

Unsaturated Carbenes

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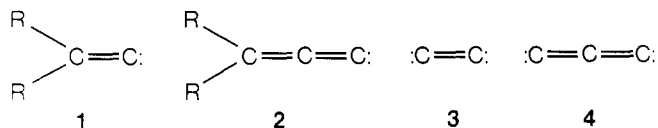
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I. Introduction

The term "unsaturated carbene" properly refers to a reactive intermediate where the electron-deficient carbon is an integral part of an unsaturated system as in **1** and **2**. To date, two main classes of such species are known: alkylidene carbenes (**1**) and vinylidene carbenes (**2**). Besides these two species, C_2 (**3**) and C_3 (**4**) belong to this class of intermediates. Despite the wide



occurrence of C_2 and C_3 in the Universe,¹ mostly in comets and carbon stars, their somewhat unusual terrestrial generation via flames and carbon arcs places them outside of every day organic chemistry. Furthermore, they have been recently reviewed,² and therefore this report will deal only with alkylidene and vinylidene carbenes.

Although unsaturated carbenes have not been seen as stable entities nor to date observed spectroscopically, their existence is clearly demonstrated by their chemical behavior. Pioneering work, primarily by Hartzler, Köbrich, Newman, and their col-

laborators,³ which established unsaturated carbenes as viable reaction intermediates was carried out during the 1960s. The characterization of their exact nature and the full development of their chemistry and uses are still continuing. Compared to the activity and plethora of results in saturated carbenes,⁴ unsaturated carbene chemistry is still in its infancy. Hence, it is a particularly appropriate time for a critical review and perhaps some stimulus and influence on the future growth and development of this area of chemistry.

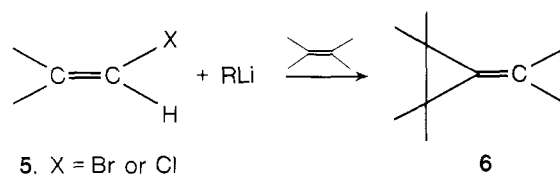
This review will treat in separate sections the generation, nature, and reactions of alkylidene (**1**) and vinylidene (**2**) carbenes, respectively. A separate part will deal with the increasing number of transition metal complexes of unsaturated carbenes, along with a brief summary and extrapolation into the future.

II. Generation of Alkylidene Carbenes

A. α -Elimination Methods

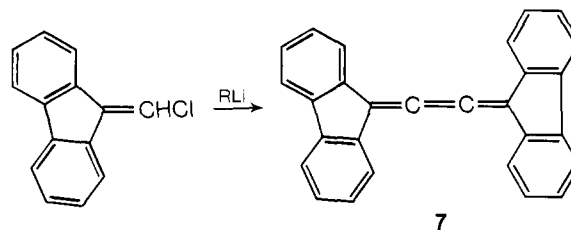
The most general method for the generation of **1** is α -elimination from a variety of vinylic progenitors. The most widely investigated of these reactions are α -eliminations of 1-halo-olefins with bases. The base-promoted reaction of arylvinyl halides, the so-called Fritsch-Buttenberg-Wiechell rearrangement,⁵ used to produce the corresponding acetylenes has been known since the 1890s, although the exact nature of the reaction was not established until much later (see section IV.A).

α -Elimination from a wide variety of primary alkylvinyl halides **5** and strong bases has been observed, usually in olefins that serve as both substrate and solvent. These reactions are gen-

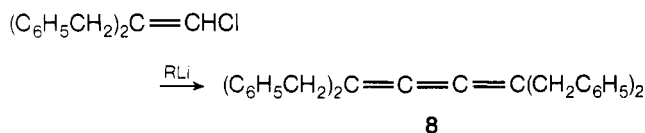


erally accompanied by isomerization of the starting vinyl halides and tar formation with the carbene-derived methylenecyclopropane **6**, products being formed to the extent of only 20–40%. These reactions proceed via carbenoids and organometallic intermediates rather than free carbenes (see section III.B).

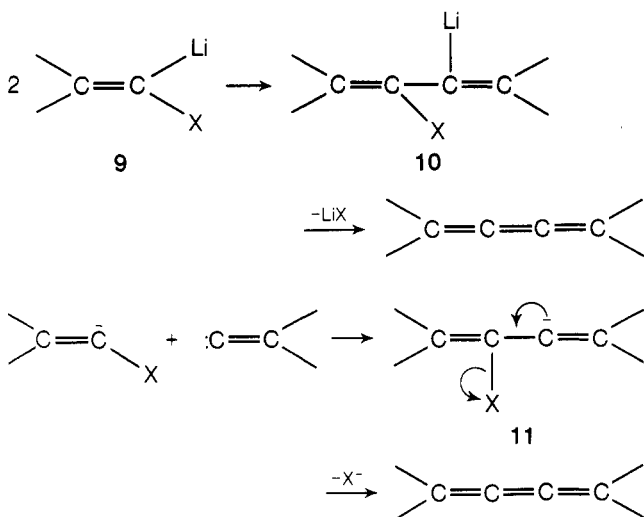
In the absence of olefins or other suitable traps, butatriene products such as **7**⁷ and **8**⁸ have been observed. It is unlikely that



