield (%)	Ratio **188a** : **188b**
Me	68	5 : 1
Pr^i	72	6 : 1
cyclo-C_6H_{11}	78	7 : 1
Ph	80	5 : 1
$Bu^tMe_2SiOCH_2$	72	95 : 5

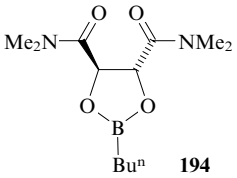
Tartrates are often used for the chiral induction in the preparation of optically active compounds from prochiral substrates. The possibility of using tartrates in the synthesis of optically active cyclopropanes was demonstrated by the example of cyclopropanation of enol **189a**.[220, 221] Under the action of the Furukawa reagent in the presence of L-(+)- or D-(−)-diethyl tartrate (DET), this reaction gave *syn*- and *anti*-bicyclopropanes **190a** (*dr* = 6 : 1) and **190b** (*dr* = 6 : 1). Treatment of alcohol **189a** in the absence of tartrates resulted in a 1 : 1 mixture of two diastereomers **190a**,**b** in 82% total yield.[218, 222] However, note that the diastereoselectivity of cyclopropanation strongly depends on the configuration of substituents in the three-membered ring and at the double bond. Cyclopropanation of compound **189a** in the absence of tartrates affords mainly *anti*-isomer **190b** (*dr* = 9 : 1).



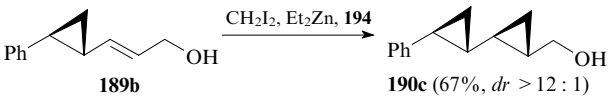
Another approach to the synthesis of optically active bicyclopropanes consists in the use of the Yamamoto method of cyclopropanation, that is, preliminary preparation of chiral unsaturated acetals.[220] Cyclopropanation of the product of condensation, *i.e.*, unsaturated aldehyde **191**, by L-(+)-diisopropyl tartrate (DiPT) is highly diastereoselective.[218, 223] The products of mono- (**192**) and bisaddition (**193**) have been isolated.[218]



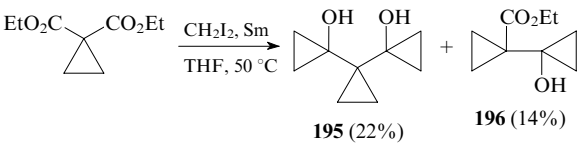
The enantioselective version of the Simmons–Smith reaction developed by Charette *et al.*[224] in 1994 is worth noting. It involved the use of chiral boron derviative of tartaric acid diamide **194**.



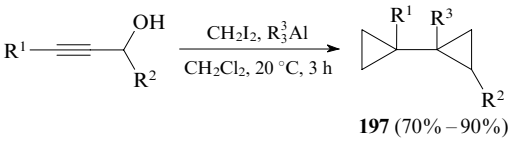
Cyclopropanation of isomer **189b** has been used by Barrett and Kasdorf in the total synthesis of natural compounds U-106305[225] and FR-900848.[226]



Besides zinc carbenoids, organometallic derivatives of other metals have been used for cyclopropanation. Thus, samarium carbenoid *in situ* generated from samarium and diiodomethane (substrate : CH_2I_2 : Sm = 1 : 6 : 8) was used for the transformation of cyclopropane-1,1-dicarboxylate into substituted tri- (**195**) and bicyclopropanes **196**.[227]

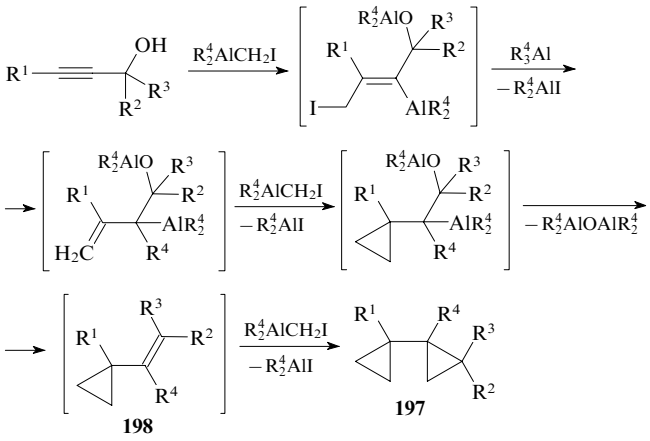


Substituted propargyl alcohols react with aluminium carbenoids with the formation of 1,1′-disubstituted bicyclopropanes **197** in high yields.[228]



