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Carbenes, related intermediates, and small-sized cycles: contribution from Professor Nefedov's laboratory

Yury V. Tomilov,[a] Leonid G. Menchikov,[a] Evgeny A. Shapiro,[b] Valentin D. Gvozdev,[a] Konstantin N. Shavrin,[a] Nikolay V. Volchkov,[a] Maria B. Lipkind,[a] Mikhail P. Egorov,*[a] Sergey E. Boganov,[a] Valery N. Khabashesku[c] and Esfir G. Baskir[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: mpe@ioc.ac.ru*
[b] *TAMI-IMI Institute for Research and Development, Haifa Bay 26111, Israel*
[c] *Department of Materials Science and Nanoengineering, Rice University, Houston, TX 77005, USA*

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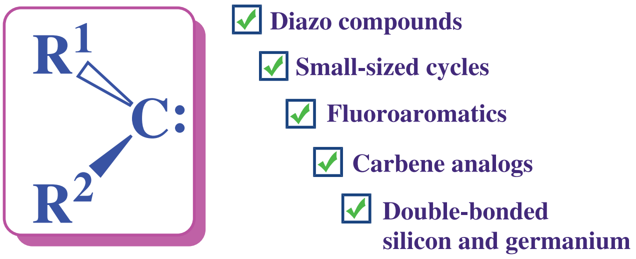
The review summarizes some of the most prominent results obtained in the laboratory headed by Academician Oleg M. Nefedov at the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences in the field of chemistry of carbenes, their heavy analogs, and related intermediates, as well as small-sized cycles. Those include elaboration of safe methodology of cyclopropanation using diazomethane, development and extension of synthetic applications of diazoesters and other diazo compounds in the preparation of valuable chemical products, design of functionalized alkynylcyclopropanes on the basis of alkynylcarbene reactions, creation of versatile synthetic approaches to preparation of various practically useful fluoroorganic compounds on the basis of reactions of fluorocarbenes, development of synthetic applications of heavy carbene analogs and synthesis of small-sized heterocycles containing silicon and germanium atoms, analysis of mechanisms of some important reactions of carbenes, their analogs and related intermediates on the basis of physicochemical studies, direct spectroscopic studies of various labile intermediates of chemical reactions.



Keywords: carbenes, diazo compounds, cyclopropanation, cyclopropanes, cyclopropenes, fluoroaromatics, carbene analogs, double bonded silicon and germanium, radicals.

Dedicated to the 90th birthday of Academician Oleg M. Nefedov

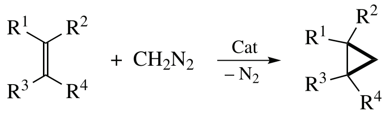
Introduction

According to the IUPAC Gold Book definition,[1] carbenes are 'the electrically neutral species H_2C: and its derivatives, in which the carbon is covalently bonded to two univalent groups of any kind or a divalent group and bears two nonbonding electrons, which may be spin-paired (singlet state) or spin-non-paired (triplet state)'. The existence of carbenes, which were initially (at the end of the 19th century) expected to be stable but difficult to synthesize compounds, and then (at the beginning of the 20th century) considered as elusive intermediate species,[2] had found its firm confirmation only in the 50–60s of the last century based on detailed analysis of the mechanisms of a series of chemical transformations with their participation and the applications of spectroscopic methods to their direct detection.[2–4] Since that time, this class of species has been transformed 'from fleeting intermediates to powerful reagents'.[5] The reactions with the participation of labile carbenes can largely be controlled at present, while their stable representatives and their transition metal complexes are widely used in synthetic applications.[3,5–16] Nevertheless, chemistry of carbenes and related chemical fields, even now, often brings new unusual results.

One of the participants in the research and development of the vast field of chemistry of carbenes almost from the very beginning has been the laboratory of Oleg M. Nefedov at the N. D. Zelinsky Institute of Organic Chemistry. In this focus article, we would like to dwell on the contributions made by this laboratory to understanding the reactivity of carbenes, to the development of synthetic approaches based on reactions of carbenes and diazo compounds, which often but not always act as precursors of carbenes, to the studies of further transformations of formed small-sized cycles, and to direct spectroscopic detection of carbenes of different types and related intermediates. To keep the bibliography short enough, only the most relevant studies are cited in the following text. More detailed information on each topic considered, as well as additional references to related work by other research groups can be found in the cited original articles and in a number of reviews.[5–27]

1. Development of safe methodology of cyclopropanation of unsaturated compounds with diazomethane

The most convenient source of methylene, which is the simplest carbene, is diazomethane (CH_2N_2). Among reactions of methylene, processes of [1+2]-cycloaddition with the formation of cyclopropane products are of the greatest importance. However, simple thermal and photolytic reactions of diazomethane with olefins have in general no preparative value and can proceed through the intermediate formation of pyrazolines, which are products of 1,3-dipolar cycloaddition.



R^1–R^4 = H, Alk, Ar, HetAr
Cat = $Pd(acac)_2$, $Pd(OAc)_2$, $(PhCN)_2PdCl_2$, $Pd_2(dba)_3$, CuOTf, CuCl, $Cu(acac)_2$, FeTPPCl, *etc.*

Scheme 1

At present, the catalytic cyclomethylenation of double bonds (including non-activated ones) with diazomethane has become one of the important general methods of preparative synthesis of various cyclopropanes (Scheme 1).[28–30] The most effective catalysts for this reaction are palladium compounds that provide high product yields with minimal consumption of diazomethane.

For a long time, methods for the synthesis of cyclopropane compounds based on diazomethane developed slowly, and the

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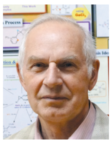


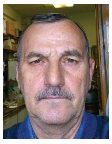
Professor **Yury V. Tomilov** is the head of the Laboratory of Chemistry of Diazo Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of chemistry of carbenes and other unstable molecules, chemistry of aliphatic diazo compounds, and small-rings compounds.

Dr. **Leonid G. Menchikov** is the Research Fellow at the Laboratory of Chemistry of Diazo Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of carbene chemistry, small-ring chemistry, germanium chemistry, and phase transfer catalysis.

Professor **Evgeny A. Shapiro** was the Leading Research Fellow at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, in the laboratory of Carbene Chemistry and Small-sized Cyclic Compounds under leadership of Prof. O. M. Nefedov until 1993. From 1994 to 2016, he was the Senior Researcher Fellow at IMI (TAMI) Institute for Research and Development, LTD. He is a specialist in process and product development in the fields of fine chemicals, pharmacy, and pesticide chemistry.

Dr. **Valentin D. Gvozdev** is the Senior Research Fellow at the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of chemistry of carbenes, small-sized cycles, and phase transfer catalysis.

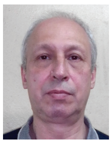
Dr. **Konstantin N. Shavrin** is the Senior Research Fellow at the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of chemistry of carbenes, small-sized cycles, and phase transfer catalysis.



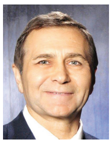
Dr. **Nikolay V. Volchkov** is the Senior Research Fellow at the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of chemistry of carbenes, small-sized cycles, and fluoroorganic compounds.

Dr. **Maria B. Lipkind** is the Research Fellow at the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. She is an expert in the areas of chemistry of carbenes, small-sized cycles, and fluoroorganic compounds.

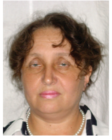
Professor **Mikhail P. Egorov**, Full Member of the Russian Academy of Sciences, is the Director of the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, and head of the Laboratory of Carbene Analogs and Related Intermediates at this Institute. He is an expert in the areas of carbene chemistry, organic reactions and reactive intermediates.



Dr. **Sergey E. Boganov** is the Senior Research Fellow at the Laboratory of Carbene Analogs and Related Intermediates at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the area of matrix IR spectroscopy.



Professor **Valery N. Khabasheskuu** is a faculty member of the Department of Materials Science and Nanoengineering at Rice University, Houston, TX, USA; previously, head of the Nanotechnology Center of Excellence at Baker Hughes oil field services company, research professor in the Departments of Chemical Engineering at the University of Houston and Chemistry at Rice University. Until 2000 he was the Senior Research Fellow at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, in the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds under leadership of Professor O. M. Nefedov. He is an expert in the areas of physical organic, organometallic and nanomaterials chemistry and applications.



Dr. **Esfir G. Baskir** is the Senior Research Fellow at the Laboratory of Carbene Chemistry and Small-sized Cyclic Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. She is an expert in the areas of matrix IR spectroscopy, quantum chemical calculations, chemistry of carbenes and radicals.

synthetic possibilities of this reaction were studied fragmentarily. This was mainly because extremely explosive and toxic gaseous diazomethane had to be used.

The situation changed in 1992, when the first safe method of catalytic cyclopropanation with *in situ* generated diazomethane was elaborated.[31] It is based on the slow addition of *N*-methyl-*N*-nitrosourea (a source of diazomethane) to a two-phase mixture of an olefin solution with added catalyst (0.5 mol%) in CH_2Cl_2/Et_2O and a concentrated aqueous KOH at 12–18 °C at such a rate that the resulting diazomethane passed into the organic phase, fully reacted and did not accumulate, thus providing its low current concentration. $(PhCN)_2PdCl_2$, $[(PhO)_3P]_2PdCl_2$, $Pd(acac)_2$ and $Pd(OAc)_2$ proved to be effective catalysts for cyclopropanation of various unsaturated compounds using this technique.[32,33] This method made it possible to overcome serious limitations in the widespread use of diazomethane and revived interest in its chemistry.

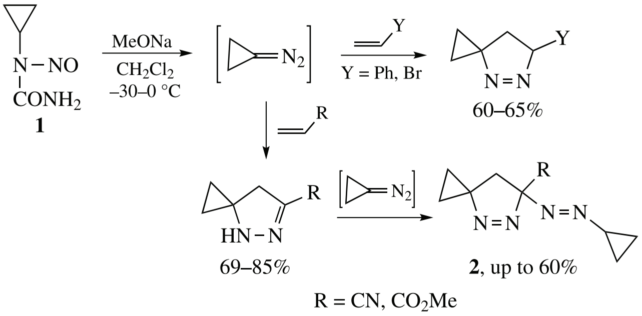
Possibilities of application and prospects for the use of catalytic methylenation with diazomethane in the synthesis of cyclopropanes are summarized in reviews.[28,30] A systematic study of these reactions made it possible to establish the basic rules governing the cyclopropanation of various double bonds, to evaluate the effectiveness of various catalysts, and to propose the mechanisms of their action. The method of catalytic cyclomethylenation with diazomethane is especially promising for the preparation of compounds that do not contain activating donor–acceptor substituents in the cyclopropane ring, in particular, terpenes, steroids, lipids, antibiotics, and other natural and practically valuable compounds.[21,34,35] The safe methods for the preparation of cyclopropanes developed to date open up perspectives for their wider application in organic synthesis and industry. This favorably distinguishes them from frequently used alternative synthetic approaches (in particular, based on the use of zinc and aluminum carbenoids) to cyclopropane structures.

2. The use of diazocyclopropane and cyclopropyldiazonium in the synthetic practice

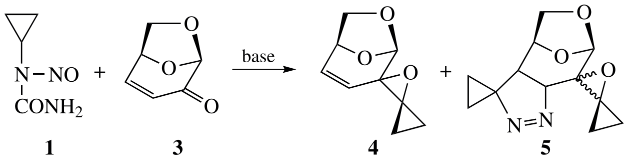
The study of highly reactive intermediates has always been one of the main directions of the work in the laboratory of Academician O. M. Nefedov. Therefore, it is not surprising that another aspect of research in the field of chemistry of diazo compounds was the study of the possibility of using diazocyclopropane in organic synthesis.[36] Though this extremely unstable compound has not yet been isolated in a pure form, its formation *in situ*, as well as the generation of its 2,2-dimethyl and 2,2-dichloro derivatives and even diazospiropentane, can be judged by their chemical trapping leading to the formation of products of the 1,3-dipolar cycloaddition preserving the cyclopropane moiety.[36,37]

A systematic study of the 1,3-dipolar cycloaddition of diazocyclopropane to unsaturated compounds dates back to the early 1990s. The reaction of diazocyclopropane generated *in situ* by the action of sodium methoxide on nitrosocyclopropyl urea **1** with unsaturated compounds containing a bicyclo[2.2.1]heptene fragment leads to the formation of the corresponding spiro[1-pyrazolinecyclopropanes].[38] Benzvalene and 3,3-disubstituted cyclopropenes, as well as styrene, vinyl bromide and unsaturated compounds with electron-withdrawing substituents, in particular, acrylic acid derivatives, turned out to be good substrates for reaction with diazocyclopropane[36,39] (Scheme 2). These transformations are of interest for the synthesis of pyrazolines with spiro-fused cyclopropane moieties, as well as cyclopropylazopyrazolines **2**.

