Thermally Induced Cyclopropene–Carbene Rearrangements: An Overview
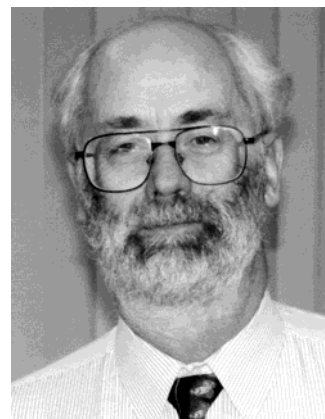
Mark S. Baird

Department of Chemistry, University of Wales, Bangor LL57 2UW, U.K.

Contents

Mark Baird graduated from Queen Mary College, London, in 1965 and went on to obtain a Ph.D. in Cambridge under the supervision of Colin Reese. After postdoctoral work including a year with Harry Wasserman at Yale, he was appointed in 1970 to the academic staff of the University of Newcastle upon Tyne. In 1990, he moved to the University of Wales, Bangor, as Professor of Organic Chemistry. His research interests focused initially on carbene chemistry and, in particular, on cyclopropylidenes. Arising from this he carried on extensive studies on the chemistry of cyclopropenes. This has led to an interest in cyclopropene fatty acids and, more recently, in the very long chain cyclopropane fatty acids present in the walls of many bacterial cells.

I. Introduction

Cyclopropenes are highly strained molecules and, not surprisingly, seek to relieve that strain by reaction with other species, through dimerization, or through rearrangement. For cyclopropenes carrying a hydrogen at C-3, the strain is often reduced through dimerization by an ene reaction; in other cases the cyclopropene forms an apparent [2+2] cycloadduct. When there is no hydrogen at C-3 or in the gas phase where the rate of dimerization is reduced, cyclopropenes often undergo ring opening on heating. Thus, the thermolysis of tetramethylcyclopropene (**1**) at 490 or 260−298 °C leads to dimethylpenta-1,3-dienes **2** and **3**,[1,2] while the bicyclic cyclopropene **4** is converted at 225 °C in a base-washed Pyrex sealed tube at low pressure into the alkyne **5** together with a small amount of diene **6**. This latter reaction is in marked contrast to the photochemical ring opening of **4**, which leads to the allene **7**.[3]
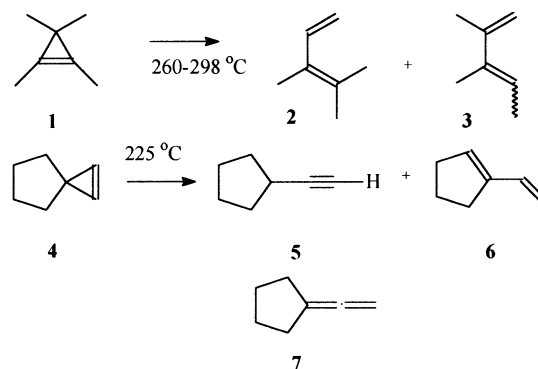

This review will cover an analysis of such processes occurring under thermal conditions. It will not include directly either photochemical examples or those induced through catalysis by a metal-containing species.[4−6] It will also not include the rearrangement

processes of arylcarbenes, which can occur through cyclopropene intermediates.

The literature concerning routes to cyclopropenes[7] contains examples of three types of carbene precursors, vinylcarbenes **8**, cyclopropylidenes **9**, and methylenecarbenes (vinylidenes) **10**, or related carbenoids (Scheme 1). By far the most common of these reactions is the cyclization of a vinylcarbene, often generated by thermolysis of the sodium salt of a tosylhydrazone.[8,9] There are very few examples of the conversion of cyclopropylidenes into cyclopropenes,[10] although 2-silyl systems **9** do rearrange in this way.[11]

Scheme 1
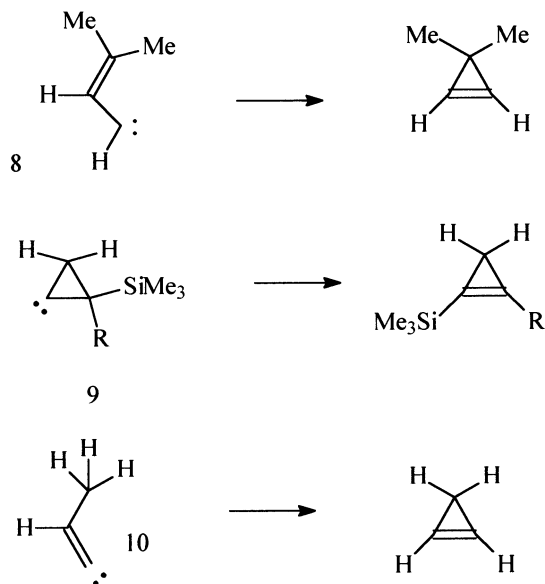
The insertion of a vinylidene, **10**, into an adjacent C—H bond to produce a cyclopropene is also not common in thermal reactions;[12] when observed, it is not usually a high-yield process, and generally competes with other carbene reactions:[13]
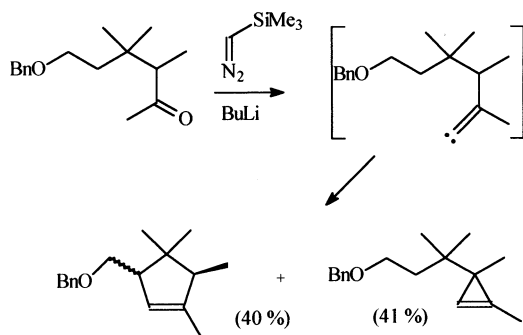

In other cases, products apparently formed by further reaction of a cyclopropene derived in this way have been reported.[14−16] The insertion is seen more frequently in photochemical processes.[17,18]

Each of the general reactions in Scheme 1 has also been observed in the reverse direction, leading to the potential for a series of equilibria, illustrated below for the parent system:
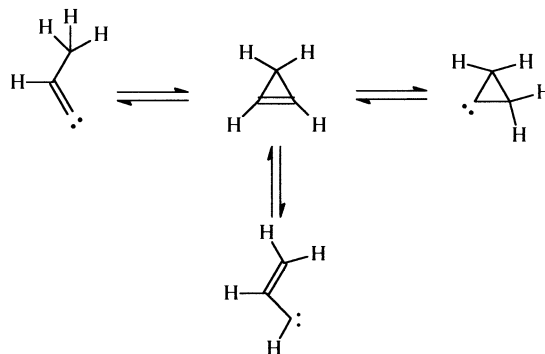
The intermediates or transition states in the reactions involving vinylidenes and cyclopropylidenes only require what may be regarded as second-order changes in the geometry of the carbon skeleton. In the case of singlet vinylcarbenes a monorotation is necessary as shown below; indeed the product on the singlet energy surface has been described as either a vinylcarbene or a diradical, and the reality may depend on the degree of planarity of the product. Moreover, the presence of suitable substituents may dramatically distort the charge distribution in the vinylcarbene, leading to a planar (or indeed nonplanar) structure that can be described as a dipole. The situation is further complicated by the possibility of inversion or rotation at the carbene center, leading to a stereoisomeric *anti* (*trans*) vinylcarbene.
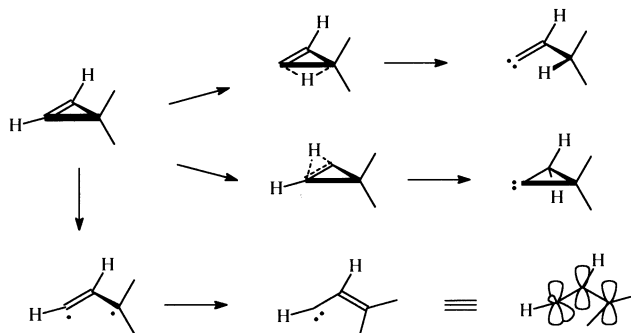
This set of reactions has been extended to try to explain the thermal racemization of allenes,[19] and the thermal interconversion of allenes and alkynes. Indeed, the thermolysis of alkynes under FVP conditions is well established to produce vinylidenes that may again be trapped in a variety of intramolecular processes,[20] while thermolysis of allenes can lead to vinylcarbenes which may be trapped in intramolecular processes:[21]
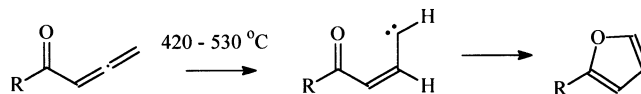
II. The C₃H₄ Energy Surface

Although it undergoes very rapid oligomerization through an ene reaction at below ambient temperature,[7] thermolysis of cyclopropene in the gas phase and at high dilution occurs primarily through a unimolecular isomerization to propyne ($\log A = 13.1$, $E_{act} = 37.3$ kcal/mol). A minor product is allene, which appears to form by two pathways including a radical one.[22] The kinetic data for the isomerization of allene

to propyne have been interpreted in terms of cyclopropene as an intermediate,[23] and deuterium labeling studies produce relative rates that suggest that 50−100% of allene derived from propyne is formed through cyclopropene.[24] Shock tube experiments at 800−1200 K and calculations have confirmed that cyclopropene is an intermediate and produced revised values for transition-state energies.[25,26]

Experimental and theoretical analysis of the structure of vinylmethylenes provided evidence for both *cis*- and *trans*-isomers of ground-state triplets.[27−31] Later calculations of the C_3H_4 energy surface showed that both prop-1-en-1-ylidene and cyclopropylidene have singlet ground states and suggested that the two geometrical isomers of the ground-state triplet vinylcarbene are degenerate. Vinylmethylene was found to be a key intermediate in the various isomerizations on the surface, though the singlet diradical form was found to be more stable than the vinylcarbene.[32,33] Ab initio calculations predict that thermal ring opening of cyclopropene itself will proceed through the cleavage of a C−C single bond in a process which retains the initial structure up to an opening angle of 110° and finally involves synchronous rotation and bond reorganization to give a stable carbenic species. This recyclizes easily though not spontaneously, and thus, competing reactions can occur.[34,35] Calculations using MCSCF and CI show that the singlet vinylmethylene has four isoenergetic energy minima, two *cis* and two *trans*, which are allylic in nature with the terminal hydrogen somewhat above the plane of the three carbons in both forms. The singlet species are all rather unstable toward ring closure to cyclopropene with a barrier of just 1.3 kcal/mol for the *cis*-form. A direct reaction path exists from cyclopropene to the *cis*-form with an energy barrier of 36.5 kcal/mol, while that to the *trans*-form is 3.7 kcal/mol higher. The ring opening of cyclopropene to prop-1-en-1-ylidene (the reverse of the final reaction of Scheme 1) is predicted to be a concerted reaction occurring by a 1,2-hydrogen migration with a barrier of 41.5 kcal/mol, and the barrier for the reverse process is 20.5 kcal/mol; hence, unlike the reactions involving vinylmethylene, the process is product forming.[36,37] The calculations confirm that cyclopropene is an intermediate and produce energy barriers in excellent agreement with experiment.[22] The thermal allene to propyne isomerization proceeds in four steps, via vinylmethylene, cyclopropene, prop-1-en-1-ylidene, and then propyne. A direct pathway does not exist on the ground-state energy surface, and cyclopropylidene is not involved.[38] The potential surfaces for the propyne−cyclopropene−allene interconversion, a process thought to be important in the initiation of soot formation through the production of propargyl radicals that go on to form C_6 species, and for the formation of cyclopropene from singlet methylene and ethyne, have been modeled on the basis of rate measurements using laser flash photolysis.[39,40]
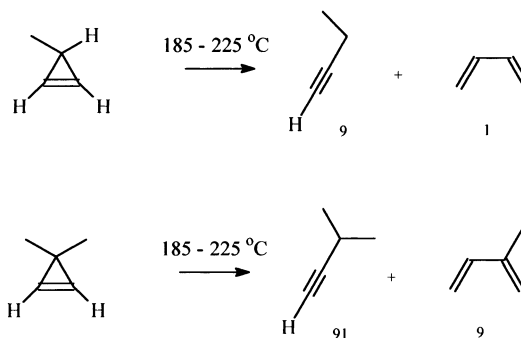
III. Alkylcyclopropenes

The most common products of gas-phase thermolysis of simple alkylcyclopropenes having a hydrogen

at either C-1 or C-2 are alkynes. Although these reactions were initially formulated as diradical processes,[2,22,41] the calculations discussed above suggested that prop-1-en-1-ylidene is involved in the rearrangement of cyclopropene itself.[37] In the case of 3-alkyl- and 3,3-dialkylcyclopropenes, the corresponding 1,2-hydrogen shift would lead to a vinylidene, **11**, that would be expected to rearrange very rapidly by a second 1,2-hydrogen shift to an alkyne—a hydrogen shift being known to occur much more rapidly than an alkyl shift in such systems:[12]
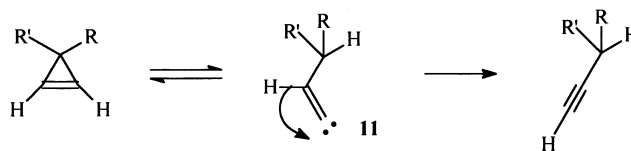
Indeed, 3-methylcyclopropene[2] and 3,3-dimethylcyclopropene[2,42] both rearrange on heating to 185−225 °C, and the corresponding alkyne makes up over 90% of the product. The rates are similar to those for cyclopropene itself:


In the case of 1-methylcyclopropene, the product is again the corresponding alkyne, but-2-yne (91−94%), together with small amounts of buta-1,3-diene and buta-1,2-diene.[41] In this case, however, the vinylidene intermediate must rearrange by a shift of one or the other methyl group:
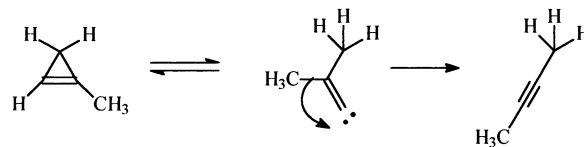
As in the cases of 3,3-dimethyl- and 3-methylcyclopropenes and cyclopropene itself, this rearrangement is characterized by a large negative entropy of activation; this presumably corresponds to a highly ordered transition state in the initial hydrogen migration leading to the vinylidene. The methyl group decreases the rate of ring opening. The rate of alkyne formation is also unusually low for 1,3,3-trimethylcyclopropene, about 0.1, compared to 3,3-dimethylcyclopropene, and the reaction at 483−525

K leads to a complex product mixture including just 22% of the alkyne **14**:
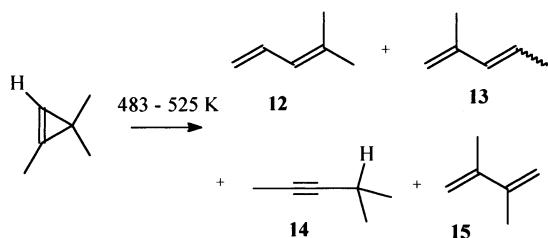
This is taken as evidence against a diradical-type intermediate and in favor of a route to the alkyne **14** via the carbene **16** (R = Me). The second step, a migration of one or the other alkyl group, is again much slower than the corresponding migration of hydrogen in **16** (R = H), the intermediate formed from 3,3-dimethylcyclopropene; carbene formation being reversible, the alternative dienic products from a vinylcarbene species are obtained in competition with alkyne formation.[43]
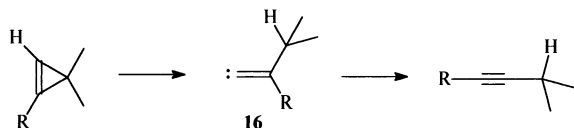
The labeled cyclopropene **17** rearranges thermally at 260 °C to give the alkyne **19** (together with dienes), labeled equally at each alkyne carbon. This process can be explained in terms of approximately equally likely migrations of methyl and isopropyl groups in **18**, but is not consistent with a diradical or vinylcarbene intermediate. Under the reaction conditions, the alkyne itself does not undergo scrambling of the label.[44]
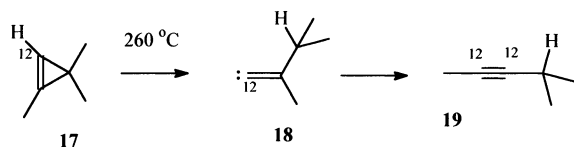

The labeling study also shows that the first two dienes shown above, **12** and **13**, are formed through cleavage of the more substituted ring bond of the cyclopropene to give a formal diradical intermediate. In an elegant extension of this experiment, thermolysis of the deuterated cyclopropene **20** was shown to lead to a small amount of exchange of the deuterium and the 2-propyl hydrogen, confirming that the ring opening of the cyclopropene to the methylenecarbene is reversible:[44]
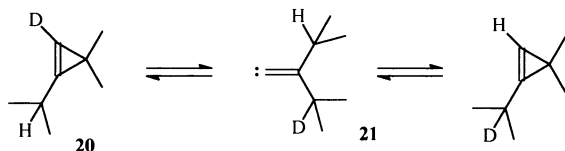

In the case of 1-*tert*-butyl-3,3-dimethylcyclopropene (**22**), thermal rearrangement in benzene between 150

and 195 °C leads to a complex mixture:[45]
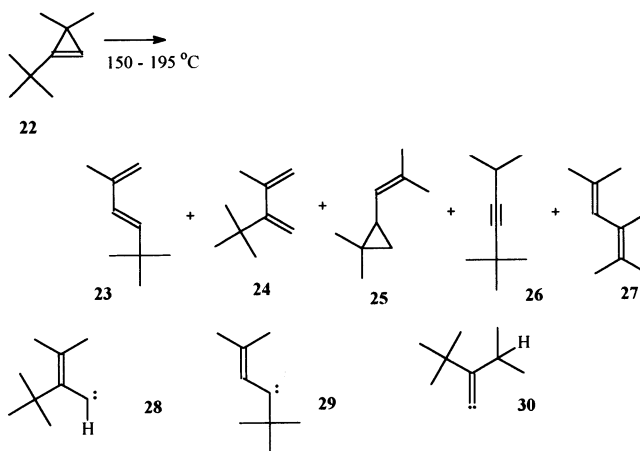
The first two products (13, 4%) arise by formal 1,4-hydrogen shifts in the two alternative vinylcarbenes **28** and **29**, a reaction that has been shown to occur in related carbenes using deuterium labeling.[46] Although there may be alternative explanations for these two products, the third product, **25** (26%), is characteristic of an intramolecular insertion by the carbene **29** into a C−H bond of one of the *tert*-butyl methyl groups, while the final product **27** (35%) can readily be explained by a 1,2-methyl shift in the carbene **29**.[45] The alkyne **26** (22%) may, on the basis of the evidence presented above, arise through a 1,3-hydrogen shift in **22** to produce a vinylidene intermediate, **30**, followed by an alkyl shift. The overall reaction, which shows a first-order decay of the cyclopropene, has a large negative enthalpy of activation (−17.8 eu; activation energy 29.8 ± 1.1 kcal/mol), which is not consistent with a simple ring opening and may again suggest more highly structured intermediates. Similar thermolyses of 1-alkyl-3,3-dimethylcyclopropenes (ethyl, isopropyl, butyl, isoamyl) occur by unimolecular processes. In the final two cases they lead to cyclopentenes such as **33**, formed in 5.5% yield by thermolysis in a sealed deactivated Pyrex tube (log A = 13.4 ± 0.2, E_{act} = 37.4 ± 0.6 kcal/mol), demonstrating the involvement of vinylidene intermediates such as **32**. Substantial yields of 2,4-alkadienes and dramatic rate increases for these cyclopropenes relative to the 1-methyl compound are explained in terms of vinylcarbene intermediates.[47,48]
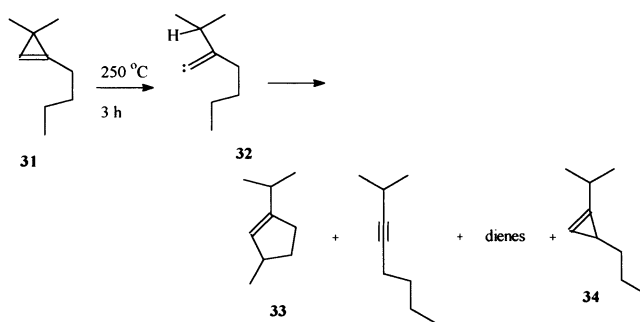