R^1 = Alk, Ph; R^2 = H, Me; R^3 = Et, Bu^i

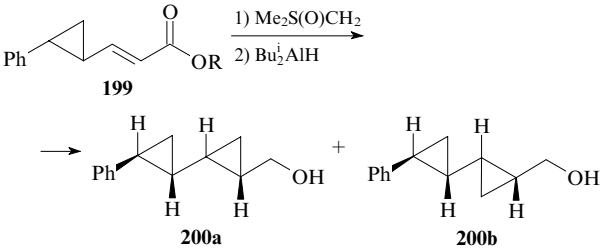
Aluminium carbenoids were generated by the interaction of Et_3Al or Bu^i_3Al with CH_2I_2. It is interesting that aluminium carbenoid obtained from Me_3Al does not show any reactivity in this reaction. Presumably, the reaction occurs *via* the intermediate formation of alkenylcyclopropanes **198**.



Under the action of lithium carbenoid generated from MeLi and $ClCH_2I$, cyclopropanecarboxylic acid anhydride was converted to to 1-cyclopropylcyclopropan-1-ol in 45% yield.[229]

10. Reactions with the involvement of sulfur ylides

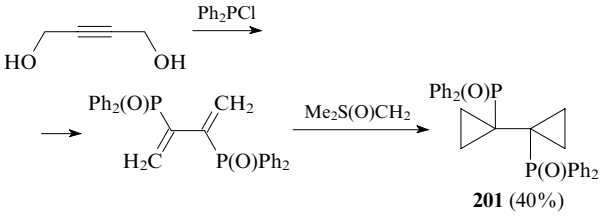
Sulfur ylides did not find wide application in the synthesis of polycyclopropane compounds. Out of the examples given in the literature, the preparation of bicyclopropanes by addition of sulfoxonium ylide to electron-deficient vinylcyclopropanes **199** could be mentioned (see pathway *d* in Scheme 4).[230] As a result, a mixture of isomers **200a**,**b** was obtained in 95% yield. Low stereocontrol and little preference for the formation of *anti*-isomer **200b** in these reactions



R = Me, Et, Bu^t

are similar to those observed for cyclopropanation of allylic alcohols by zinc carbenoids.

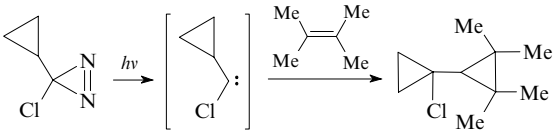
In order to obtain the organophosphorus ligand based on bicyclopropane, the cyclopropanation of 2,3-bis(diphenylphosphinyl)-1,3-butadiene into 1,1′-bis(diphenylphosphino)bicyclopropane **201** in 40% yield was performed.[231] It should be noted that the attempts to obtain compound **201** by [2 + 3]-cycloaddition of CH_2N_2 to 1,3-diene with the subsequent decomposition of an adduct have failed.