At the same time, the interaction of diazocyclopropane with levoglucosenone **3** proceeds mainly at the carbonyl group and, depending on the conditions, leads predominantly to oxaspiropentane **4** or to 1-pyrazolines **5** (Scheme 3).[40]



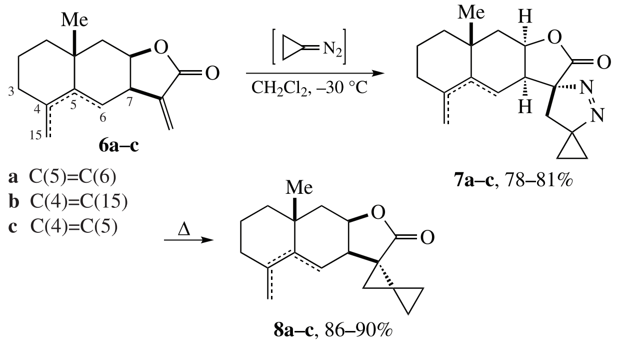
Scheme 2



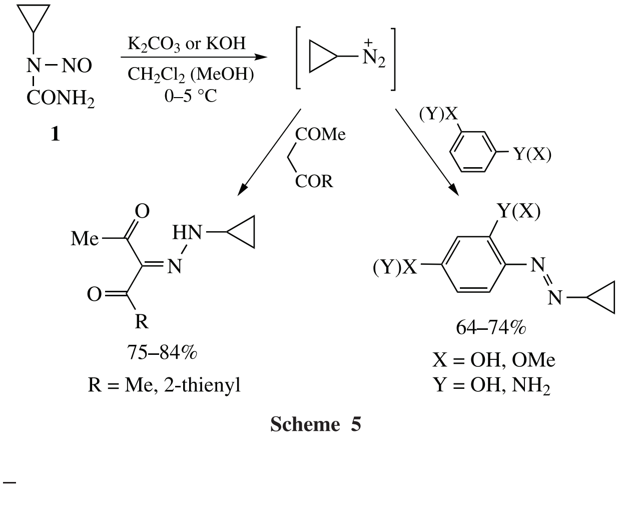
Conditions and yields:		
MeONa, MeOH, –30 °C	75%	15% (*dr* ~4 : 1)
K_2CO_3, CH_2Cl_2, 5 °C, excess of **1**	11%	72% (*dr* ~3 : 1)

Scheme 3

The interaction of diazocyclopropane with alanto-, isoalanto-, and alloalantolactones **6a–c** are examples of the reactions of diazocyclopropane with natural sesquiterpene lactones, which attract attention due to their high and diverse biological activities.[41] In all cases, these reactions proceeded in a similar manner and with high regio- and stereoselectivity, leading to the spiro-fused pyrazolines **7a–c**. It was shown that the obtained pyrazolines are capable of eliminating nitrogen during thermolysis at 195–210 °C, giving corresponding lactones **8a–c** with a spiropentane fragment (Scheme 4).



Scheme 4



Scheme 5

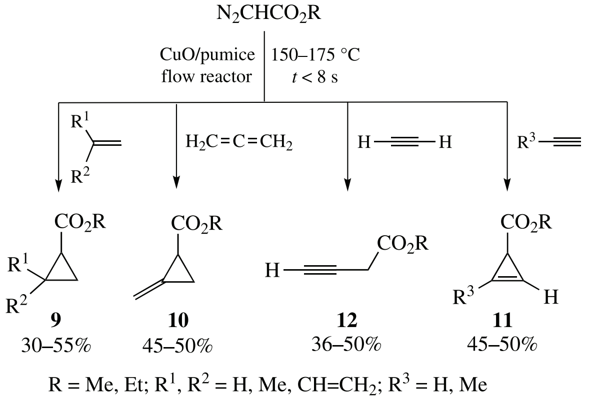
However, more unexpected was the fact that diazocyclopropane is able to exist in an equilibrium with its protonated form (cyclopropyldiazonium cation) and react like aromatic diazonium salts.

Thus, decomposition of urea **1** in the presence of aliphatic CH-acids, for example, β-diketones or malononitrile, as well as polyoxyarenes and aminophenols, leads to azo coupling reactions, which proceed quite efficiently[42,43] (Scheme 5).

3. α-Diazoesters in the synthesis of cyclopropanes and other strained molecules

Another synthetically useful type of diazo compounds is α-diazocarbonyl compounds, particularly, diazoesters. Compared with simple diazoalkanes, they are characterized by higher stability, and the processes of cyclopropanation with their participation make it possible to form three-membered cycles, which already bear an ester moieties, in one synthetic step.

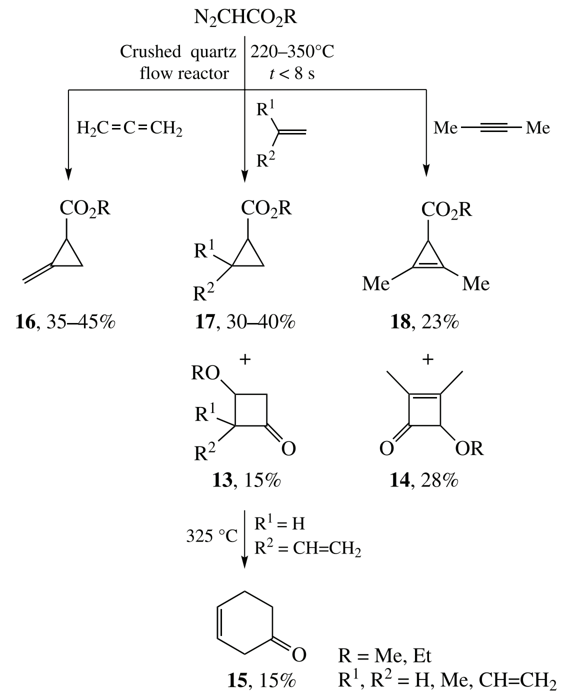
In the second half of the 1970s, the investigation of transformations of ethyl and methyl diazoacetates in flow reactors at 150–175 °C and contact time < 8 s was implemented. It was found that the dediazotization of these diazoacetates in a stream of gaseous unsaturated hydrocarbons (ethene, propene, 2-methylpropene, 1,3-butadiene, allene, acetylene, and propyne) over a pumice-supported copper catalyst resulted in the formation of cyclopropanecarboxylates **9**, methylenecyclopropanecarboxylates **10**, cycloprop-2-enecarboxylates **11**, as well as 3-alkynoates **12** (Scheme 6).[44,45]



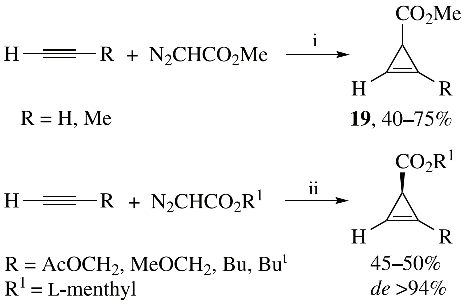
Scheme 6

Thermal decomposition of alkyl diazoacetates over crushed quartz led to the corresponding alkoxycarbonylcarbenes, which partially underwent the Wolf rearrangement into the corresponding alkoxyketenes. Both species reacted with multiple bonds of unsaturated acceptors to afford cyclobutanone (**13**), cyclobutene (**14**), and cyclohexanone (**15**) derivatives along with cyclopropanecarboxylates **16**–**18**[46,47] (Scheme 7).

Preparative methods for the synthesis of cycloprop-2-enecarboxylates **19** by the direct catalytic cyclopropenation of acetylene and its closest analogs in the liquid phase with alkyl diazoacetates have been developed[48] (Scheme 8). The simplest methyl cycloprop-2-encarboxylate appeared to be unstable at room temperature and was isolated as the cycloadduct with cyclopentadiene. Subsequently, Nefedov's students, in collaboration with colleagues abroad, showed that this reaction can be carried out stereospecifically using chiral rhodium complexes as catalysts.[49]



Scheme 7



Scheme 8 *Reagents and conditions*: i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, $Rh_2(5S\text{-}MEPY)_4$.

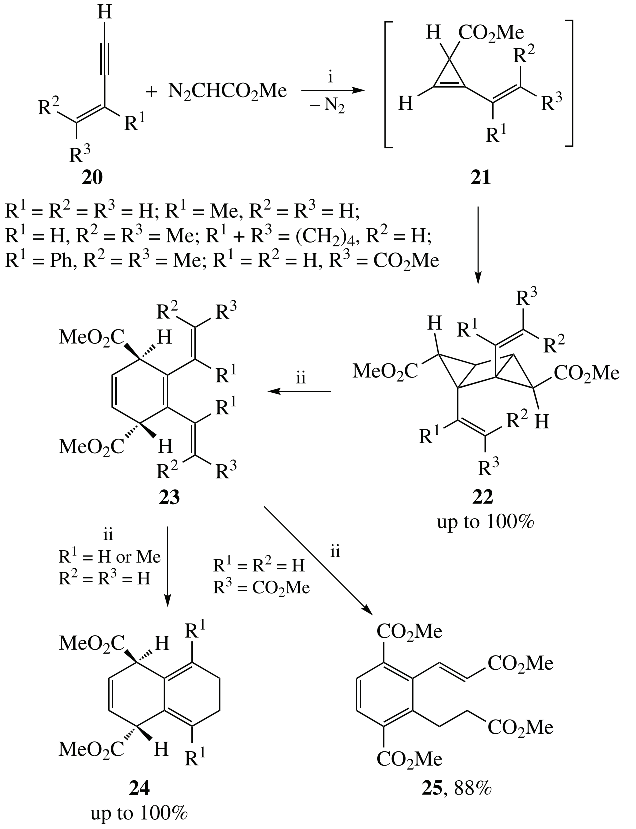
It was established that under similar conditions reactions of alkyl diazoacetates with conjugated enynes **20** having terminal triple bonds predominantly proceeded at these triple bonds, resulting in unstable alkenylcyclopropenecarboxylic esters **21**.[50,51] The latter underwent [2+2] cycloadditions *in situ*, forming tricyclohexane derivatives **22**, which were found to be transformed into more stable cyclohexadienes **23** and, then, to tetrahydronaphthalenes **24** or terephthalic acid derivatives **25** (Scheme 9).

With the use of chiral Rh-catalysis, these reactions could be performed stereoselectively.[49]

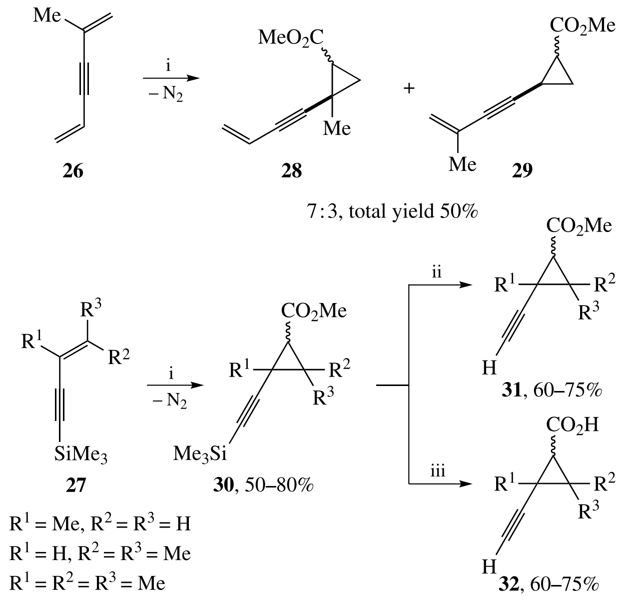
At the same time, internal enynes **26** and enynes **27** with triple bonds protected by a trimethylsilyl group reacted exceptionally at the double bonds to afford cyclopropanecarboxylates **28**–**30**. Compounds **30** can easily be desilylated to the corresponding esters **31** or acids **32** in acceptable yields (Scheme 10).[52]

The developed facile method for the preparation of cycloprop-2-enecarboxylates made it possible to study the chemistry of these compounds and discover their new transformations. They include the catalytic addition of proton-donor reagents to the saturated C(1)–C(2) bonds with the formation of esters of 4-substituted but-3-enecarboxylic acids **33**, the addition of thiols to the double bonds leading to thiocyclopropanes **34**, the selective cyclopropanation of norbornene-type double bonds with the formation of corresponding polycyclic compounds **35** with a vinylcyclopropane fragment, and stereospecific dimerization of cyclopropene esters into esters of substituted hexatriene dicarboxylic acids **36** (Scheme 11).[53]

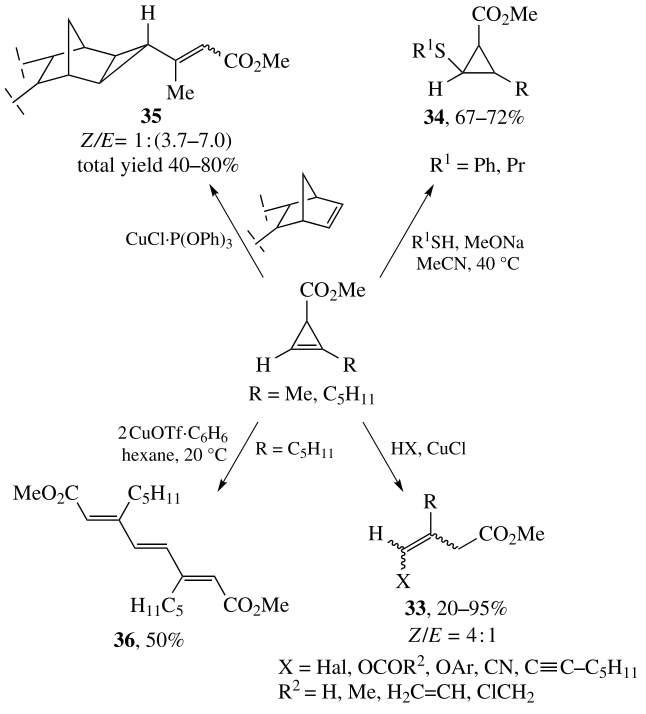
A series of functionally substituted esters of diazoacetic acid were synthesized (Scheme 12), and their catalytic dediazotation reactions were studied.[54] Most of the esters were obtained in high yields (60–80%) by diazotization of the corresponding



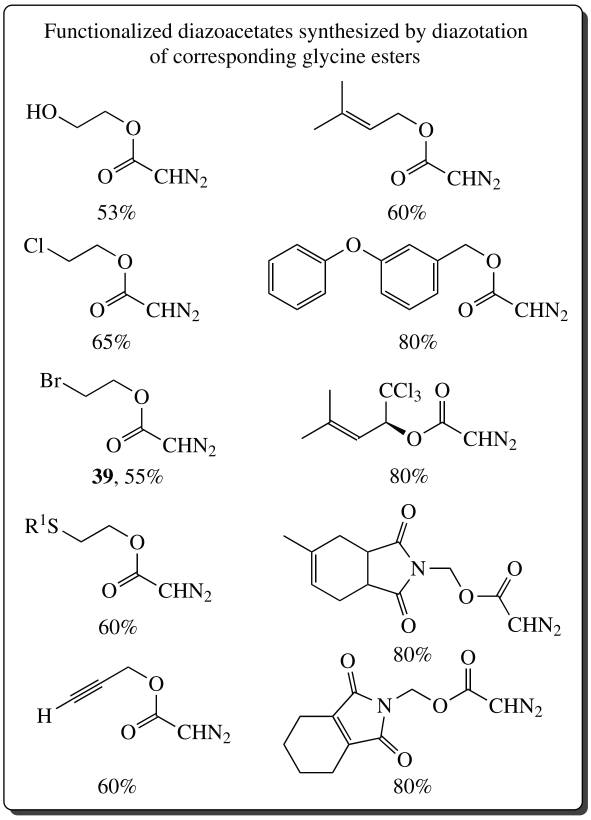
Scheme 9 *Reagents and conditions*: i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, *m*-xylene, reflux.

