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CHAPTER 6

Carbenes and Nitrenes

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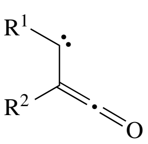
Reviews

The rearrangements, mechanisms, and conformations of alkylcarbenes have been reviewed.[1] A review of Shpolskii matrix-isolated aromatic carbenes, the study of their conformational isomerism, and the determination of the zero-field splitting parameters of their excited triplet states has appeared.[2] Reviews have also appeared on laser flash photolysis of carbonyl carbenes,[3] 1,2-hydrogen migration of singlet carbenes and the mechanistic issues involved in the use of diazirine precursors,[4] the insertion of carbenes to give compounds containing bridgehead double bonds,[5] asymmetric carbene transformations,[6] mechanisms and applications of 1,4-addition reactions of carbenes to dienes,[7] stereoselective intramolecular C−H insertion reactions of metal carbenes,[8] the formation and reactions of donor-substituted carbenes,[9] and the thermally induced isomerizations of vinylsilanes.[10]

Structure and Reactivity

At the HF/6−31G* level, ketenyl carbenes (**1**) were calculated to be intermediates in the decarbonylation of 1,2-bisketenes (**2**) to form cyclopropenones.[11] At the MP2/6−31G* and B3LYP levels, however, decarbonylation was predicted to form the cyclopropenones directly. The *anti*-ketenyl carbenes were found to be 2.2−5.4 kcal mol^{-1} higher in energy than the *syn* isomers (**1**). The mechanism of reaction of [1.1.1]propellane with singlet dihalocarbene has been reported.[12]



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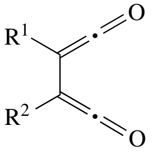

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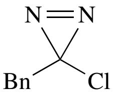

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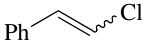

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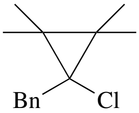

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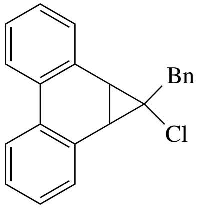

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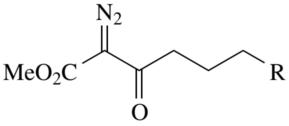
F_2C:, formed in the initial pyrolysis of perfluoro(methylcyclopropane), is proposed to recombine to form biradicaloid C_2F_4*.[13] Time-resolved electron paramagnetic resonance spectroscopy has been used to study the lowest excited triplet state of Ph_2C:, generated by photolysis of the corresponding diazo compound at low temperature.[14] The zero-field splitting parameters $|D|(-0.142\,\mathrm{cm}^{-1})$ and $|E|(-0.0033\,\mathrm{cm}^{-1})$ were obtained.

Photolysis of benzylchlorodiazirine (**3**) in the presence of tetramethylethylene (TME) is known to produce (E)- and (Z)-β-chlorostyrene (**4**) and the cyclopropane (**5**). Plots of [**5**]/[**4**] vs [TME] are curved, consistent with the existence of two pathways for the formation of the alkenes (**4**). Benzylchlorocarbene (BnClC:) was generated by laser flash photolysis of the phenanthrene (**6**) in the presence of TME.[15] In this case, plots of [**5**]/[**4**] vs [TME] are linear, ruling out the possibility that the second pathway to the alkenes (**4**) involves reaction of a carbene–alkene complex. Time-resolved IR spectroscopy revealed that diazirine (**3**) rearranges to the corresponding diazo compound, but this process is too inefficient to account for the curvatures. It is proposed that the second pathway to alkene formation involves the excited state of the diazirine.

In contrast to 2-alkylarylcarbenes, triplet carbonyl carbenes do not abstract H from δ- or ε-CH bonds.[16] Photolysis of diazo compounds (**7**) in methanol gave products due to Wolff rearrangement (**8**) and O–H insertion (**9**). Sensitized photolysis led, in addition, to the H-abstraction product (**10**). Analysis of the results indicated that a large proportion of the insertion product (**9**) arises from the excited diazo compound and that spin inversion of the triplet carbene is faster than H-abstraction from the solvent. Intersystem crossing to the singlet state is a major reaction of all triplet carbonyl carbenes that are not rapidly scavenged intramolecularly.

The absolute rate constants for reaction of p-tolyl(trifluoromethyl)carbene, generated by laser flash photolysis of the corresponding diazirine, with pyridine ($4 \times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in Freon-113), ketones [$(1.5\text{–}9.8) \times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}}$ in hexafluorobenzene], and quenchers of biological interest have been obtained.[17] The results support a triplet ground state with a small ($0.5\text{–}1.5\,\mathrm{kcal\,mol^{-1}}$) singlet–triplet energy gap.



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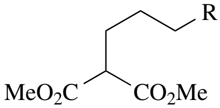

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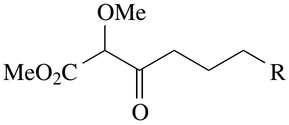

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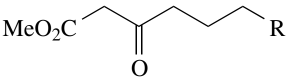

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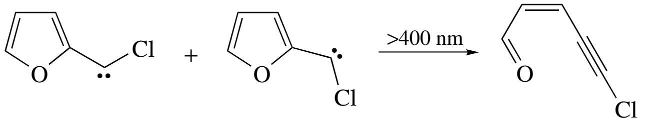
2-Furylchorocarbene (**11**), generated by irradiation of the corresponding diazirine in a nitrogen matrix at 8 K, was characterized by IR spectroscopy, which revealed two species, one of which was destroyed on irradiation to form the aldehyde (**12**).[18] The experimental and calculated spectra were in accord with two conformations of the carbene, one of which decomposes to the aldehyde.