The isolation of 2−5% of a second cyclopropene, **34**, in this reaction provided early evidence for cyclopropene−cyclopropene rearrangements. An indication of this possibility is also given by the thermal inter-

conversion of **35** and **36**, although in these cases the intermediate is probably a vinylcarbene:[49]
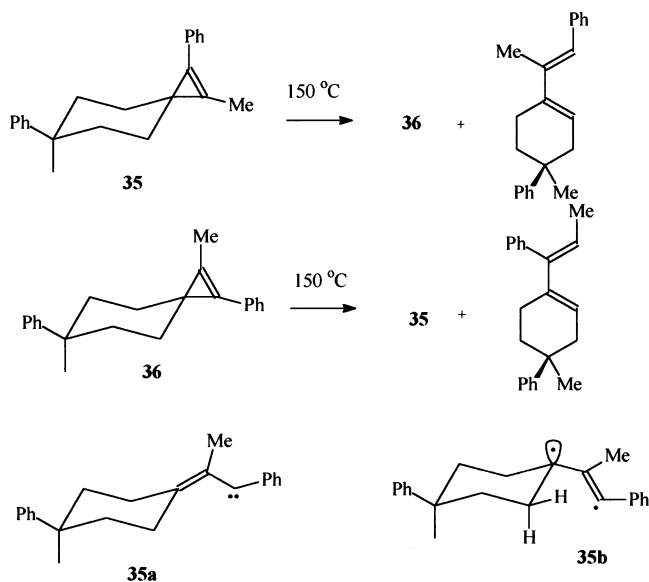
The isolation of different diene products in each of these thermal reactions of **35** and **36** suggests remarkable stereospecificity in the ring-opening processes and/or subsequent hydrogen shift, given the temperatures involved and the likely barriers to chair–chair interconversion. In each case the formal pseudoaxial C–C bond of the cyclopropene breaks. This could lead to the "planar" vinylcarbene **35a** or indeed to a nonplanar diradical such as **35b**. It would be interesting to know whether the hydrogen migrates from the axial or the equatorial position. If this same process leads to the interconversion of **35** and **36**, the C–C bond of the cyclopropene must reform either by closure from a pseudoequatorial position or by a sequence of cyclohexane chair–chair interconversion, pseudoaxial C–C bond formation, and then a second ring flip.

The above mechanisms involving vinylidene intermediates may also explain the fact that 1,3-diethylcyclopropene racemizes in the gas phase at 160–190 °C (E_{act} = 32.6 kcal/mol) 9 times faster than it rearranges,[50] a process that has previously been explained in terms of a vinylcarbene intermediate. Again, one of the major products of this reaction is an alkyne:
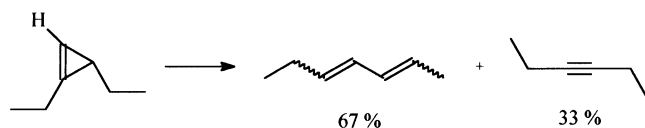
In support of this, thermal interconversion of 1,3-dimethylcyclopropene and 1-ethylcyclopropene, a process that can be explained by two alternative alkyl migrations in an intermediate vinylidene, has been found to occur in competition with the formation of pent-2-yne. The rate of ring opening of each cyclopropene was estimated to be about twice the rate of alkyne formation.[51] By determining the various rates for the sequence shown below in the thermolysis of 2-deuterio-1,3-dimethylcyclopropene, it has been pos-

sible to establish that there is a small primary isotope effect for the hydrogen migration, suggesting this is concerted with vinylidene formation.[52]
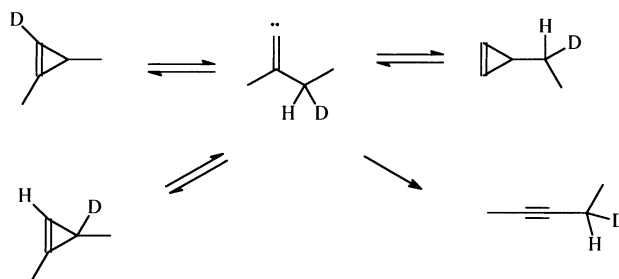
Using labeled 1,3-dimethylcyclopropene and 1,3,3-trimethylcyclopropene, it has been shown that the relative migratory aptitudes of alkyl groups in vinylidenes are Me:Et:*i*-Pr = 1:3.1:1.5. The sequence is thought to result from a combination of an increased rate due to electronic effects and a reduced rate due to steric effects.[52,53] Kinetic analysis also allows relative rates of 1,3-insertion of dialkylvinylidenes into C–H bonds to be determined as primary:secondary:tertiary = 1:16.5:46.4.[53] Also observed is a marked increase in the rate of formation of diene products from 1-alkylcyclopropenes, which can be explained by either hyperconjugative stabilization of vinylcarbene intermediates or their different rates of 1,2-hydrogen shift.[53] Calculations using density functional theory have been used to analyze the various intermediates involved in the reactions of 2-methylbut-1-en-1-ylidene and 2,3-dimethylbut-1-en-1-ylidene. These show that, for the former at 298 K, the migration rates should be in the order methyl migration < C–H insertion < ethyl migration, whereas for the latter the order should be methyl migration < isopropyl migration < C–H insertion.[54]

In contrast to the above cyclopropenes that all have at least one alkene hydrogen, thermolysis of 1,2-dimethylcyclopropene does not produce any alkyne; instead it rearranges to isoprene with an activation energy of 44 kcal/mol and $\Delta S^{\ddagger}$ = +3.4 eu.[55] The positive entropy of activation suggests a mechanism different from that involving the vinylidene intermediate above leading to alkynes; instead it may involve the formation of a vinylcarbene or the corresponding diradical. The fact that the reaction is 4 times slower than the ring opening of 1-methylcyclopropene presumably simply reflects the fact that the hydrogen shift to form a vinylidene intermediate is not available in this case. The effect may however arise instead due to stabilization of the ground-state cyclopropene.[2] Like the 1,2-dimethyl-compound, tetramethylcyclopropene rearranges thermally to give a mixture of dienes, and alkynes are not observed.[2]

The kinetic data for the various rearrangements of alkylcyclopropenes are collected in Table 1.

IV. Halogenated Cyclopropenes

Gas-phase thermolysis of halogenated cyclopropenes has only been studied for a few examples. In the

**Table 1. Gas-Phase Thermolysis of Alkylcyclopropenes**

cyclopropene	major product (%)	log A	E_{act} (kcal/ mol)	$\Delta S^{\ddagger}$ (eu)	ref
cyclopropene	propyne (90–99)	13.3	37.5	−3.9	22, 23
			35.2		2
1-methyl-	but-2-yne (90–94)	12.9	38.1[a]	−10.3	41
		11.4	34.7		2, 56
1-ethyl-		13.4	38.4[a,c]		51
3-methyl-	but-1-yne (90)	13.6	37.6		55
			37.6		2
3,3-dimethyl-	3-methylbut-1-yne (90)	13.3	37.3		42, 57
1,2-dimethyl-	isoprene (>96)	13.6	43.9	+3.4	55
1,3-dimethyl-	complex	13.4	39.7[b]		51
1,3,3-trimethyl-	2-methylpenta-1,3-diene (complex mixture)	13.4	39.0		43
			39.0		2
tetramethyl-	isomeric dienes	12.5	39.9		2
1,3-diethyl-	hept-3-yne	11.8	32.6		50
1-tert-butyl-3,3-dimethyl-			29.8	−17.8[a]	

[a] Data are for the overall process. [b] For rearrangement to 1-ethylcyclopropene log A = 12.3 and E_{act} = 39.7 kcal/mol; for rearrangement to 2-methylbut-1-ylidene log A = 13.3 and E_{act} = 38.6 kcal/mol. [c] For rearrangement to 1,3-dimethylcyclopropene log A = 12.3 and E_{act} = 37.5 kcal/mol; for rearrangement to 2-methylbut-1-ylidene log A = 12.9 and E_{act} = 37.9 kcal/mol.

case of the halocyclopropenes **37** and **38**, gas-phase pyrolysis in a Vycor tube at 375–650 °C and 0.5–1 Torr is reported to lead to the corresponding allene **39** or **40**, contaminated in the case of **37** (X = Br) by some propargyl bromide. In the same way, tetrachlorocyclopropene rearranges to tetrachloroallene under these conditions. No firm mechanism is indicated, though the formation of a vinylcarbene followed by a 1,2-halogen shift is favored. Given the well-known trapping of tetrachloroprop-2-en-1-ylidene in the thermolysis of the tetrachloride in the presence of alkenes (vide infra), such a mechanism seems likely at least in the case of this compound.[58]

$$X,Y = Cl,Cl;\ Cl,Br;\ Me_3Si,Cl$$
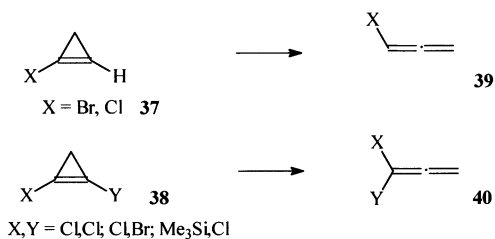
A calculation of the pathway for the rearrangement of 1,2-dichlorocyclopropene using QCISD(t)/6311G*/B3LYP/6311G* gave the energies shown in Figure 1.
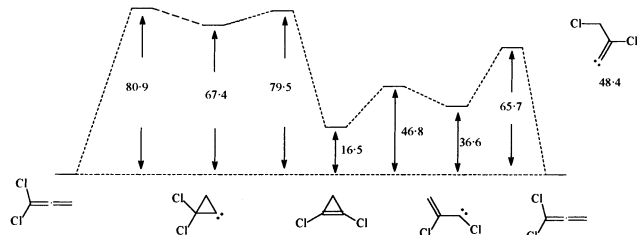
Figure 1. Calculated energies for species on the rearrangement path for 1,2-dichlorocyclopropene (kcal/mol).

On this basis, it is clear that the favored ring opening in this case also should be to the vinylcarbene, 1,2-dichloroprop-2-en-1-ylidene. The barrier to this ring opening is calculated to be 30.3 kcal/mol,

while that for recyclization is just 10.2 kcal/mol.[59] It is interesting to note that similar calculations for the ring opening of cyclopropene itself lead to corresponding barriers of 35.8 and 4.5 kcal/mol. The barrier to rearrangement of the dichlorovinylcarbene to 1,1-dichloroallene, in contrast, is calculated to be relatively high.[59]

Thermal ring opening of halogenated cyclopropenes has been studied widely in solution, as discussed later.

V. Tetrachlorocyclopropene

The thermal ring opening of tetrachlorocyclopropene at 150–170 °C over a period of 15–20 h in the presence of a wide range of alkenes leads to adducts derived by apparent trapping of tetrachloroprop-2-en-1-ylidene (**41**), which is in equilibrium with the cyclopropene:[9,60–63]
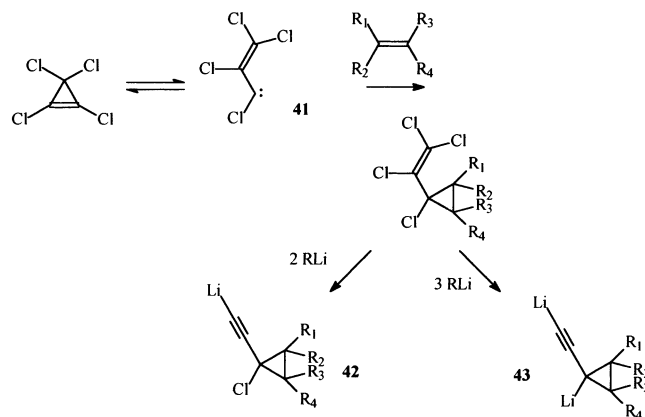
The carbene adds to cis- and trans-alkenes with retention of the alkene stereochemistry; although the reaction occurs only in low yield with acrylonitriles, addition to acrylates occurs efficiently.[63] In general, there is a moderate endo/exo-selectivity with both electron-rich and electron-poor alkenes, though in some cases this may be higher:[60,63]
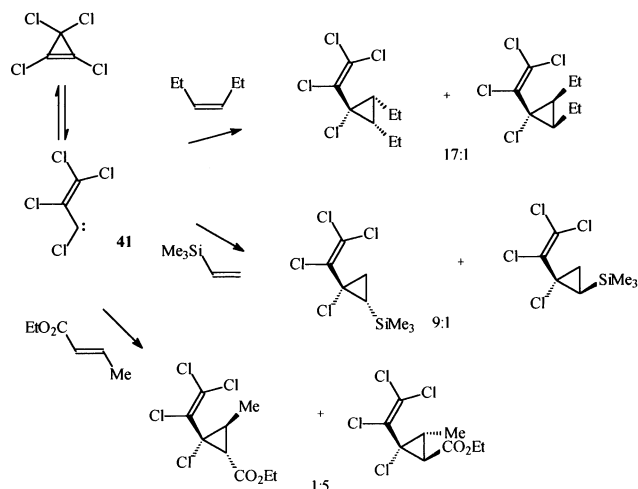
The carbene has a selectivity index toward alkenes of ca. 0.38, corresponding to its being an electrophilic species.[64] The adducts with alkenes are intermediates in a wide variety of transformations;[63] for example, they are readily converted by reaction with 2 or 3 molecular equivalents of an alkyllithium into the mono- and dilithio species **42** and **43**, and these can be trapped by a range of electrophiles.

The carbene also inserts into C–H single bonds in alkanes (e.g., into each C–H bond of hexane), into the bridgehead bond of adamantane,[62,63] into a C–H bond α to oxygen in ethers,[65] and into the methyl group of *tert*-butyl methyl ketone.[65]

VI. 1,2-Dihalocyclopropenes

In the absence of an alkene or alkyne, the dichlorocyclopropene **44** decomposes in 18 h at 20 °C in ether solution to give **47**, a product characteristic of insertion of a vinylcarbene, **45**, into a C–H bond adjacent to oxygen. The neat cyclopropene also decomposes over a period of 18 h at 20 °C to give a triene, **48**; although this is the formal dimer of the carbene **45**, it is more likely to be produced by reaction of the carbene **45** with the cyclopropene, for example, to produce the adduct **49**, which subsequently rearranges.[66] Although the dichlorocyclopropene **44** reacts only slowly at ambient temperature
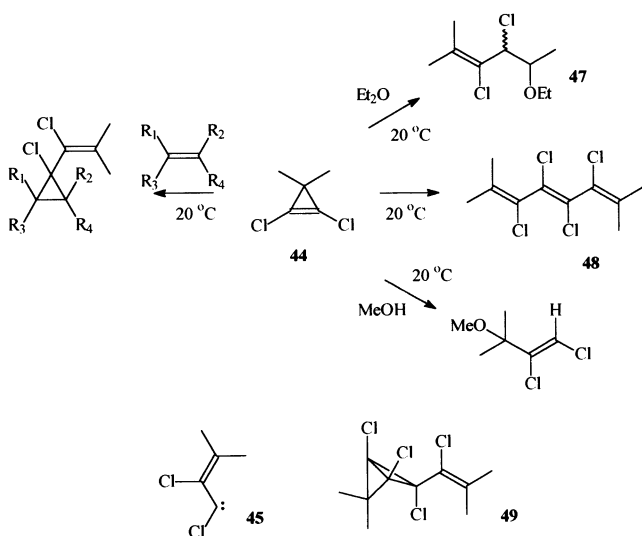

under the above conditions, it is consumed much more rapidly in the presence of an alkene, to give a cyclopropane.[67] This has been interpreted in terms of an equilibrium between the cyclopropene and the corresponding vinylcarbene **45** which is trapped in the presence of an alkene. It is interesting to note the calculations for the rearrangement of 1,2-dichlorocyclopropene described above which suggest a lower barrier to ring opening to the corresponding vinylcarbene than in the case of a simple alkylcyclopropene, a very low barrier to recyclization to the cyclopropene, and a rather high barrier to rearrangement to 1,1-dichloropropa-1,2-diene.[59]

In the case of the addition of **45** to simple alkyl-substituted alkenes, the stereochemistry of these is maintained in the product cyclopropane, suggesting the addition of a singlet carbene derived by ring opening of the cyclopropene; with *cis*-but-2-ene there is a 5.5:1 selectivity for the cyclopropane with the alkenyl group *trans* to the methyl substituents. In the case of electron-poor alkenes, the substituent in the product is apparently *cis* to the alkene group as in **46**, while, with dimethyl maleate, the stereochemistry about the alkene is partly lost in the addition.
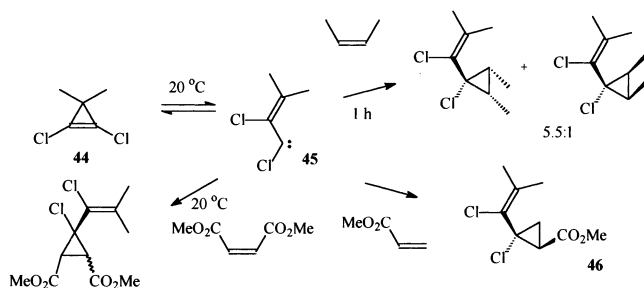