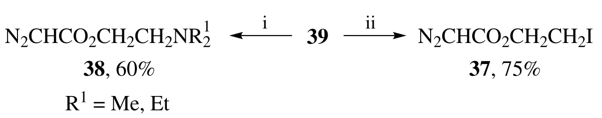


Scheme 10 *Reagents and conditions*: i, N_2CHCO_2Me, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, KOH, EtOH, <–5 °C; iii, KOH, EtOH, reflux.



Scheme 11


Functionalized diazoacetates synthesized by diazotation of corresponding glycine esters



$$\underset{\mathbf{38},\ 60\%}{N_2CHCO_2CH_2CH_2NR^1_2} \xleftarrow{\text{i}} \mathbf{39} \xrightarrow{\text{ii}} \underset{\mathbf{37},\ 75\%}{N_2CHCO_2CH_2CH_2I}$$

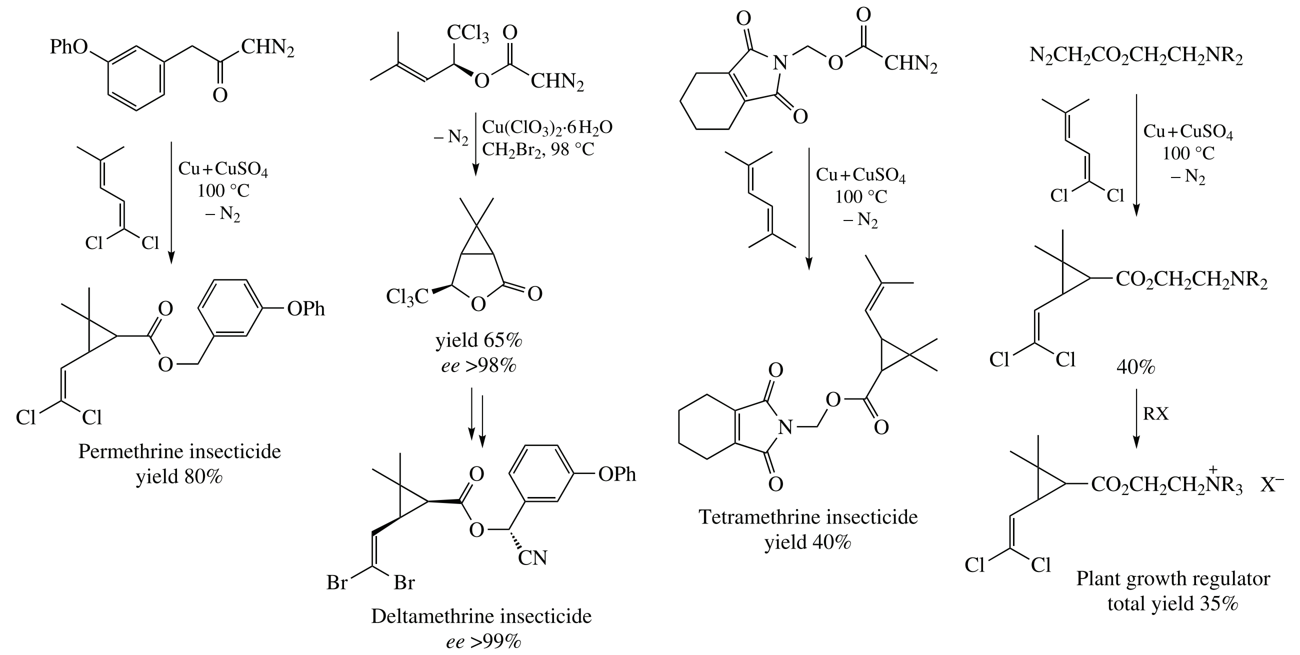
R^1 = Me, Et

Scheme 12 *Reagents and conditions*: i, NHR^1_2, K_2CO_3, MeCN; ii, NaI, acetone.

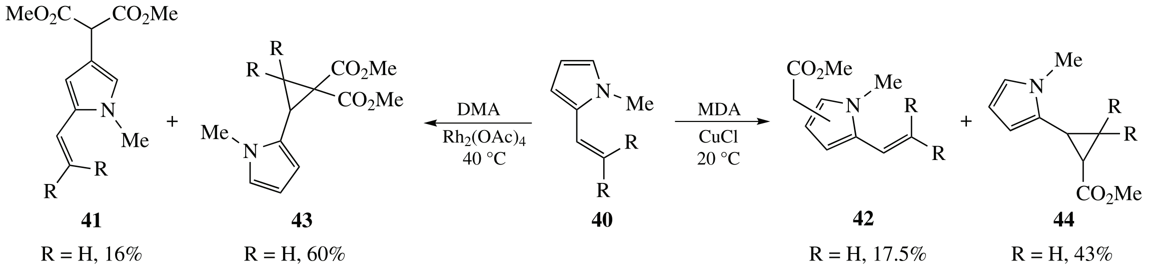
glycine esters with $NaNO_2$ in CH_2Cl_2–acetate buffer two-phase system at pH 3–5. Some esters such as **37** and **38** were prepared by transformations of 2-bromoethyl diazoacetate **39**. Starting glycinates were synthesized by the direct esterification of glycine with corresponding alcohols in the presence of acids (HCl or *p*-toluenesulfonic acid). In the case of acid sensitive alcohol components, N-protection of glycine was used.

The catalytic dediazotation of most of these compounds proceeds *via* the carbene pathway and, in the presence of unsaturated acceptors, leads to the formation of cyclopropane and cyclopropene adducts in moderate to high yields. The fundamental possibility of using diazo compounds of this type for the direct synthesis of synthetic pyrethroids and other biologically active compounds of the cyclopropane series has been demonstrated (Scheme 13).[55,56]

A significant attention in Nefedov's laboratory was paid to the study of selective reactions of diazoesters with alkenyl-



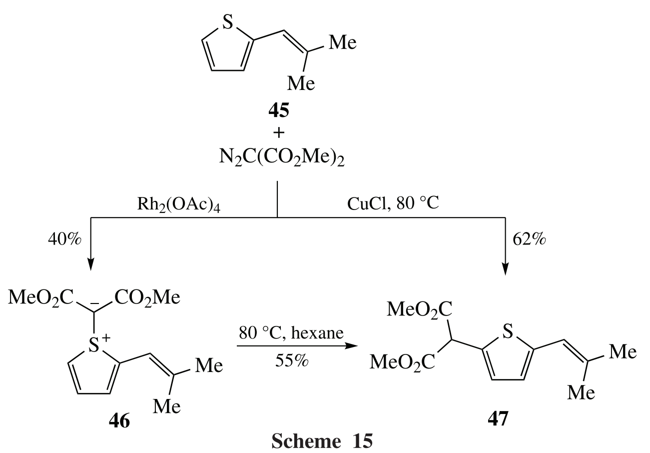
Scheme 13



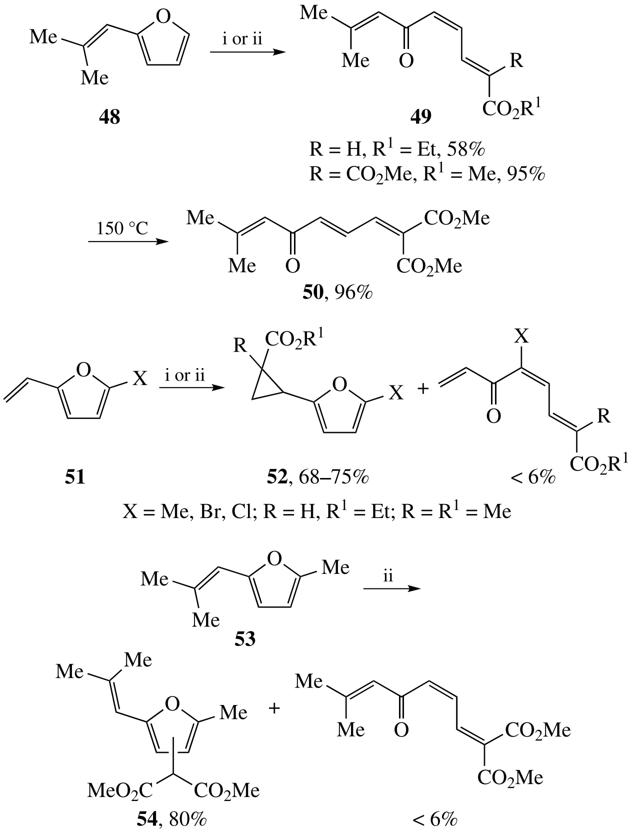
Scheme 14

substituted heteroaromatic compounds: pyrroles, thiophenes, and furans. In the case of 1-methyl-2-alkenylpyrroles **40**, there is a possibility of competition between the carbene attack to the pyrrole ring and the alkenyl group. As a result, along with the products **41**, **42** of the C–H insertion, products of cyclopropanation of the *exo*-cyclic double bonds **43**, **44** were also formed (Scheme 14).[57] The ratio between these directions of the reaction depends on diazoester used and, to a smaller extent, on the substituents at the double bond. In reaction with dimethyl diazomalonate (DMA), the cyclopropanation of the double bond dominates, whereas methyl diazoacetate (MDA) attacks both the pyrrole ring and the double bond.

The reaction of DMA with 2-(2-methylpropen-1-yl)thiophene **45** in the presence of $Rh_2(OAc)_4$ proceeds exclusively at the S-atom, leaving the *exo*-double bond intact (Scheme 15). The



Scheme 15



Scheme 16 *Reagents and conditions*: i, N_2CHCO_2Et, CuCl, 80 °C; ii, $N_2C(CO_2Me)_2$, $Rh_2(OAc)_4$, 20 °C.

forming stable *S*-ylide **46** transforms to corresponding 1,5-disubstituted thiophene **47** upon heating.[58,59]

The main pathways of interactions of DMA and ethyl diazoacetate (EDA) with 2-alkenylfurans, *e.g.*, 2-(2-methylpropen-2-yl)furan **48**, lead to *Z*-5-oxa-1,3-dienecarboxylates **49**, which are formed in moderate to high yields (Scheme 16). These compounds were transformed into more stable *E*-isomers **50** upon heating.[60–62] α-Substituted 5-vinylfurans **51** predominately react with EDA and DMA due to the double bond of the vinyl substituent to furnish cyclopropane adducts **52**. However, under the action of DMA, furan **53** bearing the methyl group in position 5 gives products of the substitution of hydrogen atoms in positions 3 and 4 of the furan ring (compound **54**).

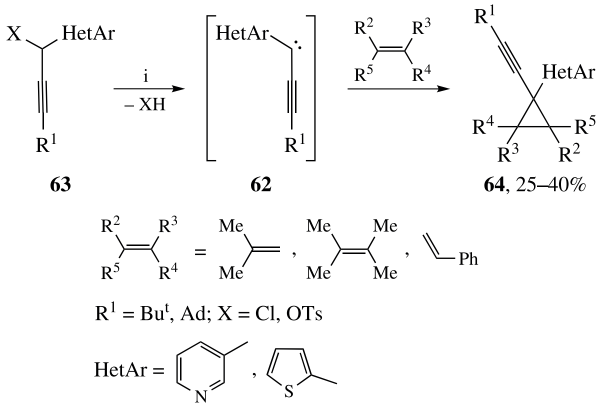
4. Alkynylcarbenes with functional substituents at the carbene center in the synthesis of functionalized alkynylcyclopropanes and further chemical transformations of the latter

Among the numerous types of carbenes, unsaturated carbenes and, in particular, alkynylcarbenes, in which the carbene center is adjacent to the triple bond, are of special interest. This is connected both with the development of theoretical concepts, since such a combination allows for a better understanding of the nature of conjugation, and with synthetic applications aimed at the synthesis of strained ethynylcyclopropanes. Over the past several decades, in the laboratory of Academician Nefedov, a number of methods for the generation of alkynylcarbenes with various substituents at the carbene center were developed.