Irradiation of 2-diazomethylbiphenylene gives the carbene (**13**), which possesses an antiaromatic ring.[19] Insertion into the C—H bond of cyclohexane and addition to alkenes with retention of stereochemistry suggest reactions via the singlet state. ESR spectroscopy allowed the estimation of zero-field splitting parameters of the two conformational isomers of (**13**). Both were $S = 1$ species displaying slightly more delocalization than the corresponding naphthylcarbenes.

t-Butylphenylmethylene (**14**) is calculated to have a singlet–triplet gap of 5–6 kcal mol^{-1} with a triplet ground state.[20] The larger angle at the carbene carbon in the triplet (138.5°) compared with the singlet (119.3°) reduces steric interactions and allows the phenyl ring to adopt a position in which maximum overlap with the carbene *p*-orbital can occur. The Me—C$_\alpha$—C$_{\text{carbene}}$ angle θ is 101°, indicating some stabilization of the carbene by the adjacent C—C σ-bond. The barriers for 1,3-CH insertion and C—C migration were calculated to be 1.8 and 3.8 kcal mol^{-1}, respectively, in good agreement with the experimentally determined ratio of these processes.



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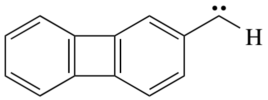

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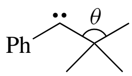

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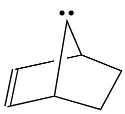

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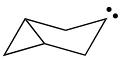

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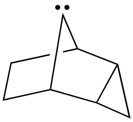

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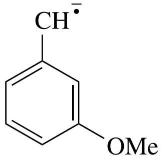
Calculations at the B3LYP/6–31G*//B3LYP/6–31G* level were used to evaluate the stabilization energy of the singlet carbene (**15**) as 15.56 kcal mol^{-1}.[21] Similar calculations on singlet 3-carbenabicyclohexane (**16**) and the tricyclooctane (**17**) gave values of 3.27 and 14.06 kcal mol^{-1}, respectively. The calculated geometries of (**15**) and (**17**) showed a significant leaning of the carbenic carbon over the π system or cyclopropane. This distortion was absent in the triplet structures, which were found to lie well above the singlets (by 27.82 and 25.74 kcal mol^{-1}, respectively). Singlet carbenes (**15**) and (**17**) appear to be strongly homoaromatic, whereas (**16**) is only weakly so.

Abstraction of H_2^+ from 3-methylanisole, generated in a flowing afterglow triple quadrupole apparatus, gives the radical anion (**18**). This species undergoes electron transfer to F_2 followed by attack of fluoride ion at the methoxy methyl group to give the distonic carbene ion (**19**).[22] Carbene (**19**) displays reactivity characteristic of a singlet species and calculations at the B3LYP/cc-pVTZ level predict a singlet ground state with singlet–triplet gap of 3 kcal mol^{-1}. Kinetic protonation on oxygen is predicted to give a ground-state triplet. *C*-protonation is predicted to give a triplet biradical 22.6 kcal mol^{-1} more stable than the *O*-protonated form. Insight into the origin of spin–orbit coupling in carbenes and the heavy atom effect of substituents was gained by calculations on **:**CH_2, **:**CHF, **:**CHCl, and **:**CHBr.[23] Photolysis of 1,4-bis(diazomethylbenzene) in an N_2 matrix at 10 K produced a species attributed by IR and UV–Visible spectroscopy to *p*-phenylenebismethylene as its biradical (**20**).[24] The biscarbene (**20**) was trapped by HCl to form 1,4-di(chloromethyl)benzene and by oxygen to form the bis(carbonyl *O*-oxide).



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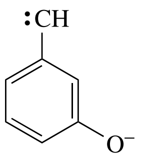

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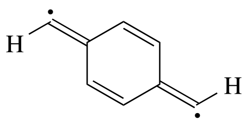
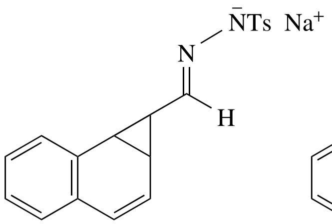


(**20**)

Both thermal (120 °C at 0.005τ) and photochemical decomposition of the tosylhydrazone salt (**21**) were proposed to proceed by initial formation of the cyclopropylcarbene followed by fragmentation to biradicals (**22**) and (**23**), which proceeded to 1- and 2-vinylnaphthalene and benzobarrelene (**24**).[25]



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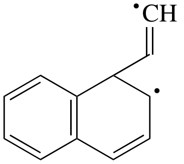

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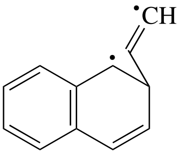

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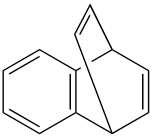

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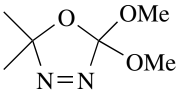
Thermolysis of the oxadiazoline (**25**) in the gas phase using a CO_2 laser as directed heat source gives products including acetone, tetramethoxyethene, and dimethyl oxalate.[26] Subtraction of the photoelectron spectra of these species from the spectrum of the product mixture leaves a simple photoelectron spectrum attributed to dimethoxycarbene in the W conformation (**26**). Photoelectron spectra for two stable carbenes (**27**; R = Et and R = ^{i}Pr) have been recorded.[27] The first ionization potentials were found to be 7.71 and 7.56 eV, respectively. Calculations of the first adiabatic ionization potentials of eight electronically diverse carbenes were performed using a variety of levels of theory. Calculations using the CBS-4 model and those using B3LYP/6−31 + G* were shown to give good agreement with experiment.



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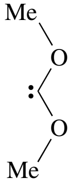

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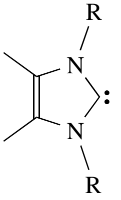

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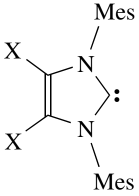
1,3-Dimesitylimidazol-2-ylidene (**28**; X = H) reacts with CCl_4 to give carbene (**28**; X = Cl), which showed enhanced stability towards air, moisture, and acidic halogenated solvents.[28] An X-ray crystal-structure determination was obtained. Both carbenes (**28**; X = H or Cl) react with tellurium to give the corresponding tellurone. The strong σ electron-withdrawing effect of the chlorine atoms is evidenced by the very downfield ^{125}Te resonance of this species (−4 ppm compared with −150 ppm for the non-chlorinated tellurone).

Proton abstraction from the imidazolium chloride (**29**) by KO^{t}Bu gave the carbene (**30**) originally postulated, but not isolated, by Wanzlick.[29] An X-ray structure determination of the carbene (**30**) showed the expected near-planarity of the imidazole ring and an NCN angle of 102.1°, characteristic of a singlet carbene.