Addition also occurs to dimethyl acetylenedicarboxylate, leading to cyclopropene **50**, apparently derived following a rearrangement of the initial adduct.[66]
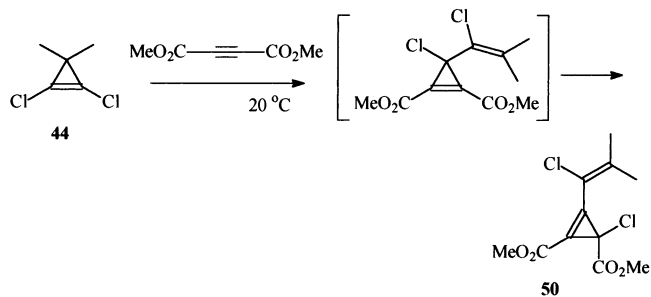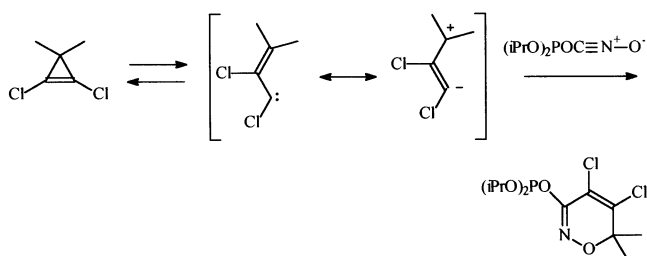

The carbene is also trapped by addition to ketene-alkyl silyl acetals:[68]
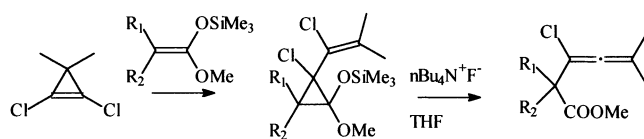

It is trapped by dienes to give dichlorocyclohepta-1,4-dienes, after a Cope rearrangement of a mixture of *cis*- and *trans*-divinylcyclopropanes:[69,70]
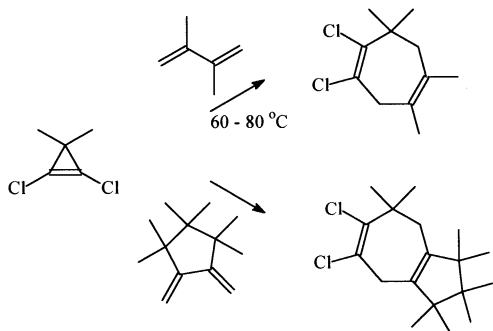
The dichlorocyclopropene is also reported to react with a nitrile oxide in an apparent three-center plus three-center [4+2]cycloaddition:[71]


The introduction of a different substitutent onto C-3 of the cyclopropene as in **51** can lead to a highly stereoselective ring opening in which the products **52** and **53** of addition of the carbene **54** rather than **55** are obtained in the presence of appropriate alkenes, again in reactions which occur over a few hours at 20 °C:[72,73]
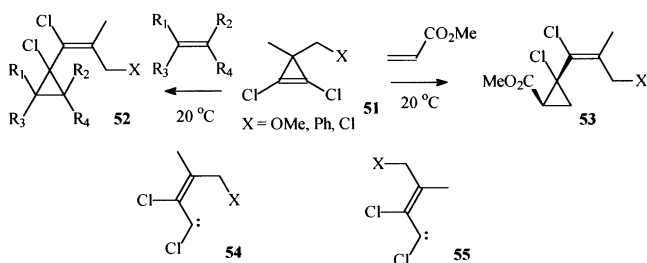
Once again, the additions to *cis*- and *trans*-but-2-enes lead to retention of alkene stereochemistry in the product cyclopropane, but addition to dimethyl maleate leads to partial loss of alkene stereochemistry. Even the cyclopropene **51** (X = OCMe$_2$OMe) carrying a very large substituent ring opens at ambient temperature, and the corresponding carbene **54** (X = OCMe$_2$OMe) is again trapped.[74]

The ring opening of cyclopropenes **51** (X = C$_6$H$_4$Y) occurs more rapidly when Y is an electron-releasing group and the rate of cyclopropanation of 2,3-dimethylbut-2-ene correlates with σ_I of the substituent with a ρ-value of -0.8. A comparison of the relative rates of addition of **54** (X = H) and **54** (X = OMe) to a series of alkyl-substituted alkenes shows them to be of about equal selectivity, but there is not a good linear correlation with the relative selectivities of dichlorocarbene. A good linear correlation is obtained with the relative rates of addition of tetrachloropropen-1-ylidene[64] to alkenes.[75]

In the absence of an alkene trap, the cyclopropene **51** (X = Ph) rearranges slowly to diene **56**, a product that can be explained either by an insertion of the carbene **54** (X = Ph) into a C–H bond of the benzyl group to give a cyclobutene, which then ring-opens to the diene or, more likely given that the reaction occurs at 20 °C, by a 1,4-hydrogen shift in the carbene.[76,77] A similar reaction is observed for **51** (X = OMe), though in this case the diene reacts further with starting cyclopropene.[72,77]
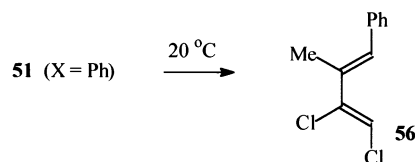

The rearrangement of **51** has been analyzed using quantitative SCF-MO calculations at the PM3 level and the preference for the carbenes **54** rather than **55** explained in terms of stereoelectronic effects between the cleaving σ-bond and the σ^*-orbital of the C–X bond.[78] In contrast, cyclopropenes bearing bulky nonpolar groups at C-3 are predicted to ring-open to place these *trans* to the developing carbene center, as seen experimentally below.

Reaction of the dichlorocyclopropenes **44** and **51** with a phosphaalkyne in ether solution at 25 °C leads to a phosphirene, **58**, the product of a 1,3-chlorine shift in the initial adduct **57**:[79]

X = H, Cl, OMe, R = t-Bu, CMe$_2$Et, 1-adamantyl
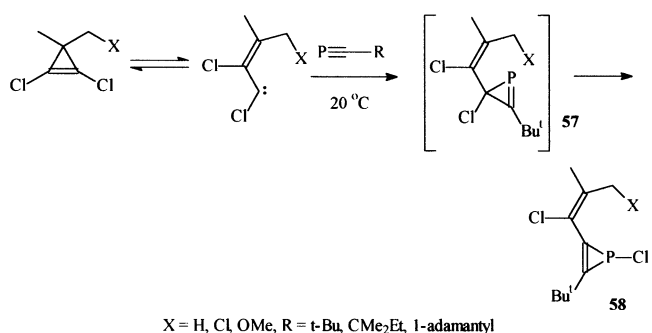
Heating the phosphaalkyne with tetrachlorocyclopropene at 200 °C leads to a similar phosphirene, albeit in low yield.[79]

The product 1-chloro-2-vinyl-1*H*-phosphirene reacts with an alkyllithium in two stages, first undergoing alkylation on phosphorus and then, with a second equivalent, forming a phosphino-1,2,3-butatriene:[80]
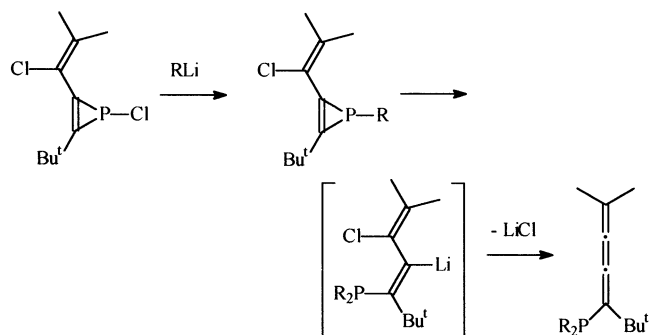
In another unusual reaction, the dichlorocyclopropene **51** (X = Cl) reacts with propanone to give **59**, the product of an apparent 1,6-hydrogen shift in an intermediate ylide:[81]
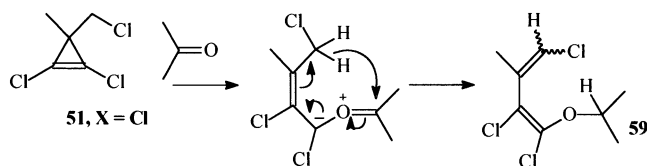

The reaction of the cyclopropene with other ketones and aldehydes leads to more complex products.

In the case of the alcohol **60**, reaction with methyllithium leads to an allene that has been explained in terms of a complex series of reactions involving the vinylcarbene **61**:[82]
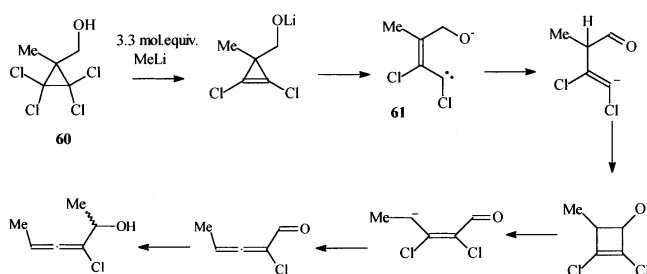

The corresponding 1,2-dibromide **62** also ring-opens at 0−20 °C to the vinylcarbene **63**; this again may be trapped by addition to electron-rich alkenes with retention of stereochemistry. It also adds to electron-poor alkenes H$_2$C=CHX to give cyclopropanes in which the dibromovinyl group and the X group are *cis*. The corresponding substituted systems **64** (X = OMe, Br) ring-open under similar conditions, in each case to two isomeric vinylcarbenes **65** with essentially no stereoselectivity, unlike the substituted dichlorides described above.[83]
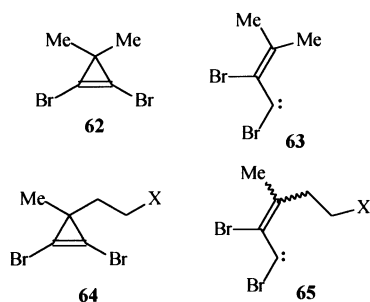

In the case of the dibromides **67** having a single alkyl substituent at C-3, ring opening again occurs in the presence of an electron-rich or an electron-poor alkene to give the adducts **68** and **69** derived by trapping of a vinylcarbene, though in these cases it was the (*Z*)-carbene **70**. The addition to *cis*-but-2-ene again proceeds with retention of alkene stereochemistry. In the absence of an alkene trap the cyclopropene rearranges in the reaction solution from the tetrabromide **66** in ether to give the alkyne **71**:[84,85]
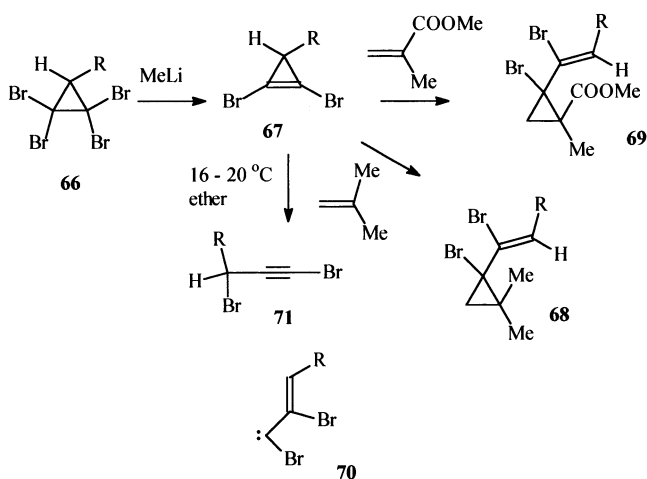
Moreover, even the cyclopropene with no substituent at C-3, 1,2-dibromocyclopropene, is reported to react with alkenes in solution at ambient temperature to produce vinylcyclopropanes **73**, again apparently by trapping of the ring-opened vinylcarbene **72**:[86]
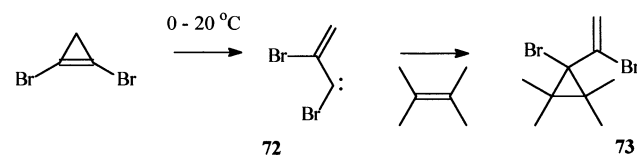
In the case of 1-bromo-2-chloro-3,3-dimethylcyclopropene **74** (X = Br), ring opening again occurs at ambient temperature and leads to a ca. 1:1 mixture of isomeric vinylcarbenes **75** and **76** which are trapped by an added alkene.[87] However, 1-fluoro-2-chlorocyclopropene **74** (X = F) ring-opens highly selectively, and only 1-chloro-2-fluoro-3-methylbut-2-en-1-ylidene **77** is trapped by an added alkene. This may be explained by the strong effect of fluorine in stabilizing an anion at the β-carbon in the transition state, leading to the dipolar resonance form of the carbene or in weakening of the opposite C−C bond of the cyclopropene.[88]
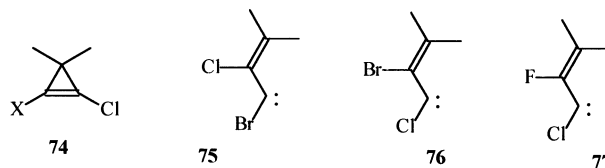
VII. Monohalocyclopropenes

Monocyclic monohalocyclopropenes are also rather labile, but in general they rearrange to alkynes. Thus, the labeled monochloride **78** rearranges slowly in ether−CDCl$_3$ at 20 °C to give C-2-labeled alkyne **79**, while the bromide **80** again rearranges regioselectively:[89−91]

$$X = Cl, 10\ d, 20\ °C, CDCl_3$$
$$X = Br, 2\ h, 20\ °C, CDCl_3$$
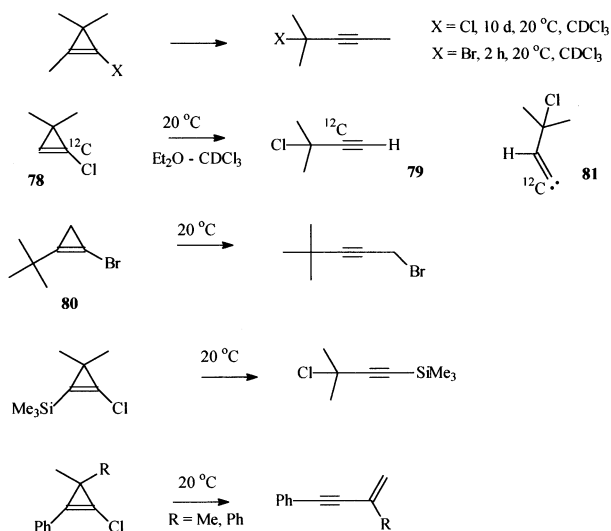
Although these reactions can be explained in terms of a 1,2-halogen shift in an intermediate vinylcarbene, there is no evidence of trapping of these by an added alkene. At first sight, the alkynes may also again arise through a methylenecarbene such as **81** from **78**, in this case derived by a 1,3-halogen shift, followed by a 1,2-alkyl, hydrogen, or trimethylsilyl shift; however, the labeling pattern in **79** is not consistent with this as the favored 1,2-hydrogen shift in such an intermediate carbene would lead to an alkyne labeled at the CH carbon. It is also possible that ionic processes are occurring, catalyzed by halide ion, or in some cases that the reactions are promoted by lithium ion present in the solution used to generate the cyclopropene.[91,92] The reactions do proceed, albeit more slowly when the cyclopropene has been distilled, but addition of lithium bromide to a solution of **80** in CDCl$_3$ leads to a rate that is very similar to that for distilled material. Vinylcarbenes have also been implicated as intermediates in the formation of by-products in the reactions of 1,1,2-trihalocyclopropanes with base.[67,93,94]

It is interesting to note that 3-ethoxy-1-chlorocyclopropene **82**, generated by the halodesilylation of 1,1-dichloro-2-trimethylsilyl-3-ethoxycyclopropane, is trapped in situ by diphenylisobenzofuran, though when **82** is generated by dehydrochlorination of the dichloride with KO-t-Bu in tetrahydrofuran in the presence of the furan, a most unusual allene, **83**, is isolated:[95]
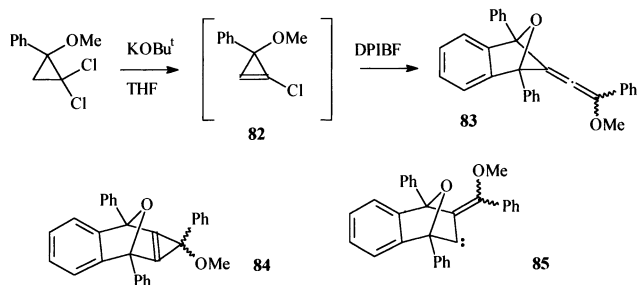
Although a mechanism can be written involving ring opening of **82** to a vinylcarbene and trapping of this, it seems more likely that the cyclopropene undergoes [4+2] cycloaddition to the furan and that

further dehydrochlorination under the reaction conditions then leads to a second cyclopropene, **84**, which ring-opens to a vinylcarbene, **85**, and rearranges through a 1,2-alkyl shift.

