Russian Chemical Reviews **62** (10) 935–950 (1993)
©1993 Russian Academy of Sciences and Turpion Ltd

UDC 547.548 + 547.592.2 + 541.254.9 + 595.1

Reactions of cyclopropene derivatives with electrophiles

V R Kartashov, E V Skorobogatova, N S Zefirov

Contents

I. Introduction 935
II. The influence of the nature of the reagent on the reactions of cyclopropene derivatives 935
III. The mechanisms of the interaction of cyclopropene derivatives with electrophiles 947

Abstract. A systematic account is given of data on the reactions of cyclopropene derivatives with acids, halogen- and sulfur-containing electrophiles, and mercury salts. The influence of the nature of the electrophile and of the structure of the cyclopropenes on processes with retention and opening of the ring, on the stereochemistry of the addition of reactants to the cyclopropene bond, and on the stereochemistry of the formation of the ring opening products is examined. The reaction mechanisms are discussed. The bibliography includes 120 references.

I. Introduction

Cyclopropene derivatives as highly strained systems[1–11] have aroused much scientific interest. For a long time, the study of the physicochemical properties and reactivities of cyclopropene derivatives was held back by the difficulty of their synthesis. However, since the appearance in the 1960s of new methods of synthesis which have made these compounds entirely available, such studies have developed vigorously. The chemical properties of cyclopropenes in the diene synthesis,[3,4,12–15] dipolar addition,[3,4,16–20] and cyclodimerisation[21–23] reactions as well as reactions with electrophiles have been investigated systematically. Cyclopropene derivatives have proved convenient substances for the synthesis of a wide variety of heterocyclic and polycyclic systems.[3,4,12–23] Numerous studies have been devoted to the molecular and orbital structures of cyclopropenes, the main results of which may be found in the relevant publications[1,2,7–9,24–26] and in the literature quoted therein.

A large number of studies have led to the need for a systematic arrangement of the literature data. However, there have been very few review publications[3,4,27,28] and none whatever exist for reactions of cyclopropenes with electrophiles.

The aim of the present review is to survey the experimental data on the reactions of cyclopropene derivatives with electrophiles. Some information about these reactions has been published in review articles[3,4,27] and where necessary it is considered in the context of the data discussed in the present communication.

Although in the description of the literature data the probable reaction mechanisms are also considered, we thought it desirable to describe in a separate section of the review, on the basis of the data presented, the most general mechanisms of these reactions and also to consider in greater detail the publications devoted specifically to these problems. The review reflects the state of the problem at the end of 1992.

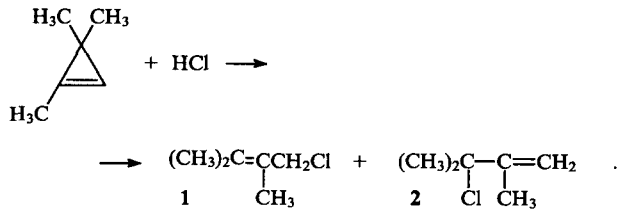
V R Kartashov, E V Skorobogatova Department of Physical and Colloid Chemistry at the Nizhny Novgorod State Technical University, ul. Minina 24, 603600 Nizhny Novgorod, Russian Federation.
Fax (7-831) 236 93 57
N S Zefirov Department of Organic Chemistry, Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow.
Fax (7-095) 939 01 26

Received 25 June 1993
Uspekhi Khimii **62** (10) 991 – 1006 (1993); translated by A K Grzybowski

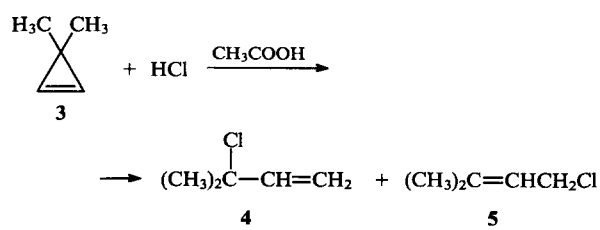
II. The influence of the nature of the reagent on the reactions of cyclopropene derivatives

1. Reactions of cyclopropenes with protic and Lewis acids

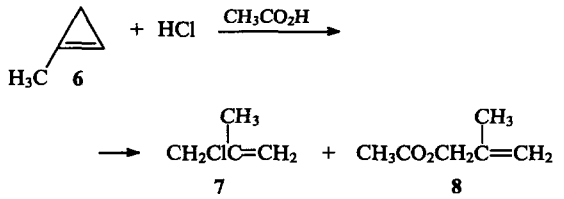
The reactions of propenes with protic acids usually lead to ring opening products. Thus the reaction of 1,3,3-trimethylcyclopropene with dry hydrogen chloride at –50 °C leads to the formation of 1-chloro-2,3-dimethylbut-2-ene **1** and 3-chloro-2,3-dimethylbut-1-ene **2** with compound **1** predominating.[3]



The reaction of 3,3-dimethylcyclopropene **3** with hydrogen chloride in acetic acid takes place similarly to the preceding reaction and involves the formation of 3-chloro-3-methylbut-1-ene **4** and 4-chloro-2-methylbut-2-ene **5**, the product ratio **4**:**5** varying during the course of reaction and amounting to 42 : 58 on extrapolation to zero time.[29]

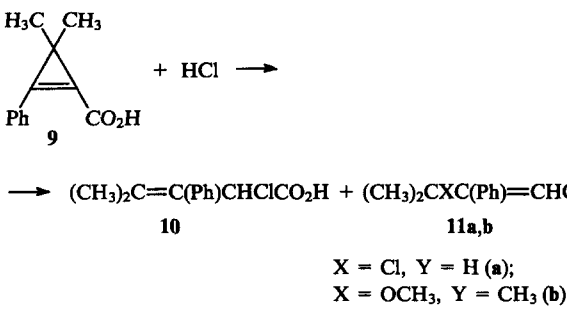


Under the same conditions, the interaction of 1-methylcyclopropene **6** with hydrogen chloride leads to a mixture of methylallyl chloride **7** and methylallyl acetate **8**.[29]



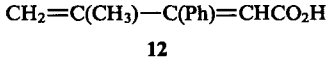
The formation of compound **8** with participation of the solvent indicates the cationoid nature of the intermediate, while the presence of the isomeric products of types **4** and **5** is evidence for its allylic structure.[29]

The reactions involving cyclopropene derivatives containing an electron-accepting substituent at the double bond, which hinders the formation of an allylic intermediate, proceed with formation of a cationoid intermediate. Thus 3,3-dimethyl-2-phenylcyclopropene-1-carboxylic acid **9** is converted into 2-chloro-4-methyl-3-phenylpent-3-enoic acid **10** and 4-chloro-4-methyl-3-phenylpent-2-enoic acid **11a** on treatment with hydrogen chloride.[30]

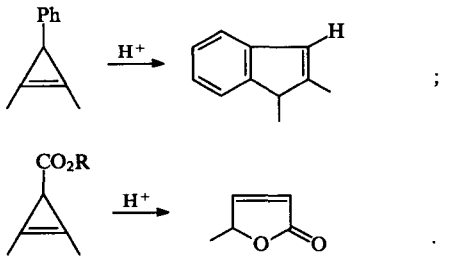


At 40–80 °C, compound **10** is formed preferentially (**10**:**11a** = 4:1, overall yield 60%), whilst at 20 °C the main product is compound **11a** (**10**:**11a** = 3:7).[30] The reaction of hydrogen chloride with the cyclopropene derivative **9** in methanol affords methyl 4-methoxy-4-methyl-3-phenylpropene-2-carboxylate **11b**.[31]

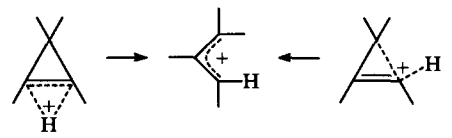
On treatment with toluene-4-sulfonic acid in boiling toluene, compound **9** is converted into 4-methyl-3-phenylpenta-2,4-dienoic acid **12**.[30]



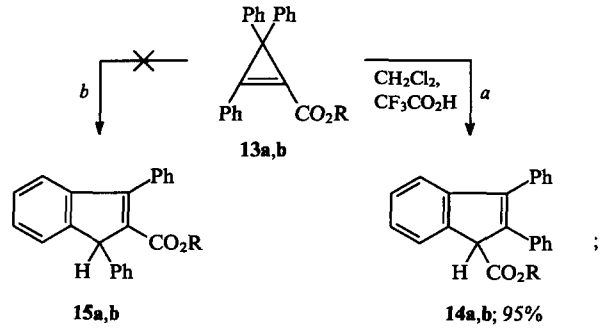
In the presence of a nucleophilic substituent at the methylene fragment of the cyclopropene derivative, treatment with acid leads to the isomerisation of the substrate.[3,27]



It has been suggested that this is a result of the protonation of the double bond or electrophilic attack on the C–C bond.[3,27]

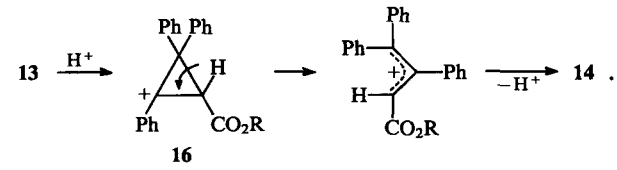


The occurrence of the reaction via the first mechanism is apparently more likely. This is indicated, for example, by the isomerisation of the esters of 2,3,3-triphenylcyclopropene-1-carboxylic acid **13**, which results in the exclusive formation of the indenes **14**.[32,33]

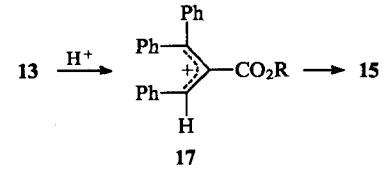


R = CH_3 (**a**), C_2H_5 (**b**).

The authors propose the following mechanism for the formation of the indenes **14**:



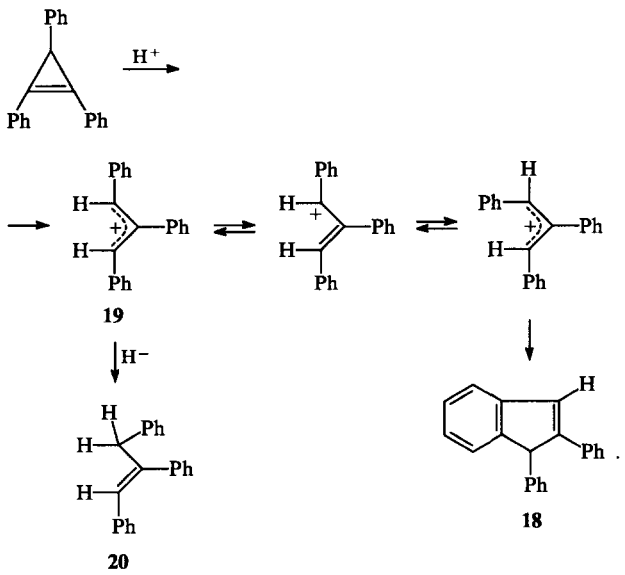
In the alternative version, one should expect the formation of the intermediate **17** and hence of the indenes **15**.



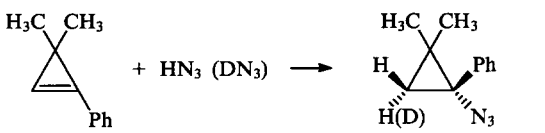
The question of the involvement in the reaction of the cyclopropyl type intermediate **16** is extremely controversial.[3] It is more probable that the allylic intermediate is formed directly as a result of the interaction of the electrophilic hydrogen with the double bond. This mechanism will be analysed in detail in the subsequent sections.

Kudryavtseva and Nesmeyanova[34] attempted to obtain data confirming the formation of the allylic intermediate in the reactions of cyclopropene derivatives with protic acids. For this purpose, a study was made of the isomerisation of 1,2,3-triphenylcyclopropene catalysed by trifluoroacetic acid in methylene chloride using triethylsilane as the donor of a hydride ion. Under the usual conditions, 1,2,3-triphenylcyclopropene is converted on

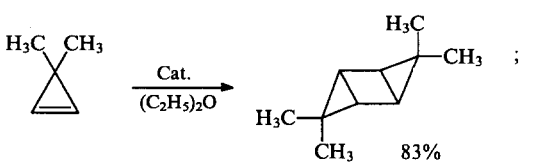
treatment with acid into 1,2-diphenylindene **18**. On the other hand, in the presence of triethylsilane, *cis*-1,2,3-triphenylpropene **20** is formed in a quantitative yield, which indicates the involvement of the allylic intermediate **19** in the reaction.