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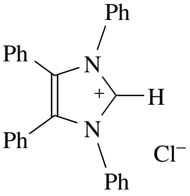

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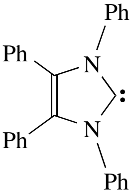

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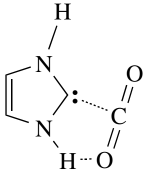
Irradiation of matrix-isolated imidazole-2-carboxylic acid gave the 2,3-dihydroimidazol-2-ylidene–CO_2 complex (**31**) characterized by IR spectroscopy and calculated to lie 15.9 kcal mol^{-1} above the starting material.[30] A series of non-aromatic nucleophilic carbenes (**32**) were prepared by desulfurization of the corresponding thiones by molten potassium in boiling THF.[31] The most hindered of the series (**32**; R = ^{t}Bu) is stable indefinitely under exclusion of air and water and can be distilled without decomposition. The less hindered carbenes slowly dimerize to the corresponding alkenes. Stable aminoxy- and aminothiocarbenes (**33**; X = O, S) were prepared by deprotonation of iminium salts with lithium amide bases.[32] The carbene carbon resonance appears at 260–297 ppm in the ^{13}C NMR spectrum and an X-ray structure determination of an aminooxycarbene indicated that electron donation from the nitrogen is more important than that from oxygen. These carbenes do not dimerize.

The observed IR spectrum of the initial product of irradiation of *p*-diazidobenzene in an argon matrix at 12 K was in excellent agreement with that calculated for the bisnitrene (**34**).[33] Calculations indicated that (**34**) has a singlet ground state and small singlet–triplet gap. The decay of (**34**) gave rise to a species assigned as (**35**) which, in turn, fragmented to acetylene and the alkene (**36**).



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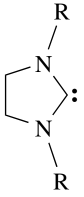

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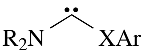

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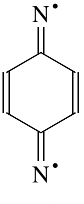

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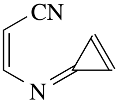

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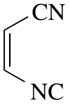

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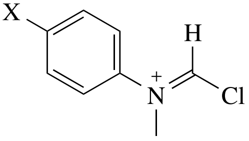
Generation

Extrusion of F_2C**:** from the CF_3 group adjacent to the radical centre of an initially formed biradicaloid isomer in the pyrolysis of hexafluoropropylene was proposed.[34] The activation energy for this extrusion was 30 ± 2.5 kcal mol^{-1} and $(F_3C)FC$**:** was not observed. Thermal decomposition of $CHCl_3$ in krypton was found to proceed by elimination to form HCl and Cl_2C**:** in a laser Schlieren density gradient study.[35] Chlorine atom formation is entirely due to the thermal reactivity of Cl_2C**:**. MNDO calculations have been used to study the reaction of CCl_4 with magnesium to form Cl_2C**:**.[36]

Deprotonation of Vilsmeier reagents (**37**) by tertiary amine bases has been proposed to give nucleophilic aminochlorocarbenes (**38**), which react with (**37**) to produce the observed enediamine products (**39**).[37]



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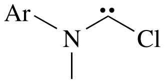

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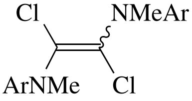

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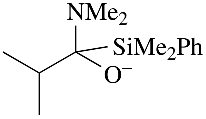

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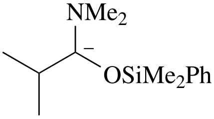

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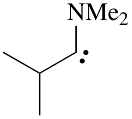

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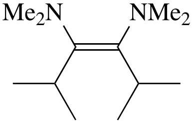

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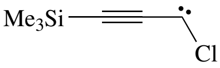

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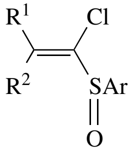
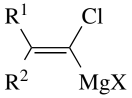


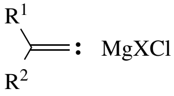
(**45**)

Reaction of an amide with $PhMe_2SiLi$ was proposed to proceed via addition to the carbonyl (**40**), Brook rearrangement to (**41**), and loss of $PhMe_2SiO^-$ to give the carbene (**42**), which dimerizes to the enediamine product (**43**).[38] The carbene could be trapped by a second equivalent of silyl lithium reagent to give $R(Me_2N)CLi(SiMe_2Ph)$.

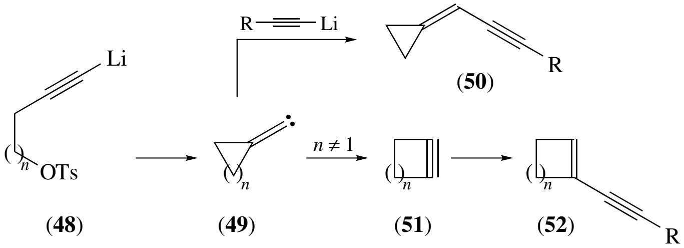
Chloro(trimethylsilylethynyl)carbene (**44**) was formed by α-elimination of HCl from trimethylsilylethynyldichloromethane with KO^tBu.[39] Cycloaddition to alkenes gave the corresponding cyclopropanes. Treatment of 1-halovinyl sulfoxides (**45**) with EtMgX gave rise to the corresponding magnesium alkylidene carbenoids (**46**), which could be trapped by electrophiles to give vinyl chlorides.[40] Carbenoids (**46**) were



(**46**)



(**47**)

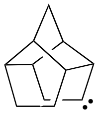


(**48**) (**49**) (**50**) (**51**) (**52**)

configurationally unstable and exchanged Cl with Br on magnesium, suggesting an equilibrium with the alkylidene carbene–magnesium halide complex (**47**).

An *exo*-type cyclization, proceeding through a cycloalkylidene carbene (**49**; $n = 1$, 3, 4), was proposed to explain the formation of enynes (**50**) and (**52**) from alkynyl lithium species (**48**).[41] The proposed carbene (**49**) could be trapped by addition to cyclohexene and the cycloalkyne intermediate (**51**) was trapped by Diels–Alder reaction with 1,3-diphenylisobenzofuran.