Calculations on 1-fluorocyclopropene using DFT, CCSD, CCSD(T) methods show that it can undergo automerization involving a 180° rotation of its methylene group through a carbene-like transition state but without an intermediate carbene or diradical.[96]
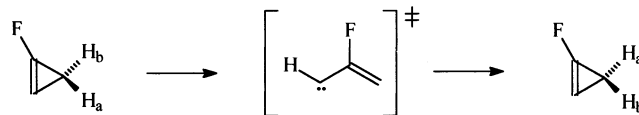
The rearrangement of fluoroallene to singlet fluorovinylmethylene has also been examined by ab initio calculations which show that 1,2-fluorine migration is less favorable than 1,2-hydrogen migration.[97]

VIII. 3-Arylcyclopropenes

It has been known since 1967 that the thermolysis of molten tetraphenylcyclopropene **86** (R = H) at 235−240 °C leads to the formation of triphenylindene **88** in a reaction that shows first-order kinetics in diphenyl ether−quinoline with $E_{act} = 40 \pm 1$ kcal/mol and log $A = 14.0 \pm 0.5$. The process, which is sensitive to traces of acid or oxygen, was rationalized in terms of a diradical intermediate, **87** (R = H), or the related carbene which can formally insert into a C−H bond, although an electrocyclic closure followed by a hydrogen migration seems more likely, particularly in view of the formation of **89** as one product from the mesityl system **86** (R = Me):[98]
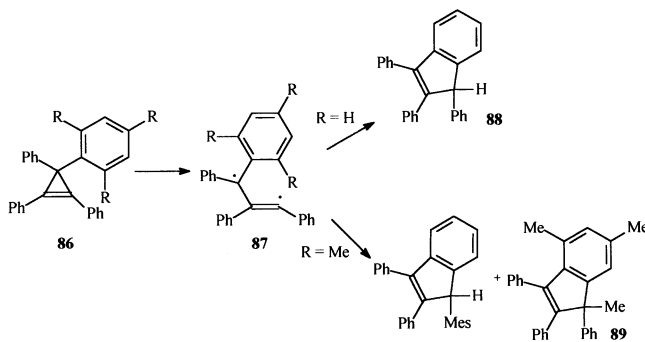
3,3-Diphenylcyclopropene also rearranges at 200 °C, giving phenylindene in 80% yield.[99] In the case of 3-methyl-3-phenylcyclopropene, thermolysis at 180 °C leads to the formation of the indene **91**, again explained in terms of the intramolecular cyclization of the ring-opened vinylcarbene **90**. In the presence of a very large excess of 2,3-dimethylbut-2-ene, this may indeed be trapped as the cyclopropane **92**.[100] There is some evidence that the carbene may also be trapped by electron-poor alkenes such as ethyl crotonate. It is interesting to note that there is no evidence in these systems of the 1,2-hydrogen shift from C-1 to C-3 of the cyclopro-

pene leading to a vinylidene and then an alkyne as seen, e.g., in the case of 3,3-dimethylcyclopropene above.
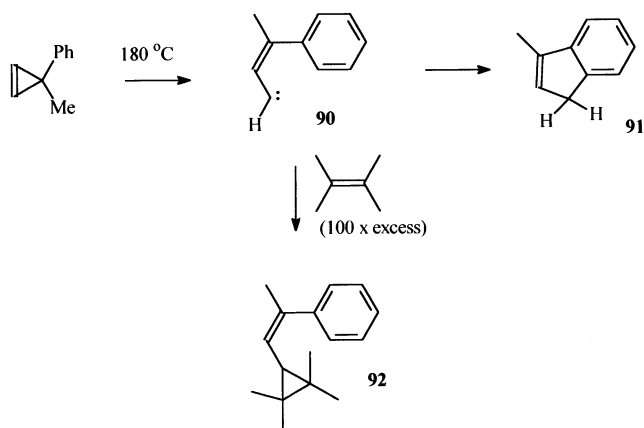
In the case of unsymmetrically 1,2-substituted cyclopropenes, selective formation of single indenes may occur as shown below. Cyclization also occurs into heterocycles at the 3-position of the cyclopropene:[98,101−104]
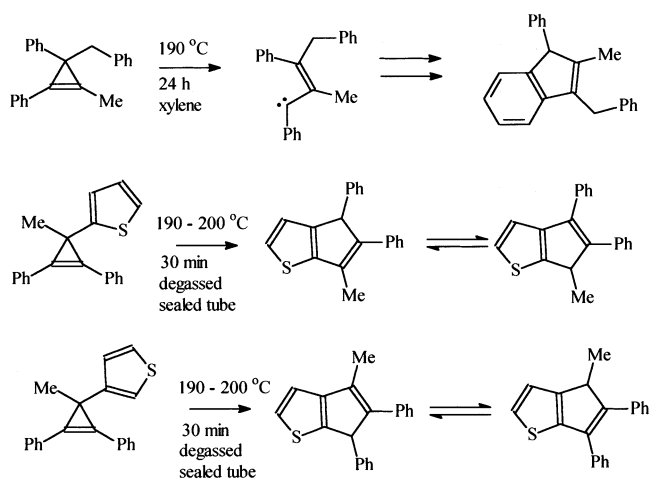
In other cases, the intermediate may react further, in the following example by an ene reaction:[101]

Similar reactions have also been reported for 3-ferrocenyl-3-phenylcyclopropenes.[105−107] It is notice-
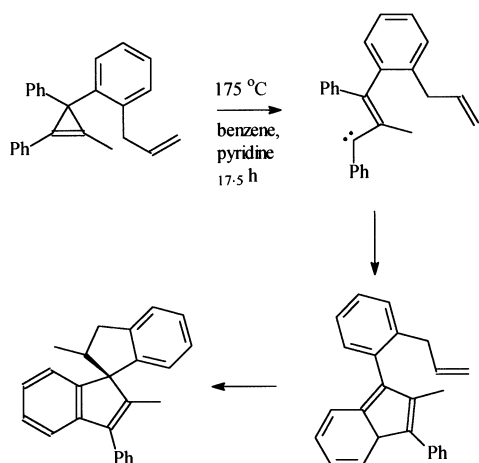
able that, in almost all cases, the cyclopropenes described above are tetrasubstituted. The less substituted systems have not been widely studied or react in different ways; 1,3-diphenylcyclopropene, for example, undergoes rapid dimerization through an ene reaction even at below ambient temperature.[108]

Similar cyclizations leading to indenes are observed when 3-aryl-1,1,2,2-tetrachlorocyclopropanes are treated with methyllithium at ambient temperature and below, apparently through rearrangement of the derived 3-aryl-1,2-dichlorocyclopropenes, although these may not be isolated:[109]
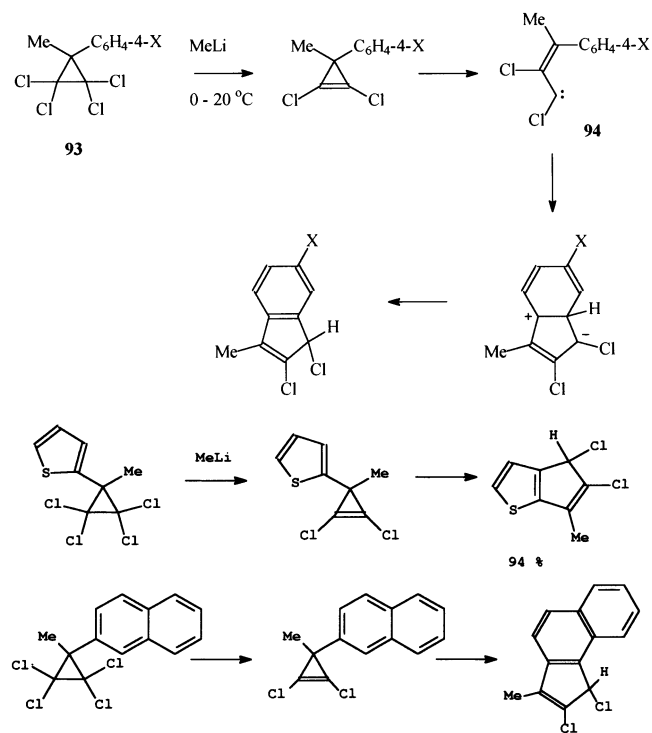
In the case of **93** (X = H), carrying out the reaction in the presence of a large excess of 2,3-dimethylbut-2-ene leads to a small amount of the cyclopropane derived by addition of **94** (X = H) to the alkene.

When there is an isoxazole at position 3 of the cyclopropene as in **95**, ylide formation followed by fragmentation is observed:[110]
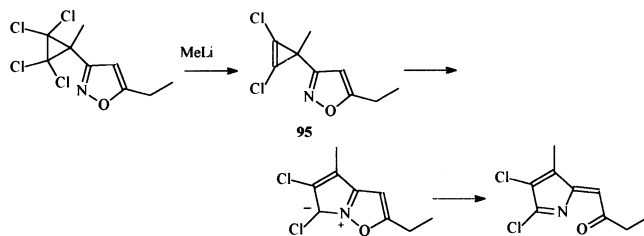
In the case of the 2-oxa-3-azabicyclo[3.1.0]hex-3-enes **96** and **98**, fragmentation to pyrroles or methylenepyrroles occurs, apparently by cyclization of the vinylcarbene intermediate to give a pyrrole such as **99**, followed in the latter case by rearrangement to **100**; the equivalent intermediate in the case of **96** presumably undergoes tautomerism to give the observed product.[110]

96

97
R = Et, 82 %
R = Bu, 85 %

98

99

100
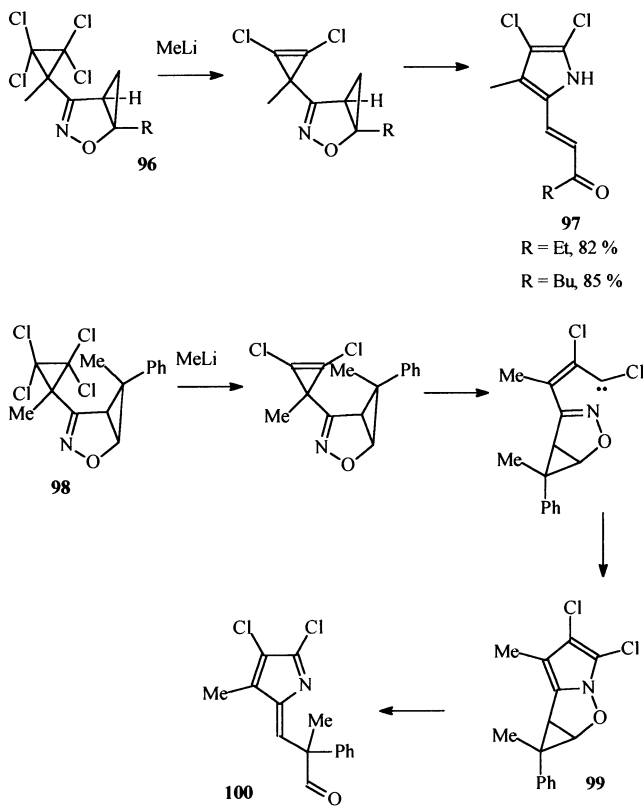
IX. Vinylcyclopropenes

In a reaction similar to that above of 3-arylcyclopropenes, 3-vinylcyclopropene rearranges cleanly to cyclopentadiene on flash vacuum pyrolysis at 250 °C.[111] In contrast, 3-ethynylcyclopropene is stable to FVP at this temperature, though it does rearrange at above 500 °C to a 5:1 mixture of penta-1,4-diyne and penta-1,2-dien-4-yne.

The barriers for ring opening of 1-vinylcyclopropene to penta-1,4-dien-3-ylidene and to 2-vinylprop-2-en-1-ylidene have been found by MINDO/3 semiempirical calculations to be 41.2 and 52.3 kcal/mol, respectively.[112] Given these barriers, it is not surprising that 1-vinylcyclopropenes usually undergo other reactions to relieve their strain.[71,111,113,114] The former process has however been implicated in the photolysis of the cyclopropene.[113] It is interesting that this process could in principle lead to a cyclopropene–cyclopropene interconversion; although a suitable system to study this has been reported, no evidence for the isomerization is presented:[115]
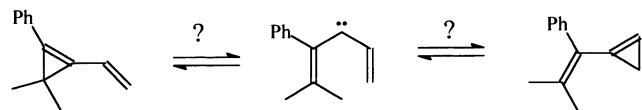

X. Cyclopropenecarboxylates and Related Systems

The ester **101** undergoes dimerization at 0−20 °C over a period of several days to produce the bicyclobutane **102** which itself rearranges to triene **103**. Although the bicyclobutane can reasonably be explained in terms of the addition of the ring-opened carbene **104** to the starting cyclopropene, the carbene

could not be intercepted by the addition of a large excess of 2,3-dimethylbut-2-ene.[116]

101   **102**   **103**

104
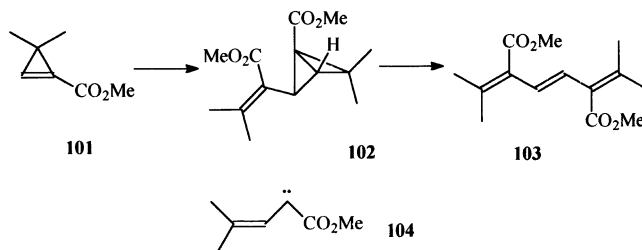
At a pressure of 8 kbar, **101** reacts at 20 °C to give a mixture of triene **103** and the epimer of **102** at C-4.[117]

Trienes are also obtained from the thermolysis of the corresponding 2-phenylcyclopropene, though in this case the opposite regiochemistry is observed:[118]

175 °C
72 h
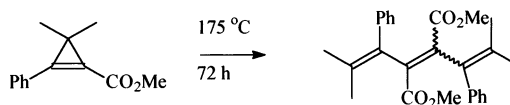
The activation energy for the thermal isomerization of esters of 2,3,3-triphenylcyclopropenecarboxylic acid, which leads to 2,3-diphenyl-1-indenecarboxylates, has been found to be 25 ± 1 kcal/mol, with an entropy of activation of −22.4 eu in tetrachloroethylene at 160 °C. The reaction is not greatly accelerated by a polar solvent (though the rate does increase considerably in trifluoracetic acid, possibly due to reaction through a cation). Although the reaction may occur through the formation of a vinylcarbene, the large negative entropy of activation is more consistent with a concerted mechanism involving ring opening and rotation of C-3 of the cyclopropene through 90°.[119,120] It is interesting to note that in this process the bond to the ester substituent is cleaved whereas in the corresponding photochemical process the other σ-bond breaks.

30 min
180 °C
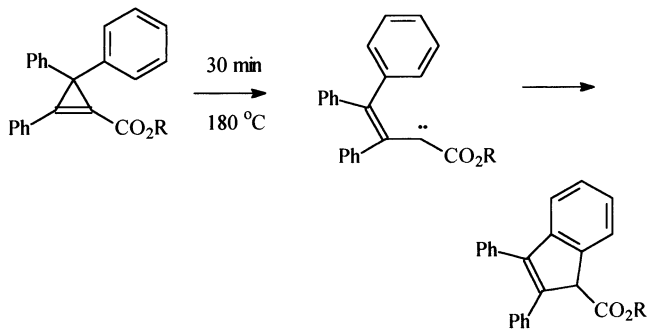
The diesters **105** (R = Me, CH$_2$Ph) rearrange in d_6-benzene at 154 and 138 °C, respectively, with first-order rates of 4×10^{-4} and 3.6×10^{-5} s^{-1}, leading in each case to a diene, **106**. The isomeric esters **107** (R = Me, CH$_2$Ph) are both stable at these temperatures but rearrange to complex mixtures at 190 °C.[121]

Experimental parameters have been determined for the unimolecular isomerization of 1,2-dicarbomethoxy-3,3-dimethylcyclopropene, and calculations have been carried out at the ab initio level using 1-methoxycarbonyl-3-methylcyclopropene as a
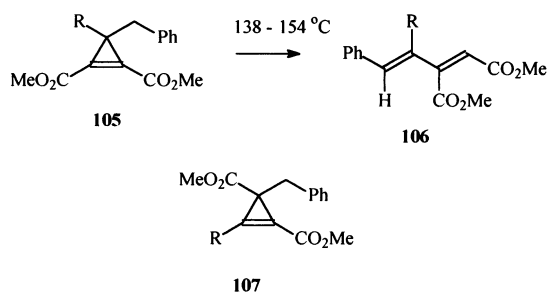
model.[122] The dibenzoyl system **108** rearranges at room temperature to give a diketone and an α-pyran:[123]
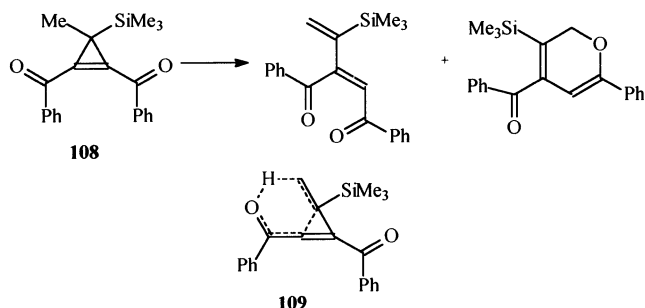
The activation parameters for the rearrangement are $\Delta H^{\ddagger}$ 18.4 ± 0.6 kcal/mol and $\Delta S^{\ddagger}$ −24.7 eu in toluene. They are relatively similar in nitrobenzene, although this has a very different dielectric constant; the reaction rate is only increased by a factor of 1.4 in the latter at 100 °C. Given these data it seems likely that this reaction does not proceed through a carbene intermediate but that a concerted retro ene reaction as in **109** may be involved.

There are few examples of the ring opening of simple cyclopropene-3-carboxylates. In one, a most unusual cycloheptatriene is isolated, but this is most likely derived by formal reaction of ethoxycarbonyl-carbene with the solvent:[124]

XI. Alkoxy Substituents

The 3-alkoxycyclopropene **110** ring-opens only under vigorous conditions, and the only products observed are those apparently derived from the thermodynamically more stable carbene **111**:[95]
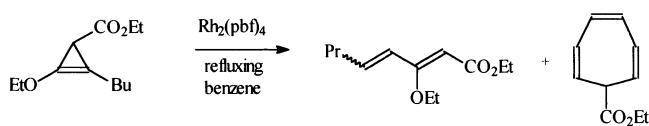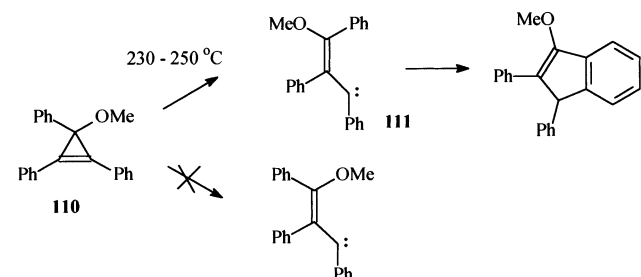
There seem to be no examples of ring opening to carbenes in simpler alkoxy-substituted cyclopropenes.