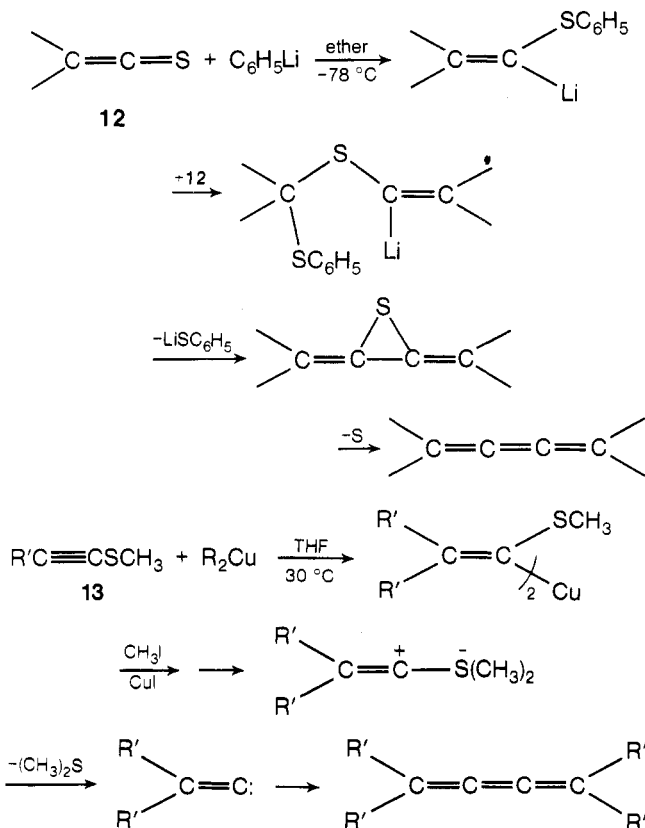
these products arose via dimerization⁹ of the respective carbenes. More likely is the interaction of two anions, **9**, with for-



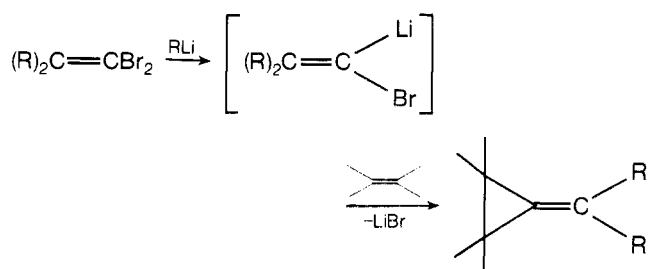
mation of **10** and subsequent loss of LiX; or trapping of the carbene by the anion, with formation of **11** and subsequent loss of X⁻.⁹



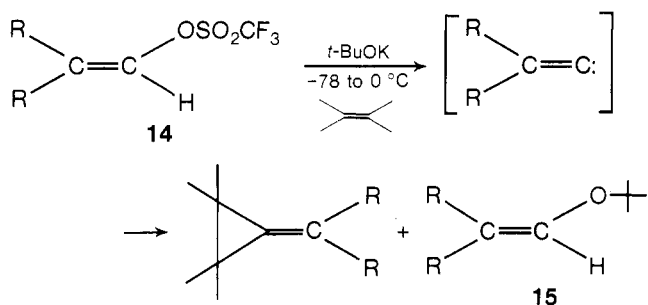
Similar triene products have recently been observed in the interaction of phenyllithium with dialkylthioketenes¹⁰ **12** and thioalkynes¹¹ **13** with organocopper reagents. Although the possible involvement of alkylidene carbenes **1** in these reactions cannot be completely ruled out, other processes are more likely:



1,1-Dibromoolefins and alkyllithiums readily underwent halogen-metal exchange, α-elimination, and methylenecyclopropane formation:¹²

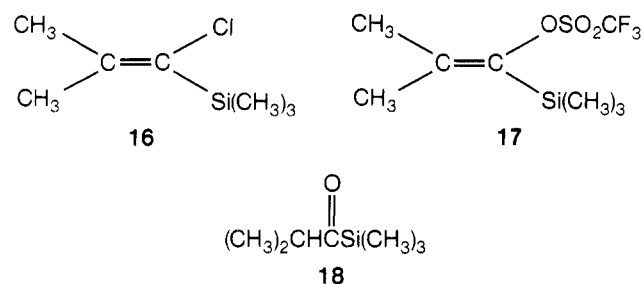


Nearly quantitative carbene-derived products were obtained by the use of primary vinyl trifluoromethanesulfonates¹³ (triflates) **14** and *t*-BuOK.¹⁴ Along with the olefin adducts, *tert*-butyl vinyl ethers **15** were observed as minor products.