The reactivity of cage-annulated carbene (**53**) was found to depend markedly on the method of its formation.[42] Pyrolysis of the corresponding tosylhydrazone sodium salt gave products of intramolecular CH insertion or H-abstraction. Photolysis of a diazirine precursor gave only azine products by reaction of the carbene with the precursor or diazo compound. Treatment of the *gem*-dibromoalkane with BuLi gave products due to intermolecular insertion of the carbene into CH bonds of the solvent.



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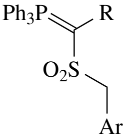

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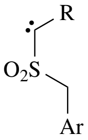
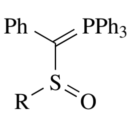


(**55**)

Flash vacuum pyrolysis (600 °C) of arylmethylsulfonyl-stabilized phosphorus ylides (**54**) gave products resulting from initial extrusion of Ph_3P to form the sulfonyl carbene (**55**) followed by 1,2-, 1,3-, or 1,5-CH insertion and loss of SO_2.[43] 1,3-Insertion gives a thiirane dioxide, which loses SO_2 to produce an alkene ArCH=CHR. Flash vacuum pyrolysis of alkane sulfinyl ylides (**56**; R = alkyl) gave thioesters (**58**) by extrusion of Ph_3P to give the α-sulfinyl carbenes (**57**) followed by 1,2-oxygen transfer.[44] The corresponding arylsulfinyl ylides (**56**; R = aryl) give, in addition, ketones (**60**) via



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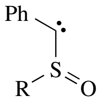

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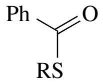

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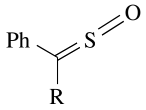

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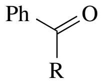
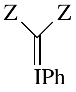


(**60**)



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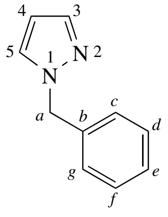

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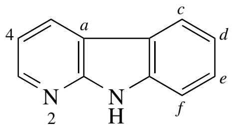

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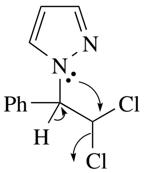

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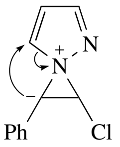
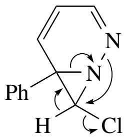
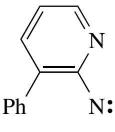


(**65**)



(**66**)



(**67**)

Wolff-like rearrangement of the carbenes (**57**) to the sulfines (**59**), which rearrange with loss of sulfur. The remaining minor products were postulated to arise by loss of Ph_3PO to give the sulfenyl carbene RS(Ph)C**:**.

Phenyliodonium ylides (**61**; $Z = CO_2R$, SO_2Ph, COR) react in the presence of Rh(II) catalysts with the same selectivity in cyclopropanations as the corresponding diazo compounds and intramolecular CH insertions occur with identical enantioselectivities.[45] This strongly suggests the intermediacy of Rh carbenoids in reactions of the ylides. Copper(I)-catalysed cyclopropanation of alkenes with diphenylsulfoniumethoxycarbonylmethylide also gave *cis:trans* ratios and *ee*s identical with those formed using ethyl diazoacetate. $Rh_2(OAc)_4$-catalysed alkene aziridination using NsN=IPh(Ns = *N*-*p*-nitrobenzenesulfonyl) is stereospecific, CH insertions occur with retention of stereochemistry, chiral ligands on rhodium give enantio-enriched products, and no ring opening is observed in the CH insertion reactions of alkylcyclopropanes.[46] A single-step mechanism involving a metal-complexed nitrene is proposed for both reactions.

A series of substituted or ^{13}C- or ^{15}N-labelled 1-arylmethylpyrazoles (**62**) were used to identify the origin of the atoms in the α-carboline (**63**) formed by pyrolysis in the presence of chloroform.[47] The proposed mechanism involves insertion of dichlorocarbene into a benzylic CH bond to give (**64**). Loss of HCl gives (**65**), which undergoes a Stevens-type rearrangement to (**66**) followed by rearrangement to the nitrene (**67**), which closes on to the phenyl ring to give the α-carboline (**63**).

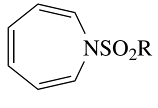
Treatment of sulfonylamide tetrabutylammonium salts $RSO_2NH^-Bu_4N^+$ in benzene with XeF_2 gives the corresponding *N*-sulfonylazepines (**68**) via a proposed sulfonyl nitrene intermediate.[48]

Addition

Ab initio and RRKM calculations indicate that the reactions of C, CH, and $^1(H_2C\mathbf{:})$ with acetylene occur with no barrier.[49] Laser flash photolysis of the cyclopropanes (**69**) and (**70**) was used to generate the corresponding dihalocarbenes.[50] The absolute rate constant for the formation of a pyridine ylide from $Br_2C\mathbf{:}$ was $(4-11) \times 10^{-9}\,\mathrm{l\,mol^{-1}\,s^{-1}}$. The rates of additions of these carbenes to alkenes were measured by competition with pyridine ylide formation and the reactivity of $BrClC\mathbf{:}$ was found to resemble that of $Br_2C\mathbf{:}$ rather than $Cl_2C\mathbf{:}$.

Theoretical studies on the cyclopropanation of ethene with lithium carbenoid and zinc carbenoid (Simmons–Smith reagent) revealed that both methylene-transfer and carbometallation pathways are fast for lithium whereas only the former is fast enough to be experimentally observed for the zinc carbenoid.[51] Treatment of trimethyl orthoformate with Me_3SiCl and zinc amalgam in the presence of alkenes gave rise to the corresponding alkoxycyclopropanes (**71**) via a postulated zinc carbenoid (**72**).[52] The reaction showed a preference for electron-rich alkenes, proceeded with retention of configuration on the alkene, and gave predominantly the more hindered *endo* isomer (**71**).

7-Norbornylidene carbene (**73**) was generated by treatment of the corresponding dibromomethylene species with butyllithium.[53] The carbene reacted with alkenes with retention of configuration, a characteristic of singlet carbenes. No evidence of 1,2-C shift to the corresponding alkyne was seen. Similar observations were made with the heptacyclic analogue (**74**).