XII. Cyclopropenone Acetals

Cyclopropenone acetals ring-open readily at between 20 and 80 °C to give species that can be described as planar delocalized vinylcarbenes or as the dipolar form, e.g., **112**. This can be seen in the [3+2] trapping by a ketone to give **113**, or by pyrones substituted with electron-withdrawing groups:[125−128]
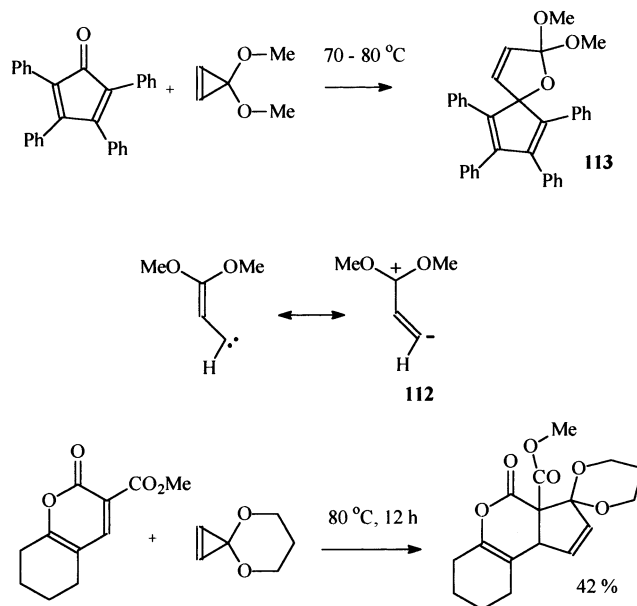
These "carbenes", which are formed reversibly, are nucleophilic and add readily to a wide range of electron-poor alkenes to give cyclopropanes, though when the alkene carries two electron-withdrawing groups, a formal [3+2] dipolar cycloaddition is observed.[126,128,129] Mechanistic studies indicate that [3+2] additions may proceed with partial loss of alkene stereochemistry in a process for which both the rate and stereoselectivity are solvent independent. Triplet carbene traps and radical traps do not react. These studies rule out a concerted $[\pi 2_a + \pi 2_s]$ cycloaddition, a stepwise addition−cyclization involving a singlet delocalized vinylcarbene and a zwitterionic intermediate, and an addition involving a triplet vinylcarbene or rearrangement of an unobserved initial [1+2] carbene adduct. However, they are consistent with a [3+2] process that proceeds by a mechanism involving single electron transfer from an electron-rich π-delocalized singlet vinylcarbene to the electron-poor alkene.[129]

However, reaction with 2-cyclopropylmethylene-malononitrile, an alkene designed to undergo extremely rapid rearrangement should a cyclopropyl-methyl radical center be generated in this way, led to no rearrangement.

In general, the major [1+2] cycloadduct with alkenes having a single electron-withdrawing group often has this group and the ketene acetal group *cis*,[130−133] though ratios do depend on the alkene substituents, reaction solvent, and nature of the substituents on the cyclopropenone acetal.[126] This effect apparently arises through an attractive interaction between the electron-withdrawing substituent and the cationic end of the dipolar singlet vinylcarbene.
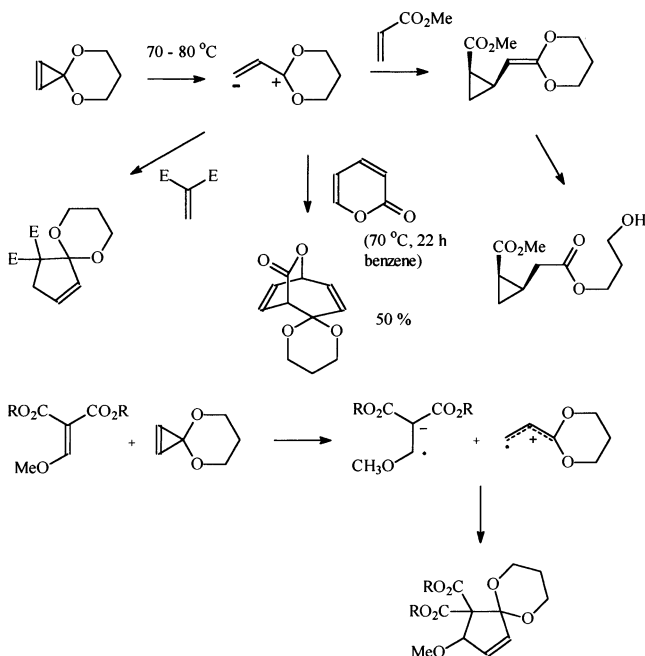
With α-pyrones, a four-center plus three-center dipolar addition can occur:[126,129,133,134]
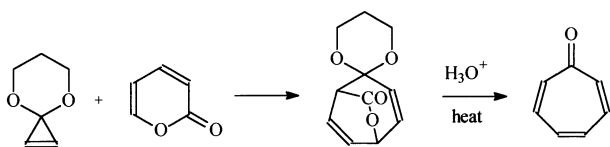
This has been applied in a key step in a formal synthesis of colchicine:[134,135]
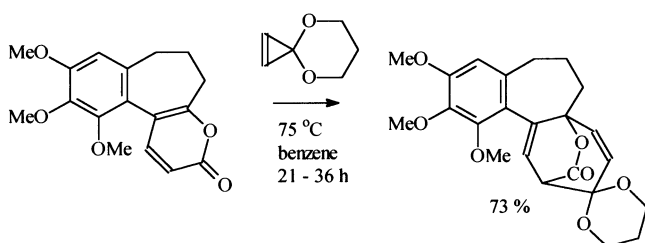
Addition to carbonyl groups leads to butenolide ortho esters, the products of a formal three-carbon plus two-carbon cycloaddition. These are hydrolyzed in the presence of acid:[126,127]
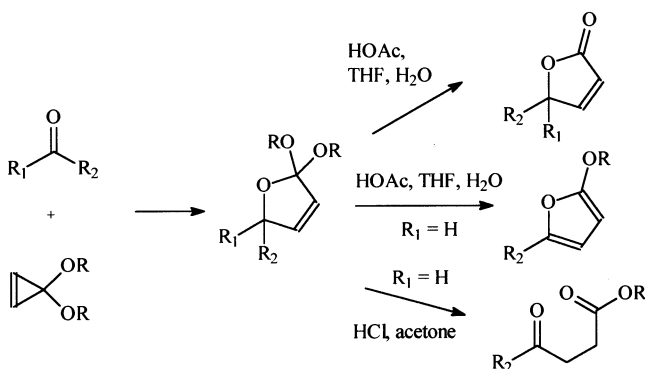
The carbenes **114** are also trapped by the addition of alcohols, leading to ortho esters.[136] Related species also apparently "insert" into the C−H bond of a terminal alkyne, although both of these reactions are rather different from a normal carbene insertion, when both bonds are formed to the same atom:[126]
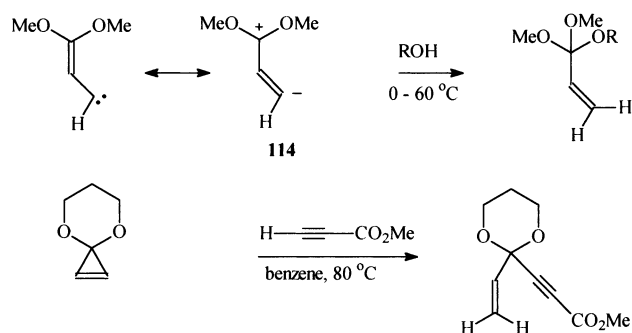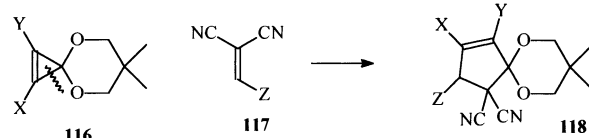
If the alcohol is replaced by water, the product is an acrylate ester; by using 25 M D_2O in acetonitrile, it can be shown that the hydrogen added is entirely *cis* to the ester. At lower D_2O concentrations, the stereoselectivity is lower, apparently due to isomerization of the vinylcarbene to the *anti*-form **115**.[137] This indicates a relatively low barrier for interconversion of the two forms, which have been calculated to be of nearly equal energy.[133]
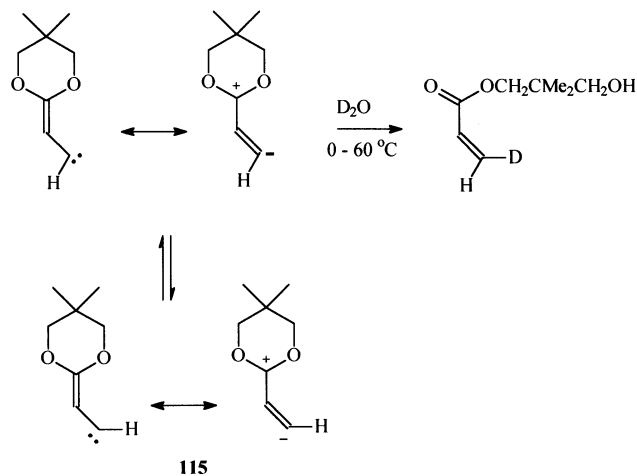
The addition of substituents onto the cyclopropene double bond has a marked effect on the ring opening in the presence of water. While an ethyl substituent slows the reaction and leads to complex products, and a phenyl group leads to cleavage of both the cyclopropene σ-bonds with only low selectivity, SPh and COOR substituents lead to reactions at room temperature and with high regioselectivity:[137]

X = SPh, 89 %, E:Z 100:0

X = CO_2CHMe_2, 90 %, E:Z 77:23
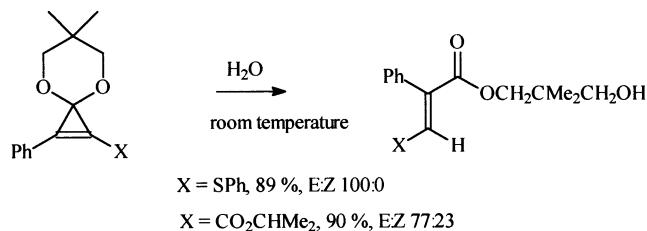
The introduction of substituents onto the cyclopropene double bond also controls the regioselectivity of

Table 2. Typical Reactions of Cyclopropenone Acetals 116 with Dinitriles 117

X	Y	Z	solvent	temp (°C)	time (h)	yield (%)
H	Et	Ph	toluene	150		82[a]
Ph	H	Ph	benzene	75	15	76
SiMe$_3$	H	Ph	toluene	100	7	62
SPh	Et	Ph	THF	15	5	64
SPh	Ph	Ph	THF	0	5	63
COO-i-Pr	Ph	Ph	THF	25	14	64

[a] In a 71:29 ratio with **118** (X = Et, Y = H, Z = Ph).

the addition process with alkenes carrying one electron-withdrawing substituent:[131,137]

R = Et, Ph, SiMe$_3$ X = CO$_2$Me, CN
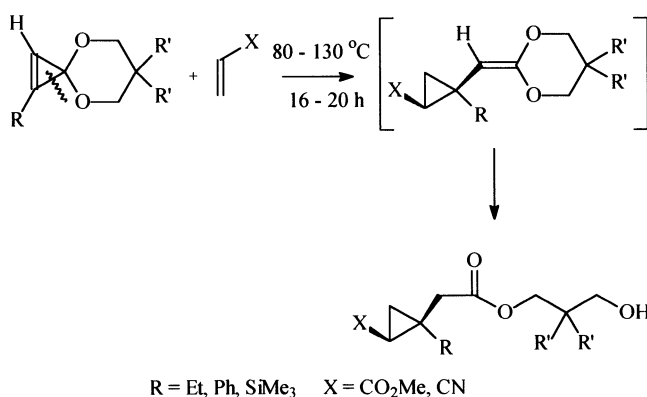
It is noteworthy that the ring opening is highly regioselective, placing aryl, silyl, phenylthio, and ester groups selectively at the carbene carbon; once again, it is also highly stereoselective, placing the substituent X and the derived ester *cis*. However, as the alkene concentration is increased, the regioselectivity drops. This has been interpreted in terms of the formation of regioisomeric vinylcarbenes derived by cleavage of both cyclopropene σ-bonds, and selective trapping of the more reactive carbene.

Again, with an alkene having two geminal electron-withdrawing substituents such as **117**, a cyclopentene **118** is formed (Table 2).[137] When one of X or Y is hydrogen, the products derived by cleavage of the more substituted cyclopropene σ-bond are formed exclusively, except in the case of **116** (X = H, Y = Et, Z = Ph).

With disubstituted systems, the bond carrying SPh or ester substituents is cleaved preferentially. Although the lower reaction temperatures observed may reflect selective ring opening of the cyclopropene to a single carbene, it is again possible that the two regioisomeric carbenes are both formed in equilibrium with the cyclopropene and that only one of them is trapped.[137] Although an SET process is not formally discussed in this case, it must as in earlier examples be a possibility.

3,3-Dimethoxycyclopropene reacts with triazines in toluene solution at 50 °C over a period of about 6 h to give the products of a three-center plus two-center cycloaddition, **119** when R$_2$ ≠ H and **120** when R$_2$ =

H.[138] The formation of **121** and **122** suggests that the addition occurs at whichever C−N bond bears a hydrogen on carbon.

(25 %)

R$_1$ = CF$_3$, Ph, H,CO$_2$Et   R$_2$ = H, CF$_3$ R$_3$ = SMe, Ph

17 - 51 %
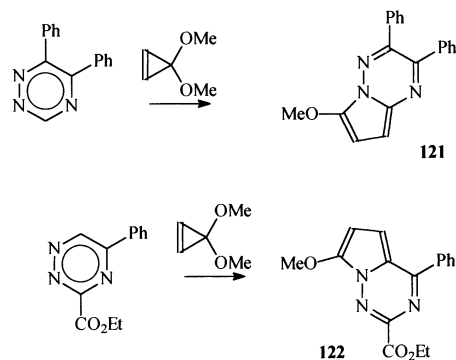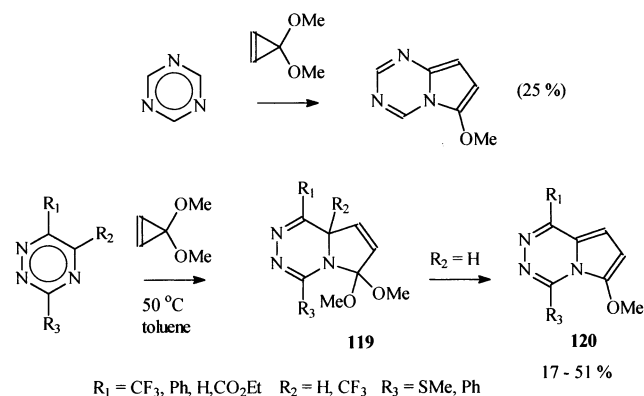
Among the alkenes that trap vinylcarbenes derived from cyclopropenone acetals are C$_{60}$. A [1+2] adduct is formed at 80 °C, but at above 140 °C, the predominant products are derived by [3+2] cycloaddition.[139,140]

XIII. Silicon Substituents

The section above covering alkylcyclopropenes (section III) shows that those carrying a hydrogen on the 1-position of the double bond rearrange thermally to alkynes by a 1,3-hydrogen shift to produce a vinylidene, with subsequent rearrangement by a 1,2-hydrogen or -alkyl shift. Calculations of the isomerization of silylallene using ab initio molecular orbital theory show that the silyl group is expected to migrate more easily than a hydrogen in the parent allene; in particular, the 1,3-silyl-migration that would interconvert silylallene and silylpropyne has barriers for the forward and backward reactions that are about half the migration barriers in allene itself. Silylcyclopropene **123** is predicted to rearrange with the lowest activation barrier by a shift of silicon from C-1 to C-3 to give **124**; the next lowest activation energy (QCISD(T)) is for a 1,3-hydrogen shift to produce **125** (Scheme 2).[141]

The cyclopropene **126** rearranges in the gas phase almost exclusively to the alkyne **128**. The activation energy is found to be 37.2 kcal/mol,[42] very close to that for 3,3-dimethylcyclopropene and to that calculated for path D in Scheme 2. A very low log A value is also consistent with an ordered transition state with migration of the alkene hydrogen to C-3 to produce a vinylidene, **127**.[42] The reaction does, however, occur more slowly than that of 3,3-dimethyl-

Scheme 2
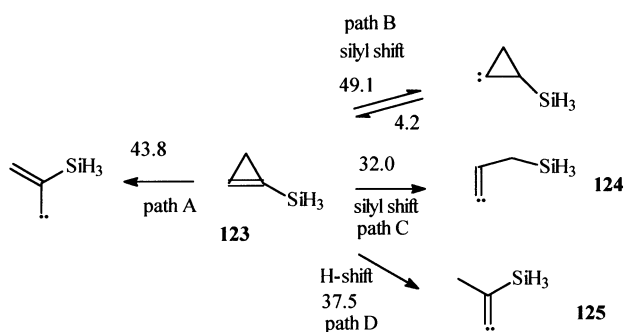
cyclopropene itself. There seems to be no product derived from a silyl shift from C-1 to C-3 of the cyclopropene (path C in Scheme 2); perhaps in this case this is disfavored over a hydrogen shift on steric grounds.
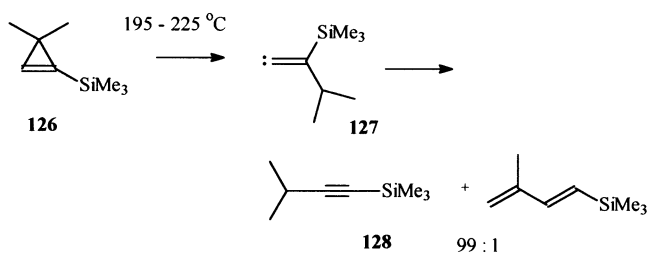
The three silyl-substituted cyclopropenes **129**−**131** rearrange thermally as shown with activation energies of 45.9 (log A = 13.4), 44.1 (log A = 13.5), and 29.8 (log A = 12.2) kcal/mol, respectively, and in each case the corresponding allene is the major product.[142,143]

In the first case, the allene appears to be derived by a silyl shift in the ring-opened vinylcarbene **132** or diradical **132a**. The second example, **130**, is characterized as reacting through a 1,2-silicon shift to generate the corresponding cyclopropylidene **133**. Although 1,2-shifts in cyclopropylidenes or related carbenoids are not common, the reverse of the silyl

shift converting **120** into **133** does occur efficiently,[11] as predicted in Scheme 2, path B, above:

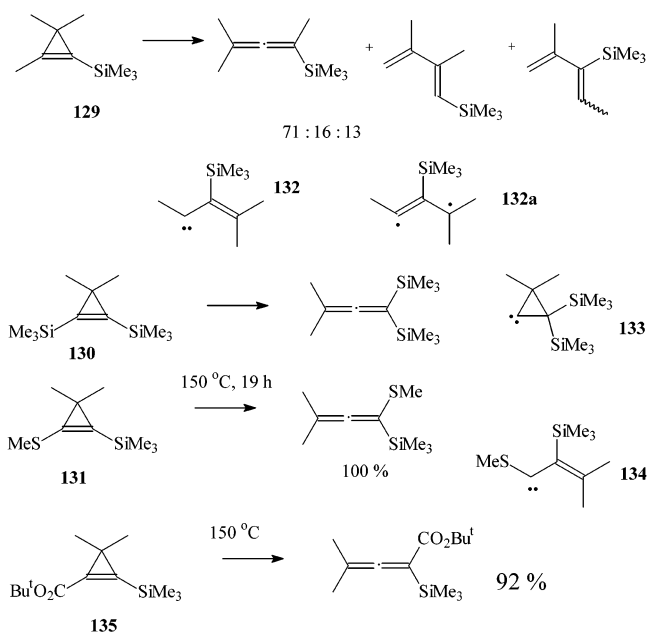R_1 = H, Me; R_2 = H, Me, Bu, Oct; SiR_3 = $SiMe_3$, $SiMe_2Ph$
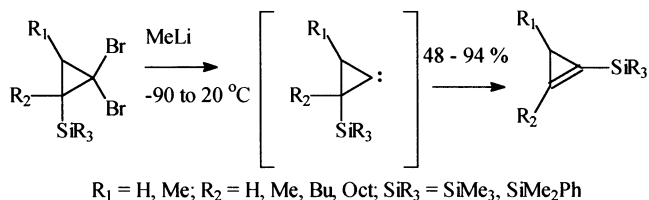
The third reaction above, leading to the allene from **131**, has been explained in terms of a vinylcarbene intermediate, **134**. The ester **135** also rearranges cleanly to allene.[142]