In the light of the data described above, the results of the reaction of 3,3-dimethyl-1-phenylcyclopropene with hydrazoic acid and deuterium azide were unexpected. Only adducts having the *cis*-configuration are formed in 60% and 38% yields respectively.[35]

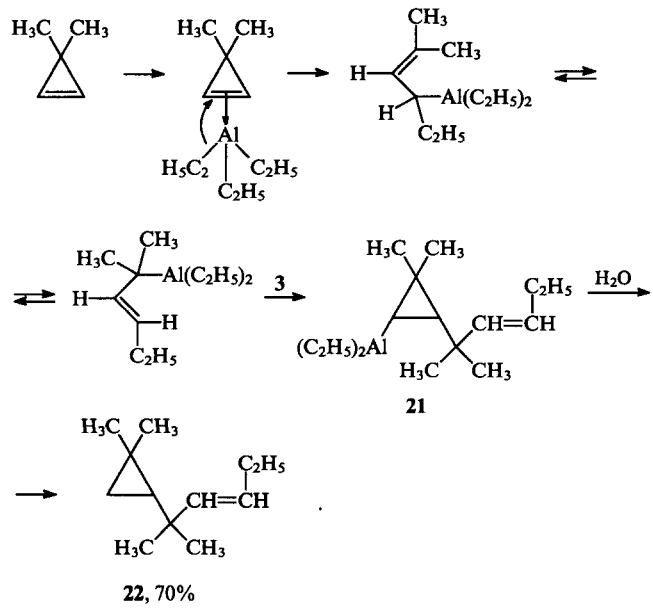


Extensive studies have been carried out on the reactions of cyclopropenes on treatment with Lewis acids. A characteristic feature of these processes is the wide variety of products and modes of reaction, which are determined mainly by the nature of the Lewis acid. For example, the cyclodimerisation of 3,3-dimethylcyclopropene[36] takes place smoothly on treatment with a number of Lewis acids and leads to the formation of *trans*-3,3,6,6-tetramethyltricyclo[3.1.0.0^{2,4}]hexane.



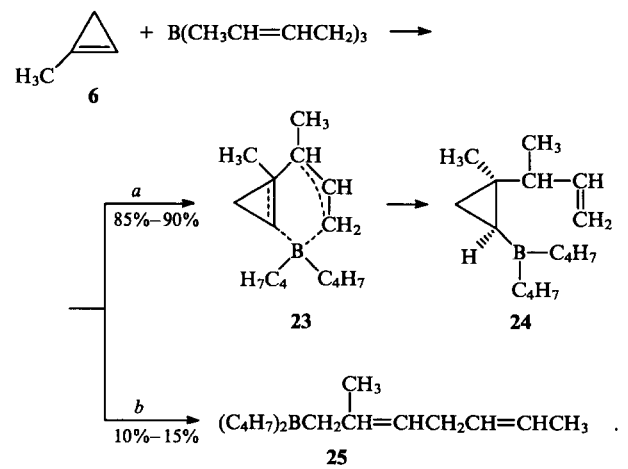
Cat. — $BF_3O(C_2H_5)_2$, $AlCl_3O(C_2H_5)_2$, $B(C_2H_5)_3$, $Al(C_2H_5)_3O(C_2H_5)_2$.

If the triethylaluminium dimer is used as the catalyst, then the process takes place differently and involves the formation of the product **21**, which affords *trans*-2-methyl-2-(2′,2′-dimethylcyclopropyl)hex-3-ene **22** after hydrolysis.

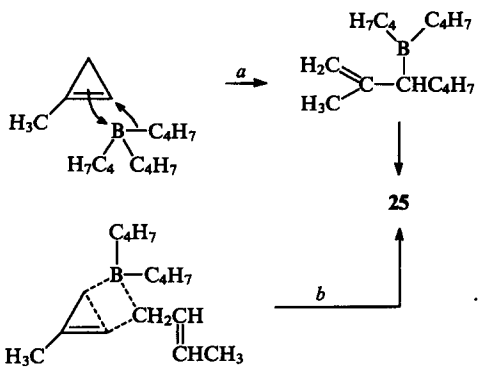


22, 70%

1-Methylcyclopropene **6** cyclodimerises in the reaction with boron trifluoride diethyl etherate,[36] but, when it is treated with triethylborane,[37] triallylborane,[38] and tricrotylborane,[39] the reagent adds to the cyclopropene with retention or opening of the ring. Thus, in the last case the products are *cis*-2-(but-3-en-2-yl)di(but-2-enyl)(2-methyl-1-cyclopropyl)borane **24** and di(but-2-enyl)(2-methylhepta-2,5-dien-1-yl)borane **25**.

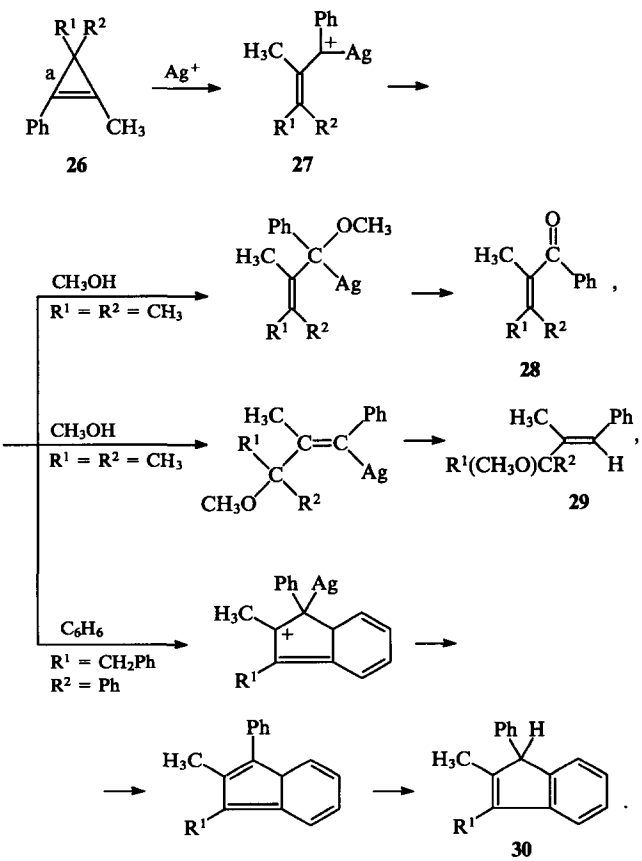


According to Bubnov et al.,[39] the formation of compound **24** shows that the addition of allylboranes to the double bond in cyclopropene derivatives is accompanied by the allyl rearrangement, apparently via the six-centred transition complex **23** with cyclic electron transfer. The formation of compound **25** can be represented by alternative schemes, according to which tricrotylborane attacks the double bond of the cyclopropene (pathway *a*) or the single C3–C2 σ-bond (pathway *b*). The latter scheme appears less likely according to the authors,[39] as the location of the boron atom at the trigonal rather than the tetragonal carbon atom in the transition state is energetically more favourable.

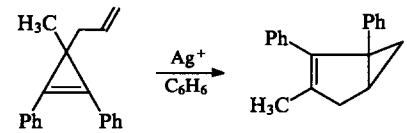


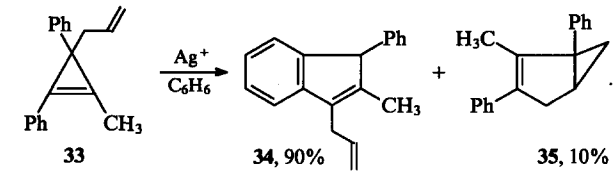
On treatment with silver perchlorate in benzene and methanol, the regio-selective opening of the ring compound **26** takes place with rupture of the single bond 'a'.[40] The structure of the product depends on the nature of the substituents. Thus 2,3,3-trimethyl-1-phenylcyclopropene **26** ($R^1 = R^2 = CH_3$) affords a mixture of 2,3-dimethyl-1-phenylbut-2-en-1-one **28** (65%) and 3-methoxy-2,3-dimethyl-1-phenylbut-1-ene **29** (45%). On the other hand, 3-benzyl-2-methyl-1,3-diphenylcyclopropene **26** ($R^1 = CH_2Ph$, R^2 = Ph) in benzene is converted into 3-benzyl-2-methyl-1-phenylindene **30** in a quantitative yield.

It is believed[40] that the silver ion, which is a strong Lewis acid, attacks the cyclopropene ring, forming the intermediate **27**, the stabilisation of which by the phenyl group determines the selectivity of the ring opening at the bond 'a'.

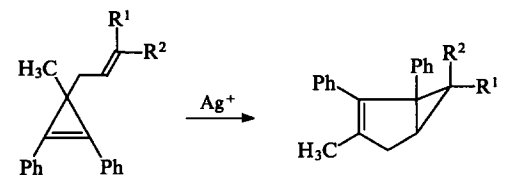


3-Allyl-3-methyl-1,2-diphenylcyclopropene **31** is converted into 3-methyl-1,2-diphenyl-bicyclo[3.1.0]hex-2-ene **32** in the presence of silver ions in benzene, while its analogue 3-allyl-2-methyl-1,3-diphenylcyclopropene **33** affords 3-allyl-2-methyl-1-phenylindene **34** and 2-methyl-1,3-diphenylbicyclo[3.1.0]hex-2-ene **35**.





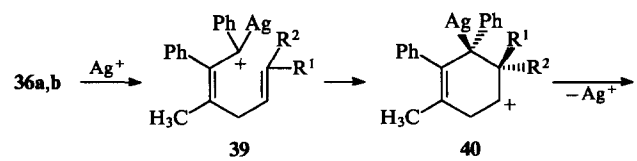
The isomerisation of (*E*)- and (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-but-2-enes **36a, b** takes place stereoselectively under these conditions with formation of *exo* and *endo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-enes **37** and **38** respectively.[40]



$R^1 = CH_3$; R^2 = H (**a**)
R^1 = H; $R^2 = CH_3$ (**b**)

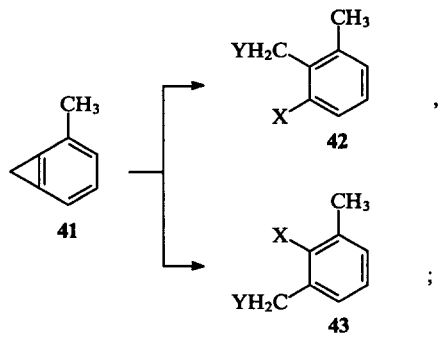
37: $R^1 = CH_3$; R^2 = H; 96%
38: R^1 = H; $R^2 = CH_3$; 97%

The authors[40] explain the stereoselectivity of the latter reaction within the framework of the mechanism of the formation of the argentocarbonium ion **39** and the subsequent interaction of the terminal double bond with the carbonium ion centre. The intermediate **40** formed under these conditions is converted into the products **37** and **38** after the elimination of silver.



The way in which the cyclopropene ring is opened in the reactions of methylbenzocyclopropenes depends on the nature of the electrophiles.[41] On reaction with silver nitrate in ethanol or

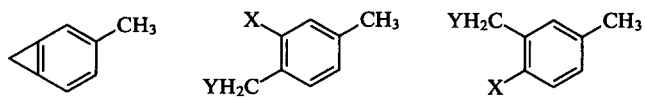
aniline, 2-methylbenzocyclopropene **41** affords compounds **42e, f** as the main products, whereas the reactions with bromine, iodine, and hydrogen chloride give rise to compounds **43a, c, d** as the main products. The overall yield of the products **42** and **43** in these reactions ranges from 54% to 70%.



41 **42** **43**

X = Y = Br (**a**); X = Br, Y = H (**b**); X = Y = I (**c**);
X = H, Y = Cl (**d**); X = H, Y = OC_2H_5 (**e**); X = H, Y = NHPh (**f**)

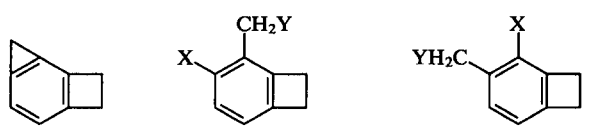
Similarly 3-methylbenzocyclopropene **44** reacts with silver nitrate to form mainly the *p*-xylenes **45**, while the reactions with the halogens and hydrogen chloride afford compounds **46**.



44 **45** **46**

X = H, Y = OC_2H_5, NHPh

Cyclopropa-3,4-benzocyclobutene **47** also affords various products on reaction with silver nitrate and the halogens, but in this case the reaction with hydrogen chloride leads to the same type of compound **49** as the reaction with silver nitrate.



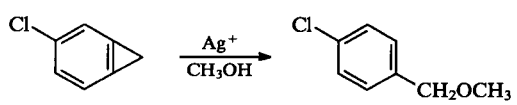
47 **48** **49**

X = Y = I (**a**)
X = Y = Br (**b**)
X = Y = H (**c**)

X = Y = I (**a**)
X = H, Y = Cl (**b**)
X = H, Y = OC_2H_5 (**c**)
X = Y = H (**d**)

The different behaviour of compounds **41**, **44**, and **47** in relation to two types of electrophiles has been explained[41] as due to the attack by silver ions (and the proton in the case of the reaction of compound **47**) on the σ-electrons of the cyclopropene ring, while other electrophiles attack the π-system of the benzene ring.