The main attention in these efforts was paid to alkynylhalocarbenes, as they are the most synthetically useful, whereas the possible approaches to their generation seem to be the simplest. The first communication describing the generation of some alkynylchloro- and alkynylbromocarbenes **55** (X = Cl, Br) from corresponding 1,1-dihaloalk-2-ynes **56** on treatment with Bu^{t}OK or KOH under the phase transfer catalysis conditions was published[63] in 1987. Later on, this methodology was considerably improved, and four years later, a general effective method for the preparation of various alkynylhalocyclopropanes **57** based on the [1+2] cycloaddition of alkynylhalocarbenes to alkenes was elaborated[64] (Scheme 17). Using trimethylsilyl protection made it possible to propose[65] a new simple route to 1-chloro-1-ethynylcyclopropanes **58**, which are versatile polyfunctional synthons. Another original approach[66,67] to alkynylhalocarbenes and the corresponding alkynylhalocyclopropanes **57**, which was developed later, consists in the triple dehydrobromination of readily available tetrahalopropanes **59**. Using this method, alkynylfluorocarbenes **55** (X = F) producing alkynylfluorocyclopropanes **57** (X = F) in the reaction with alkenes were generated for the first time.[67]

Besides cyclopropanation of double bonds, alkynylchlorocarbenes are able to selectively insert[68] into α-C–H-bonds of primary and secondary alkali metal alkoxides with subsequent nucleophilic ring closure, which results in the formation of alkynyloxiranes **60**. Generation of these carbenes in the presence of diphenylacetylene made it possible to obtain[69] highly conjugated alkynylcyclopropenium salts **61** (see Scheme 17).

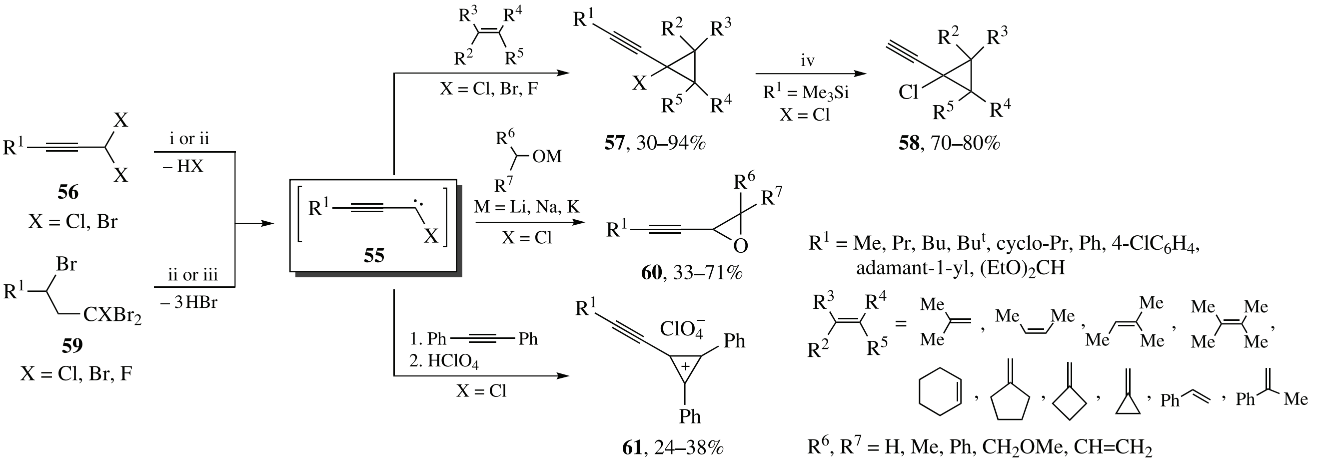
An α-elimination-based strategy was also used[70] for the generation of alkynyl(pyridyl) and alkynyl(thienyl)carbenes **62** as the first examples of (alk-1-ynyl)carbenes with hetaryl substituents at the carbene centers. They arise upon treatment of corresponding tosylates or chlorides **63** with Bu^{t}OK in nonpolar solvents and give cyclopropanation products **64** with some electron-rich and conjugated alkenes (Scheme 18).



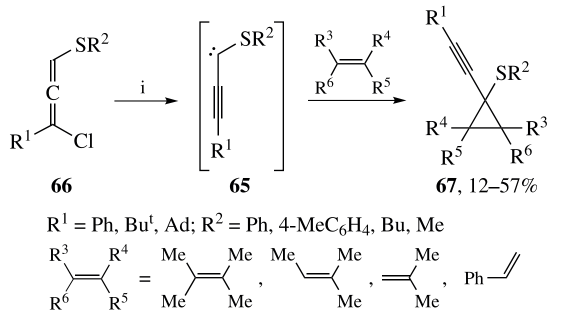
Scheme 18 *Reagents and conditions*: i, Bu^{t}OK, hexane, –20 to +80 °C.

Structurally similar (alkylthio)alkynylcarbenes **65** were successfully generated[71,72] by γ-elimination of HCl from 3-alkylthio-1-chloropropadienes **66**. Although their addition to alkenes proceeds less efficiently than analogous processes with alkynylchlorocarbenes, this reaction still remains the only known direct method for the preparation of 1-alkynyl-1-alkylthiocyclopropanes **67** (Scheme 19).

Recently it was shown that some alkynylcarbenes can be obtained photolytically from the corresponding 3-alkynyl-3*H*-pyrazoles **68** (Scheme 20). This technique made it possible to conduct comprehensive matrix IR-spectroscopic and quantum-chemical studies of (4-methylpent-3-en-1-ynyl)methylthiocarbene **69** (X = SMe)[73] and (4-methylpent-3-en-1-ynyl)chlorocarbene **69** (X = Cl).[74] For both species, structural parameters and pathways of further phototransformations were determined,

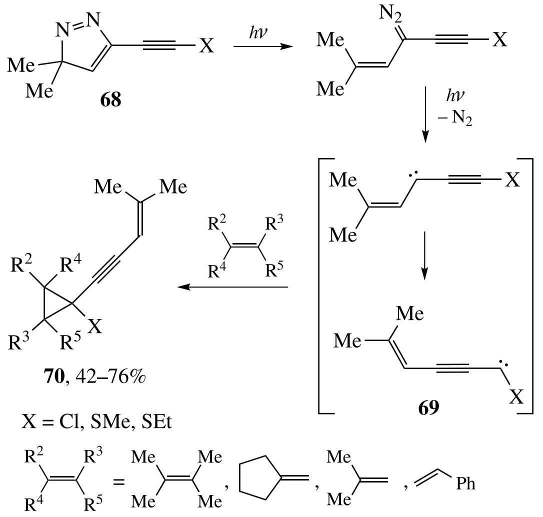


Scheme 17 *Reagents and conditions*: i, Bu^{t}OK, pentane, –20 °C; ii, KOH/BTEAC, CH_2Cl_2, 20 °C; iii, Bu^{t}OK, hexane, 20–60 °C; iv, KF·2 H_2O, DMF.



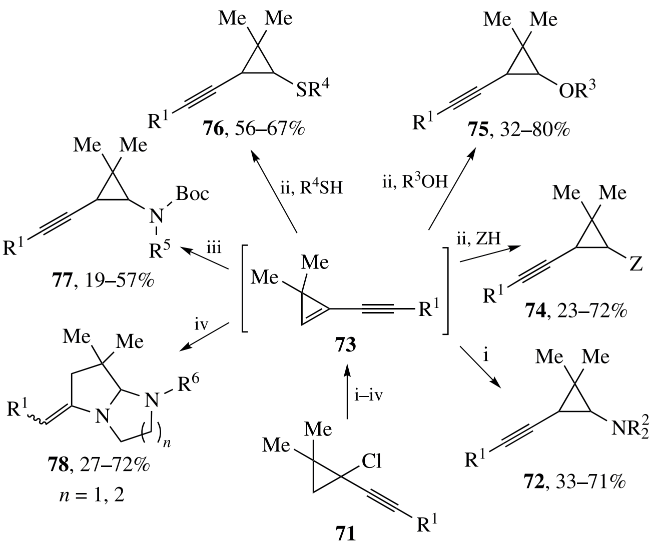
R^1 = Ph, Bu^t, Ad; R^2 = Ph, 4-MeC$_6$H$_4$, Bu, Me

Scheme 19 *Reagents and conditions*: i, Bu^{t}OK, hexane, 20 °C.



X = Cl, SMe, SEt

Scheme 20



R^1 = Ph, Bu^t, adamant-1-yl
R^2 = Me, Et, PhCH$_2$
$R^2 + R^2$ = (CH$_2$)$_4$, (CH$_2$)$_5$, (CH$_2$)$_2$O(CH$_2$)$_2$, (CH$_2$)$_2$NH(CH$_2$)$_2$
R^3 = Me, Et, Pr^i, Ph, (CH$_2$)$_2$OH, (CH$_2$)$_2$NH$_2$, (CH$_2$)$_2$NHMe
R^4 = Ph, 4-MeC$_6$H$_4$
R^5 = Me, Pr, Bu^i, CH$_2$CH$_2$OMe, PhCH$_2$
R^6 = H, Me
ZH = imidazole, 2-methylimidazole, pyrazole, 2,4-dimethylpyrazole

Scheme 21 *Reagents and conditions*: i, R^2_2NLi, THF, 20–40 °C; ii, KOH, DMSO, 90–100 °C; iii, R^5NHBoc, Bu^{t}OK, DMSO, 70 °C; iv, R^6NLiCH$_2$(CH$_2$)$_n$NH$_2$, THF, 20 °C.

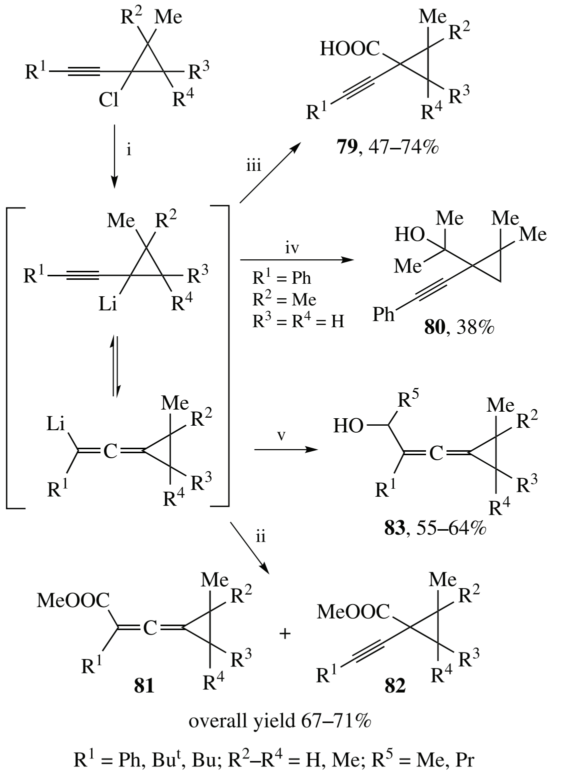
as well as an evidence of their singlet nature was obtained, which agrees with their chemical behavior. Preparative photolysis of pyrazoles **68** in the presence of alkenes represents[74,75] an original method of synthesis of alkynylchloro- and (alkylthio)alkynylcyclopropanes **70** in the absence of bases.

Alkynylchlorocyclopropanes are highly reactive compounds having at least three reaction centers: the strained three-membered ring, a chlorine atom at the propargylic position, and a triple bond. Two pathways of their further transformation were investigated in detail. The first one is based on the generation of conjugated alkynylcyclopropenes under the action of strong bases and their further reactions (Scheme 21).

It was found[76,77] that chlorocyclopropanes **71** react with an excess of lithium derivatives of dialkylamines in THF, forming dialkylaminocyclopropanes **72** with yields up to 71%. The intermediate participation of cyclopropenes **73** in these reactions was proved by the isolation of a number of these compounds in the reaction of chlorocyclopropanes **71** with sterically hindered lithium dialkylamides.[76]

For the synthesis of cyclopropanes **74**–**76**, heating of starting chlorides **71** with an appropriate nucleophile (primary and secondary alcohols, phenol, azoles and arenethiols) in DMSO in the presence of KOH was found to be the optimal conditions.[77–79] Introduction of an *N*-Boc-alkylamino group with formation of aminocyclopropanes **77** was successfully performed using Bu^{t}OK in DMSO as a base.[80] Unexpected domino reaction, involving all reaction centers of starting cyclopropanes **71**, occurs in case of reaction of the latter with lithium derivatives of aliphatic 1,2- and 1,3-diamines.[81,82] As a result, three new C–N bonds are formed, giving rise to N-heterocyclic compounds **78** with an exocyclic double bond. Formation of these compounds occurs *via* intermediate alk-4-ynylideneamines, which are the condensation products of the corresponding alk-4-ynals with diaminoalkanes. Taking this in account, a new one-pot transition metal-free strategy for the synthesis of various nitrogen-containing fused heterocycles was developed.[83–89]

Another type of chemical transformation of alkynylchlorocyclopropanes comprises the lithium-for-chlorine exchange and subsequent reactions of the lithium derivatives with electrophilic



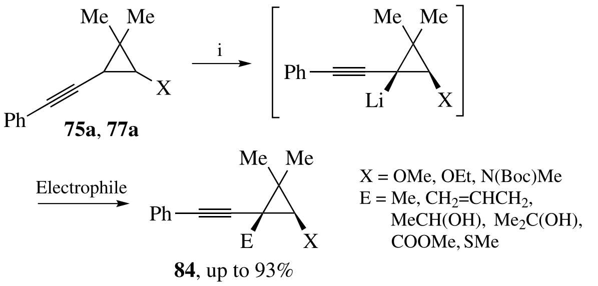
overall yield 67–71%

R^1 = Ph, Bu^t, Bu; R^2–R^4 = H, Me; R^5 = Me, Pr

Scheme 22 *Reagents and conditions*: i, BuLi, –40 to 0 °C, THF; ii, ClCOOMe; iii, 1. CO$_2$, 2. HCl; iv, Me$_2$CO; v, R^5CHO.

reagents. It was shown[90] that this exchange proceeds smoothly with BuLi in THF, and the subsequent treatment of the reaction mixture with carbon dioxide gives rise to 1-alkynylcyclopropanecarboxylic acids **79** in good yields (Scheme 22). Similar regioselective functionalization with formation of tertiary alcohols **80** occurs when acetone as an electrophile is used. However, other electrophilic reagents behave less selectively. Employing methyl chloroformate yields mixtures of isomeric cyclopropylacetylenic (**81**) and vinylidenecyclopropanic (**82**) esters, and aliphatic aldehydes produce only corresponding allenic alcohols **83**. Thus, these reactions can be considered as an efficient synthetic approach to functionalized alkynyl- and vinylidenecyclopropanes.