The introduction of a silyl group onto one of the methyl substituents as in **136** leads to a marked rate increase compared to that of 3,3-dimethylcyclopropene and provides evidence of a 1,4-trimethylsilyl migration in an intermediate formulated as a biradical **137**, leading to the *cis*-silyl diene **138**. A second product, **139**, formed in about equal yield, apparently arises by a 1,4-hydrogen shift in the same diradical. In the case of **140**, the rate is about 400 times that for the rearrangement of 1,3,3-trimethylcyclopropene and the major product apparently arises by a 1,2-silicon shift in the diradical **141**. The radicals are thought to be stabilized by the β-effect of silicon.[144]
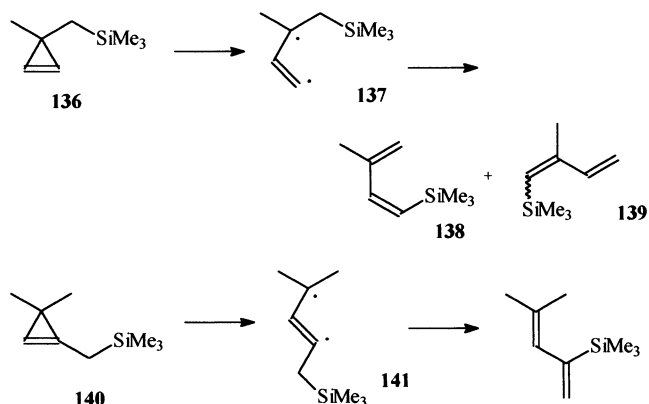
The 3-vinylcyclopropenes **142** (X = Si, Ge) rearrange in hexane in a high-pressure Schlenk tube to give mixtures of alkynes and allenes:

| X = Si | 5 | | 1 |
| X = Ge | 2 | | 1 |
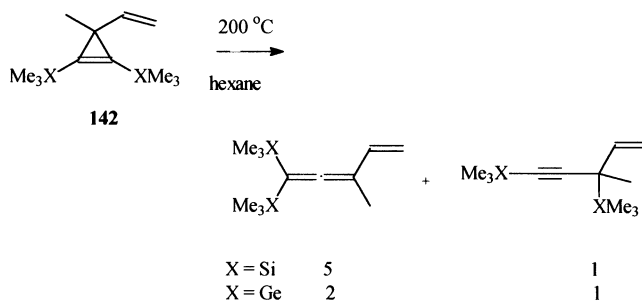
The allene is thought to arise by a 1,2-shift of XMe_3 in a diradical or vinylcarbene intermediate. It is, however, difficult to rule out an intermediate cyclopropylidene, especially by analogy with the reaction of **130**. The alkyne apparently results from a similar shift in a vinylidene.[145]

Table 3. Relative Rates of Selected Cyclopropene Rearrangements at 500 K

cyclopropene	product	rate constant (10^{-4} s^{-1})	k_{rel}/degeneracy[a]	ref
3,3-dimethyl-	3-methylbut-1-yne	9.5	58.4	42
1,3,3-trimethyl-	4-methylpent-2-yne	0.52	6.4	43
3-methyl-3-(trimethylsilyl)methyl-	*cis*1-trimethylsilyl-3-methylbuta-1,3-diene	43.0	265	144
3-methyl-3-(trimethylsilyl)methyl-	1-trimethylsilyl-2-methylbuta-1,3-diene	40.6	125	144
3,3-dimethyl-1-(trimethylsilyl)methyl-	2-trimethylsilyl-4-methylpenta-1,3-diene	306	3774	144
3,3-dimethyl-1-trimethylsilyl-	1-trimethylsilyl-3-methylbut-1-yne	3.5	42.8	42

[a] Relative to cyclopropene.

The tetrasilylcyclopropene **143** rearranges quantitatively at 200−252 °C in d_8-toluene to allene **144**. Kinetic studies indicate a first-order reaction with an activation energy of 37.5 kcal/mol (log A = 11.75). The activation energy is 6.8 kcal/mol lower than that for 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene.

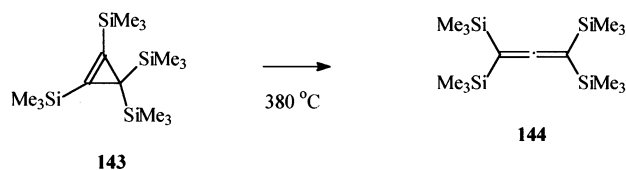The reaction was formulated as occurring via either a cyclopropylidene or a vinylcarbene. To try to trap an intermediate cyclopropylidene, the trisilyl species **145** have been prepared and their thermal reactions studied—in the hope of observing an intramolecular addition of the carbene intermediate to the alkene. In the cases of **145** (n = 1 or 3), only the products of apparent cyclopropylidene−allene rearrangement, **146**, were isolated; with **145** (n = 2), the product was **147**, derived by an intramolecular ene reaction of the cyclopropene. There was no evidence of intramolecular trapping of an intermediate cyclopropylidene by the vinyl group, even though such a reaction is known for other cyclopropylidenes.[146]
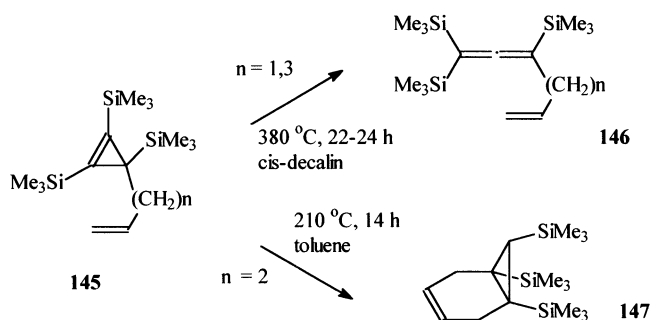
In a similar attempt to trap a cyclopropylidene by intramolecular addition to an alkene, the photolysis of cyclopropenes **148** and **149** has been examined. Again, only allenes were isolated.[146]
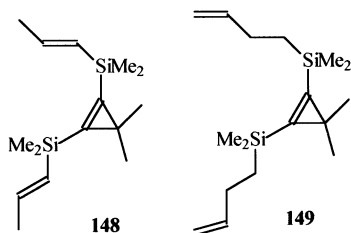
Quantum mechanical ab initio calculations for 1-silylcyclopropenes show that for the 1-trimethylsilyl-3,3-dimethyl compound there is good agreement between observed and predicted product distribution and activation energies and confirm that alkyne formation occurs through a vinylidene intermediate derived by an initial 1,3-hydrogen shift. A comparison between the calculations for this silane and for 1-silyl-3,3-dimethylcyclopropene shows that the latter is not a good model for trimethylsilyl substituents in these systems. For the tetrasilyl cyclopropene, calculations on the desmethyl model **150** suggest a concerted ring opening via a vinylidene-like transition state but predict an activation barrier that is not consistent with experiment. However, steric effects in the methylated version may explain the differences. The calculations indicate that the polysilylated systems should rearrange through vinylcarbenes and that cyclopropylidenes can be excluded as intermediates.[146]
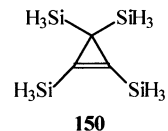
Some relative rates of rearrangement are collected in Table 3.

XIV. Sulfur Substituents

Ring opening to a vinylcarbene, apparently in an equilibrium process, and trapping by furan have also been observed for a cyclopropene-1-sulfoxide, **151** (R = H), even at −20 to +20 °C, though the methyl-substituted analogue **151** (R = Me) does not trap alkenes even at 80 °C:[147]
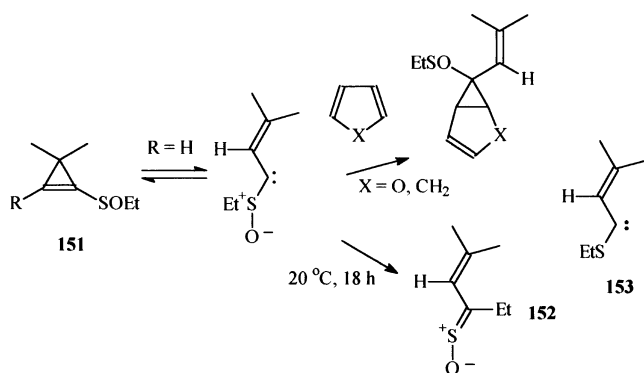
In the absence of furan the cyclopropene rearranges at 20 °C to the diene **152**.[117] The correspond-

ing sulfone also ring-opens to the vinylcarbene at room temperature, and this can be trapped by furan.[148] In contrast, the corresponding thioether is too unstable to isolate and rearranges to 3-methylbuta-1,3-dienyl ethyl thioether, derived by an apparent 1,4-hydrogen shift in an intermediate carbene, **153**, and 2,7-dimethyl-4,5-ethylthioocta-2,4,6-triene, a formal dimer of the carbene.[117,149]

As indicated above, thioether **131** rearranges in 10 h at 150 °C to allene either by ring opening to the vinylcarbene **134** followed by a silyl shift or by a 1,2-silyl shift to give the cyclopropylidene, and then rearrangement to the allene **154**. It is not possible to trap either intermediate by intermolecular addition to an alkene, and the activation energy for the process is about 4 kcal/mol higher than that observed for 3-isopropyl-1-methylthio-2,3-diphenylcyclopropene.[142]

The thioether **155** rearranges under relatively mild conditions by cleavage of the σ-bond to the carbon bearing the sulfur substituent, and products are observed from both stereoisomeric vinylcarbenes:[95]
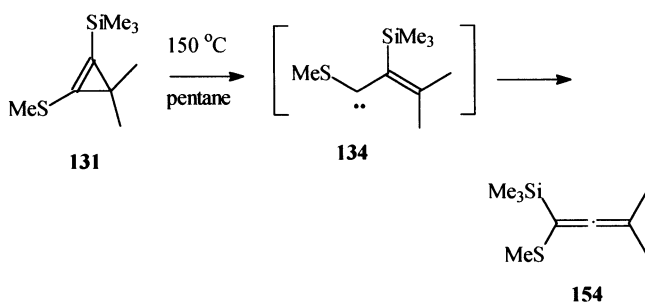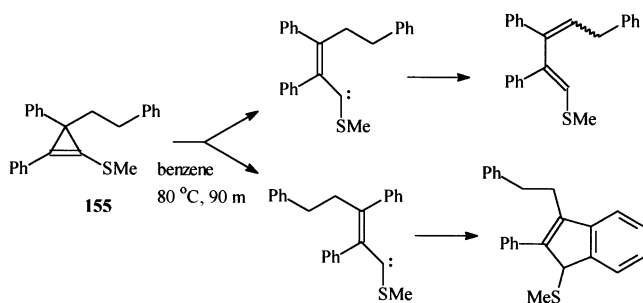

In related systems, the rearrangement in refluxing benzene leads to the more stable sulfur-substituted carbene **157** rather than **158**. It is interesting to note that the isomeric cyclopropene **159** does not rearrange under these conditions. In the case of 3-iso-propyl-2,3-diphenyl-1-thiopropylcyclopropene, the rate of rearrangement is only slightly changed in different solvents; the activation energy for the rearrangement in methanol has been determined to be 23.6 kcal/mol.[150,151]

Cyclopropenes such as **160** carrying a second heteroatom substituent also rearrange to indenes **161** under similar conditions, again provided the thio-

alkyl group is on C-1 — compound **162** being unreactive:[152]
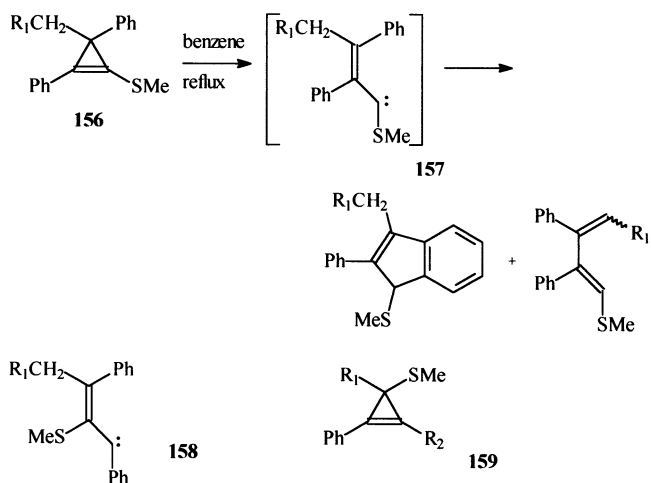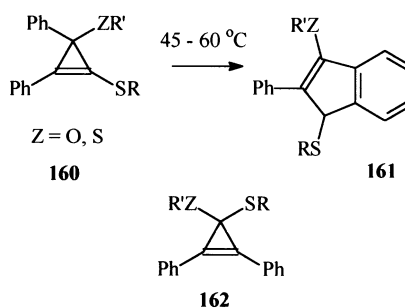
R	R'Z	E_{act} (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
Me	4-ClC$_6$H$_4$O	21.5 ± 05	−10.1 ± 1.3 (CCl$_4$)
Me	4-ClC$_6$H$_4$S	21.5 ± 0.1	−10.1 ± 0.1

In other cases, the intermediacy of a carbene is only implied from the products. Thus, trapping of tri-2-propylthiocyclopropenium ion (**163**) by sodium aryl-sulfinates in dry acetonitrile or benzene at reflux leads to products **164** and **165**, consistent with vinylcarbene intermediates:
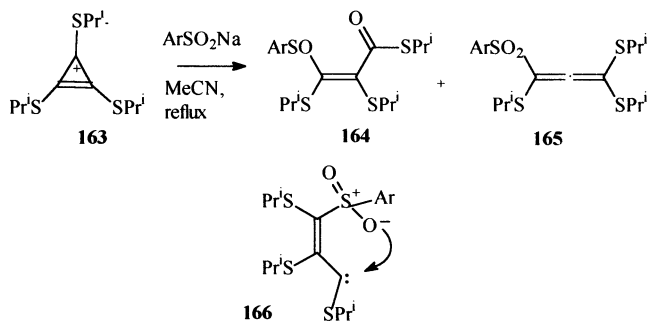
The allene **165** can be explained in terms of a 1,2-shift in the carbene **166**, derived from an initially formed cyclopropene (which can be isolated if the reaction is carried out at room temperature). Cyclization of the carbene as shown, followed by fragmentation, would lead to the enone **164**.[153] The cyclopropenium ion also reacts with

naphthylamines in refluxing acetonitrile or dimethylformamide at 85 °C to give the tricycle **168**. This is apparently derived by initial formation of a 3-aminocyclopropene, ring opening to the corresponding vinylcarbene **167**, and then insertion of this into the α-CH bond of the remote ring, followed by loss of one molecule of thiol. In a similar way, the anion of pyrrole reacts with the cyclopropenium ion in dimethyl sulfoxide at 25 °C over 1.5−2 h to give **169**.[154]
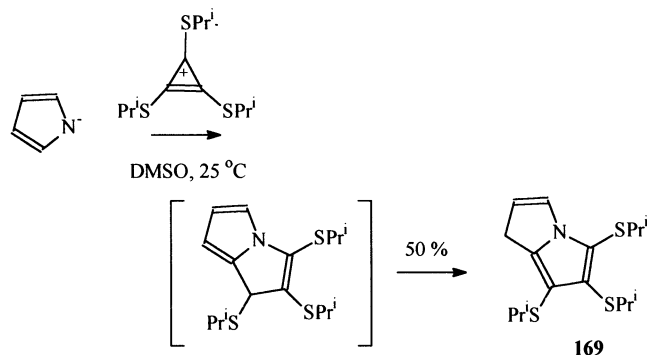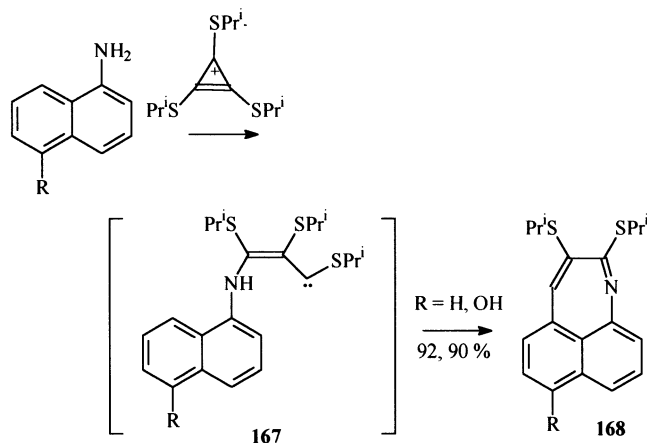
XV. Aminocyclopropenes

If the alkylthio group in cyclopropenes such as **155** and **156** is replaced by an amino substituent, amino-indenes are isolated on heating in benzene. These are again derived by cleavage of the heteroatom-substituted σ-bond. In other solvents, however, carbenium ion rearrangements are observed leading to isomeric indenes **170**:[155]
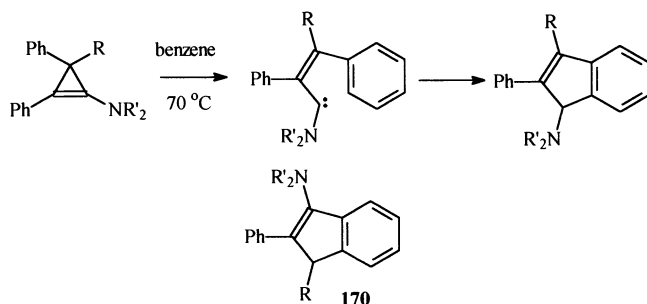
The bicyclic cyclopropene **171** carrying a 3-amide substituent rearranges in benzene in 4 h at 154 °C in a sealed tube, giving a low yield of **172**, apparently

derived by intramolecular trapping of a vinylcarbene:[156]
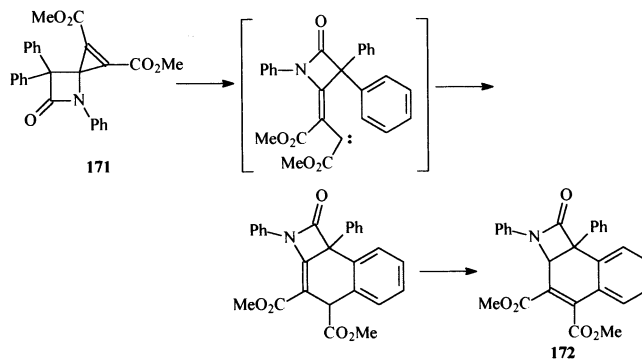
XVI. Nitrocyclopropenes

1-Nitro-2-phenyl-3,3-dimethylcyclopropene undergoes an unusual cycloaddition to furan, leading to the bicycle **173**, apparently derived by addition of the vinylcarbene **174** to the alkene:[157]
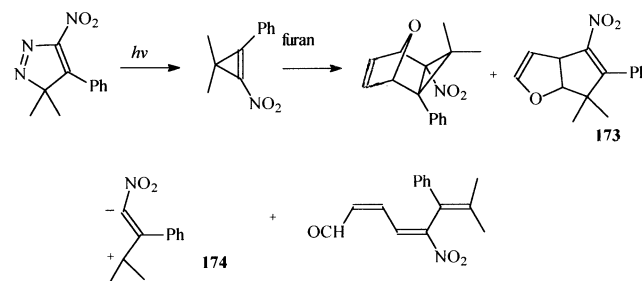
It is not clear, however, whether all the products are actually derived from thermal reactions of the cyclopropene.