In the silver ion-catalysed reaction of 3-chlorobenzocyclopropene **50** with methanol, only one product is formed.[42]

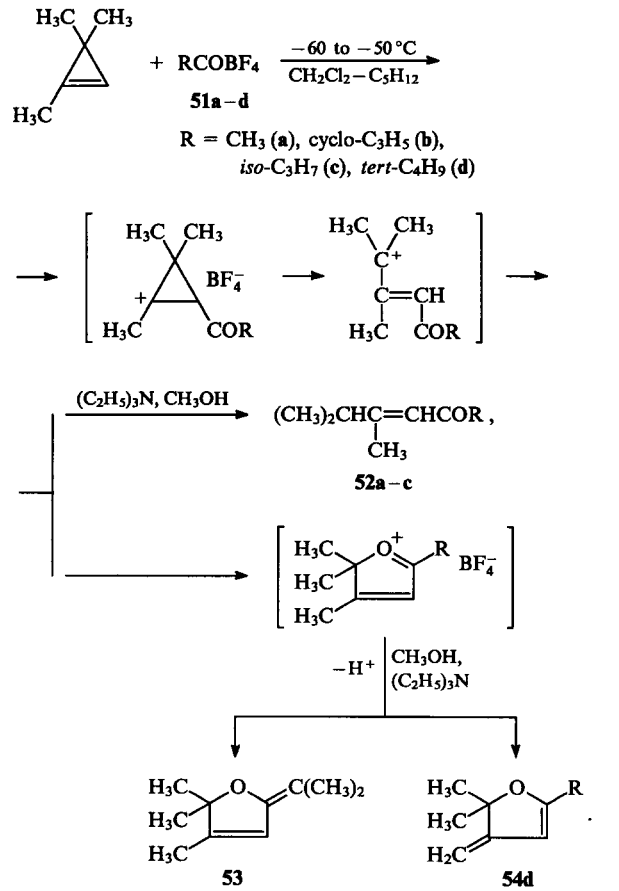


50

A reaction with ring opening is characteristic also of other electrophiles.

The acyl tetrafluoroborates **51a–d** react with 1,3,3-trimethylcyclopropene to form the acyclic ketones **52a–c** and the products **53** and **54** (Scheme 1).[43]

Scheme 1



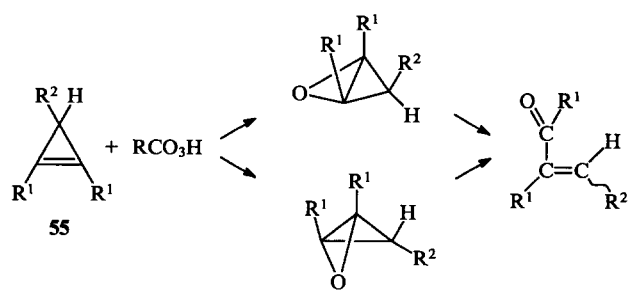
51a–d

R = CH_3 (**a**), cyclo-C_3H_5 (**b**), *iso*-C_3H_7 (**c**), *tert*-C_4H_9 (**d**)

52a–c

53 **54d**

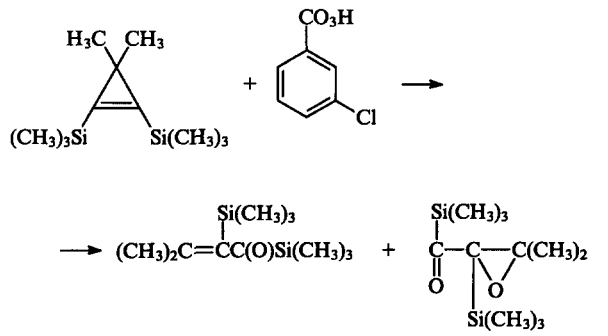
The opening of the cyclopropene ring has also been observed in the epoxidation reactions.[44–47] On treatment with peracids, compounds **55** are converted into acyclic ketones.[47]



55

R^1 = R^2 = Ph (Ref. 44); R^1 = Ph, R^2 = CH_2OH, CH_2OCH_3 (Ref.45);
R^1 = CH_2CH_3, R^2 = $CO_2C_2H_5$, CH_2OH (Ref. 46).

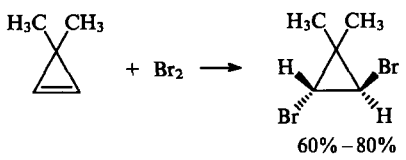
3,3-Dimethyl-1,2-bis(trimethylsilyl)-cyclopropene undergoes a similar reaction on treatment with *m*-chloroperbenzoic acid (reactant ratio 1 : 1, overall yield 65%).[47]



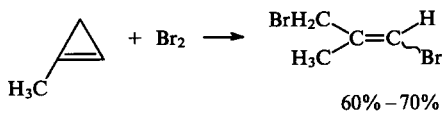
2. Reactions with the halogens and halogen-containing reagents

Cyclopropene combines with bromine and iodine in carbon tetrachloride with retention of the ring.[48] On bromination, a *trans*-adduct with a small admixture of the *cis*-isomer is formed in 57% yield.

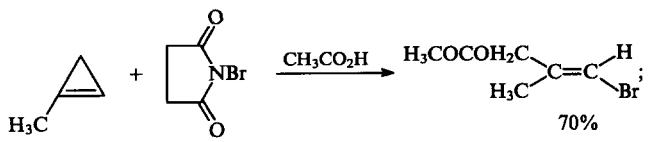
The bromination of 3,3-dimethylcyclopropene **3** in methylene chloride (−50 °C),[49] carbon tetrachloride, acetonitrile, and nitromethane[50] leads to *trans*-1,2-dibromo-3,3-dimethylcyclopropane.

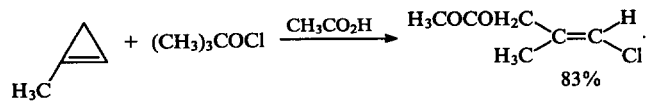


On passing from compound **3** to 1-methylcyclopropene **6**, the mode of addition changes. In this case, the reaction with bromine in carbon tetrachloride,[50] chloroform,[51] or methylene chloride[52] results in the formation of 1,3-dibromo-2-methyl-1-propenes as a mixture of the (*Z*) and (*E*)-isomers (*E* : *Z* = 1 : 2 in CCl_4 and 3 : 1 in $CHCl_3$ and CH_2Cl_2).

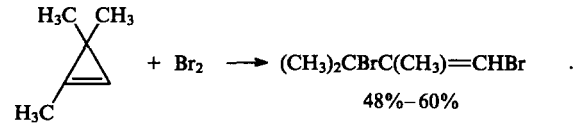


Complete ring opening is observed also in the reactions of 1-methylcyclopropene with *N*-bromosuccinimide (NBS)[51,52] and *tert*-butyl hypochlorite[52] in acetic acid, which results in the formation of the corresponding haloacetates with the (*E*)-configuration.

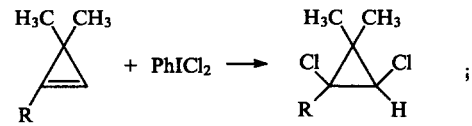




1,3,3-Trimethylcyclopropene reacts similarly with bromine (CCl_4, CH_2Cl_2, C_5H_{12}, T = 30 to −110 °C).[53]



In the reaction with chlorine under the same conditions, it affords a complex and a virtually unidentified mixture of acyclic products,[53] whereas treatment with dichlorophenyliodine resulted in the formation of 1,2-dichloro-1,3,3-trimethylcyclopropane **56a** in 50% − 70% yield. The reaction with 3,3-dimethylcyclopropene also takes place similarly (the yield of compound **56b** is 50%).

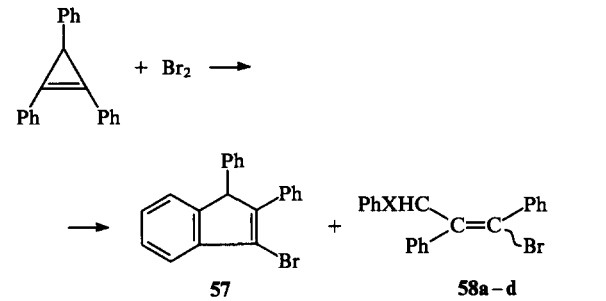


R = CH_3 (**a**), H (**b**). **56a,b**

It has been suggested[53] that the reaction of dichlorophenyliodine takes place in one stage, possibly via a concerted mechanism, whereas chlorination with free chlorine results in the formation of cationoid or radical intermediates.

The data presented show that the presence of a methyl substituent at the double bond of cyclopropene intensifies the tendency towards the formation of products with ring opening.

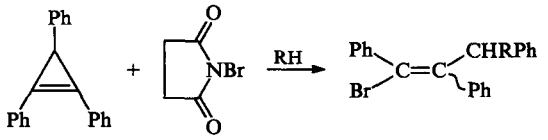
On interaction of 1,2,3-triphenylcyclopropene with bromine in acetic acid or nitromethane, virtually one product of intramolecular alkylation is formed — 3-bromo-1,2-diphenylindene **57**, whereas the reaction in methanol and aqueous acetic acid led to the isolation, together with compound **57**, of the acyclic solvatoadducts **58a − c** and that in acetonitrile led to the dibromo-derivative **58d**.[54]



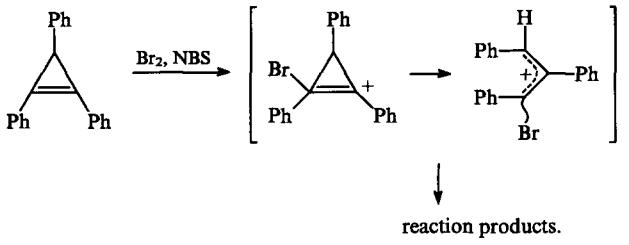
X = OCH_3 (**a**), $OCOCH_3$ (**b**), OH (**c**), Br (**d**).

Solvent	Yield of products (%)				
	57	**58a**	**58b**	**58c**	**58d**
CH_3OH	30	45	–	–	25
80% CH_3CO_2H	30	–	40	30	–
CH_3CO_2H	100	–	–	–	–
CH_3CN	90	–	–	–	10
CH_3NO_2	100	–	–	–	–

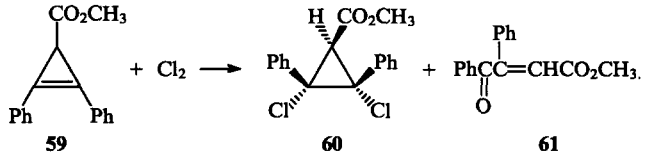
Bromination of 1,2,3-triphenylcyclopropene with *N*-bromosuccinimide in polar solvents affords a mixture of acyclic stereoisomeric products with the (*E*)-isomer predominating.[55]



The authors[54,55] proposed the following mechanism for the above reactions of triphenylcyclopropene with bromine and NBS. As will be shown below, this mechanism is consistent with the nonstereoselectivity of the process:



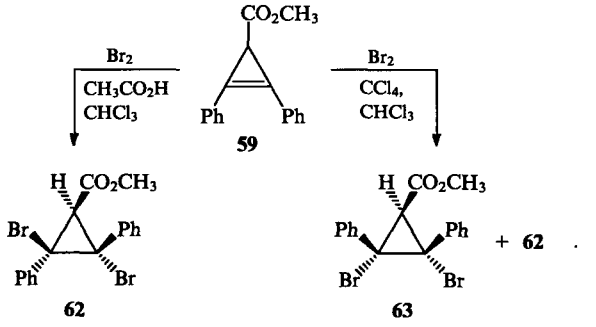
The tendency towards ring opening decreases sharply after the introduction of a carboxylate substituent into the cyclopropene ring. Thus the main pathway in the reaction of chlorine with methyl 2,3-diphenylcyclopropene-2-carboxylate **59** is its addition, which takes place stereoselectively in the *cis*-position regardless of the conditions (acetic acid or carbon tetrachloride in scattered light and under irradiation) with formation of methyl 2,3-dichloro-*cis*-*cis*-2,3-diphenylcyclopropanecarboxylate **60**.[56] Methyl 3,4-diphenylbut-2-en-4-oate **61** is formed at the same time, but the mechanism of its formation was not established.[56]



Reaction conditions	Yield of **60** (%)	Yield of **61** (%)
CCl_4, dispersed light, 0 °C	41	22
CH_3CO_2H, −12 to 13 °C	35	25
CCl_4, light irradiation (500 W electric lamp)	71	8

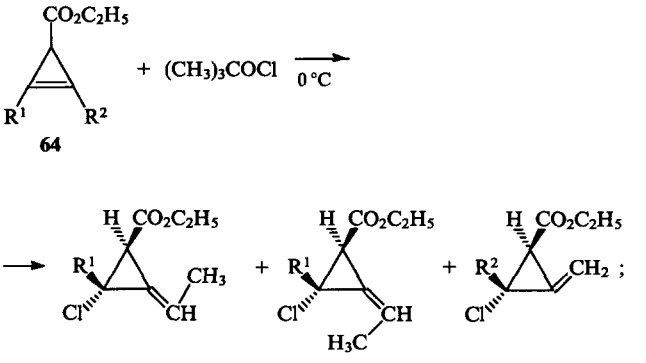
The following features are noteworthy: (a) the addition reaction proceeds not only stereoselectively but also regioselectively—the attack on the double bond takes place from the sterically less hindered side in the *anti*-position relative to the carboxylate group; (b) in acetic acid, where an electrophilic mechanism is most probable, the contribution of the pathway with retention of the ring diminishes compared with the reactions which probably proceed via a radical mechanism (CCl_4, irradiation). According to Grigorova and Komendantov,[56] this may be evidence for the greater stability of the intermediate cyclopropyl radical compared with the cationic species of the cyclopropyl type.