Synthesized alkynylcyclopropanes **75a**, **77a** with alkoxy- and *tert*-butoxycarbonylamino moieties in the β-position also undergo selective displacement of the hydrogen atom in the propargylic position by the lithium atom.[80,91] Owing to the pronounced directing effect of neighboring substituents having lone electron pairs, this process is highly stereoselective, providing alkynylcyclopropanes **84** with *cis*-arrangement of both functional groups (Scheme 23).

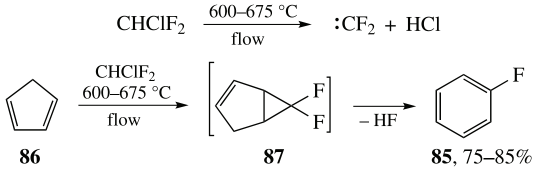


Scheme 23 *Reagents and conditions*: i, BuLi, –70 °C, THF.

5. Synthesis of fluorinated arenes, alkenes and dienes using carbene cyclopropanation reactions and rearrangements of fluorohalocyclopropanes

One of the traditional areas of fundamental, synthetic and applied research of the laboratory of Academician O. M. Nefedov is associated with the development of methodology and new methods for the synthesis of fluoroorganic compounds based on the processes of cyclopropanation of unsaturated substrates using fluorocarbenes and ring-opening transformations of fluorohalocyclopropanes.

The simplest example of the practical use of the carbene methodology in the synthesis of organofluorine compounds is the original one-stage process for the production of fluorobenzene **85** by gas-phase copyrolysis of cyclopentadiene **86** and $CHClF_2$ in a flow reactor at 600–675 °C developed by Nefedov and Ivashchenko in the late 60s (Scheme 24).[92–99]

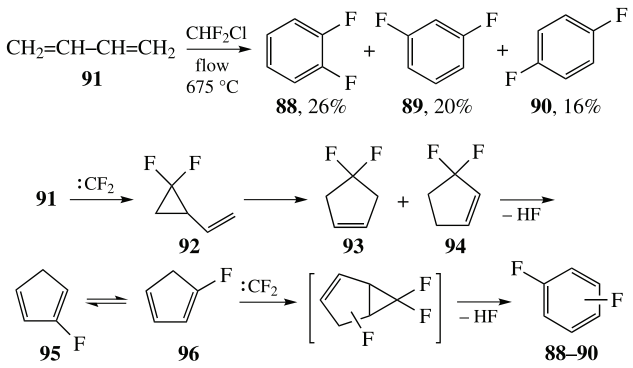


Scheme 24

The process is based on the known ability of $CHClF_2$ to undergo thermal fragmentation to difluorocarbene, which adds to cyclopentadiene **86** to give labile difluorobicyclo[3.1.0]-hexene **87**. The latter is converted into fluorobenzene as a result of ring-expansion and elimination of HF. The optimized process was implemented in the corresponding pilot-industrial technology of commercial production of fluorobenzene.

Similarly,[97,98] fluorotoluenes and 2-fluoronaphthalenes can be obtained by the copyrolysis of $CHClF_2$ with methylcyclopentadienes or indenes.

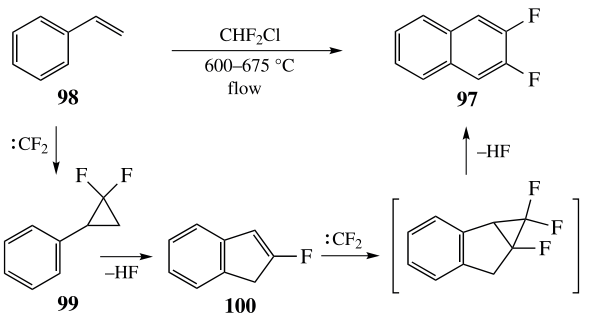
The carbene method can also be successfully applied for the synthesis of difluoroarenes. The most interesting and practically important example is the original one-step synthesis of difluorobenzenes **88**–**90** by copyrolysis of $CHClF_2$ and buta-1,3-diene **91** at 620–700 °C in a flow reactor (Scheme 25).[92–94,97,98,100–103] According to detailed studies,[97,98,103] the process occurs through a sequence of reactions, including the intermediate formation of vinyldifluorocyclopropane **92**, difluorocyclopentenes **93**, **94** and fluorocyclopentadienes **95**, **96**.



Scheme 25

Based on this process, a pilot-industrial technology for the production of difluorobenzenes was developed, including a one-step synthesis of technical mixtures of isomeric difluorobenzenes **88**–**90** followed by their separation by fractional and extractive distillation giving individual isomers with 98–99% purity.[97] The 1,2-difluorobenzene **88** obtained by this procedure was used for the commercial production of 3,4-difluoroaniline and fluoroquinolone antibacterial agent Pefloxacin. Samples of thus obtained 1,3-difluorobenzene **89** were used for the development of a technology for the production of the insecticide Diflubenzyron.

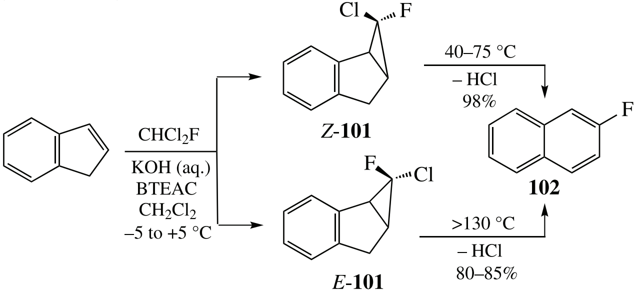
Another original process is a one-step synthesis of 2,3-difluoronaphthalene **97** by copyrolysis of $CHClF_2$ and styrene **98** (Scheme 26).[97,101,104] The reaction proceeds through the intermediate formation of phenyldifluorocyclopropane **99** and 2-fluoroindene **100**.[97,104]



Scheme 26

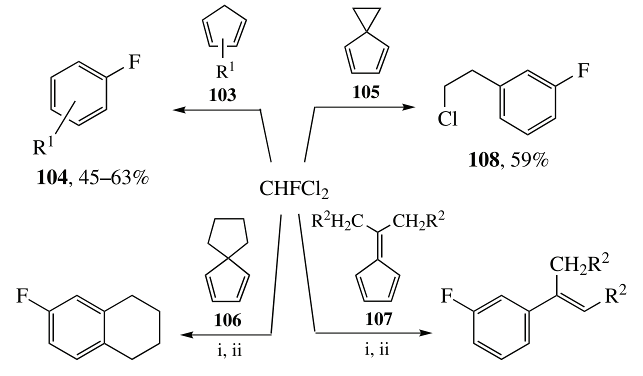
Efficient methods of regioselective C–H-functionalization of naphthalene **97** leading to 2,3-difluoronaphthalene derivatives containing various functional groups in almost any position were developed.[97,105] Among the obtained functional difluoronaphthalenes, compounds with anti-inflammatory, antifungal and cytotoxic activity were found.

In addition to the pyrolytic gas-phase processes, liquid-phase carbene syntheses of fluoroarenes were developed.[97,106,107] The processes are based on the generation of chlorofluorocarbene from $CHCl_2F$ by the action of KOH under the conditions of phase transfer catalysis. Thus, the reaction of $CHCl_2F$ with indene in the presence of aqueous KOH and a catalytic amount of benzyltriethylammonium chloride (BTEAC) at –5 to +5 °C results in two isomeric cyclopropane adducts *Z*- and *E*-**101**, which are converted into 2-fluoronaphthalene **102** at 40–150 °C (Scheme 27).[97,107]



Scheme 27

Similar reactions of alkylcyclopentadienes **103** with $CHCl_2F$ result in the corresponding alkylfluorobenzenes **104** (Scheme 28).[97,106,107]

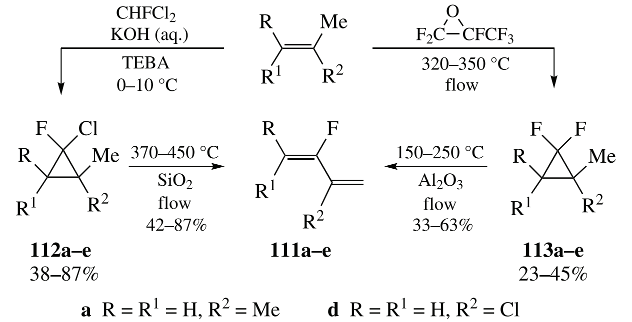


R^1 = Me, Et, Pr^i
R^2 = H, $R^2 + R^2 = (CH_2)_2, (CH_2)_3$

Scheme 28 *Reagents and conditions*: i, KOH (aq., 50%), BTEAC (cat.), CH_2Cl_2, 0–5 °C; ii, 50–150 °C.

Spiro-fused cyclopentadiene derivatives **105** or **106** and fulvenes **107** can also be used in similar syntheses as starting substrates to give 6-fluorotetralin **108**, chloroethyl-3-fluorobenzene **109** or alkenyl-substituted fluorobenzenes **110** (see Scheme 28).[97,106]

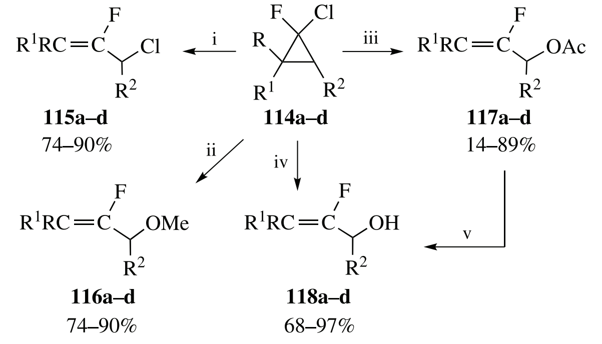
The carbene methodology can also be successfully applied for the preparation of fluorinated dienes.[108–111] Two effective procedures for the synthesis of 2-fluorobut-1,3-dienes **111** from *gem*-chlorofluorocyclopropanes **112** or *gem*-difluorocyclopopanes **113** by gas-phase pyrolysis at 370–450 °C or by gas-phase heterogeneous thermolysis in the presence of aluminum oxide at 150–250 °C were elaborated (Scheme 29).[109–111]



a R = R^1 = H, R^2 = Me
b R^1 = R^2 = H, R = Me
c R = R^2 = H, R^1 = Me
d R = R^1 = H, R^2 = Cl
e R = R^1 = R^2 = Me

Scheme 29

As a result of studies carried out in the last decade, the ability of copper salts to catalyze liquid-phase cyclopropyl–allyl rearrangements of *gem*-chlorofluoro- and *gem*-fluorobromocyclopropanes was established, and new methods for the preparation of fluorohaloalkenes, fluorohaloalkadienes and functional fluoroalkenes from *gem*-fluorohalocyclopropanes were developed (Schemes 30, 31).[112–114] It was found that alkyl- and aryl-substituted *gem*-chlorofluorocyclopropanes **114a–d** undergo cyclopropyl–allyl isomerization when heated in acetonitrile in the presence of catalytic amounts of CuCl to form 2-fluoroallyl chlorides **115a–d** with a yield of 62–98% (see Scheme 30).[112] Under similar conditions, vinylchlorofluorocyclopropanes are isomerized to 2-fluoro- and 4-fluoro-5-chloropenta-1,3-dienes, and 2-fluoro-2-chloro-1,1′-(bicyclopropane)isconvertedinto(*E*)-6-chloro-2-fluorohexa-1,3-diene.[112]



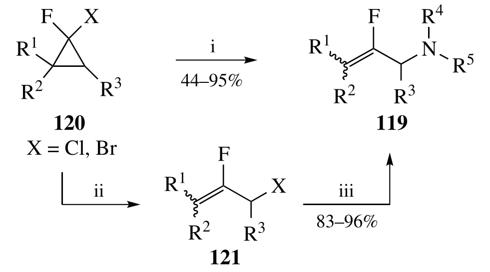
a R = Ph, R^1 = R^2 = H
b R = R^1 = Me, R^2 = H
c R = R^2 = Me, R^1 = H
d R = H, $R^1 + R^2 = (CH_2)_4$

Scheme 30 *Reagents and conditions*: i, CuCl, MeCN, 80 °C; ii, CuCl, MeOH, 60–150 °C; iii, CuCl, NaOAc, AcOH, 100 °C; iv, CuCl, H_2O, dioxane, 100 °C; v, K_2CO_3, MeOH, 20–25 °C.