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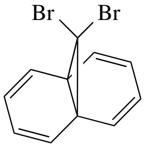

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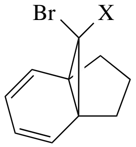
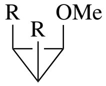


(**70**)

X = Br, Cl



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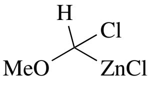

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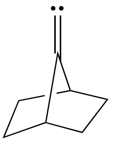

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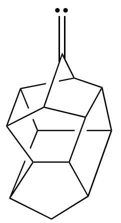

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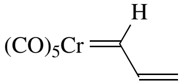

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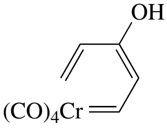

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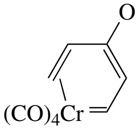

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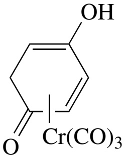


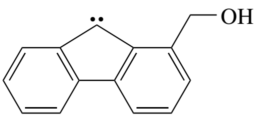
(**78**)

Density functional calculations on the Dötz reaction leading from chromium carbene (**75**) with acetylene to give the phenol (**78**) suggested a new mechanism involving the formation of a chromahexatriene complex (**77**) from the initially formed vinylallylidene complex (**76**).[54] Complex (**77**) then collapses to the phenol complex (**78**).

Insertion and Abstraction

Laser flash photolysis of phenylchlorodiazirine was used to measure the absolute rate constants for intermolecular insertion of phenylchlorocarbene into CH bonds of a variety of co-reactants.[55] Selective stabilization of the carbene ground state by π-complexation to benzene was proposed to explain the slower insertions observed in this solvent in comparison with those in pentane. Insertion into the secondary CH bond of cyclohexane showed a primary kinetic isotope effect $k_\mathrm{H}k_\mathrm{D}$ of 3.8. 1-Hydroxymethyl-9-fluorenylidene (**79**), generated by photolysis of the corresponding diazo compound, gave aldehyde (**80**) in benzene or acetonitrile via intramolecular H-transfer.[56] In methanol, the major product was the ether, formed by insertion of the carbene into the MeO−H bond, and the aldehyde (**80**) was formed in minor amounts through H-transfer from the triplet carbene to give a triplet diradical which can relax to the enol.

Flash vacuum pyrolysis of 3,5-diphenylpyrazole (**81**) gave rise to products of intramolecular CH insertion of the resulting vinylcarbene (**82**).[57] The barrier to nitrogen extrusion is $20 \pm 3\,\mathrm{kJ\,mol^{-1}}$ and $\log A = 13.1 \pm 0.1\,\mathrm{s^{-1}}$.



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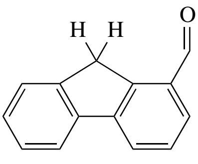
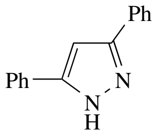
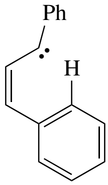


(**80**)



(**81**)



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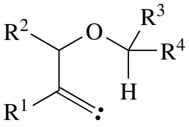

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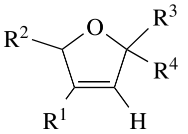

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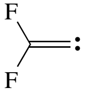

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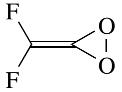


(86)

1,5-CH insertion of vinylidenecarbenes (**83**), generated from the corresponding ketones by treatment with lithio(trimethylsilyl)diazomethane, gave rise to 2,5-dihydrofurans (**84**).[58] The use of aldehydes ($R^1 = H$) gave rise to alkynes by 1,2-H shift in the corresponding carbenes. Matrix-isolated difluorovinylidene (**85**) was generated by photo-induced 1,2-F shift from difluoroacetylene.[59] The reaction of vinylidene (**85**) with CO_2 leads, by electrophilic attack on the oxygen of CO_2, to difluoroketene and CO. The reaction of (**85**) with molecular dioxygen produces $F_2C\mathbf{:}$ and CO_2 and is postulated to proceed via difluoromethlene dioxirane (**86**).

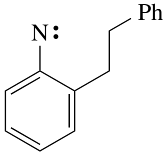
The deuterium kinetic isotope effect for intramolecular CH insertion of the nitrene (**87**), generated by photolysis of the corresponding azide, is 14.7 ± 0.3 at 20 °C and is consistent with the H-abstraction–recombination mechanism from the triplet state.[60] The temperature dependence of the kinetic isotope effect suggests that quantum mechanical tunnelling is important in this process.

Rearrangement

A density functional study has been made of the competition between Wolff rearrangement and [1,2]-H shift in β-oxy-α-diazocarbonyl compounds.[61] Silver-catalysed decomposition of α-diazoketones (**88**; $n = 0$), derived from *N*-tosyl α-amino acids in methanol, gave rise to mixtures of products of Wolff rearrangement (**89**) and direct insertion of the carbene into the NH bond (**90**).[62] The β-amino acid derived species (**88**; $n = 1$) gave rise to products of Wolff rearrangement.

Dimethylcarbene and dimethylcarbene-d_6 were generated by laser flash photolysis of the corresponding diazirines.[63] In perfluorohexane, the carbenes decay by rearrangement to propene with barriers of 2.56 ± 0.05 and $5.63 \pm 0.03\,\text{kcal mol}^{-1}$, respectively. The results, in comparison with calculations, indicate that quantum mechanical tunnelling is significant for dimethylcarbene, but makes only a minor contribution for dimethylcarbene-d_6.