The stereochemistry of the bromination of the ester **59** depends on the reaction conditions.[57] In chloroform or acetic acid in the dark or in the light, bromine adds in accordance with a *trans*-mechanism to form methyl *cis*, *trans*-2,3-dibromo-2,3-diphenylcyclopropanecarboxylate **62** in 30%–39% yield. The rest of the mixture was not identified. On irradiation with light in carbon tetrachloride, bromine adds to the ester **59** mainly with formation of methyl 2,3-dibromo-*cis*,*cis*-2,3-diphenylcyclopropanecarboxylate **63**. The *trans*-adduct **62** is obtained under these conditions in insignificant amounts (5%). As in chlorination, the double bond is attacked from the sterically less hindered side.

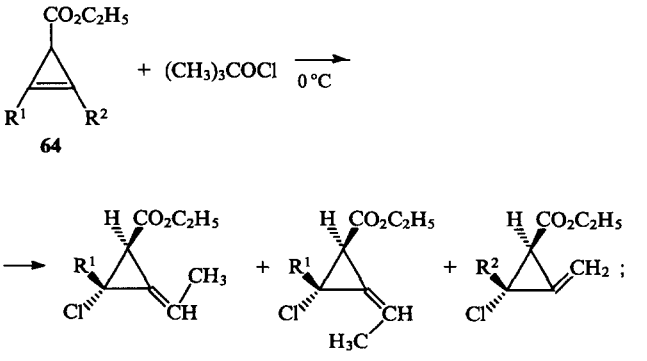


The halogenation of the esters of cyclopropene-2-carboxylic acid **64** by *tert*-butyl hypochlorite leads to isomerisation and the formation of a mixture of the products of the *cis*- and *trans*-addition of chlorine.[58,59]

At temperatures below 0 °C, the first pathway predominates (overall yield 50%), whereas at 60 °C the yield of the adducts increases (overall yield 85%).



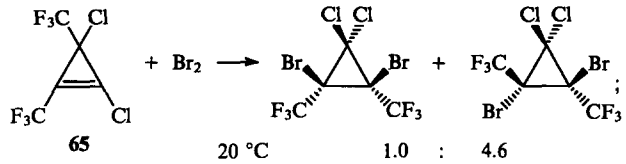
$R^1 = CH_3, C_2H_5$; $R^2 = C_2H_5$.



$R^1 = CH_3, C_2H_5$; $R^2 = C_2H_5$.

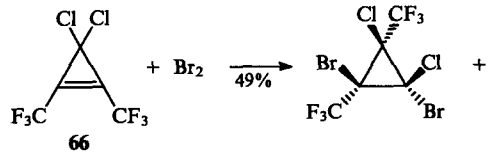
Choubani and coworkers[58,59] considered these results from the standpoint of a radical mechanism. There is no doubt that the cyclopropene derivatives **65** and **66** are brominated in the gas phase via a radical mechanism,[60] which results in the formation of

a mixture of *cis*- and *trans*-adducts. For compound **66**, the ratios of the reaction products are 4.0 : 2.2 : 1.1 : 1.0 with an overall yield of 49%.

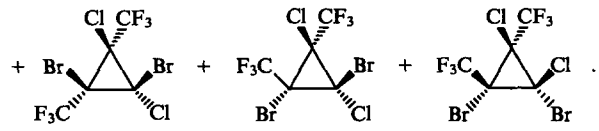


65

20 °C 1.0 : 4.6
70 °C 1.0 : 3.0

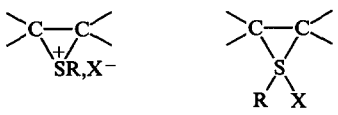


66



3. Reactions with sulfur-containing electrophiles

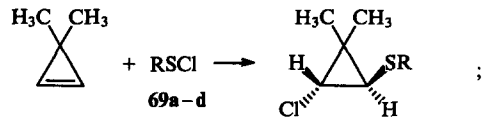
The reaction of sulfenyl halides with alkenes is one of the most thoroughly investigated reactions of the Ad_E type. It is characterised by a high *trans*-selectivity of the addition with a low tendency towards molecular rearrangement under the usual conditions. When the reaction is carried out in nucleophilic solvents, the products of the addition of the reagent are obtained as a rule as a mixture of regioisomers. The formation of mixed adducts with participation of the solvents, which is characteristic of the vast majority of electrophiles, is not observed in this case.[61-65] Salt additives exert an effective influence on this reaction (the phenomenon of the doping effect).[66-72] Under the conditions of the doping effect, there is a possibility of a series of unusual pathways in the reaction, which greatly extends its synthetic potential.[72] It has now been established that the above features are due to the formation in the sulfenyl halogenation of alkenes of a cyclic intermediate, the cationoid component of which is the highly symmetrical and relatively stable episulfonium ion **67**, which reacts selectively with the counterion. In weakly polar media, one cannot rule out the possibility of the formation of the species **68**, having the sulfurane structure, as intermediates.



67 **68**

A salt-like compound of type **67** was isolated in a stable form and its structure was determined by X-ray diffraction.[73] It is of interest to discover the extent to which the above rules hold for unusual systems such as cyclopropene derivatives.

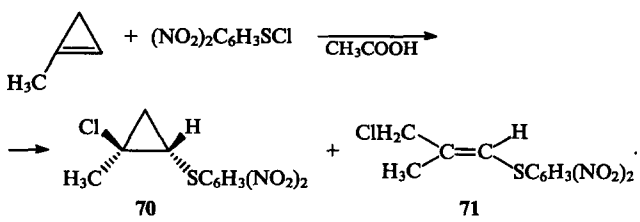
It has been established[74-76] that 3,3-dimethylcyclopropene reacts with benzene- and 2,4-dinitrobenzene-sulfenyl chlorides in acetic acid[74] and with sulfenyl halides **69a-d** in other solvents [$(C_2H_5)_2O$, CCl_4, $CHCl_3$],[75,76] forming *trans*-1-aryl(alkyl)thio-2-chloro-3,3-dimethylcyclopropanes in high yields (80% - 90%).



69a-d

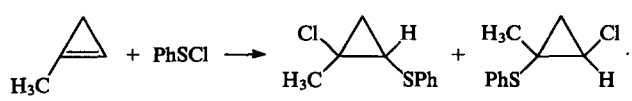
R = CH_3 (**a**), C_2H_5 (**b**), C_6H_5 (**c**), 2,4-$(NO_2)_2C_6H_3$ (**d**).

The same stereochemistry of the addition reaction has been observed in the reaction of 1-methylcyclopropene with 2,4-dinitrobenzenesulfenyl chloride. The structure of *trans*-1-chloro-2-(2′,4′-dinitrophenyl) thio-1-methylcyclopropane **70** was determined by X-ray diffraction.[52] It is noteworthy that the addition of the reagent takes place in accordance with the Markovnikov rule (overall yield 90%).[52]

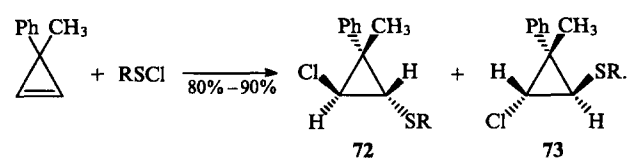


70 **71**

In contrast to this reaction, the addition of benzenesulfenyl chloride leads to a mixture of regioisomers in proportions which depend on the nature of the solvent.[29]



The reaction of 3-methyl-3-phenylcyclopropene with sulfenyl halides results in the formation of a mixture of isomers,[75,76] each of which was obtained from the *trans*-addition of the reagent.

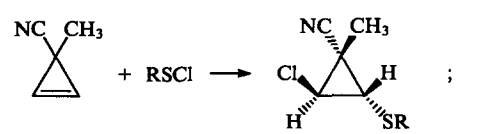


72 **73**

R	Solvent	72 : 73 Ratio
CH_3	$(C_2H_5)_2O$	1.0 : 1.5
	CH_3CN	2.5 : 1.0
C_2H_5	$(C_2H_5)_2O$	1.0 : 1.8
	CH_3CN	1.7 : 1.0
Ph	CCl_4	1.0 : 2.0
	CH_3CN	3.0 : 1.0

The product ratio depends on the polarity of the solvent: in weakly polar solvents (ether, CCl_4), the isomers **73** predominate, whereas in the appreciably more polar acetonitrile mainly the isomers **72** are formed.

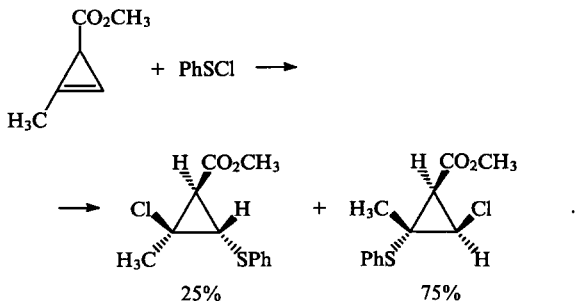
The data presented show that the general principle of *trans*-addition of the reagent holds in the sulfenyl halogenation of cyclopropenes. This postulate remains valid also for the substrates where there is a strongly electronegative group in the methylene unit. Thus 3-cyano-3-methylcyclopropene reacts smoothly with methane- and benzene-sulfenyl chlorides, forming *trans*-adducts, the nitrile and sulfide groups being in the *syn*-positions.[75,76]



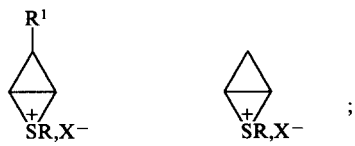
R = CH_3 (93%), Ph (94%).

The authors explain this mode of addition[75,76] by the attractive interaction in the transition state between the electrophile and the cyano-group.

The occurrence of *trans*-addition has also been established in the reaction of methyl 1-methylcyclopropene-3-carboxylate with benzenesulfenyl chloride, which results in the formation of a mixture of regioisomers in an overall yield of 85%–90%.[77] It is interesting to note that in this case the electrophile attacks the double bond from the *anti*-side relative to the ester group, in contrast to the preceding reaction.



The results demonstrate that, for the sulfenyl halogenation of cyclopropenes, the *trans*-addition principle is just as fundamental as for the unstrained systems. The introduction of highly negative groups undoubtedly renders the intermediate **74** less stable compared with its unsubstituted analogue **75**, but the sulfenyl halogenation of cyclopropenes, even when the latter contain electronegative substituents, is nevertheless exclusively *trans*-stereoselective.



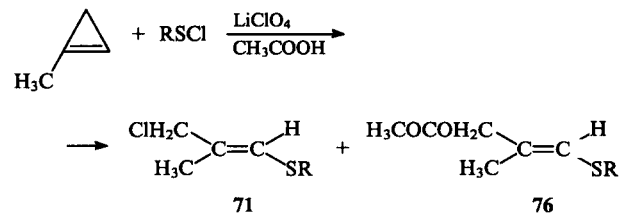
74 **75**

R^1 = electronegative group.

As can be seen from the data presented, the dominant pathway in the reaction of benzene- and alkane-sulfenyl halides with cyclopropenes involves the formation of cyclic adducts. However, the specific properties of the substrate can be manifested in this reaction too.

The introduction of electronegative substituents into the reagent and the presence of an electron-donating group at the cyclopropene double bond promote the occurrence of a reaction with ring opening. Thus the ring opening product (*E*)-3-chloro-1-(2,4-dinitrophenyl)thio-2-methyl-1-propene **71** is formed together with the cyclic adduct in the reaction of 1-methylcyclopropene with 2,4-dinitrobenzenesulfenyl chloride.[52] The amount of the acyclic compound **71** increases with increasing polarity of the medium and in solvents such as nitromethane and acetonitrile its yield reaches 50%. The (*E*)-configuration of compound **71** was established on the basis of ^{13}C and ^1H NMR spectroscopic data.[52]

The reaction of sulfenyl halides with cyclopropenes proved to be extremely sensitive to the addition of lithium perchlorate. In solution in acetic acid, the yield of compound **71** does not exceed 13%. If the reaction is carried out in the presence of a fivefold excess of $LiClO_4$ relative to RSCl, it takes place entirely with ring opening, which results in the formation of compound **71** and the product of the reaction with participation of the solvent—(*E*)-3-(2,4-dinitrophenyl)thio-2-methyl-propene-2-acetate **76**.[69]



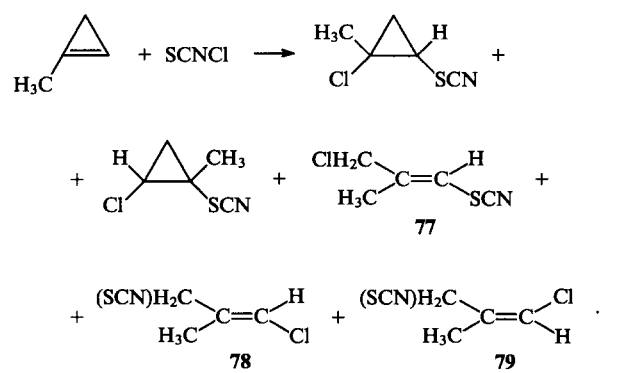
71 **76**

R = 2,4-$(NO_2)_2C_6H_3$.