The CuCl catalyzed ring-opening of chlorofluorocyclopropanes **114** in protic O-nucleophilic solvents (MeOH, HOAc, H_2O) leads to fluoroallyl methyl ethers **116**, fluoroallyl acetates **117** or fluoroallylic alcohols **118** (see Scheme 30).[113] In addition to the direct hydrolysis of chlorofluorocyclopropanes, an alternative way to fluoroallylic alcohols **118** by reaction of the corresponding acetates **117** with K_2CO_3 in MeOH was also developed (see Scheme 30).[113]

Based on the catalytic transformations of *gem*-fluorohalocyclopropanes, an efficient method for the preparation of various fluoroallylamines **119** was also found (Scheme 31).[114]

Two versions of such syntheses were developed, including ring-opening of *gem*-fluorohalocyclopropanes **120** in the presence of amines, or a two-step process involving preliminary



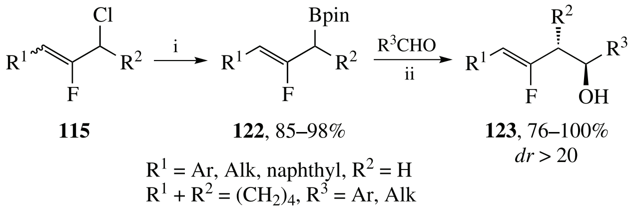
a R^1 = Ph, R^2 = R^3 = H
b R^1 = R^2 = Ph, R^3 = H
c $R^1 + R^2 = (CH_2)_4$, R^3 = H
d $R^2 + R^3 = (CH_2)_4$, R^1 = H
e R^1 = cyclopropyl, R^2 = R^3 = H

R^4, R^5 = Bn, 4-$MeOC_6H_4$, Me, OMe, $(CH_2)_3CH(CO_2Me)$, *c*-C_6H_{11}
$R^4 + R^5 = (CH_2)_2O(CH_2)_2$

Scheme 31 *Reagents and conditions*: i, HNR^4R^5, CuBr, DIPEA, dioxane, 100 °C, 5 h; ii, CuBr, MeCN, 100 °C, 5 h; iii, HNR^4R^5, K_2CO_3, MeCN, 20–25 °C, 2 h.

isomerization of cyclopropanes **120** into 2-fluoroallyl halides **121** followed by nucleophilic substitution of a halide by amines (see Scheme 31).[114]

The found method of catalytic isomerization of *gem*-fluorohalocyclopropanes stimulated a number of new studies related to the synthesis of fluorinated organoelement compounds. Thus, in a recent work by Novikov and Nefedov,[115] an efficient method for the synthesis of (2-fluoroallyl)pinacolboronates **122** with high *Z*-selectivity was developed. The method is based on Pd-catalyzed borylation of 2-fluoroallyl chlorides **115** prepared by catalytic isomerization of alkyl- and arylsubstituted *gem*-chlorofluorocyclopropanes **114**. The obtained fluoroallylboronates **122** showed high efficiency as reagents for diastereoselective 2-fluoroallylboration of aromatic and aliphatic aldehydes producing *anti*-3-fluorohomoallylic alcohols **123** (Scheme 32).



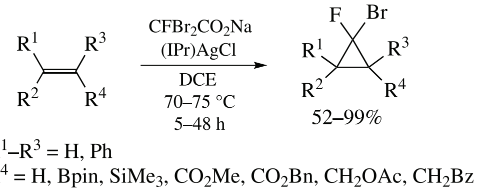
115

122, 85–98%

123, 76–100%
dr > 20

Scheme 32 *Reagents and conditions*: i, B_2pin_2, $[(2\text{-MeAll})PdCl]_2$ (2 mol%), TMEDA, DCE, 60 °C, 3–24 h; ii, R^3CHO (1.2 equiv.), room temperature, 1–3 days.

Among the latest interesting developments of the laboratory in the field of fluorocarbene and fluorocyclopropane chemistry, the recently found new effective method for bromofluorocyclopropanation of alkenes based on the decomposition of $CFBr_2CO_2Na$ catalyzed by silver N-heterocyclic carbene complexes should be noted (Scheme 33).[116]



Scheme 33

In contrast to the commonly used processes for generating bromofluorocarbene from $CHBr_2F$ by the action of alkali bases under the conditions of phase transfer catalysis, the newly found method can also be successfully used to obtain fluorobromocyclopropanes with electron-acceptor substituents, as well as groups sensitive to strong bases or acids (silyl and boronyl substituents).

6. Group 14 carbene analogs

Various species possessing electronic structures analogous to those of carbenes exhibit a reactivity pattern, which is also similar to that of carbenes. It is reasonable to consider them as carbene analogs. The definition of the latter term given by Volpin *et al.*[117] was refined by Nefedov and Manakov:[118] carbene analogs are species having (i) at least one lone pair of s or p electrons or two unpaired electrons on the central atom, (ii) at least one unoccupied p orbital or two electrons in two p orbitals, (iii) no unoccupied d level with a quantum number lower than that of the valence p electrons, and (iv) can form one sp^2 or two sp^3 covalent bonds. Thus, according to this definition, neutral derivatives of monovalent B and Al, divalent Si, Ge, Sn, and Pb, and monovalent N, P, As, and Sb should be considered as carbene analogs. This meaning of the term ‘carbene analogs’ is relevant to this day.[119]

While studying chemistry of carbenes, it was reasonable to pay attention to chemistry of carbene analogs as well. Therefore, many studies in the laboratory were devoted to exploration of reactions with participation of the Group 14 carbene analogs and investigations of these carbene analogs themselves using various physicochemical methods.

In 1966, the first stable complex of germylenes with n-donor molecules was synthesized by the reaction of trichlorogermane, $HGeCl_3$, with an excess of 1,4-dioxane (Scheme 34).[120]

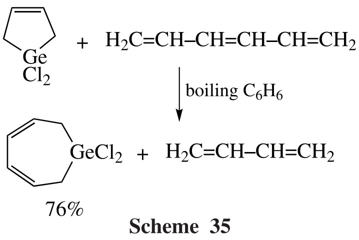
$$HGeCl_3 + C_4H_8O_2 \xrightarrow[\text{temperature}]{\text{room}} \underset{100\%}{GeCl_2{\cdot}Diox + HCl}$$

Scheme 34

By that time, germylenes, derivatives of divalent germanium, and, in particular, $GeCl_2$, were already known as labile intermediates. Moreover, GeI_2 and GeF_2 were isolated as stable salts, and GeI_2 underwent some reactions characteristic of carbenes, but under rather vigorous conditions, which were, apparently, necessary to shift the equilibrium between the salt and monomeric forms to the latter.[118] The synthesis of $GeCl_2{\cdot}Diox$, which is rather low sensitive to oxygen and moisture from air and completely stable under an inert atmosphere, demonstrated for the first time a principal possibility of transformation of a labile intermediate into a rather stable reagent with analogous reactivity. The $GeCl_2{\cdot}Diox$ was characterized by different spectroscopic methods and X-ray analysis.[121,122] A number of other crystalline complexes of $GeCl_2$ coordinated to O, N, P, and As atoms were synthesized from this complex and characterized by different physicochemical methods.[121,123]

The reactivity of $GeCl_2{\cdot}Diox$ was studied in detail. It was shown that it actively reacts with organic halides with mobile halogen atoms by the carbene mechanism.[124,125] As was revealed in a kinetic study, in the case of the interaction with benzyl chloride, the reaction occurs *via* the step of dissociation of the complex into free $GeCl_2$ and dioxane. The activation energy for the $GeCl_2$ insertion into the C–Cl bond of benzyl chloride (14.1 ± 1.5 kcal mol^{-1}) was obtained, which presented the first experimentally measured activation energy for insertion of any germylene into single bonds.[124] The study of reactions of different $GeCl_2{\cdot}B$ complexes with conjugated polyenes showed that they often lead to products of formal [1+4]- and even [1+6] cycloadditions, and the [1+4] cycloaddition is concerted.[126] In the course of the latter series of studies, an unusual reaction of 1,1-dichloro-1-germacyclopent-3-ene with 2,3-dimethylbuta-1,3-diene and hexa-1,3,5-triene was revealed,[127] which was called transgermylenation reaction (Scheme 35).

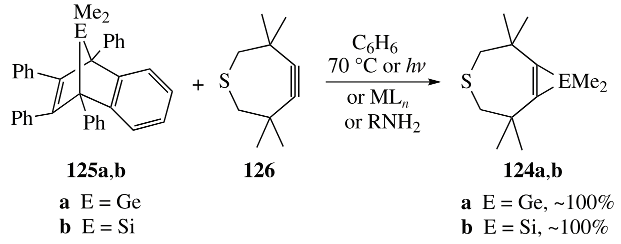
Due to availability, stability and high reactivity, the dioxane complex of $GeCl_2$ has found wide applications in the synthesis of germanium containing compounds. The similar 2,2′-bipyridyl complex of $SiCl_2$, *viz.* $SiCl_2{\cdot}(Bipy)_2$, was synthesized only three years later.[128] However, it turned out to be not so attractive from a synthetic point of view. Synthetically convenient complexes of $SiCl_2$, *viz.* N-heterocyclic carbene stabilized dichlorosilylenes,



Scheme 35

NHC·$SiCl_2$, where NHC is 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene or 1,3-dimesitylimidazol-2-ylidene, were obtained only recently.[129]

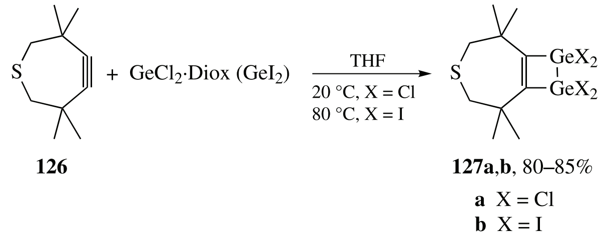
One of the important ways for the synthesis of cyclopropenes is the [2+1] cycloaddition of carbenes to alkynes.[9] Therefore, the cyclopropene chemistry is closely related to the carbene chemistry. The first 1-silacycloprop-2-enes, silicon containing cyclopropene analogs, were obtained by a similar reaction of silylenes in the mid-1970s.[130,131] The first germirene **124a** in the pure form was obtained in a quantitative yield by the reaction of Me_2Ge generated from **125a** with an equimolar amount of acetylene **126** (Scheme 36) under the framework of collaboration of the laboratory of Nefedov with the Institute for Organic Chemistry and Biochemistry of Hamburg University and characterized by X-ray diffraction.[132] To compare structural characteristics and reactivities of germirenes and silirenes, analogous silirene **124b** was obtained by the reaction of Me_2Si photochemically generated from **125b** with acetylene **126** (see Scheme 36).[133,134]



Scheme 36

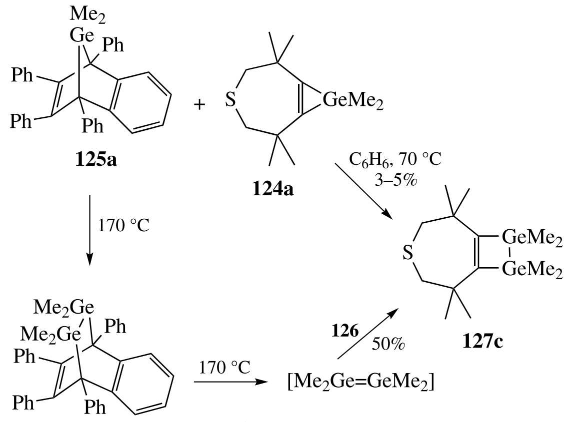
Like silirene **124b**, germirene **124a** is characterized by anomalously low-field signals of double bonded carbon atoms in the ^{13}C NMR spectra (158 and 154 ppm for **124b** and **124a**, respectively). According to X-ray data, the most distinctive feature of both silirene **124b** and germirene **124a** is a considerable shortening of the E–C(sp^2) single bonds in the three-membered rings in comparison with the corresponding acyclic compounds, which could be related to some aromaticity of these heterocyclopropenes. Germirene **124a** was found to be extremely stable (up to 200 °C in vacuum), although sensitive to oxygen. Its reactions mainly proceed with the rupture of one of the Ge–C(sp^2) bonds. According to semi-empirical calculations, the reluctance of both **124a** and **124b** to thermal destruction into starting acetylene and EMe_2 is related to the ring strains in 1-thiacyclohept-4-yne **126**.

Interaction of $GeCl_2$·Diox (THF, 20 °C) and GeI_2 (THF, 80 °C) with **126** produced the corresponding 1,1,2,2-tetrahalo-1,2-digermacyclobut-3-enes **127a**,**b** (Scheme 37).[135,136] These compounds were the first representatives of digermacyclobutenes.



Scheme 37

Soon after that, digermacyclobutene with alkyl substituents at the germanium atoms, 1,1,2,2-tetramethyl-1,2-digermacyclobut-3-ene **127c**, was obtained both by the interaction of digermene $Me_2Ge{=}GeMe_2$ with acetylene **126** and by the insertion of $GeMe_2$ into the endocyclic Ge–C bond of germirene **124a** (Scheme 38), although in a very low yield in the latter case.[137]

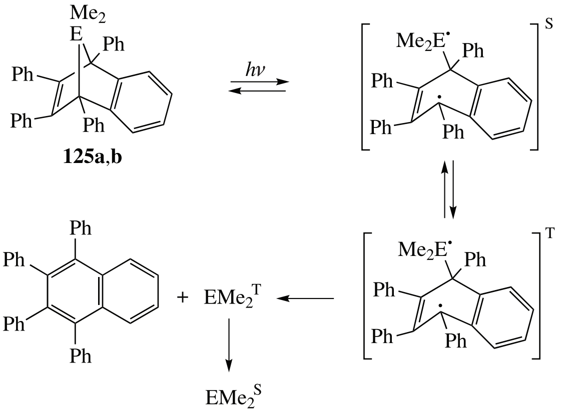


Scheme 38

The latter reaction represented the first example of [2+2] cycloaddition of digermenes to multiple bonds.