A detailed reinvestigation of the products and kinetics of reactions of benzylchlorocarbene, generated by photolysis of the corresponding diazirine, indicated that the



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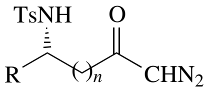

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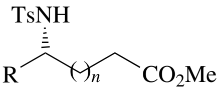

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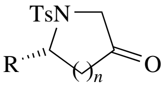


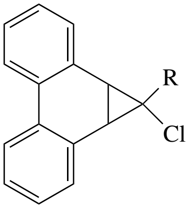
(90)

curvature observed in the Arrhenius plots ($\ln k$ vs $1/T$) for the rate constants of 1,2-H shift in hydrocarbon solvents is mainly due to competitive intermolecular reactions (azine formation and solvent insertion) down to −70 °C.[64] The barrier to [1,2]-H shift is ca 4.8 kcal mol^{-1} in hydrocarbons and ca 3.2 kcal mol^{-1} in polar solvents (e.g. tetrachloroethane). Quantum mechanical tunnelling does not appear to play a major role in the [1,2]-H shift of benzylchlorocarbene at ambient temperature in solution.

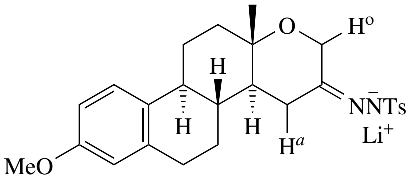
Previous studies of the photochemistry of alkylchlorodiazirines have shown that the yield of trappable carbene is sensitive to the alkylcarbene structure. A laser flash photolysis study of phenanthridenes (**91**), precursors of alkylchlorocarbenes, in the presence of pyridine, has ruled out the intermediacy of a carbene–pyridine complex which partitions between pyridine–ylide formation and [1,2]-H shift.[65]

Substituent effects at the migration origin on the rate of rearrangement of several alkylchlorocarbenes have been studied at the B3LYP/6−311G**//B3LYP/6−31G* level.[66] [1,2]-H shifts are accelerated in the order Ph > Me > F > Cl > H. The exclusive [1,2]-H shift observed in Bn(Cl)C**:** is not due to a migratory preference of H over Ph, but is the result of the greater acceleration of [1,2]-H shift by the Ph group than of the [1,2]-Ph shift by an adjacent H. The relative effect of ring-alkyl vs ring-oxygen on the [1,2]-migration of hydrogen (H^a vs H^o, respectively) to the steroidal carbene formed by thermal or photochemical decomposition of the *N*-tosylhydrazone lithium salt (**92**) showed that ring-oxygen is a more powerful activator than ring-alkyl by a factor of 12:1 in thermolysis at 170 °C and by 14:1 in photolysis at −70 °C.[67]

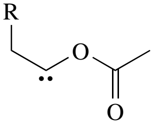
A study of the absolute rate constants for [1,2]-H and [1,2]-acyl shifts in a series of alkylacetoxycarbenes (**93**), generated by photolysis of the corresponding diazirines, showed that an α-methyl group is ca 12 times more effective at promoting [1,2]-H shift than an α-Ph group.[68]



(**91**)



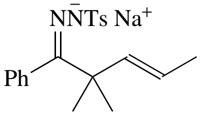
(**92**)



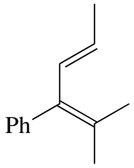
(**93**)

Photolysis of the tosylhydrazone sodium salt (**94**) in diglyme gave, as the major product, 1,3-diene (**95**) by [1,2]-vinyl shift in the intermediate carbene.[69] Vinyl migration occurs with retention of configuration and is postulated to occur in the singlet manifold.

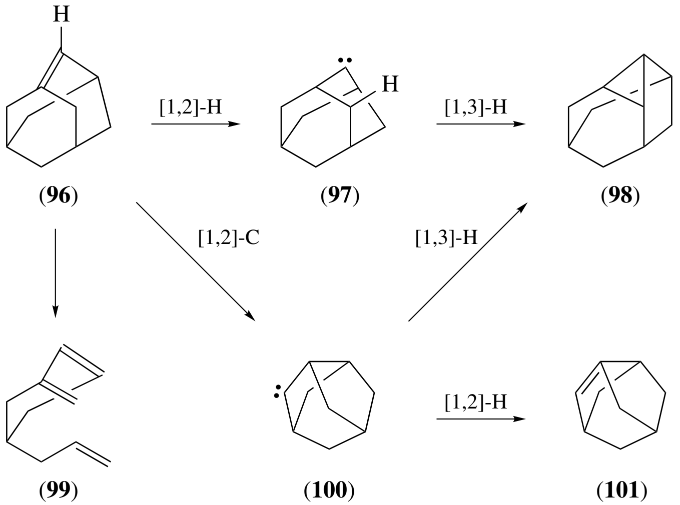
B3LYP calculations indicated that 2-adamantene (**96**) is 17.4 kcal mol^{-1} more stable than $^1A_1$-adamantylidene (**97**).[70] The barrier to interconversion of (**96**) to (**97**) by [1,2]-H shift is 69.1 kcal mol^{-1}, much higher than that for [1,2]-C migration



(**94**)

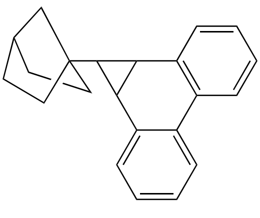


(**95**)



to 4-propoadamantylidene (**100**) (30.3 kcal mol^{-1}) or for retro-Diels–Alder reaction (20.5 kcal mol^{-1}) to form the triene (**99**). The singlet carbene (**100**) rearranges via [1,3]-H and [1,2]-H shifts with identical barriers (8.8 kcal mol^{-1}). The predicted distribution of products (**99**) $\gg$ (**98**) $\approx$ (**101**) is in agreement with experiment.

The non-nitrogenous carbene precursor (**102**) was used for the photochemical generation of the carbene (**103**) without complications due to reactions of diazirine or diazo species.[71] In the presence of alkenes, carbene (**103**) gave rise to cyclopropanes and in the absence of alkenes was proposed to undergo [1,2]-C shift to form (**104**), which suffered retro-Diels–Alder reaction to give a triene.



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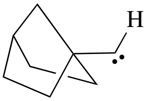

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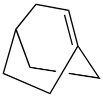
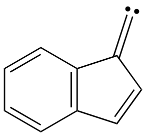


(**104**)

Calculations at the BLYP/6–311G** level were found to give a good estimate of the barrier (33.2 kcal mol^{-1}) of the benzyne to cyclopentadienylidenecarbene (CPDC) rearrangement.[72] Similar calculations on polycyclic arynes (e.g. naphthalynes) identified three distinct types of rearrangement. Only type I, e.g. of 1,2-naphthalyne, to produce relatively stable CPDCs [such as (**105**)] with aromatic conjugation unaffected by the cyclopentadienylidene moiety are observed experimentally.