201 (40%)

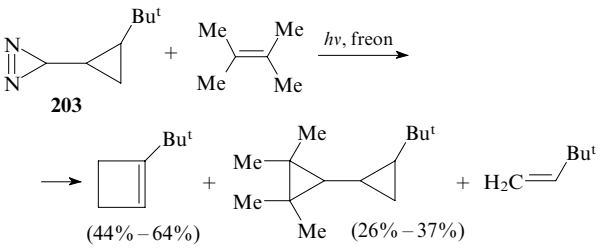
11. Cyclopropanation with cyclopropylcarbene

Cyclopropylcarbenes may be easily obtained by photochemical and thermal decomposition of diazirines (see Scheme 4, pathway *e*). Chlorocyclopropylcarbene may be of great interest because the chlorine atom stabilizes the singlet state of carbene and favours the addition to alkenes.[232] The rate of addition to the double bond and the yield of bicyclopropanes well correlate with the nucleophilicity of the unsaturated compound.[233] In the reaction of chlorocyclopropylcarbene with tetramethylethylene, along with the formation of the addition product **202a**, the formation of minor quantities of 1-chlorocyclobutene was also observed. The latter was formed as a result of rearrangement of chlorocyclopropylcarbene. Under certain conditions (thermolysis in CCl_4 at 100 °C or photolysis in pentane), 1-chlorocyclobutene is the major reaction product.

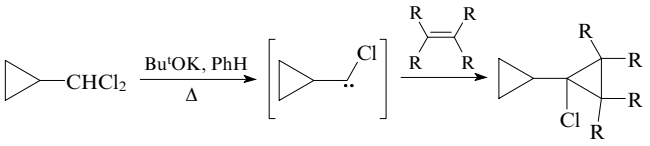


202a (78%)

Upon generation of cyclopropylcarbene from diazirine **203** in the presence of alkenes (*e.g.*, tetramethylethylene), it mainly rearranged and a mixture of products formed.[234]



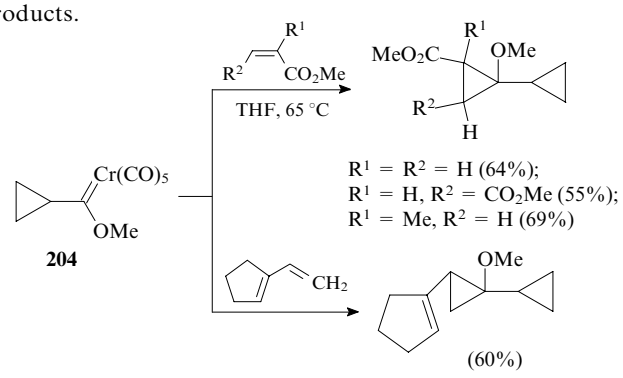
Chlorocyclopropylcarbene has also been generated by the action of potassium *tert*-butoxide on dichloromethylcyclopropane, but the yields of corresponding addition products **202a**,**b** did not exceed 25%. The formation of 1-chlorocyclobutene was also the main side reaction.[235]



R = Me (**a**, 18%), H (**b**, 25%) **202a**,**b**

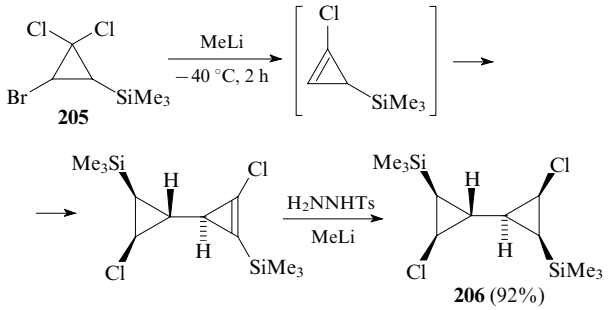
12. The use of the chromium complexes

Dotz and Fischer[236] have first accomplished the cyclopropanation of alkenes by arylalkoxycarbene complexes of chromium and tungsten. Though this reaction is universal and suitable for transforming a wide range of functionally substituted alkenes into cyclopropanes, the reaction with 1,3-diene still results in cyclopropanation of only one double bond. It was possible to obtain bicyclopropane using cyclopropyl-containing carbene complex of chromium **204**,[237–239] which easily reacts with conjugated dienes, α,β-unsaturated esters and amides. More reactive unsaturated compounds, such as vinyl methyl ketone, more rapidly undergo side reactions and do not form the cycloaddition products.