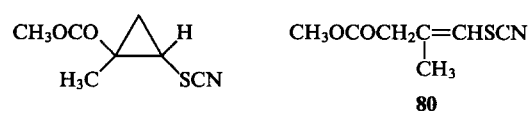
Thiocyanato-reagents interact with cyclopropenes in a more complex manner than sulfenyl halides, although both types of reagents have the same electrophilic centre. The main difference between these reactions consists in the fact that, in the substitution of thiocyanato-groups into cyclopropenes, the contribution of the pathway with ring opening is greater.

1-Methylcyclopropene reacts with thiocyanogen chloride in chloroform, affording up to 50% of acyclic products.[78,79]

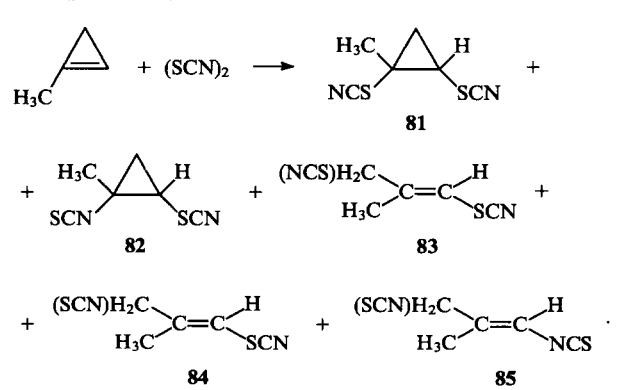
Chloro-2-methylpropen-1-yl thiocyanate **77** has the (*E*)-configuration, while 3-chloro-2-methylpropen-2-yl isothiocyanates **78** and **79** consist of a mixture of the isomers (*E*)-**78** and (*Z*)-**79** in proportions of 9 : 1.[79]



When the reaction is carried out in acetic acid, the products of solvo-addition are formed together with those indicated above:[79] 2-acetoxy-2-methyl-cyclopropyl thiocyanate and 3-acetoxy-2-methylpropen-1-yl thiocyanate **80** (overall yield 85%–90%).



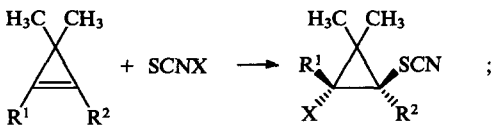
The reaction of 1-methylcyclopropene with thiocyanogen in chloroform and acetic acid results in the formation of the products **81**–**85** (yield 85%).[79,80]



The fraction of the acyclic products is in this case 42% – 43%. Ring opening takes place fully stereoselectively with formation of products having the (*E*)-configuration.[79]

It is striking that in the reactions indicated fundamentally different pathways leading to the synthesis of the acyclic products are observed. The formation of compounds **77** and **80**, (*E*)-2-methyl-1,3-dithiocyanato-1-propene **83**, and (*E*)-3-isothiocyanato-2-methylpropen-1-yl thiocyanate **84** is presumably induced by the electrophilic attack on the double bond in 1-methylcyclopropene by the sulfur atom, whereas compounds **78** and **79** are obtained in the reaction with thiocyanogen chloride as a result of the attack on this bond by the chlorine atom and (*E*)-1,3-diisothiocyanato-2-methyl-1-propene **85** is formed in the reaction with thiocyanogen as a result of the attack by the nitrogen atom on the double bond. One cannot rule out the possibility that thiocyanogen chloride and thiocyanogen exhibit the properties of an ambident electrophile in these reactions.[49,79]

As in the reactions with other electrophiles, substitution of the thiocyanato-group into 3,3-dimethylcyclopropene results in the formation of only the *trans*-adducts.[78]



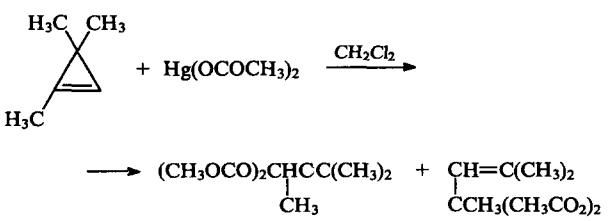
X = Cl, SCN;
$R^1 = R^2 = H$ (96%); $R^1 = H$, $R^2 = CH_3$ (81%);
$R^1 = R^2 = CH_3$ (100%); R^1 = Ph, $R^2 = CH_3$ (87%).

4. Reactions with mercury salts

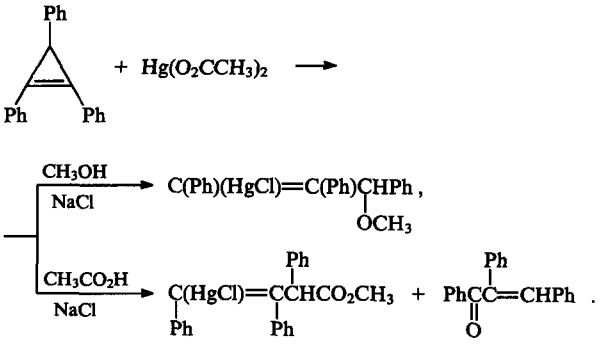
The reaction of mercury salts with cyclopropenes has aroused special interest for a long time. It follows from a large number of studies that a characteristic feature of the mercuration of unsaturated compounds, which distinguishes this reaction from others of the Ad_E type, is its high sensitivity to the structure of the substrate. Whereas mercury salts react with unstrained systems in accordance with the general *trans*-addition mechanism, the mercuration of strained unsaturated compounds, particularly those having a bridged structure, proceeds as a *cis*-process, frequently simultaneously with *trans*-addition.[81,82] Although the claim that the strain in the structure is the main cause of the 'anomalous' stereochemistry is not open to doubt, the specific mechanism of its influence on the *cis*-addition is very complex.[81,82] This is clearly manifested, for example, by the fact that in certain cases opposite stereochemical results are obtained for the same substrate depending on the reaction conditions.[81–85] However, it is noteworthy that quantum-chemical calculations have led to the conclusion that the *cis*-addition is determined not by the structural strain but by the unusual structure of the intermediate.[86]

Cyclopropene derivatives constitute a good model for testing the relationship between the process stereochemistry and the structure of the substrate because steric factors do not play a significant role in these systems, in contrast to bridged systems.

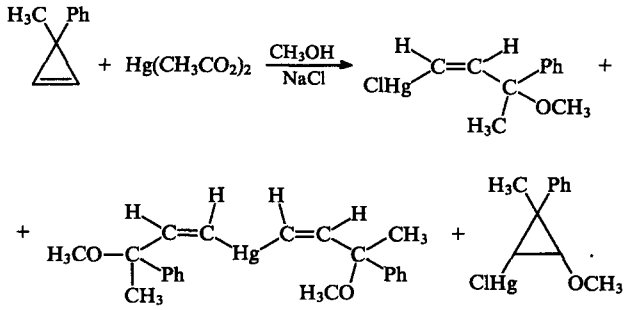
First attempts to elucidate the stereochemistry of the mercuration of cyclopropene derivatives were not successful, as mercury salts react with the simplest cyclopropenes to form acyclic compounds which do not contain mercury.[82,87,88] A characteristic example of reactions of this type is that between 1,3,3-trimethylcyclopropene and mercury acetate in methylene chloride.[87,88]



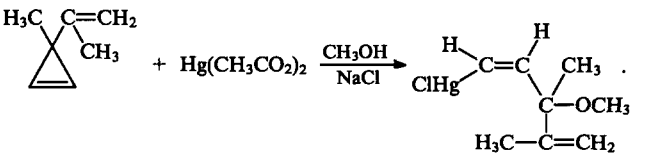
1,2,3-Triphenylcyclopropene interacts with mercury acetate in methanol and acetic acid with ring opening.[89]



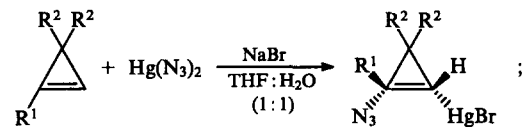
It has been shown in relation to the mercuration of 3-methyl-3-phenylcyclopropene that the acyclic products obtained in the reaction have the (*Z*)-configuration.[90]



A similar stereochemical result was obtained in the reaction with 3-isopropenyl-3-methylcyclopropene (yield of reaction product 10%).[90]



The results of the study of Galle and Hassner[35] constituted an important step in the investigation of the stereochemistry of the addition of mercury salts to cyclopropenes. It was established that mercury azide adds to a number of cyclopropenes with formation of *cis*-adducts.

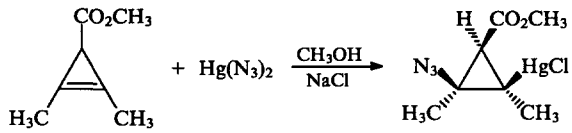


$R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_3$;
$R^1 = R^2 = CH_3$; R^1 = Ph, $R^2 = CH_3$.

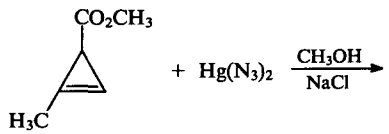
The esters of cyclopropene-2-carboxylic acids are a convenient model for the study of the stereochemistry of the mercuration of cyclopropenes as well as certain other aspects of this reaction. They react smoothly with mercury salts, affording products containing a three-membered ring, the nature of the reaction remaining unchanged on variation over a wide range of the electronic properties of the substituents at the double bond.

The azidomercuration of methyl 2,3-dimethylcyclopropene-2-carboxylate **86** and methyl 2-methylcyclopropene-2-carboxylate **87**, like that of cyclopropene hydrocarbons, proceeds in accordance with the *cis*-mechanism. In the reaction of

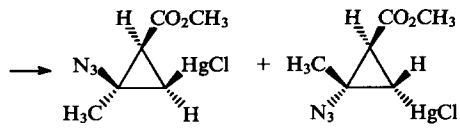
mercury azide with the ester **87**, a mixture of *cis*-2-azido-*cis*-3-chloromercurio-*trans*-2-methyl- and *trans*-2-azido-*trans*-3-chloromercurio-*cis*-2-methylcyclopropanecarboxylic acids was obtained after the exchange reaction with NaCl (**88**:**89** = 1:1).[91]



86 52%



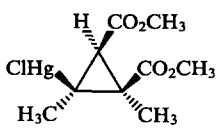
87



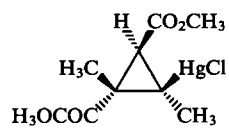
88 **89**

The use of mercury azide as the reagent made it possible to discover, in relation to monocyclic unsaturated compounds, a clear relationship between the strain in the substrate and the probability of the *cis*-addition. In contrast to the reactions with cyclopropenes, the azidomercuration of the less strained cyclobutene affords a mixture of the *cis*- and *trans*-azidomercurio-derivatives in proportions of 60:40,[92] while the reaction with cyclohexene results in the formation of only the *trans*-adduct.[85]

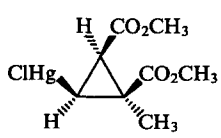
It follows from the data presented that mercury azide is a specific *cis*-azidomercurating agent for cyclopropene derivatives. The reactions with other mercury salts are nonstereoselective. The interaction of the esters **86** and **87** with mercury acetate in acetic acid results in the formation of mixtures of the methyl esters of *trans,trans*- and *trans,cis*-2,3-dimethyl-*cis*-3-chloromercurio-2-acetoxycyclopropanecarboxylic acids (compounds **90** and **91**) and the methyl esters of *trans*- and *cis*-2-methyl-*cis*-2-chloromercurio-2-acetoxycyclopropanecarboxylic acids (compounds **92** and **93**) in the proportions **90**:**91** = 31:46 and **92**:**93** = 4:1.[91]



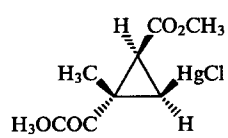
90



91

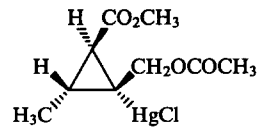


92



93

Furthermore, the methyl ester of *trans*-3-chloromercurio-*trans*-2-methyl-3-acetoxymethylcyclopropanecarboxylic acid **94** was isolated after the reaction with compound **87**. The mechanism of the formation of compound **94** has not been investigated (the overall yield of the products of the reactions indicated was 85%–90%).[91]

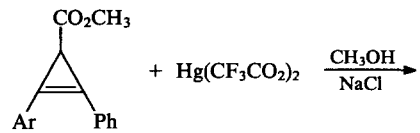


94

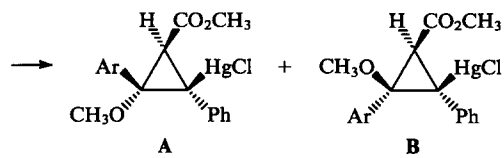
Although mercuration with mercury acetate takes place nonstereoselectively, nevertheless in this case too there is a tendency towards a decrease in the amount of *cis*-adducts with decrease in the substrate strain energy. For example, in the reaction of mercury acetate with cyclobutene in methanol, the amount of the *cis*-adduct does not exceed 7%, while in solution in acetic acid it is not formed at all.[92]

It follows from the data considered that the influence of strain on the degree of *cis*-addition of mercury salts depends radically on the nature of the reagent and the solvent. A convincing argument confirming this postulate is provided by the results of the mercuration of the methyl esters of 2-aryl-3-phenylcyclopropene-2-carboxylic acids. In this case, the influence of the reaction conditions on the process stereochemistry is so great that the strain factor is almost completely abolished.