The ^{13}C-labelled cycloalkyne (**106**) generated by treatment of the corresponding vinyl bromide with a strong base (LDA), was proposed to undergo [1,2]-C rearrangement to the vinylidenecarbene (**107**) in which the label is scrambled between the two *sp*^{2} carbons. Carbene (**107**) was trapped by cycloadditions to alkenes.[73] The reverse process, rearrangement of vinylidenecarbene (**107**) to the cycloalkyne (**106**), was shown not to occur because formation of (**107**) from the corresponding ^{13}C-labelled dibromomethylene precursor (**108**) gave products in which no scrambling of the label was observed. The cycloalkyne was calculated to lie 8.3 kcal mol^{-1} above the carbene.



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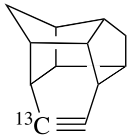

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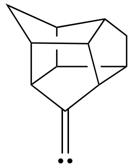
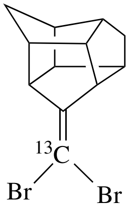


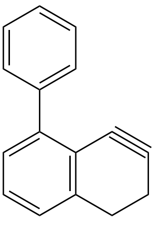
(**107**)



(**108**)

The cyclodehydration of 1-phenylnaphthalene has been studied by BLYP/6–311G** calculations.[74] A minor pathway involving two consecutive losses of H to give the naphthalyne (**109**), which rearranges to the CPDC (**110**) (with a barrier of 30.3 kcal mol^{-1}), that can insert into the *ortho*-H of the phenyl ring (barrier 3.0 kcal mol^{-1}) was identified.

Attempted formation of the 4-silyl-substituted nucleophilic carbene (**111**) by deprotonation of the corresponding triazolium salt with KH led to the triazole (**112**), the product of apparent [1,2]-Si migration.[75] A crossover experiment indicated that silyl transfer is intermolecular.



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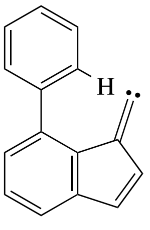

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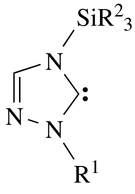

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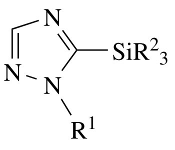

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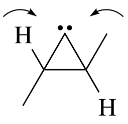

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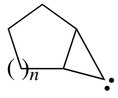

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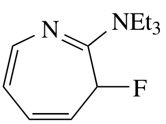

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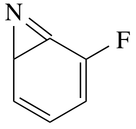

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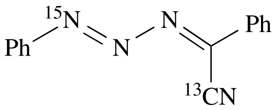

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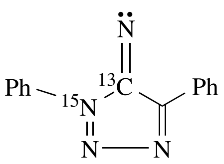


(**118**)

Calculations on the ring opening of *trans*-cyclopropylidene (**113**) to 1,3-dimethylallene predicted a barrier of 4.2 kcal mol^{-1} via initial disrotatory motion of the substituents followed by a change to conrotatory motion.[76] The *cis*-cyclopropylidene rearrangement is barrierless and, in agreement with the elusive nature of 1,2-cycloheptadiene, the barrier to ring opening of bicyclic cyclopropylidene (**114**; $n = 2$) cannot be overcome at low temperatures.

Irradiation of *o*-fluorophenyl azide in the presence of diethylamine gives the single azepine (**115**), suggesting that the ring closure of *o*-fluorophenylnitrene occurs away from the substituent to give azirine (**116**).[77] Only in azides bearing two *ortho*-fluorine substituents is ring expansion sufficiently retarded to allow the singlet nitrene to react with diethylamine.

Thermal decomposition of a doubly labelled azidotriazole gave rise to the open-chain triazine (**117**) in which the labels were not scrambled.[78] Laser flash photolysis of the triazole leads to (**117**) within 20 ns with no observable intermediate. *Ab initio* calculations indicate that a dynamic equilibrium between the open-chain triazine (**117**) and a cyctic nitrene (**118**), as originally proposed,[79] is highly disfavoured.

Nitrenium ions

Calculations of the singlet–triplet energy gaps of a series of nitrenium ions [X(H)N:]$^+$ in the gas phase and in solution indicate that the gap decreases in the order $X = H > CN > F$ as a result of stabilization of the singlet state by π-donation from the substituent. For strong π-donors (Cl, F), the singlet state is more stable than the triplet.[80]

Calculations on the isoelectronic series Me(Ph)B$^-$, Me(Ph)C:, and [Me(Ph)N:]$^+$ show that the singlet-state geometries are different, reflecting differences in the orbital interactions between the hypovalent atom and the π-system.[81] The high calculated barrier (21.5 kcal mol^{-1}) for [1,2]-H shift in the nitrenium ion is the result of migration using the orbital which is conjugated with the π-system.

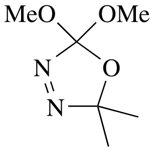
Nucleophiles and Electrophiles

The yields of CO production in the reaction of BrFC**:** with substituted benzaldehydes are dependent on the electronic effects of *para* substituents.[82] Carbonyl ylide intermediates were trapped with dimethyl acetylenedicarboxylate. Sterically hindered tetraphenylcyclopentadienone gave a high yield of CO and no ylide could be trapped in this case.

The absolute rate constants for oxygen and sulfur transfer to a range of carbenes (dialkyl, cycloalkylidene, alkylchloro, diaryl, arylchloro, arylalkoxy, and dialkoxy), generated by laser flash photolysis of diazirine or oxadiazoline precursors, were determined.[83] No evidence was seen for ylide formation and a concerted mechanism via an ylide-like transition state was proposed.

Ab initio and density functional calculations indicate that the first step of the abnormal Reimer–Tiemann reaction involves barrierless formation of an intermediate by nucleophilic attack on **:**CCl_2 of the β-carbon of pyrrole anion.[84] This is followed by a single, concerted step to give the product, 3-chloropyridine.