Digermacyclobutenes **127** are thermally stable (up to *ca.* 200 °C) and, in contrast to disilacyclobutenes known to date, are insensitive to oxygen of air. Like germirenes, digermacyclobutenes are characterized by low-field signals (163–175 ppm) of double bonded carbon atoms in the ^{13}C NMR spectra. According to the X-ray data, the four-membered cycles of these compounds are flat, the C=C bonds are slightly shortened, while the Ge–Ge bonds are significantly more shortened than in acyclic compounds. The chemical behavior of digermacyclobutenes **127** is determined by the high reactivity of the strained Ge–Ge bond, which is prone to rupture. The effect of substituents at the germanium atoms manifests itself in the fact that **127c** more easily reacts with nucleophilic reagents, while **127a** is more inclined to reactions with electrophiles.

In collaboration with the Institute of Chemical Kinetics and Combustion of the Russian Academy of Sciences, the mechanism of photochemical generation of EMe_2, E = Si, Ge, from 7-heteronorbornadienes **125b** and **125a**, respectively, was explored using the methods of spin chemistry.[138,139] According to the data obtained with the use of the CIDNP ^1H technique and by detection of magnetic field effects, the photoinduced decomposition of **125a** and **125b** proceeds as shown in Scheme 39.



Scheme 39

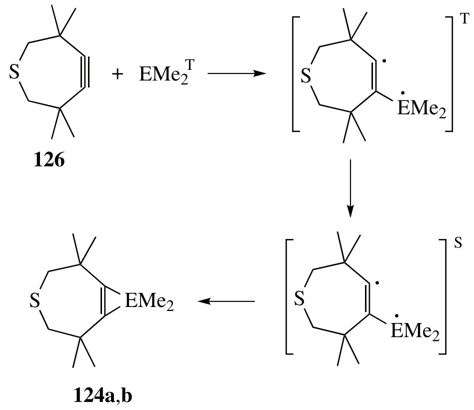
An analysis of the CIDNP effects observed in the course of insertions of thus formed $SiMe_2$ and $GeMe_2$ into the C–Br bond of $PhCH_2Br$ and into the Sn–Cl bond of Me_3SnCl, respectively, showed that the reactions proceed with singlet EMe_2 species by an abstraction–recombination mechanism *via* intermediate formation of singlet radical pairs (Scheme 40) rather than by a one-step concerted mechanism often assumed for such insertion reactions.[138]

$$EMe_2^S + RHal \rightarrow [R^{\bullet\bullet}EMe_2Hal]^S \rightarrow REMe_2Hal$$

$$E = Si,\ RHal = PhCH_2Br;\ E = Ge,\ RHal = Me_3SnCl$$

Scheme 40

At the same time, when thiacycloheptyne **126** was used as a scavenger, a triplet EMe_2 trapping (Scheme 41) was detected by the CIDNP ^{1}H technique.[140] Thus, in this case, the rates of the additions of triplet EMe_2 to acetylene **126** turned out to be higher than those of the intersystem crossing, and thiacycloheptyne **126** proved to be highly reactive not only towards singlet, but also to triplet carbene analogs.[140] This was the first observation of any reactions with participation of triplet silylenes or germylenes. Later on, triplet $SiMe_2$ was also trapped with CCl_4 under the same conditions.[141]



Scheme 41

In collaboration with the Institute of Chemical Physics of the Russian Academy of Sciences using laser flash photolysis techniques, rate constants for reactions of $GeMe_2$ in its ground singlet state with a number of substrates were measured in solutions.[142] Though, apparently, the obtained values were somewhat affected by the $GeMe_2$ complexation with the precursor and photolysis co-product molecules as it was shown in further time resolved gas-phase kinetic studies (*vide infra*), together with other studies of liquid-phase kinetics carried out by that time, they provided the first quantitative ideas about the reactivity of germylenes. In addition, the ability of $GeMe_2$ to form a complex with PPh_3, a rather strong Lewis base, was revealed.[143] Later on, it was shown that $SiMe_2$ forms complexes with CCl_4 and $CHBr_3$.[141,144]

In collaboration with the laboratory of P. P. Gaspar (Department of Chemistry, Washington University, St. Louis, Missouri, USA), the first germylene radical anion together with its tin analog were obtained (Scheme 42) and characterized by ESR spectroscopy.[145] A UV spectrum of the germylene radical anion was also recorded. Both radical anions were shown to be π-radicals according to the traditional σ,π-nomenclature.[145] Until now, chemistry of radical ions of carbene analogs remains a rather poorly studied area.

In the mid-1990s, a collaboration with the Laboratory of Chemical Kinetics at the Department of Chemistry of University of Reading, GB, was started. In the course of it, under the guidance of R. Walsh, the first absolute rate constants and activation parameters were obtained for a series of germylene reactions. We will not dwell on these results here as they were analyzed in detail in reviews by Becerra and Walsh.[146,147] It should be mentioned, however, that the kinetics of the majority of reactions of both silylenes and germylenes[146,147] indicates the involvement of weakly bound complexes between the reactants, which are formed at the first step due to an electrophilic attack of the carbene analog to the substrate typically representing a weak Lewis base. Additional important experimental evidences for the existence of such complexes were obtained in the studies of kinetic isotope effects.[148] Quantum chemical calculations also corroborate the existence of the complexes.[146–148] However, direct spectroscopic evidences of their existence were obtained only recently (*vide infra*).

$$[(Me_3Si)_2CH]_2E \xrightarrow[\text{room temperature (Ge) or −80 °C (Sn)}]{\text{Na, THF}} [(Me_3Si)_2CH]_2E^{-\bullet}\,Na^+$$

$$E = Ge,\ Sn$$

Scheme 42

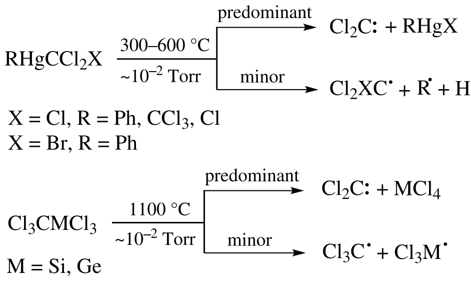
7. Matrix IR studies of carbenes, carbene analogs, and related intermediates

Direct spectroscopic detection of labile intermediates is the best way to confirm their existence. In addition, studies of this kind provide valuable information concerning the spatial and electronic structures of the detected intermediates, making these elusive species closer to stable compounds in terms of their understanding. One of the powerful experimental methods of investigating chemical intermediates is matrix isolation combined with conventional spectroscopic methods. Matrix isolation IR spectroscopy studies were started in the laboratory of O. M. Nefedov in the late 60s. They included investigations of carbenes, carbene analogs, compounds with double bonded silicon and germanium atoms, organic radicals, and other labile species. These studies were supplemented with mass-spectrometric investigations carried out partly in this laboratory and partly in the laboratory of J. Tamas at the Central Research Institute of Chemistry of the Hungarian Academy of Sciences, Budapest, and with high-temperature electron diffraction studies conducted in the laboratory of I. Hargittai at the Department of Structural Studies of the Hungarian Academy of Sciences, Budapest.

7.1. Carbenes

During the 1960s–1970s, much attention in matrix isolation studies all over the world was paid to the stabilization and investigation of triatomic carbenes.[149] Several new pyrolytic precursors of singlet dichlorocarbene, Cl_2C**:**, were investigated in Nefedov's laboratory (Scheme 43) in part in collaboration with the laboratory of J. L. Margrave, Department of Chemistry, Rice University, Houston, Texas, USA.[150–154] The use of these precursors made it possible to achieve the best resolution in IR spectra of chlorine isotopic splitting of the stretching vibrations of this species and, on this basis, to calculate the most accurate value of the valence angle in it.[153] Bromochlorocarbene, ClBrC**:**, along with $CClBr_2$, was also generated from $PhHgCClBr_2$ and stabilized in an Ar matrix.[152]

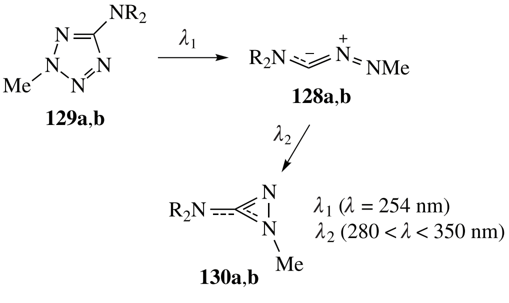
Later on, triplet $(CF_3)_2C$**:**, $(CF_3)PhC$**:** and singlet ClPhC**:**, BrPhC**:** were obtained in matrices by photolysis of corresponding diazirines, and characterized by their IR spectra and by their trapping in matrices with several scavengers.[154,155] The [1+2]



Scheme 43

cycloaddition of triplet cyclopentadienylidene to ethylene was also directly monitored by IR spectroscopy, demonstrating for the first time that the latter compound can be an efficient trapping agent for carbenes in matrices.[154,155]

C-Amino-substituted nitrilimines **128a**,**b**, exhibiting significant carbenic character, were generated[156] by photolysis of the corresponding 2,5-disubstituted tetrazoles **129**. These species, which are the primary products of the photodecomposition of tetrazoles, undergo isomerization into cyclic diazirines **130a**,**b** upon prolonged UV irradiation (Scheme 44).



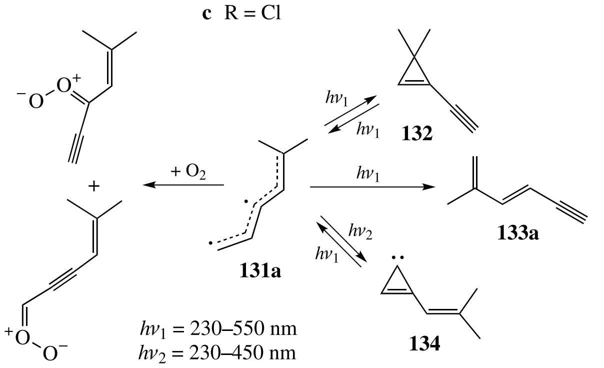
129a,**b** **128a**,**b** **130a**,**b**

a R = H
b R = Me

Scheme 44

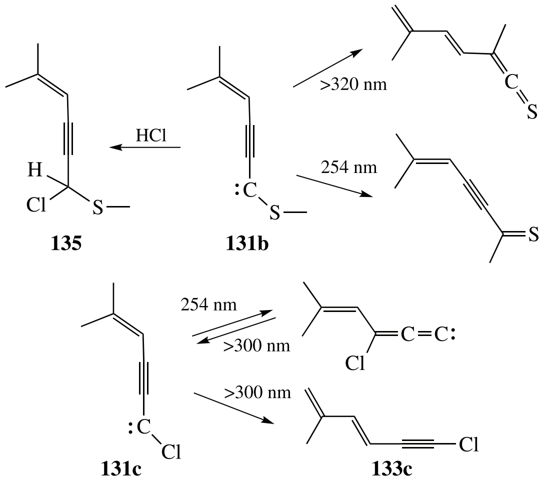
3*H*-Pyrazoles **68** were found to be good photochemical precursors of carbenes **131** with extended chains of conjugation for matrix isolation studies (Scheme 45).[73,74,157,158] Triplet 5-methylhexa-1,2,4-triene-1,3-diyl **131a** was characterized by its IR and ESR spectra.[157,158] According to the obtained experimental and theoretical data, the electronic structure of carbene **131a** has the principal features characteristic of both triplet ethynylcarbenes and triplet vinylcarbenes. However, two major photoinduced rearrangements (to **132** and **133a**) observed for this carbene were those typical of vinylcarbenes, and only the minor rearrangement (to carbene **134**) was characteristic of ethynylcarbenes (see Scheme 45). As can be expected, addition of oxygen to **131a** occurred at both ends of the propargylenic moiety (see Scheme 45).