Simple 3-nitrocyclopropenes are relatively rare. The parent is too unstable to isolate, though it is not clear to what it decomposes, while 3-cyano-3-nitrocyclopropene and silylated analogues are relatively stable and can undergo [4+2] cycloaddition to cyclopentadiene rather than ring opening or oligomerization.[158,159]

XVII. Bicyclic Systems

The ring opening of cyclopropenes to vinylcarbenes also occurs in bicyclic systems; such processes have been reviewed.[160] Thus, the 1,2-elimination of halogen from bicyclic trihalocyclopropanes such as **175** ($n = 3, 4$) often leads to the isolation of a relatively stable cyclopropene, but in the bicyclo[3.1.0] ring system **175** ($n = 1$), only the product of trapping of a ring-opened carbene by furan can be isolated:[161,162]
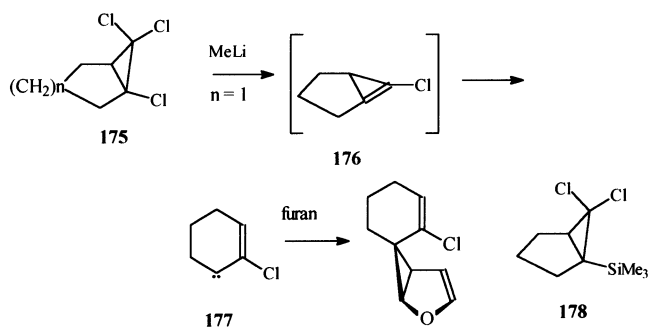
The stereochemistry assigned to related compounds on the basis of NOE experiments (see below) suggests that that assigned to the adduct above may need to be reversed, i.e. that it is actually **181** (X = CH$_2$). The cyclopropene **176** can also be generated by dehalosilylation of **178** or by dehydrochlorination of **179** (X = CH$_2$) and the derived carbene **177** trapped as above by furan and by insertion into the C–H bond α to oxygen in tetrahydrofuran.[163]

In the same way, reaction of **179** (X = O) with potassium *tert*-butoxide leads to elimination to cyclopropene **180** (X = O), which may be trapped as a [4+2] cycloadduct with diphenylisobenzofuran but in the presence of furan undergoes ring opening and is trapped as **181**. The corresponding cyclopropene **180** (X = S) does not ring-open to carbene and is trapped in [4+2] cycloadditions.[161,164]
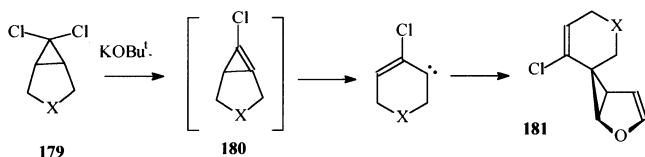
The tetrahalide **182** reacts with methyllithium by two rather different routes. One of these involves a 1,2-dehalogenation leading to the cyclopropene **183**. Ring opening produces the vinylcarbene **184** which inserts into the solvent, ether, to give a pair of diastereomeric ethers **185**:[165]
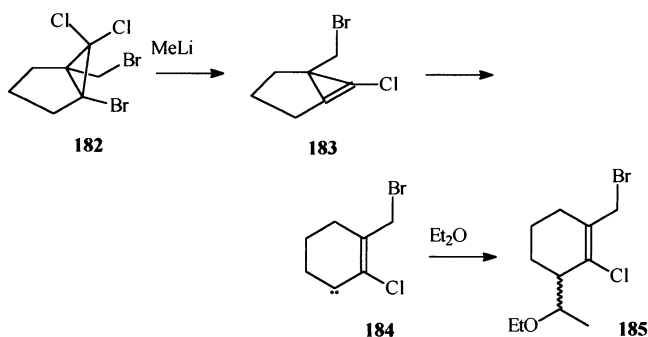
This pathway is favored at low temperature. It is interesting to note that no product of a 1,2-hydrogen shift in the carbene is observed.

The highly strained cyclopropenes **186** are only kinetically stabilized by a low barrier and have also been shown to isomerize thermally even in an argon matrix at 10 K to carbenes **187**.[166–168] The cyclopropene is transformed directly into triplet carbene, and intersystem crossing is rate determining; at low
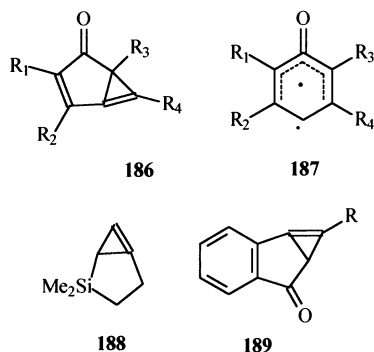
temperature the rates are independent of temperature, indicating a quantum mechanical tunneling process. In contrast, 4,4-dimethylcyclohexa-2,5-dienylidene undergoes an irreversible cyclization to 4,4-dimethylbicyclo[3.1.0]hexa-1(6),2-diene in an argon matrix at 10 K.[169]

It is interesting to note that the silicon species 4,4-dimethyl-4-silacyclohexa-1,4-dien-6-ylidene ring-contracts to the cyclopropene **188**,[170,171] while **189** ring-opens to the corresponding indenonylcarbene.[171]

In the bicyclo[4.1.0]heptene series, **190** is reported to form 2-chlorocyclohepta-1,3-diene when generated by a dehalosilylation in a vacuum gas–solid system; the reaction is thought to involve ring opening to the carbene **191**,[172] a process that apparently occurs even at −90 °C.[173] However, a later study, in which the cyclopropene was generated from 1-trimethylsilyl-7,7-dichlorobicyclo[4.1.0]heptane and tetrabutylammonium fluoride in solution, leads to the formation of the dichloride **195**, apparently derived from the alternative vinylcarbene **194**. Since the diene obtained on dehydrochlorination of **195** shows properties identical to those reported for the diene **192**, the earlier interpretation may not be correct.[163]
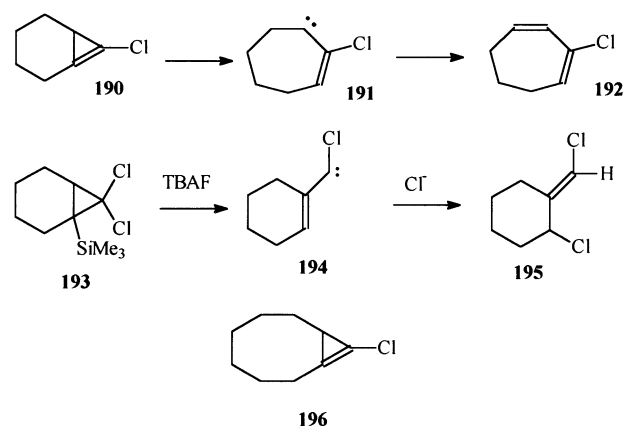
Ring expansion is also reported for the bicyclo[6.1.0]nonene **196**. Reaction with water leads to (*E*)-2-chloromethylenecyclooctanol and cycloocten-1-carboxaldehyde, a process claimed to involve the trapping of cyclooctenylchlorocarbene; reaction with oxygen is reported to lead to 2-chlorocyclonon-2-enone, a process reported to involve 2-chlorocyclonon-2-en-1-ylidene.[174] However, no trapping of the carbenes by alkenes is reported, and there are alternative non-carbene processes that may lead to the observed products.

Cyclopropenes have also been proposed as nonisolable intermediates in the generation of vinylcarbenes in polycyclic systems. Thus, although the cyclopropene **197** does not ring-open at −110 °C to produce anthracenylcarbene,[175] reaction of **198** with base leads to **199**; cleavage of the external σ-bond leads to a carbene which inserts into the C–H bonds adjacent to oxygen in tetrahydrofuran:[176,177]
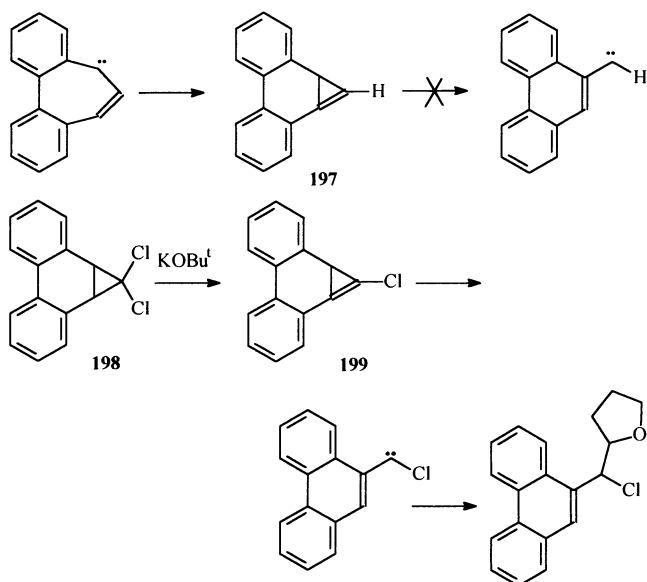
No products derived by cleavage of the internal σ-bond of the cyclopropene are observed.

When a suitable substituent is present at the 9-position of the phenanthrene ring, intramolecular trapping of the carbene is observed leading to furans or cyclopentadienes:[178,179]
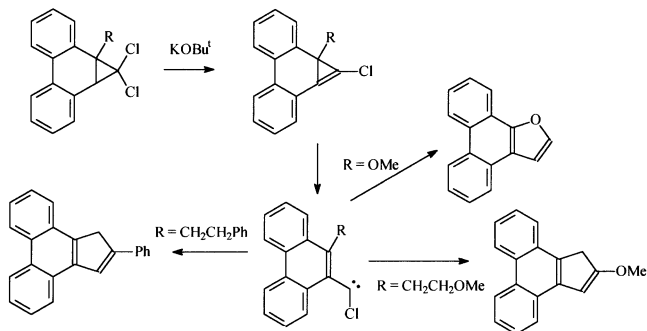
There is some evidence that vinylcarbenes are formed from a number of related bicyclo[4.1.0]-heptanes, though in most cases these are trapped as ethers by reaction with the base.

XVIII. Dicyclopropenes

Thermolysis of the dicyclopropene **200** leads to benzocyclobutene, tetralin, and styrene as the major products. These have been explained in terms of the formation and trapping of a vinylcarbene, **201**, though there is little direct evidence to support this.[180]
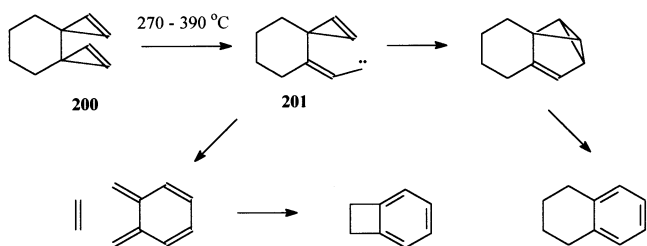
XIX. Conclusion

The thermal ring opening of cyclopropenes provides a template for the examination of the core reactions of vinylidenes and vinylcarbenes and, to a rather lesser extent, of cyclopropylidenes. In the case of cyclopropene itself and of alkylcyclopropenes, these ring-opening reactions occur only at relatively high temperatures, generally above 200 °C. When the cyclopropene has hydrogens at C-1 and C-2, the predominant reaction is a hydrogen shift from C-1 to C-3 of the cyclopropene, leading to a vinylidene (methylenecarbene), **202**, which rapidly rearranges to an alkyne through a 1,2-hydrogen shift. With a single hydrogen on the double bond, a similar 1,3-hydrogen shift occurs, but the derived vinylidene **203** now rearranges by a slower process, a 1,2-alkyl shift, and alternative products derived from a vinylcarbene are observed in competition with alkyne. Those alkylcyclopropenes with no alkene hydrogens ring-open to vinylcarbenes **204**, which usually undergo hydrogen shifts. Although intramolecular trapping of these intermediates can readily be observed, intermolecular trapping is not.
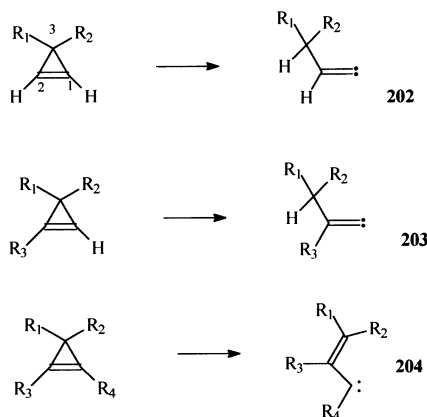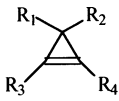
The introduction of a range of substituents can dramatically reduce the temperature at which ring opening occurs. Thus, simple 3,3-dialkoxycyclopropenes ring-open at about 80 °C, and the addition of selected substituents leads to reaction even at 0 °C, while 1,2-dihalocyclopropenes react at 0–20 °C. In both these reactions, the formal vinylcarbene intermediates may be trapped in a variety of useful intermolecular processes. Cyclopropene-1-carboxylates, cyclopropene 1-thioethers, 1-sulfoxides, and sulfones can also ring-open to vinylcarbenes at ambient temperature, although there are far fewer examples.

Alkyl- or aryl-substituted 3-arylcyclopropenes generally rearrange at temperatures of 170–200 °C and lead to indenes by apparent cyclization of a vinylcarbene intermediate, which in some cases can be trapped in intramolecular processes. Substituents such as thioether groups at C-1 dramatically reduce the reaction temperature. The corresponding 1,2-dichloro-3-arylcyclopropenes undergo a similar cyclization and cannot be isolated under the conditions of their generation at below ambient temperature. These reactions can be applied to the synthesis of a variety of polycyclic frameworks.

Despite the number of publications in this area of cyclopropene chemistry, there are still many substituent patterns for which there is no information on thermal reactions (see Table 4). It seems likely

Table 4. Some Cyclopropenes for Which Thermal Isomerization Is Not Reported

R_1	R_2	R_3	R_4	conditions	ref
H	H	SPh	Me	not reported	181
H	H	OMe	Ph	not reported	182
H	H	OSiCMe$_2$-t-Bu	SiMe$_3$	not reported	183
H	H	OEt	Ph	not reported	182
Cl	Cl	SMe	SMe	not reported	184
COOEt	H	OMe	Me	not reported	185
CH(OMe)$_2$	H	OMe	Et	not reported	186
COOEt	TMS	H	H	143 °C, xylene[a]	187

[a] Forms a [2+2] dimer.

that within these there will be additional opportunities for generating carbenes that have useful synthetic potential as well as providing fuller information on the factors that control the various ring-opening processes.