Thus the interaction of the cyclopropenes **95a–c** with mercury trifluoroacetate in methanol affords a mixture of the *cis*- and *trans*-adducts.[93–96]



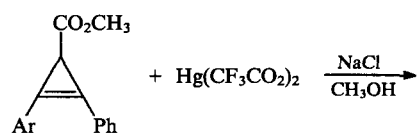
95a–c



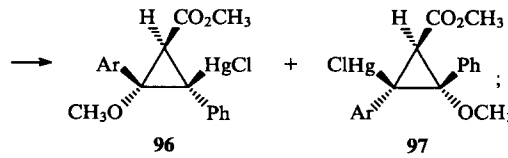
A **B**

Ar	Yield of A (%)	Yield of B (%)
4-$CH_3OC_6H_4$ (a)	42	16
4-$CH_3C_6H_4$ (b)	30	19
Ph (c)	54	4

The amount of the *trans*-adduct increases as the electron-donating properties of the aryl substituent in the substrate are weakened and the reaction of compound **95d** (Ar = 4-ClC_6H_4) proceeds mainly in accordance with the *trans*-mechanism with formation of two regioisomeric methyl esters of *cis*-2-chloromercurio-*trans*-3-methoxy-3-(4-chlorophenyl)-2-phenyl- and *cis*-2-chloromercurio-*trans*-3-methoxy-2-(4-chlorophenyl)-3-phenylcyclopropanecarboxylic acids (**96**:**97** = 33:67, overall yield 40%).[90]



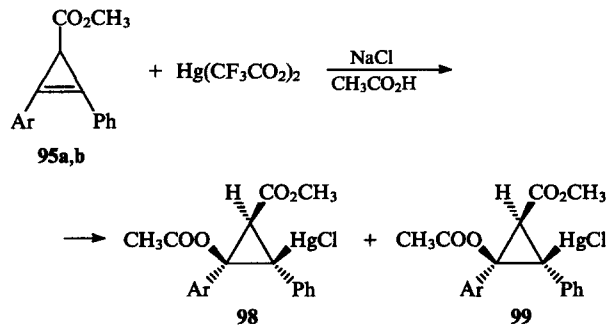
95d



96 **97**

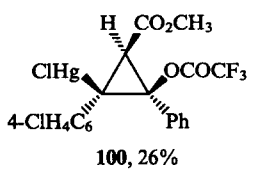
Ar = 4-ClC_6H_4.

The replacement of methanol by acetic acid makes the process *cis*-stereoselective[95-98] with formation of the adducts **98** and the solvatoadducts **99**.



Ar	Yield of **98** (%)	Yield of **99** (%)
4-$CH_3C_6H_4$ (**a**)	50	–
Ph (**b**)	30	8

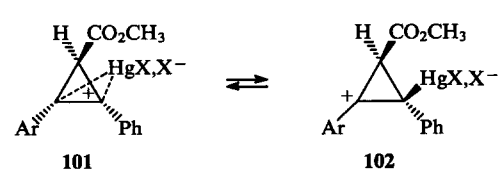
In the mercuration of compound **95d**, the change of solvent not only leads to the inversion of the stereochemistry of the process but also renders the reaction strictly regioselective with formation of methyl *cis*-2-chloromercurio-*cis*-3-trifluoroacetoxy-2-(4-chlorophenyl)-3-phenylcyclopropanecarboxylate **100**.[96]



100, 26%

As can be seen from the data presented above, in the mercuration of the esters of cyclopropene-2-carboxylic acids the carboxylate group exhibits a pronounced directing effect, as a consequence of which the substituent and the chloromercurio-group are in the *syn*-positions. The manifestation of the directing effect by functional groups in the mercuration of other unsaturated systems has been discussed.[99-102] Examination of the nature of the influence of the substituent on the course of solvatomercuration led to the conclusion that one of the causes of this phenomenon may be conformational effects.[102] Since these effects are absent for cyclopropene derivatives, the *syn*-regioselectivity indicates the interaction of the functional group and the mercury atom of the reagent.[103]

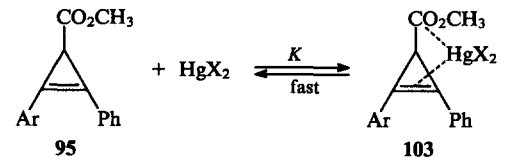
It is believed[96] that the reaction of the cyclopropene derivatives **95** with mercury trifluoroacetate in methanol leads to the formation of the mercurinium intermediate **101** (the *trans*-adduct), which is in equilibrium with the intermediate open-chain structure **102** (the *cis*-adduct).



In acetic acid, the reaction proceeds via a different mechanism. In this case, the close ion pair **102** is apparently formed as an intermediate species, which is converted into the reaction products as a result of the *cis*-addition of counterions from the solvent. The regioselectivity of the addition of the solvent to the ester **95d** is an argument in support of this hypothesis. Another no less important fact confirming the above hypothesis is that the solvatomercuration products **99** are formed as a result of the *cis*-addition of acetic acid from the sterically hindered side, i.e. the side from which the reagent attacks the double bond. This result is feasible if the solvent molecule completing the reaction is part of the solvation shell while the cation of the intermediate has an open-chain structure.

It was noted above that the regioselectivity of the mercuration of cyclopropenecarboxylic acid esters indicates the manifestation of the 'reagent–substrate' coordination. The occurrence of coordination of this type is indicated by the results of kinetic studies on the reactions of esters of cyclopropene-2-carboxylic acid **95** with mercury trifluoroacetate in methanol and acetic acid.[96]

The reaction in methanol is described by the kinetic scheme including the stage involving the formation of the pre-reaction complex **103**.



;

103 $\xrightarrow[k_1,\ \text{slow}]{CH_3OH}$ reaction products .

Under the conditions of a large excess of the mercury salt, the observed second-order rate constant depends on the initial reagent concentration $[HgX_2]_0$ in conformity with Eqn. (1), which made it possible to determine the equilibrium constant K from kinetic data.

$$\frac{1}{k_{II}} = \frac{1}{k_1}\left(\frac{1}{K} + [HgX_2]_0\right), \qquad (1)$$

where k_{II} is the observed second-order rate constant.

The equilibrium constant increases with enhancement of the electron-donating properties of the aryl substituent, which shows that not only the functional groups but also the cyclopropene double bond participates in the complex formation reaction.

The reaction in acetic acid proceeds in a more complex manner, but in this case too the kinetic data lead to the conclusion that there is a coordination interaction between the ester group and the reagent. The kinetic data are described by the equation

$$\frac{1}{k_{II}} = \frac{1}{k_1} + \frac{1}{k_1 K [HgX_2]_0}, \qquad (2)$$

which corresponds to the scheme

95 + HgX_2 $\underset{\text{fast}}{\overset{K}{\rightleftharpoons}}$ **103** ;

103 + HgX_2 $\xrightarrow[\text{slow}]{k_1}$ reaction product .

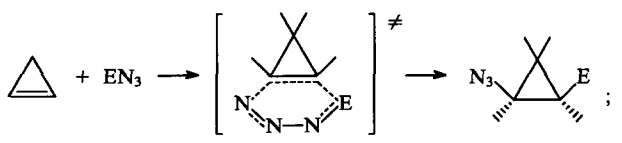
III. Mechanisms of the interaction of cyclopropene derivatives with electrophiles

It follows from the data presented that the main pathway in the reactions of cyclopropenes with electrophiles is the competitive formation of products with both retention of the ring and with its opening. The same data have shown that development of the competing pathways is influenced significantly by the substrate structure factors. Cyclopropenes with electron-donating substituents at the double bond tend more to form products with ring opening.[50-55] Conversely, electron-accepting substituents favour the formation of the products of addition to the double bond.[56,57]

Together with substrate structure factors, the nature of the electrophiles plays a major role in the development of the competing pathways. In terms of the increasing amount of acyclic products formed in the reaction, the reagents can be arranged in the sequence

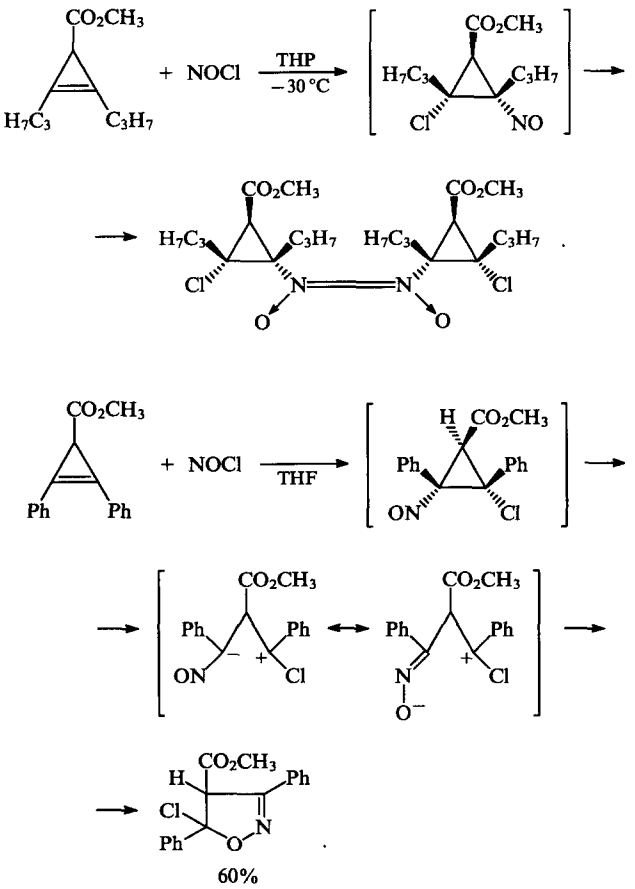
$$RS^+, I^- < SCN^+ < Br^+ \approx Cl^+ \ll H^+.$$

The view exists that the products of the addition to the double bond in cyclopropenes are formed in certain reactions via a concerted mechanism.[35,53] Indeed, a concerted mechanism is apparently most preferred for a series of reagents. Thus *cis*-adducts are probably formed via this mechanism in the reactions of cyclopropenes with hydrazoic acid[35] and mercury azide.[35,91] It may be that the high nucleophilicity of the azide group is in this case the decisive factor which determines the reaction pathway.



E = H, HgN_3 .

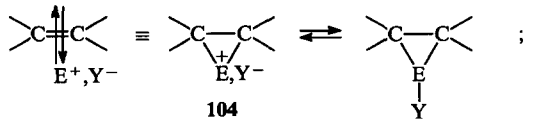
The interaction of the esters of cyclopropene-2-carboxylic acids with nitrosyl chloride, which results in the formation of either dimerisation or ring-opening products, is considered from these standpoints.[104,105]



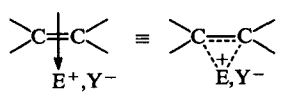
60%

It follows from stereochemical,[52,57,74-78] kinetic,[69,106] and other studies[29,52,69] that a stepwise mechanism operates for the remaining reagents of the series quoted above. As in the reactions with unstrained systems,[61,81,107] the structure of the intermediate species depends on the nature of the reagent. For reagents with a considerable tendency towards the reverse coordination, the formation of cyclic intermediates is most likely. According to Dewar's views,[109] the reverse coordination takes place as a result of the interaction of the occupied *p* or σ orbital of the electrophilic atom with the unoccupied antibonding π MO of the alkene. If the electronegativity of the electrophilic atom is comparable with that of the carbon atom, then the energies of the AO and MO are comparable and the interaction is strong. The linkage between the electrophilic atom E and the carbon atoms of the double bond is produced as a result of the formation of two usual two-electron bonds, while the intermediate has the structure of the onium species **104**.