According to the obtained data, the carbene centers in singlet (4-methylpent-3-en-1-ynyl)methylthiocarbene **131b** and (4-methylpent-3-en-1-ynyl)chlorocarbene **131c** are located at the C atoms bearing thiomethyl or chlorine substituent, respectively.[73,74] In particular, carbene **131b** readily reacts with HCl during annealing of matrices with formation of only one product **135** (Scheme 46).[73] All observed photoinduced rearrangements of **131b** involve the thiomethyl group,[73] whereas those of **131c** are analogous to rearrangements known for vinyl- and ethynylcarbenes (see Scheme 46).[74]



68a–c **131a–c** **131a** **132** **133a** **134**

Scheme 45



135 **131b** **131c** **133c**

Scheme 46

7.2. Carbene analogs

In a continuation of the studies devoted to detection of dichlorocarbene, pyrolysis of hexachlorodisilane, Si_2Cl_6, was examined using matrix IR spectroscopy, and this compound turned out to be a very good pyrolytic precursor of $SiCl_2$ (Scheme 47).[153,159] Subsequently, Si_2Cl_6 found a wide application both in matrix isolation studies and in preparative chemistry as one of the best thermal sources of $SiCl_2$.

$$Cl_3SiSiCl_3 \xrightarrow[\sim 10^{-2}\ \text{Torr}]{> 900\ ^\circ\text{C}} SiCl_2 + SiCl_4$$

Scheme 47

The obtained matrix IR spectra of $SiCl_2$[153] generated from Si_2Cl_6 as well as those of $GeCl_2$[160] generated by thermal depolymerization of $(GeCl_2)_x$ were characterized by well resolved isotopic splitting of stretching vibration bands, which was practically not complicated by matrix splitting. This made it possible to determine valence angles in these species for the first time.[153,160] The valence angles obtained later using the gas electron diffraction[161,162] proved to be very close to those calculated from IR data. The isotopic splitting of $SiCl_2$ bands comprised that due to both Cl and Si isotopes, and a significant part of the splitting components was established.[153] A later study using FTIR spectroscopy[163] made it possible to find several additional minor components and, in addition, demonstrated that $SiCl_2$ is able to form donor–acceptor complexes with N_2. This was the first observation of N_2 complexes of any silylenes, which followed by a report of Maier *et al.*,[164] who detected analogous complex of SiH_2. These results, in particular, indicate that the use of nitrogen matrices in silylene studies is undesirable.

The question of the ability of carbene analogs to form complexes with Lewis bases was of particular interest at the turn of the century, but mainly complexes of carbene analogs with relatively strong Lewis bases were known.[165] Therefore, in a series of matrix IR studies, it was demonstrated that SnF_2, one of triatomic carbene analogs, which is characterized by stretching vibrations lying in the mid-IR region, can form complexes with rather weak Lewis bases such as N_2, MeCl, PhH, PhCl, PhMe, and hept-1-yne.[166] In subsequent studies of Egorov's laboratory,[167–171] which grew out from a part of Nefedov's laboratory, a series of labile complexes of $SiCl_2$ with a number of Lewis bases (allyl chloride, allyl bromide, buta-1,3-diene, HCl, CO_2, CO) was obtained in Ar matrices and characterized using IR spectroscopy, thus showing principal ability of silylenes to form complexes with weak Lewis bases in confirmation of the conclusion made on the basis of kinetic and theoretical studies (*vide supra*). By photolysis of complexes of $SiCl_2$ with buta-1,3-diene, labile 1,1-dichloro-2-vinyl-1-silacyclopropane was obtained and characterized.[168]

7.3. Compounds with double-bonded silicon and germanium atoms

Another type of derivatives of low-coordinated Group 14 elements is represented by compounds containing double bonds at these elements. During the mid-1970s–end 1990s period, Nefedov's laboratory carried out pioneering works, both independently and through international collaboration, in the area of direct spectroscopic detection of labile derivatives of double-bonded silicon and germanium. These compounds possessing a much higher reactivity than their carbon analogs are of practical interest as monomers for the preparation of new polymers, ceramics, and semiconducting materials and also fundamentally important for basal theory of chemical structure, especially, by taking into consideration that yet in early-mid 60s the very existence of molecules with double bonds at silicon and germanium was ruled impossible.

The first direct spectroscopic evidence for the ability of silicon to form double bonds with carbon had been obtained using cryogenic matrix isolation technique in 1976 by Mal'tsev, Khabashesku, and Nefedov[172] by detection of dimethylsilene, $Me_2Si{=}CH_2$, and slightly later by Chapman *et al.*[173] and Chedekel *et al.*[174] by detection of trimethylsilene, $Me_2Si{=}CHMe$. A detailed analysis of experimentally observed vibrational frequencies of $(CH_3)_2Si{=}CH_2$, $(CD_3)_2Si{=}CH_2$, $CD_3(CH_3)Si{=}CH_2$, $(CH_3)_2Si{=}CD_2$, and $(CD_3)_2Si{=}CD_2$ made it possible to optimize the set of force field constants describing these molecules and unambiguously assign the IR band of dimethylsilene at 1003 cm^{-1} to the Si=C stretching mode.[175–177]

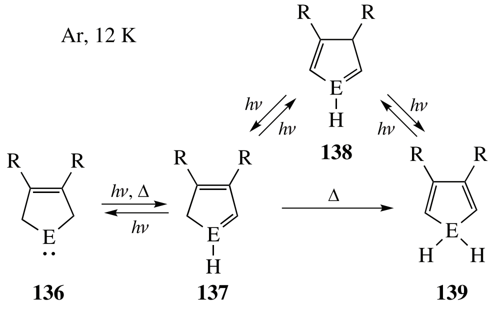
The followed up worldwide research involved labile species with double bonds formed by other elements of Group 14 with heteroatoms. Despite modern advances in the synthesis of molecules with the E=X bonds, where E is a Group 14 element, X = C, Si, Ge, N, P, O, S, *etc.*, which are stabilized due to electronic and steric effects of various specific substituents,[178–180] the studies of the species with simple substituents (H, Me, OMe, *etc.*) still retain their significance since they provide the information on the least perturbed double bonds and form a basis for benchmarking of theoretical modeling.

Later on, in collaboration with the laboratory of J. Tamás (Central Research Institute for Chemistry of Hungarian Academy of Sciences, Budapest), the mechanisms of vacuum pyrolysis of a series of potential precursors of unstable silanones $R_2Si{=}O$ were studied by pyrolysis mass spectrometry (PMS) and cryogenic matrix IR spectroscopy methods.[181–188] Diels–Alder adducts of 2,2-dimethyl- and 2,2,6-trimethyl-2-silapyranes with maleic anhydride and 6-oxa-3-silabicyclohexanes were found to be the most suitable precursors for silanones $Me_2Si{=}O$, $(MeO)_2Si{=}O$, and $Ph_2Si{=}O$, which were successfully stabilized in argon matrices.[181,184,185] An analysis of the experimentally measured frequencies of d_o- and d_6-dimethylsilanones assisted with the force field calculations made it possible to perform their complete assignment to fundamental modes, including the Si=O stretching mode [1210 cm^{-1} in $Me_2Si{=}O$ and 1215 cm^{-1} in $(CD_3)_2Si{=}O$].[182] These frequencies along with the force constant $K_{Si=O} = 8.32$ mdyn Å^{-1} and bond order $N_{Si=O} = 1.5$ were the first physical characteristics of the double bonding between the silicon and oxygen atoms in dimethylsilanone. Formation of cyclodimers of dimethyl- and dimethoxysilanones, novel 4-membered silaheterocycles unstable under ambient conditions, was also detected using PMS, and their ionization energies were measured.[183,186]

Several labile prototype species containing double-bonded Ge atoms, *viz.*, $Me_2Ge{=}O$,[189] $Me_2Ge{=}S$,[190] and $Me_2Ge{=}CH_2$,[191,192] were then stabilized in cryogenic matrices for the first time. Complete assignment of their IR bands to normal vibrational modes was carried out. The obtained characteristics of the Ge=O bond in dimethylgermanone are $\nu(Ge{=}O) = 972$ cm^{-1}, $K_{Ge=O} = 7.04$ mdyn Å^{-1}, and $N_{Ge=O} = 1.72$.[189] An IR band of $Me_2Ge{=}CH_2$ at 847.2 cm^{-1}, which lies significantly higher than the typical ν(Ge–C) bands (~600 cm^{-1}) was assigned to the Ge=C stretching mode.[191] On the basis of experimental and theoretical data, it was concluded that dimethylgermene has lower kinetic and thermodynamic stability than dimethylsilene.[192] The PMS detection of labile dimethylgermathione, $Me_2Ge{=}S$, was also performed.[190] It gave an ionization energy value that was in good agreement with the value obtained earlier by photoelectron spectroscopy.[193]

In a collaboration with laboratories of E. A. Chernyshev (State Research Institute of Chemistry and Technology of Organoelement Compounds, Moscow, RF) and J. Michl (University of Colorado, Boulder, USA), multistep thermal and photoinduced interconversions occurring in the five-membered Si and Ge containing cycles were revealed.[194–198]

These interconversions involve corresponding carbene analogs [1-sila(germa)cyclopent-3-ene-1,1-diyls **136**], isomeric sila- or germadienes **137**, **138**, and 1*H*-siloles or 1*H*-germoles [1-sila(germa)cyclopenta-2,4-dienes] **139**, respectively (Scheme 48). All species were characterized by their UV-VIS and IR spectra.[194,195,197] In addition, the ionization potential of unsubstituted silole was measured for the first time in a PMS study.[196] These studies provided the first direct spectroscopic evidence of the existence of labile parent silole and germole, synthesis of which had unsuccessfully been attempted for over 50 years. 1-Sila(germa)cyclopenta-1,3-dienes and their 1,4-isomers observed in these studies were among the first representatives of these classes of compounds revealed by that time by direct or indirect methods. The obtained data unambiguously indicated the presence of strong π-conjugation in the E=C–C=C and C=E–C=C chains, with a stronger conjugation occurring for E = Si.[197] Finally, the Ge containing system study showed a reversible character of the previously unknown germylene-to-germene photoinduced isomerization.[197,198]



E = Si, R = H, Me
E = Ge, R = H
thermal transformations (Δ) were only studied for E = Si

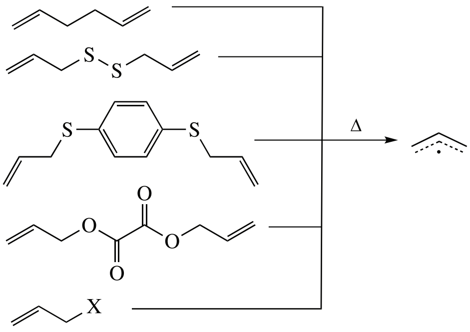
Scheme 48

7.4. Radicals

In addition to studies of carbenes and their analogs, matrix isolation was successfully used for IR spectroscopic detection of different radicals. As noted above, halogen substituted methyl radicals were formed along with carbenes during the pyrolysis of mercury derivatives $RHgCCl_2X$, X = Cl, Br, and silicon and germanium derivatives Cl_3CECl_3, E = Si, Ge (see Scheme 43).[150–154]

1-Chloro-2,2,2-trifluoroethyl radical ($CF_3HClC^\bullet$) important for atmospheric chemistry was generated by pyrolysis of halothane ($CF_3CHClBr$) and detected for the first time by matrix IR spectroscopy.[199,200] Corresponding peroxyl radical $CF_3CHClOO^\bullet$ was obtained by co-condensation of halothane pyrolysis products and molecular oxygen in argon matrices.[200] The fundamental bands of O–O and C–O stretching vibrations of this radical (1102.1, 972.7 cm^{-1}) were identified on the basis of their red shifts in the spectra of the ^{18}O substituted derivatives.

Considerable attention was paid to organic radicals containing unsaturated hydrocarbon and aromatic substituents. For some previously detected species of this type, new studies using more sophisticated technique resulted in refinement of earlier results. Allyl radical generated by vacuum pyrolysis of different compounds (Scheme 49) was detected in an Ar matrix using IR spectroscopy.[201,202] The band of ν_s(CCC) stretching vibration of allyl radical at 1242 cm^{-1} was found to lie between the corresponding frequencies typical of single and double carbon–carbon bond stretching vibrations. The structure of allyl radical was determined in electron diffraction experiments.[203] This was the first electron diffraction study of an unstable organic molecule. The results obtained by matrix IR spectroscopy and the gas-phase electron diffraction firmly indicate considerable delocalization of electron density along the π-system of allyl radical.



X = I, Cl, Br, $SiMe_3$

Scheme 49

The reaction of allyl radical with O_2 resulted in the formation of allylperoxyl radical $CH_2{=}CHCH_2OO^\bullet$ presented by two conformers. UV photolysis (λ > 250 nm) of allylperoxyl radical produced acryloyl radical $CH_2{=}CH(O)C^\bullet$.[204]

Perfluorinated allyl radical C_3F_5 formed in the pyrolysis of perfluorohexa-1,5-diene or 3-iodopentafluoroprop-1-ene was studied by pyrolytic mass spectrometry and matrix IR spectroscopy.[205] Its photolysis in matrices gave perfluoroprop-2-enyl radical ($F_2C{=}C^\bullet{-}CF_3$).[206]

Complete IR spectrum was obtained for propargyl radical generated by vacuum pyrolysis of propargyl iodide or dipropargyl oxalate, which made it possible to carry out force field calculations and reveal the unpaired electron density delocalization in this radical.[207]

IR spectra of benzyl radical and its deuterated derivatives $C_6H_5CD_2^\bullet$ and $C_6D_5CH_2^\bullet$, which were generated by vacuum pyrolysis of corresponding benzyl bromides, as well as by pyrolysis of 1,2-diphenylethane, were recorded for the first time in argon matrices.[208] The spectrum of benzyl radical was used for identification of this species by other researches.[209,210] An important feature of the IR spectrum of the benzyl radical is a significant decrease in the frequencies of stretching vibrations of the benzene ring compared to toluene. The same effect was observed for the perfluorobenzyl radical ($C_6F_5CF_2$).[211]

Concluding remarks

The results both summarized above and not included in the considerations undoubtedly contributed to the understandings of modern chemistry of carbenes, carbene analogs, related intermediates, and small-sized cycles, which is built by the joint efforts of numerous research groups around the world. Formation and development of particular fields in this area of chemistry are reflected in a number of reviews and monographs by Nefedov and co-workers.[3,4,21,30,97,118,212–223] Despite a rather long history, this area of chemistry still remains dynamically developing and constantly bringing up fundamentally new subjects, which are waiting for their detailed analysis.

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