It is also possible that the introduction of additional strain into polycyclic cyclopropenes will lead to rearrangements under very mild conditions and novel reactions of derived vinylcarbenes. One example is seen in the possible intermediacy of a vinylcarbene into generation of an anti-Bredt olefin which is subsequently trapped by diphenylisobenzofuran:

XX. References

(1) Stechl, H.-H. *Chem. Ber.* **1964**, *97*, 2681.
(2) Srinivasan, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1041.
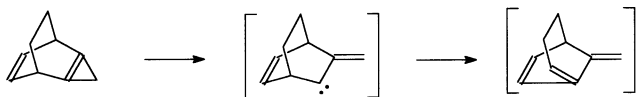(3) Steinmetz, M. G.; Yen, Y.-P.; Poch, G. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1504.
(4) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1986**, *135*, 79.
(5) Shapiro, E. A.; Protopopova, M. N.; Nefedov, O. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, 2153.
(6) Leftin, J. H.; Gil-Av, E. *Tetrahedron Lett.* **1972**, 3367.
(7) Baird, M. S. In *Methoden der Organischen Chemie, Houben Weyl*; de Meijere, A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1997; Vol. E17d, p 2695.
(8) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.
(9) Misslitz, U.; de Meijere, A. In *Methoden der Organischen Chemie, Houben Weyl*; Regitz, M., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1989; Vol. E19b, p 664.
(10) Backes, J.; Brinker, U. H. In *Methoden der Organischen Chemie, Houben Weyl*; Regitz, M., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1989; Vol. E19b, p 391.
(11) Baird, M. S.; Dale, C. M.; Al Dulayymi, J. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1373.
(12) Stang, P. J. In *Methoden der Organischen Chemie, Houben Weyl*; Regitz, M., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1989; Vol. E19b, p 84.
(13) Taber, D. F.; Yu, H. *J. Org. Chem.* **1997**, *62*, 1687.
(14) Wolinsky, J.; Clark, G. W.; Thorstenson, P. *J. Org. Chem.* **1976**, *41*, 745.
(15) Eberbach, W.; Roser, J. *Tetrahedron Lett.* **1987**, *28*, 2685.
(16) Eberbach, W.; Roser, J. *Tetrahedron Lett.* **1987**, *28*, 2689.
(17) Pascual, A.; Nishio, T.; Frei, B.; Jeger, O. *Helv. Chim. Acta* **1984**, *67*, 129.
(18) Osullivan, A.; Frei, B.; Jeger, O. *Helv. Chim. Acta* **1984**, *67*, 815.
(19) Roth, W. R.; Bastigkeit, T. *Liebigs Ann.* **1996**, 2171.
(20) Brown, R. F. C. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 655.
(21) Huntsman, W. D.; Yin, T.-K. *J. Org. Chem.* **1983**, *48*, 3813.
(22) Bailey, I. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1146.
(23) Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, 2137.
(24) Hopf, H.; Pricke, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

(25) Karni, M.; Oref, I.; Barzilaigilboa, S.; Lifshitz, A. *J. Phys. Chem.* **1988**, *92*, 6924.
(26) Kiefer, J. H.; Kumaran, S. S.; Mudipalli, P. S. *Chem. Phys. Lett.* **1994**, *224*, 51.
(27) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511.
(28) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wessermann, E. E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.
(29) Hoffmann, R.; Zeiss, G. D.; van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.
(30) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.
(31) Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699.
(32) Kakkar, R.; Padhi, B. S. *Indian J. Chem., Sect. B* **1999**, *38*, 1262.
(33) Kakkar, R.; Padhi, B. S. *Int. J. Quantum Chem.* **1996**, *58*, 389.
(34) Sevin, A.; Arnaud-Danz, L. *J. Org. Chem.* **1981**, *46*, 2346.
(35) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 4015.
(36) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Am. Chem. Soc.* **1984**, *106*, 5361.
(37) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785.
(38) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 4198.
(39) Blitz, M. A.; Beasley, M. S.; Pilling, M. J.; Robertson, S. H. *Phys. Chem. Chem. Phys.* **2000**, *2*, 805.
(40) Gates, K. E.; Robertson, S. H.; Smith, S. C.; Pilling, M. J.; Beasley, M. S.; Maschhoff, K. J. *J. Phys. Chem. A* **1997**, *101*, 5765.
(41) Hopf, H.; Wachholz, G.; Walsh, R. *Chem. Ber.* **1985**, *118*, 3579.
(42) Walsh, R.; Untiedt, S.; Stohlmeier, M.; De Meijere, A. *Chem. Ber.* **1989**, *122*, 637.
(43) Walsh, R.; Wolf, C.; Untiedt, S.; De Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 421.
(44) Likhotvorik, I. R.; Brown, D. W.; Jones, M. *J. Am. Chem. Soc.* **1994**, *116*, 6175.
(45) Streeper, R. D.; Gardner, P. D. *Tetrahedron Lett.* **1973**, 767.
(46) Perez, J. D.; Yranzo, G. I. *J. Org. Chem.* **1982**, *47*, 2221.
(47) Hopf, H.; Plagens, A.; Walsh, R. *Justus Liebigs Ann. Chem.* **1996**, 825.
(48) Hopf, H.; Plagens, A.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1467.
(49) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *47*, 3377.
(50) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.
(51) Hopf, H.; von der Schulenburg, W. G.; Walsh, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 381.
(52) von der Schulenburg, W. G.; Hopf, H.; Walsh, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1128.
(53) von der Schulenburg, W.; Hopf, H.; Walsh, R. *Chem.—Eur. J.* **2000**, *6*, 1963.
(54) Ebrahimi, A.; Deyhimi, F.; Roohi, H. *J. Mol. Struct.: THEOCHEM* **2001**, *546*, 207.
(55) Hopf, H.; Wachholz, G.; Walsh, R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1103.
(56) Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 6250.
(57) de Meijere, A.; Untiedt, S.; Stohlmeier, M.; Walsh, R. *Chem. Ber.* **1989**, *122*, 637.
(58) Billups, W. E.; Bachman, R. E. *Tetrahedron Lett.* **1992**, *33*, 1825.
(59) Croft, A. K.; Baird, M. S. Unpublished results.
(60) Liese, T.; Demeijere, A. *Chem. Ber.* **1986**, *119*, 2995.
(61) Liese, T.; Splettstasser, G.; De Meijere, A. *Tetrahedron Lett.* **1982**, *23*, 3341.
(62) Weber, W.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 138.
(63) Weber, W.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2450.
(64) Kostikov, R. R.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1528.
(65) Dehmlow, E. V.; Naser-ud-din *J. Chem. Res., Synop.* **1981**, 144.
(66) Baird, M. S.; Hussain, H. H. *Tetrahedron* **1989**, *45*, 6221.
(67) Baird, M. S.; Buxton, S. R.; Whitley, J. S. *Tetrahedron Lett.* **1984**, *25*, 1509.
(68) Slougui, N.; Rousseau, G. *Tetrahedron Lett.* **1987**, *28*, 1651.
(69) Al Dulayymi, J. R.; Baird, M.; Baran, J.; Mayr, H. Unpublished results.
(70) Baird, M. S. *Adv. Strain Org. Chem.* **1991**, *1*, 65.
(71) Al Dulayymi, J. R.; Baird, M. S.; Pavlov, V. A.; Kurdyukov, A. I. *Tetrahedron* **1996**, *52*, 8877.
(72) Al Dulayymi, J. R.; Baird, M. S. *Tetrahedron* **1989**, *45*, 7601.
(73) Al Dulayymi, J. R.; Baird, M. S.; Clegg, W. *Tetrahedron Lett.* **1988**, *29*, 6149.
(74) Al Dulayymi, J. R.; Baird, M. S.; Rajaram, L.; Clegg, W. *J. Chem. Res., Synop.* **1994**, 344.
(75) Al Dulayymi, J. R.; Baird, M. S.; Hussain, H. H. *Tetrahedron Lett.* **1989**, *30*, 2009.
(76) Al Dulayymi, J. R.; Baird, M. S.; Clegg, W. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1799.
(77) Al Dulayymi, J. R.; Baird, M. S. *Tetrahedron Lett.* **1988**, *29*, 6147.
(78) Baird, M. S.; Al Dulayymi, J. R.; Rzepa, H. S.; Thoss, V. *J. Chem. Soc., Chem. Commun.* **1992**, 1323.

(79) Memmesheimer, H.; Al Dulayymi, J. R.; Baird, M. S.; Wettling, T.; Regitz, M. *Synlett* **1991**, 433.
(80) Memmesheimer, H.; Bergstrasser, U.; Hoffmann, J.; Baird, M.; Regitz, M. *Synlett* **1992**, 635.
(81) Baird, M.; Al Dulayymi, J. R.; Hussain, H. H. Unpublished results.
(82) Al Dulayymi, J. R.; Baird, M. S. *Tetrahedron Lett.* **1992**, *33*, 835.
(83) Al Dulayymi, A. R.; Al Dulayymi, J. R.; Baird, M. S.; Rajaram, L. *Tetrahedron* **1995**, *51*, 8371.
(84) Al Dulayymi, J. R.; Baird, M. S.; Fitton, H. L. *Tetrahedron Lett.* **1992**, *33*, 4803.
(85) Al Dulayymi, J. R.; Baird, M. S.; Fitton, H. L.; Rajaram, L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1633.
(86) Al Dulayymi, J. R.; Baird, M. S. *Tetrahedron Lett.* **1995**, *36*, 3393.
(87) Baird, M. S. *Tetrahedron Lett.* **1984**, *25*, 4829.
(88) Gothling, W. Dissertation, University of Hamburg, Germany, 1985.
(89) Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845.
(90) Baird, M.; Buxton, S. R.; Hussain, H. H. *J. Chem. Res., Synop.* **1986**, 310.
(91) Al Dulayymi, J. R. Unpublished results.
(92) Pavlov, V. A.; Kurdyukov, A. I.; Moskva, V. V.; Baird, M. S. *Phosphorus, Sulfur Selenium* **1996**, *110*, 509.
(93) Sydnes, L. K.; Bakstad, E. *Acta Chem. Scand.* **1996**, *50*, 446.
(94) Sydnes, L. K. *Eur. J. Org. Chem.* **2000**, 3511.
(95) Müller, P.; Pautex, N. *Helv. Chim. Acta* **1991**, *74*, 55.
(96) Dolbier, W. R.; Shelton, G. R.; Battiste, M. A.; Stanton, J. F.; Price, D. R. *Org. Lett.* **2002**, *4*, 233.
(97) Honjou, N.; Pacansky, J.; Yoshimine, M. *J. Mol. Struct.: THEO-CHEM* **1994**, *118*, 23.
(98) Battiste, M. A.; Halton, B.; Grubbs, R. H. *J. Chem. Soc., Chem. Commun.* **1967**, 907.
(99) Snatzke, G.; Langen, H. *Chem. Ber.* **1969**, *102*, 1865.
(100) Domnin, I. N.; Kostikov, R. R.; Demaiere, A. *Zh. Org. Khim.* **1983**, *19*, 2206.
(101) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Org. Chem.* **1984**, *49*, 1353.
(102) Padwa, A.; Rieker, W. F. *J. Am. Chem. Soc.* **1981**, *103*, 1859.
(103) Chiacchio, U.; Compagnini, A.; Grimaldi, R.; Purrello, G.; Padwa, A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 915.
(104) Padwa, A.; Blacklock, T. J.; Loza, R. M. *J. Org. Chem.* **1982**, *47*, 3712.
(105) Klimova, E. I.; Ramirez, L. R.; Berestneva, T. K.; Garcia, M. M.; Moreno-Esparza, R.; Toledano, C. A.; Toscano, R. A. *Russ. Chem. Bull.* **1998**, *47*, 482.
(106) Klimova, E. I.; Garcia, M. M.; Klimova, T.; Toledano, C. A.; Toscano, R. A.; Ramirez, L. R. *J. Organomet. Chem.* **2000**, *598*, 254.
(107) Klimova, E. I.; Ramirez, L. R.; Esparza, R. M.; Berestneva, T. K.; Garcia, M. M.; Meleshonkova, N. N.; Churakov, A. V. *J. Organomet. Chem.* **1998**, *559*, 1.
(108) Komatsu, K.; Niwa, T.; Akari, H.; Okamoto, K. *J. Chem. Res., Synop.* **1985**, 252.
(109) Al Dulayymi, A. R.; Swinburn, S.; Benedetti, S.; Baird, M. S. Unpublished results.
(110) Al Dulayymi, A. R.; Baird, M. S. *Tetrahedron Lett.* **1997**, *38*, 8271.
(111) Haley, M. M.; Biggs, B.; Looney, W. A.; Gilbertson, R. D. *Tetrahedron Lett.* **1995**, *36*, 3457.
(112) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482.
(113) Billups, W. E.; Lin, L. J. *Tetrahedron* **1986**, *42*, 1575.
(114) Al Dulayymi, A. R.; Baird, M. S. *Tetrahedron* **1996**, *52*, 10955.
(115) Padwa, A.; Kulkarni, Y. S.; Terry, L. W. *J. Org. Chem.* **1990**, *55*, 2478.
(116) Baird, M. S.; Hussain, H. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1609.
(117) Franck-Neumann, M.; Miesch, M.; Barth, F.; Jenner, G. *Bull. Soc. Chim. Fr.* **1989**, 661.
(118) Padwa, A.; Kennedy, G. D.; Newkome, G. R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 137.
(119) Komendantov, M. I.; Bekmukhametov, R. R.; Domnin, I. N. *Zh. Org. Khim.* **1978**, *14*, 759.
(120) Komendantov, M. I.; Bekmukhametov, R. R.; Domnin, I. N. *Tetrahedron* **1978**, *34*, 2743.
(121) Majchrzak, M. W.; Warkentin, J.; Woollard, J. M. R. *Struct. Chem.* **1991**, *2*, 137.
(122) Han, S.; Arrowood, T.; Young, V. G.; Kass, S. R. *Struct. Chem.* **1999**, *10*, 349.
(123) Han, S. D.; Kass, S. R. *Tetrahedron Lett.* **1997**, *38*, 7503.
(124) Müller, P.; Granicher, C. *Helv. Chim. Acta* **1995**, *78*, 129.
(125) Albert, R. M.; Butler, G. B. *J. Org. Chem.* **1977**, *42*, 674.
(126) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695.
(127) Boger, D. L.; Brotherton, C. E.; Georg, G. I. *Tetrahedron Lett.* **1984**, *25*, 5615.
(128) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805.
(129) Boger, D. L.; Wysocki, R. J. *J. Org. Chem.* **1988**, *53*, 3408.

(130) Boger, D. L.; Brotherton, C. E. *Tetrahedron Lett.* **1984**, *25*, 5611.
(131) Tokuyama, H.; Yamada, T.; Nakamura, E. *Synlett* **1993**, 589.
(132) Boger, D. L.; Brotherton, C. E.; Georg, G. I. *Org. Synth.* **1987**, *65*, 32.
(133) Boger, D. L.; Brotherton, C. E. *Adv. Cycloaddit.* **1990**, *2*, 147.
(134) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6713.
(135) Boger, D. L.; Brotherton, C. E. *J. Org. Chem.* **1985**, *50*, 3427.
(136) Butler, G. B.; Herring, K. H.; Lewis, P. L.; Sharpe, V. V.; Veazey, R. L. *J. Org. Chem.* **1977**, *42*, 679.
(137) Tokuyama, H.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 5523.
(138) Frenzen, G.; Rischke, M.; Seitz, G. *Chem. Ber.* **1993**, *126*, 2317.
(139) Tokuyama, H.; Isobe, H.; Nakamura, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 935.
(140) Tokuyama, H.; Nakamura, M.; Nakamura, E. *Tetrahedron Lett.* **1993**, *34*, 7429.
(141) Shimizu, H.; Gordon, M. S. *Organometallics* **1995**, *14*, 3827.
(142) Kirms, M. A.; Primke, H.; Stohlmeier, M.; Demeijere, A. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 462.
(143) Walsh, R.; Untiedt, S.; Demeijere, A. *Chem. Ber.* **1994**, *127*, 237.
(144) Walsh, R.; Wolf, C.; Untiedt, S.; Demeijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 422.
(145) Eckertmaksic, M.; Golic, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2325.
(146) de Meijere, A.; Faber, D.; Heinecke, U.; Walsh, R.; Müller, T.; Apeloig, Y. *Eur. J. Org. Chem.* **2001**, 663.
(147) Franck-Neumann, M.-F.; Lohmann, J. J. *Tetrahedron Lett.* **1979**, 2397.
(148) Franck-Neumann, M.-F.; Lohmann, J. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 323.
(149) Franck-Neumann, M.-F.; Lohmann, J. J. *Tetrahedron Lett.* **1978**, 3729.
(150) Yoshida, H.; Kato, M.; Ogata, T.; Matsumoto, K. *J. Org. Chem.* **1985**, *50*, 1145.
(151) Yoshida, H.; Sano, H.; Kato, M.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2833.
(152) Yoshida, H.; Takahashi, Y.; Kinoshita, H.; Ukishima, S.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3565.
(153) Kojima, H.; Yamamoto, K.; Kinoshita, Y.; Inoue, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1674.
(154) Kojima, H.; Matsumura, N.; Inoue, H. *Can. J. Chem.* **1992**, *70*, 1.
(155) Yoshida, H.; Sano, H.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4341.
(156) Zoghbi, M.; Warkentin, J. *Can. J. Chem.* **1992**, *70*, 2967.
(157) Franck-Neumann, M.-F.; Miesch, M. *Tetrahedron Lett.* **1984**, *25*, 2909.
(158) O_Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1991**, *56*, 2258.
(159) O_Bannon, P. E.; Carroll, P. J.; Dailey, W. P. *Struct. Chem.* **1991**, *2*, 133.
(160) Billups, W. E.; Haley, M. M.; Lee, G. A. *Chem. Rev.* **1989**, *89*, 1147.
(161) Halton, B.; Lovett, E. G. *Struct. Chem.* **1991**, *2*, 147.
(162) Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, *24*, 605.
(163) Banwell, M. G.; Corbett, M.; Gulbis, J.; Mackay, M. F.; Reum, M. E. *J. Chem. Soc., Perkin Trans. 1* **1993**, 945.
(164) Halton, B.; Bridle, J. H.; Lovett, E. G. *Tetrahedron Lett.* **1990**, *31*, 1313.
(165) Weber, J.; Brinker, U. H. *Tetrahedron* **1996**, *47*, 14641.
(166) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346.
(167) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311.
(168) Sander, W.; Hubert, R.; Kraka, E.; Grafenstein, J.; Cremer, D. *Chem.—Eur. J.* **2000**, *6*, 4567.
(169) Albers, R.; Sander, W.; Ottosson, C. H.; Cremer, D. *Chem.—Eur. J.* **1996**, *2*, 967.
(170) Coleman, B.; Jones, M. *J. Organomet. Chem.* **1979**, *168*, 605.
(171) Padwa, A.; Krumpe, K. E.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 2633.
(172) Arney, B. E. Ph.D. Thesis, Rice University, Houston, TX, 1986.
(173) Billups, W. E.; Lee, G. A.; Arney, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 7980.
(174) Lee, G. A.; Chen, J.; Chen, C. S.; Shiau, C. S.; Cherng, C. H. *J. Chin. Chem. Soc.* **1996**, *43*, 297.
(175) Mykytka, M.; Jones, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 3.
(176) Halton, B.; Officer, D. L. *Tetrahedron Lett.* **1981**, *22*, 3687.
(177) Billups, W. E.; Reed, L. E.; Casserly, E. W.; Lin, L. P. *J. Org. Chem.* **1981**, *46*, 1326.
(178) Müller, P.; Pautex, N. *Helv. Chim. Acta* **1988**, *71*, 1630.
(179) Müller, P.; Pfyffer, J. *Chimia* **1984**, *38*, 79.
(180) Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813.
(181) Baird, M. S.; Shortt, M. F.; Hussain, H. H.; Al Dulayymi, J. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1945.
(182) Crossland, I. *Acta Chem. Scand.* **1987**, *B41*, 310.
(183) Ryu, I.; Hayama, A.; Sonoda, N.; Orita, A. *J. Am. Chem. Soc.* **1990**, *112*, 7061.

(184) Weiss, R.; Schlierf, C.; Schloter, K. *J. Am. Chem. Soc.* **1976**, *98*, 4668.
(185) Wenkert, E.; Chou, K. J.; Hatch, R. P. *Synth. Commun.* **1977**, *7*, 375.
(186) Billups, W. E. *J. Org. Chem.* **1975**, *40*, 1848.
(187) Arrowood, T. L.; Kass, S. R. *Tetrahedron* **1999**, *55*, 6739.
(188) Lee, G.-A.; Lin, Y.-H.; Huang, A. N.; Li, Y. C.; Jann, Y.-C.; Chen, C.-S. *J. Am. Chem. Soc.* **1999**, *121*, 5328.