For a highly electronegative electrophilic atom, the energy of the occupied AO is appreciably lower than that of the antibonding π MO and the reverse coordination is insignificant. For such electrophiles, the cyclic intermediate constitutes in essence the 'classical' Dewar π-complex **105** with a three-centre two-electron bond.[108,109]



104



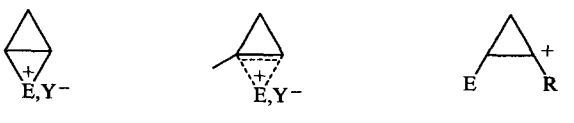
105

Within the framework of this concept of the dependence of the reaction mechanism on the electronegativity of the electrophilic atom of the reagent, there should exist a continuum of cyclic species with different degrees of reverse coordination, the intermediates **104** and **105** being the extreme members of this series.

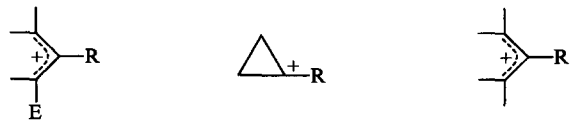
The stability of the cyclic species **104** and **105** and the reactions leading to their conversion into the final products are greatly influenced by the nature of the interaction of the electrophilic centre E^+ with the counterion Y^-. This problem has been recently investigated both experimentally and theoretically. The main results of these studies may be found in Refs 108–111.

Although the orbital structure of the cyclopropenes is more complex than that of the usual alkenes,[1,2,24-26,112] nevertheless they have an antibonding orbital similar to the π MO of the unstrained alkenes.[8] For this reason, the approach developed by Dewar is apparently valid also for the electrophilic reactions of cyclopropenes. In this case, the structures of the cyclic intermediates can be represented as **106** and **107**.

Considerations indicating that the reactions of cyclopropenes, especially with reagents having an electrophilic hydrogen atom, can proceed with participation of cyclopropyl ions **108** and the corresponding allyl ions **109** have been frequently proposed in the literature. Taking this into account, one may assume that in a multi-stage reaction of cyclopropene systems with electrophiles, the formation of the species **106**–**109** is most probable.[3,32,34,54,55]

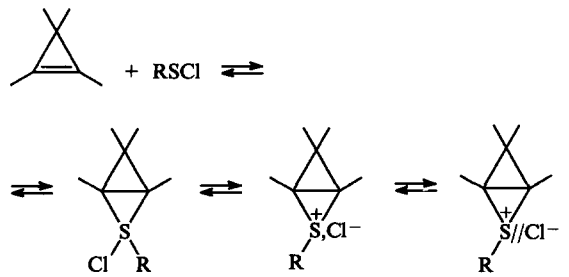


106 **107** **108**



109 **110** **111**

As mentioned above, a high *trans*-stereoselectivity of the addition to the double bond in cyclopropenes is character-istic of sulfenyl halides. Stereochemical as well as kinetic data[52,69,74,77,106] provide grounds for the assumption that, as in the sulfenyl halogenation of unstrained alkenes, this reaction results in the formation of either cyclic intermediates having the sulfurane structure **112** or the ion pairs **113** and **114** with the episulfonium cation.



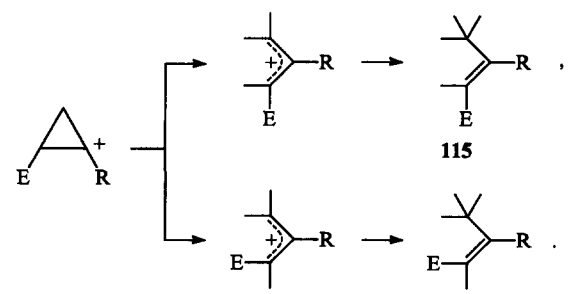
112 **113** **114**

In the reactions of cyclopropene derivatives with benzenesulfenyl chloride, only adducts are formed.[29,74-76] In contrast to this, in the interaction of 1-methylcyclopropene with 2,4-dinitrobenzenesulfenyl halides, the pathway leading to the formation of acyclic products may become the main one.[69] The electronegativity of the sulfur atom in 2,4-dinitrobenzenesulfenyl chloride is enhanced whilst the reverse coordination is diminished. This increases the electron deficiency on the carbon atoms of the three-membered skeleton in the intermediate **114**, which is in fact the reason for the occurrence of the reaction pathway involving the formation of acyclic adducts.

The sulfur atom in reagents containing the thiocyanato-group (thiocyanogen, thiocyanogen halides) is even more electronegative. For this reason, one may assume that the intermediates formed in the substitution of the thiocyanato-group into cyclopropenes have the character of π-complexes to an even greater extent and the reaction pathway involving the opening of the three-membered carbon ring becomes one of the main ones. An intermediate of type **107**, having a similar structure, is probably formed in the reactions of cyclopropenes with the halogens (Cl_2, Br_2) and their electrophilic analogues (*tert*-butyl hypochlorite, *N*-bromosuccinimide, etc.) in protic solvents.[52]

Quantum-chemical calculations have shown[113,114] that the total energy of the 1-R-cyclopropyl cations **110** is appreciably higher than the energy of the 2-R-allyl cations **111**. The relatively unstable high-energy intermediates are as a rule converted into the products or other intermediates with an insignificant activation energy. Consequently, if the formation of the ion **108** is possible in the electrophilic reactions of cyclopropenes, one should expect its conversion into the allyl cation **109** and further into acyclic products. There is also a possibility of another reaction pathway where the allyl cation **109** is obtained directly by electrophilic attack on the double bond of the cyclopropene,[3,52] by-passing the stage involving the formation of the cation **108**. However, if the substituents at the double bond are strong electron donors, the reaction can include only the stage involving the formation of a β-substituted cyclopropyl cation, which is subsequently converted into cyclic adducts. The most convincing data concerning the possibility of such a mechanism have been obtained in the reactions of esters of cyclopropene-2-carboxylic acids with mercury trifluoroacetate in acetic acid,[96,98] which were considered above.

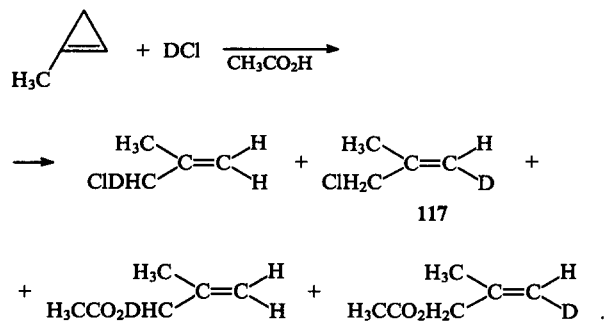
The stereochemistry of the opening of the cyclopropene ring is very important for the elucidation of the mechanism of the electrophilic reactions of cyclopropenes. In particular, it makes it possible to establish, in principle, whether the reaction proceeds via the stage involving the formation of the cyclopropyl cation **108**, which subsequently isomerises to the allyl cation **109**, or whether the latter is formed directly on electrophilic attack on the double bond of the cyclopropene. The Woodward–Hoffmann rules[115] and quantum-chemical calculations[116-119] predict a disrotatory reaction pathway **108**→**109**. There are two such procedures; if the electrophilic group E cannot make a decisive contribution to the stereochemistry of the ring opening for steric reasons, the isomeric products **115** and **116** will result. The formation reaction of the acyclic products is on the whole nonstereoselective.



115 **116**

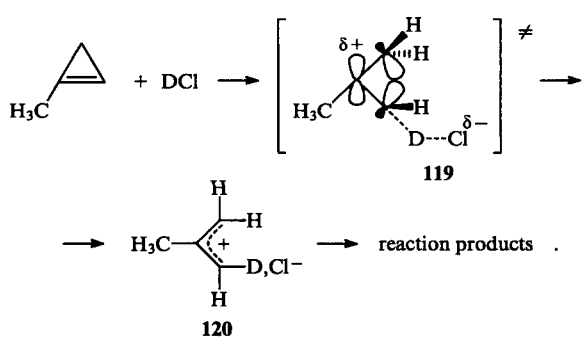
Stereoselective ring opening implies that the cyclopropyl cation of type **108** is not formed in the reaction.

It has been established[52] that the interaction of 1-methylcyclopropene with deuterium chloride entails the stereoselective opening of the cyclopropene ring and that the products of the reaction of 1-deuterio-3-chloro-2-methyl-1-propene **117** and 1-deuterio-3-acetoxy-2-methyl-1-propene **118** have the (*Z*)-configuration.



117 **118**

Within the limits of experimental error, a uniform distribution of the deuterium label is observed. This means that the reaction products are formed from the allylic intermediate **120**. The observed stereochemical result indicates a single-stage synchronous pathway leading to its formation. As the C–D bond is formed and a deficiency of electron density arises on the β-carbon atom disrotatory ring opening takes place in the transition state **119** in conformity with the stereoelectronic requirements, similarly to the behaviour manifested in the reactions involving the solvolysis of cyclopropane derivatives.[120]



119 **120**

The stereoselective formation of the product having the (*Z*)-configuration has also been observed in the isomerisation of 1,2,3-triphenylcyclopropene on treatment with trifluoroacetic acid.[34]

The reactions of 1-methylcyclopropene with 2,4-dinitrobenzenesulfenyl chloride, thiocyanogen, thiocyanogen chloride, and *tert*-butyl hypochlorite in acetic acid are likewise stereoselective, but the ring opening products have the (*E*)-configuration.[52] These data show that an intermediate with a fundamentally different structure is formed in the latter reactions. As mentioned above, it most probably has a cyclic structure.

One may conclude from the data presented that the (*Z*)-stereoselective ring opening is evidence for a single-stage formation of an allylic intermediate. If the reaction is (*E*)-stereoselective, the intermediate has a cyclic structure. More intensive stereochemical studies and theoretical calculations should show the extent to which this postulate is general and rigorous.