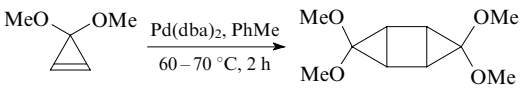
13. Miscellaneous reactions

A number of other reactions that resulted in bicyclopropanes and that did not find wide application should also be mentioned. Oligomerization of cyclopropenes is usually not selective, giving a mixture of polycyclic hydrocarbons.[240] However, in the case of 2-trimethylsilyl-1-chlorocyclopropene, which is obtained by the treatment of trihalo-substituted cyclopropane **205** by methyllithium, a regioselectivity that is unique for ene dimerization of cyclopropenes is observed. The subsequent reduction of 3-cyclopropylcyclopropene selectively results in substituted bicyclopropane **206** in high yield.[241]



206 (92%)

The reaction of [2 + 2]-cycloaddition has been used for the preparation of tricyclic compound **207** from 3,3-disubstituted cyclopropene in the presence of palladium complex.[242]

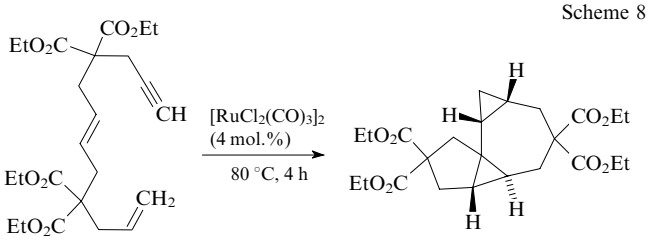


207 (74%)

dba is dibenzylideneacetone

1,6-Enynes usually rearrenge under the action of $[RuCl_2(CO)_3]_2$, but if a terminal double bond is present in the molecule (as, for example, in compound **208**), then the carbenoid intermediate gives the product of cyclopropanation **209**. This reaction also may be catalyzed by complexes of platinum, rhodium, iridium and rhenium (Scheme 8).[243]

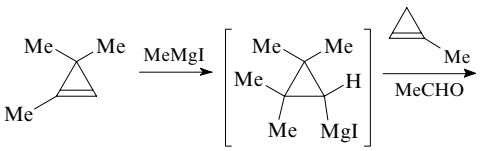
Scheme 8



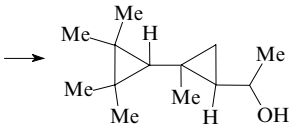
208 **209** (84%)

Catalyst	Reaction time	Yield of **209** (%)
$PtCl_2$	4 h	75
$Rh_2(O_2CCF_3)_4$	1 h	72
$[IrCl(CO)_3]_n$	4 days	54
$ReCl(CO)_5$	24 h	74

Carbometallation of cyclopropenes is a promising process, but it is still little studied as an approach to the synthesis of bicyclopropanes. Thus, a cyclopropyl magnesium derivative **210** has been obtained by the reaction of MeMgI with 1,3,3-trimethylcyclopropene and then has been used for carbomagnesation of 1-methylcyclopropene. The subsequent treatment of the reaction mixture by acetaldehyde has resulted in bicyclopropane **211** in 30% yield.[244]



210



211 (30%)

* * *

Analysis of publications on the development of methods of synthesis of bicyclo[1.1.0]butanes, spiropentanes and bicyclopropanes demonstrates that substantial advances in this field of chemistry began to appear in the 1950s – 1960s and peaked in the 1980s – 1990s. This coincides with the period of intensive progress in the carbene methods in synthetic organic chemistry. They have found the widest application in the synthesis of spiropentanes and a somewhat less extensive use in the preparation of bicyclopropanes and bicyclo[1.1.0]butanes. Such predominance of carbene methods in the synthesis of polycyclopropane compounds is caused by their efficiency. However, in spite of the diversity of the known methods of synthesis of polycyclopropanes, new techniques and their modifications appear every year, indicating the persisting interest of chemists in these unusual compounds.

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