Dimethoxycarbene $(MeO)_2C$**:**, generated by thermolysis of the oxadiazoline (**119**), was found to effect nucleophilic substitution on highly electron-deficient aryl fluorides.[85] Reaction with Sanger's reagent (2,4-dinitrofluorobenzene) gave rise to (**120**) by attack on the fluorine-bearing carbon followed by [1,2]-F shift. Thermal decarboxylation of 1,3-dimethylorotic acid (**121**; $R = CO_2H$) in refluxing benzyl bromide give rise to the 6-benzyluracil (**121**; R = Bn).[86] This process involves a C(6)nucleophile, either a zwitterion or the carbene (**122**).



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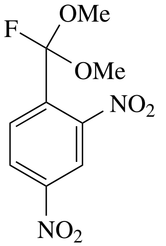
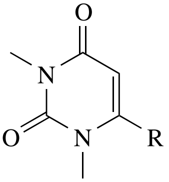
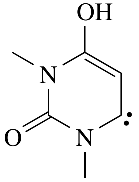


(**120**)



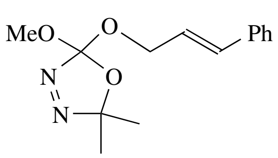
(**121**)



(**122**)

Thermolysis of the oxadiazoline (**123**) gives rise to the corresponding dialkoxycarbene, which can be trapped by reaction with *t*-butanol to form orthoesters.[87] The formation of a regioisomeric mixture of esters was explained by fragmentation of the carbene to radicals (**124**) which recombine at either end of the allyl system.

Flash photolysis of 2-diazophenylacetic acid in ^{18}O-labelled water gives mandelic acid (**127**) labelled in the carbonyl oxygen, thus ruling out a mechanism involving Wolff rearrangement of the carbene (**125**) to give a hydroxyphenylketene.[88] The results were consistent with direct conjugate addition of water to the carbene (**125**) to form the enol (**126**).



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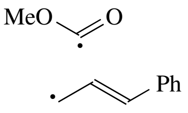
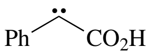


(**124**)



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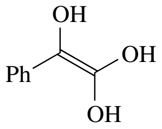
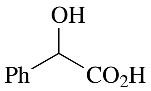


(**126**)



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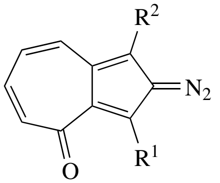

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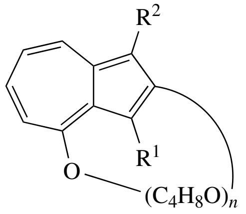


(**129**)

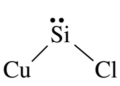
Insertion of the carbenes, via a low-lying singlet state close to the ground-state triplet, generated by photolysis of the diazo compounds (**128**), into the CO bond of cyclic ether solvents (THF, THP, dioxane) gave rise to polyether-bridged azulenes such as (**129**).[89]

$FeCl_2$ has been used to catalyse nitrene transfer from *t*-butyloxycarbonyl azide to sulfoxides (to form sulfoximides), sulfides (to give sulfimides), and a ketene acetal (to form an α-amino ester).[90]

Silylenes

Silylene (H_2Si**:**) and methylene were used to develop a general procedure for calculation of spin–orbit coupling of triplet states of organic biradicals with their singlet states.[91] The silylene (**130**) was invoked to explain the formation of ethyldichlorosilane from the reaction of metallic silicon with HCl and ethene in the presence of a CuCl catalyst.[92] Initial reaction to form the silacyclopropane (**131**) followed by reaction with 2 mol of HCl was proposed. The rate constant for insertion of Cl_2Si**:** into the CH bond of methane has been determined as $13.4\,l\,mol^{-1}\,s^{-1}$ at 921 K.[93] The decomposition of the methyldichlorosilane product is proposed to involve elimination of methane to form Cl_2Si**:** with a rate constant of $(1.5 \pm 0.2) \times 10^{-3}\,s^{-1}$ at 905 K. The results of a study of the thermal decomposition of Cl_3SiH, Cl_2SiH_2, and $ClSiH_3$ are consistent with molecular elimination reactions to give silylene intermediates (Cl_2Si**:**, Cl_2Si**:**, and HClSi**:**, respectively).[94]

An attempt to investigate the possible photochemical rearrangement of silacyclobutenylidene (**132**) to give silacyclobutadiene produced seven silylene species in the



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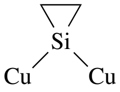
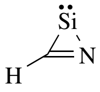


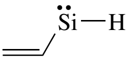
(**131**)

(**132**)

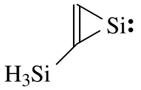


(**133**)

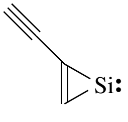
(**134**)



(**135**)



(**136**)



(**137**)

$Me_3Si—SiH(C\equiv CH)_2$

(**138**)

C_3H_4Si manifold, none of which proved to be the silacyclobutadiene.[95] Silicon atoms, generated thermally, were co-condensed in an argon matrix with HCN. The initial product **:**CH−N=Si**:** is rapidly converted into (**133**) and **:**SiH−C ≡ N.[96] The silylene (**133**) is converted into **:**SiH−N=C**:** on further irradiation and this then isomerizes to radical species.

Thermally generated silicon atoms react in an argon matrix with acetylene to give silacyclopropenylidene and in a similar way with ethylene to give silacyclopropylidene (**134**).[97] Subsequent irradiation gives the *anti*-conformer of vinylsilylene (**135**) and then a species assigned as 1-silaallene ($H_2Si{=}C{=}CH_2$). Pulsed flash photolysis of three different precursors led to matrix-isolated silacyclopropenylidene (**136**), which was converted by further irradiation into the isomeric silylenes $H_3SiC \equiv C{-}(H)Si$**:** and $H_3Si(H{-}C \equiv C)Si$**:**.[98] Calculations on five C_4H_2Si species identified the silacyclopropenylidene (**137**) as the most stable isomer.[99] Flash pyrolysis of disilane (**138**) gave rise to (**137**), which was trapped in an argon matrix at 10 K.

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