References

1. A Greenberg, T A Stevenson, in *Molecular Structure and Energetics* Vol. 2 (Eds J F Liebman, A Greenberg) (New York: VCH, 1986) p. 243
2. Kalvi Pihlaja, in *Molecular Structure and Energetics* Vol. 3 (Eds J F Liebman, A Greenberg) (New York: VCH, 1987) p. 173
3. G L Closs *Advances in Alicyclic Chemistry* Vol. 1 (Eds H Hart, G L Karabatos) (New York: Academic Press, 1966) p. 53
4. N S Zefirov, V I Sokolov *Usp. Khim.* **36** 243 (1967) [*Russ. Chem. Rev.* **36** 87 (1967)]
5. M P Kozina, V S Mastryukov, E M Mil'vitskaya *Usp. Khim.* **51** 1337 (1982) [*Russ. Chem. Rev.* **51** 765 (1982)]
6. V P Kolesov, M P Kozina *Usp. Khim.* **55** 1603 (1986) [*Russ. Chem. Rev.* **55** 912 (1986)]
7. J D Dill, A Greenberg, J F Liebman *J. Am. Chem. Soc.* **100** 6814 (1979)
8. M H Lien, A C Hopkinson *J. Mol. Struct.* **149** 139 (1987)
9. K B Wiberg, R Artis Dean, G Bonnevill *J. Am. Chem. Soc.* **113** 7969 (1991)
10. W E Billups, Gon-Ann Lee, E Arney Benny, K H Whitwire *J. Am. Chem. Soc.* **113** 7980 (1991)
11. A Padwa, M Wannamaker, S Wood *Tetrahedron* **47** 6139 (1991)
12. V V Plemenkov, L A Yanykina *Zh. Org. Khim.* **6** 2041 (1970)
13. L G Zaitseva, I V Avezov, V V Plemenkov, I G Bolesov *Zh. Org. Khim.* **10** 2227 (1974)
14. I G Bolesov, L G Zaitseva, V V Plemenkov *Zh. Org. Khim.* **14** 71 (1978)
15. V V Plemenkov, I G Bolesov *Dokl. Akad. Nauk SSSR* **248** 887 (1979)
16. D H Aue, G S Helwig *Tetrahedron Lett.* **15** 721 (1974)
17. L G Zaitseva, I V Avezov, O A Subbotin, I G Bolesov *Zh. Org. Khim.* **11** 1415 (1975)
18. I G Bolesov, A V Ignatchenko, N V Bovin, I A Prudchenko, L S Surmina, V V Plemenkov, P V Petrovskii, I V Romanov, I I Mel'nik *Zh. Org. Khim.* **26** 102 (1990)
19. K A Lukin, N V Averina, N S Zefirov *Zh. Org. Khim.* **24** 1776 (1988)
20. K A Lukin, N S Zefirov *Zh. Org. Khim.* **25** 202 (1989)
21. U Schuchardt, P Faria dos Santos Filho *Ciencia e Cultura* **30** 160 (1978)
22. A Padwa, W F Ricker *J. Am. Chem. Soc.* **103** 1859 (1981)
23. M S Baird, H H Hussain, W Clegg *J. Chem. Res.* 110 (1988)
24. A Skance *J. Mol. Struct.* **30** 95 (1976)
25. J Kao, L Radom *J. Am. Chem. Soc.* **100** 379 (1978)
26. F Allen *Tetrahedron* **38** 645 (1982)
27. M N Protopopova, E A Shapiro *Usp. Khim.* **58** 1145 (1989) [*Russ. Chem. Rev.* **58** 667 (1989)]
28. V N Plotkin, in *Sovremennye Problemy Organicheskoi Khimii* (Modern Problems of Organic Chemistry) (1991) p. 165
29. V R Kartashov, E V Skorobogatova, N F Akimkina, N S Zefirov *Zh. Org. Khim.* **18** 38 (1982)
30. R Schmitz, H Sonnenschein, R J Kuban *Tetrahedron Lett.* **26** 4911 (1985)
31. A Padwa, G D Kennedy *J. Org. Chem.* **49** 4344 (1984)
32. M I Komendantov, R R Bekmukhametov, I N Domnin *Zh. Org. Khim.* **14** 759 (1978)
33. M I Komendantov, R R Bekmukhametov, I N Domnin *Tetrahedron* **34** 2743 (1978)
34. G A Kudryavtseva, O A Nesmeyanova *Izv. Akad. Nauk SSSR, Ser. Khim.* 2357 (1974)
35. J E Galle, A Hassner *J. Am. Chem. Soc.* **94** 3930 (1972)
36. P Binger, H Schäfer *Tetrahedron Lett.* **16** 4673 (1975)
37. B M Mikhailov, Yu N Bubnov, O A Nesmeyanova, V G Kiselev, T Yu Rudashevskaja, B A Kazansky *Tetrahedron Lett.* **13** 4627 (1972)
38. Yu N Bubnov, O A Nesmeyanova, T Yu Rudashevskaya *Zh. Obshch. Khim.* **43** 127 (1973)
39. Yu N Bubnov, O A Nesmeyanova, T Yu Rudashevskaya, B M Mikhailov, B A Kazanskii *Zh. Obshch. Khim.* **43** 135 (1973)
40. A Padwa, T J Blackock, R Loza *J. Am. Chem. Soc.* **103** 2404 (1981)
41. L K Bee, P J Garratt, M M Mansuri *J. Am. Chem. Soc.* **102** 7076 (1980)
42. W E Billups, W I Chamberlain, M Y Asim *Tetrahedron Lett.* **18** 571 (1977)
43. E B Frolov, S N Anfilogova, I A Pomytkin, Yu A Luzikov, E S Balenkova *Zh. Org. Khim.* **16** 1839 (1980)
44. L E Fridrich, R A Cormier *J. Org. Chem.* **35** 450 (1970)
45. L E Fridrich, R A Cormier *Tetrahedron Lett.* **12** 4761 (1971)
46. J K Crandall, W W Conover *J. Org. Chem.* **43** 1323 (1978)
47. G D Maynard, L A Paquette *J. Org. Chem.* **56** 5480 (1991)
48. H B Wiberg, W J Bartley *J. Am. Chem. Soc.* **82** 6375 (1960)
49. E V Skorobogatova, Doctoral Thesis in Chemical Sciences, Gorky Polytechnic Institute, Gorky, 1990
50. O A Nesmeyanova, G A Kudryavtseva *Izv. Akad. Nauk SSSR, Ser. Khim.* 2629 (1982)
51. V R Kartashov, P S Afanas'ev, E V Skorobogatova, Yu K Grishin, N S Zefirov *Zh. Org. Khim.* **22** 452 (1986)
52. V R Kartashov, E V Skorobogatova, P S Afanas'ev, V A Chertkov, N M Sergeev, A N Chernov, N S Zefirov *Zh. Org. Khim.* **27** 1861 (1991)
53. L S Surmina, V A Novoselov, I G Bolesov *Zh. Org. Khim.* **12** 1594 (1976)
54. O A Nesmeyanova, G A Kudryavtseva *Izv. Akad. Nauk SSSR, Ser.Khim.* 2780 (1979)
55. O A Nesmeyanova, G A Kudryavtseva *Izv. Akad. Nauk SSSR, Ser. Khim.* 234 (1977)
56. T N Grigorova, M I Komendantov *Zh. Org. Khim.* **17** 317 (1981)
57. M I Komendantov, I N Domnin, R N Kentaeva, T N Grigorova *Zh. Org. Khim.* **9** 1420 (1973)
58. M Vincens, S Choubani, M Vidal *Tetrahedron Lett.* **22** 4695 (1981)
59. R Arnold, S Choubani, R Surba *Can. J. Chem.* **63** 2512 (1985)
60. J M Birchall, K Burger, R N Haszeidine, S N Nona *J. Chem. Soc., Perkin Trans. 1* 2080 (1981)
61. F Freeman *Chem. Rev.* **75** 438 (1975)
62. L Rasteikiene, D I Greiciute, M G Lin'kova, I L Knunyants *Usp. Khim.* **46** 1041 (1977) [*Russ. Chem. Rev.* **46** 548 (1977)]
63. W A Smit *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* 128 (1980)
64. W A Smit, N S Zefirov, I V Bodrikov, M Z Krimer *Acc. Chem. Res.* **12** 282 (1979)
65. W A Smit, N S Zefirov, I V Bodrikov *Organic Sulfur Chemistry* (Eds R R Freidline, A E Skorova) (Oxford: Pergamon Press, 1981) p. 159
66. I V Bodrikov, L G Gurvich, N S Zefirov, V R Kartashov, A L Kurts *Zh. Org. Khim.* **10** 1545 (1974)
67. V A Kartashov, I V Bodrikov, E V Skorobogatova, N S Zefirov *Zh. Org. Khim.* **12** 297 (1976)
68. V R Kartashov, I V Bodrikov, E V Skorobogatova, N S Zefirov *Phosphorus Sulfur* **3** 213 (1977)
69. V R Kartashov, E V Skorobogatova, E Yu Grudzinskaja, N F Akimkina, N S Zefirov, R Caple *Tetrahedron* **41** 5219 (1985)
70. N S Zefirov, A S Koz'min, V V Zhdankin *Tetrahedron* **38** 291 (1982)
71. N S Zefirov, A S Koz'min, V N Kirin, V V Zhdankin, R Caple *J. Org. Chem.* **46** 5264 (1981)
72. N S Zefirov, A S Koz'min *Sov. Sci. Rev B, Chem.* **7** 297 (1985)
73. G I Borodkin, Yu V Gatilov, E M Chernyak, V G Shubin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2826 (1985)
74. V R Kartashov, N F Akimkina, E V Skorobogatova *Zh. Org. Khim.* **16** 889 (1980)

75. E I Gritsenko, G G Butenko, V V Plemenkov, A I Baluev, I G Bolesov *Zh. Org. Khim.* **22** 632 (1986)
76. E I Gritsenko, G G Butenko, V V Plemenkov, I G Bolesov *Dokl. Akad. Nauk SSSR* **289** 99 (1986)
77. V R Kartashov, E V Skorobogatova, O V Vasil'eva, N V Malisova, A M Chernov, A N Pushin, N S Zefirov *Zh. Org. Khim.* **28** 934 (1992)
78. V R Kartashov, E V Skorobogatova, P S Afanas'ev, N F Akimkina, E Yu Grudzinskaya, N S Zefirov *Zh. Org. Khim.* **22** 531 (1986)
79. V R Kartashov, E V Skorobogatova, P S Afanas'ev, V A Chertkov, N M Sergeev, N S Zefirov *Zh. Org. Khim.* **28** 2477 (1992)
80. E V Skorobogatova, N F Akimkina, V R Kartashov *Zh. Org. Khim.* **15** 753 (1979)
81. R C Faney, in *Topics in Stereochemistry* Vol. 3 (Eds N Allinger, E L Eliel) (New York: Wiley, 1968) p. 237
82. T G Traylor *Acc. Chem. Res.* **2** 152 (1969)
83. R D Bach, R F Richter *J. Am. Chem. Soc.* **94** 4747 (1972)
84. V R Kartashov, T N Sokolova, O V Vasil'eva, I V Timofeev, Yu N Grishin, D V Bazhenov, N S Zefirov *Zh. Org. Khim.* **26** 1800 (1990)
85. V R Kartashov, T N Sokolova, E V Skorobogatova, Yu N Grishin, D V Bazhenov, V A Roznyatovskii, A S Koz'min, N S Zefirov *Zh. Org. Khim.* **26** 1953 (1990)
86. M J S Dewar, K M Merz Jr *Organometallics* **4** 1967 (1985)
87. T Shirafuju, I Yamamoto, H Nazaki *Tetrahedron Lett.* **12** 4713 (1971)
88. T Shirafuju, H Nazaki *Tetrahedron* **29** 77 (1973)
89. Yu S Shabarov, L D Sychkova, S G Bandaev *Vestn. Mosk. Univ., Ser. 2: Khim.* 82 (1976)
90. V S Dombrovskii, N N Yakushina, I G Bolesov *Zh. Org. Khim.* **15** 1325 (1979)
91. V R Kartashov, E V Skorobogatova, T N Sokolova, O V Vasil'eva, N V Malisova, Yu N Grishin, D V Bazhenov, N S Zefirov *Zh. Org. Khim.* **27** 1240 (1991)
92. V R Kartashov, T N Sokolova, E V Skorobogatova, Yu N Grishin, D V Bazhenov, N S Zefirov *Zh. Org. Khim.* **27** 261 (1991)
93. V R Kartashov, N V Galyanova, E V Skorobogatova, A N Chernov, N S Zefirov *Zh. Org. Khim.* **20** 2623 (1984)
94. A N Chernov, N G Furmanov, V R Kartashov, E V Skorobogatova, N V Malisova, N S Zefirov *Dokl. Akad. Nauk SSSR* **289** 1391 (1986)
95. Yu K Grishin, D V Bazhenov, Yu A Ustynyuk, E V Skorobogatova, N V Malisova, V R Kartashov, N S Zefirov *Dokl. Akad. Nauk SSSR* **289** 620 (1986)
96. V R Kartashov, E V Skorobogatova, N V Malisova, Yu K Grishin, D V Bazhenov, N S Zefirov *Zh. Org. Khim.* **27** 2490 (1991)
97. L G Kuz'mina, Yu T Struchkov, A N Chernov, V R Kartashov, N V Malisova, E V Skorobogatova *Zh. Strukt. Khim.* **28** 109 (1987)
98. V R Kartashov, N V Malisova, E V Skorobogatova, Yu K Grishin, D V Bazhenov, N S Zefirova *Zh. Org. Khim.* **22** 867 (1986)
99. H B Henbest, B Nichols, *J. Organomet. Chem.* **56** 227 (1959)
100. N S Zefirov, L G Gurvich *J. Organomet. Chem.* **81** 309 (1974)
101. J Klein, R Levene *Tetrahedron Lett.* **10** 4833 (1969)
102. P Chamberlain, G H Whitham *J. Chem. Soc. (B)* 1382 (1970)
103. L G Kuz'mina, Yu T Struchkova, V R Kartashov, N V Galyanova, E V Skorobogatova, N S Zefirov *Zh. Strukt. Khim.* **27** 120 (1986)
104. T N Grigorova, K A Ogloblin, M I Komendantov *Zh. Org. Khim.* **8** 2197 (1972)
105. T N Grigorova, K A Ogloblin, M I Komendantov *Zh. Org. Khim.* **9** 711 (1973)
106. V R Kartashov, N F Akimkina, E V Skorobogatova, E P Trub *Kinet. Katal.* **21** 1330 (1980)
107. P B D De la Mare, R Bolton *Electrophilic Additions to Unsaturated Systems* (Translated into Russian; Moscow: Mir,1968)
108. M J S Dewar, G P Ford *J. Am. Chem. Soc.* **101** 783 (1979)
109. M J S Dewar, R C Dougherty *The PMO Theory of Organic Chemistry* (Translated into Russian; Moscow: Mir, 1977)
110. I V Bodrikov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **29** 118 (1986)
111. S Yamabe, T Minato, S Inagaki *J. Chem. Soc., Chem. Commun.* 532 (1988)
112. H-L Hase, C Müller, A Schweig *Tetrahedron* **34** 283 (1978)
113. M H Lein, A C Hopkinson *J. Mol. Struct.* **121** 1 (1985)
114. S M Khalil *Z. Naturforsch. A, Phys. Sci.* **43** 801 (1988)
115. R B Woodward, R Hoffmann *Conservation of Orbital Symmetry* (Translated into Russian; Moscow: Mir, 1977)
116. H J S Dewar, S Kirschner *J. Am. Chem. Soc.* **93** 4290, 4291 (1971)
117. L Radom, P C Hariharau, J A Pople *J. Am. Chem. Soc.* **95** 6531 (1973)
118. D T Clark, G Smale *Tetrahedron* **25** 13 (1969)
119. A Jensen *Theor. Chim. Acta* **63** 269 (1983)
120. V S Aksenov, G A Terent'eva, Yu V Savinykh *Usp. Khim.* **49** 1039 (1980) [*Russ. Chem. Rev.* **49** 549 (1980)]