Reactions were carried out under heterogeneous or homogeneous conditions by the addition of anhydrous glyme and/or crown ethers¹⁵ to solubilize the base. Primary vinyl triflates are readily available¹⁴ from aldehydes via their silyl enol ethers.¹⁶

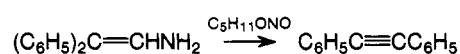
Recently an interesting indirect α-elimination route to **1** was reported by fluoride ion initiated nucleophilic attack upon α-chlorovinylsilane¹⁷ **16** and silylvinyl triflate¹⁸ **17**. Reaction of **16**



gave yields of up to 80% of carbene derived products at 25 °C in 48 h. Triflate **17** gave quantitative yields of carbene adducts with cyclohexene and ethyl vinyl ether respectively at -20 or 0 °C in 1–2 h with KF and crown ethers, with anhydrous R₄N⁺F⁻, or via KF and phase-transfer procedures.¹⁷ Chlorovinylsilanes such as **16** were prepared from vinyl halides and silylvinyl triflates such as **17** from the appropriate α-silyl ketones **18**.¹⁹ Indirect evidence¹⁸ indicated a concerted nucleophilic attack upon Si and elimination of CF₃SO₃⁻ with **17** and a stepwise process in the case of **16**. These two procedures are the best to date for the generation of alkylidene carbenes (**1**) under neutral and mild conditions.

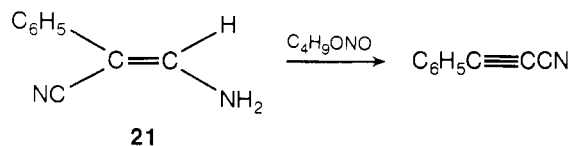
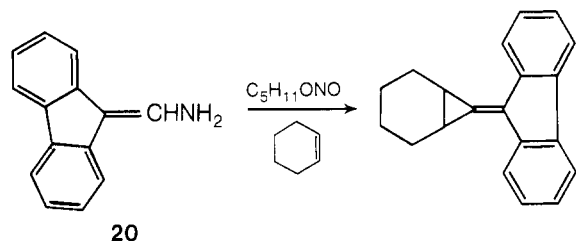
B. Deamination and Related Procedures

Certain vinylamines such as **19**, **20**,²⁰ and **21**²¹ have been reported to give carbene-derived products upon reaction with alkyl nitrites:

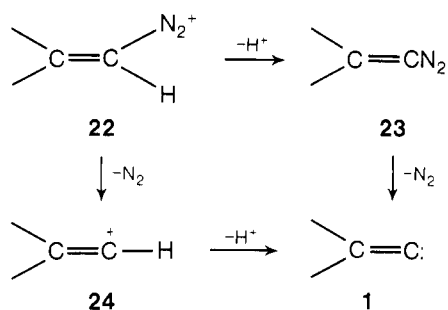


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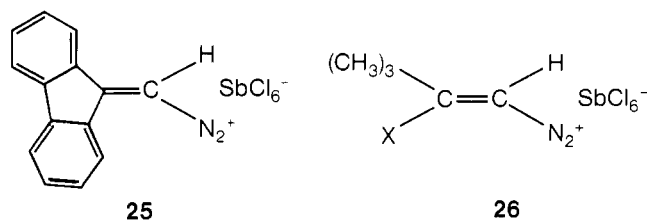
These reactions proceed via the prior involvement of vinyl-diazonium ions, **22**. However, it has not been established



whether **22** first loses a proton to form unstable diazoethylenes **23** and subsequently loses N_2 to give carbene **1**; or if **22** first loses N_2 to form a vinyl cation **24** and then a proton to give **1**:

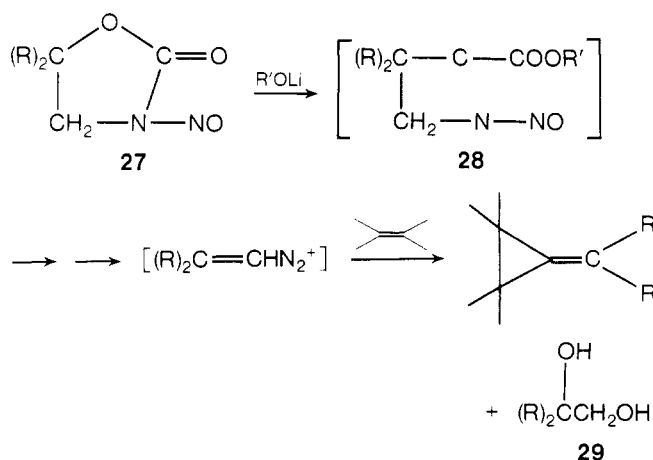


Although stable diazoethylenes **23** have not yet been reported, stable diazonium salts **22**, such as **25** and **26**, have been isolated and characterized.²² Their direct involvement in alkylidene carbene generation has not yet been investigated. Both routes

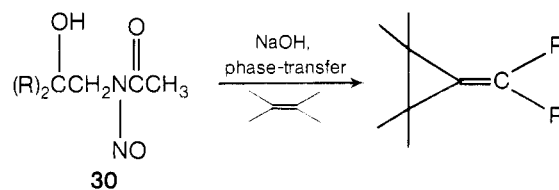


may be feasible, but formation of another high-energy reactive intermediate such as a primary vinyl cation²³ would, in this reviewer's opinion, seem less likely than involvement of diazoalkenes **23**.

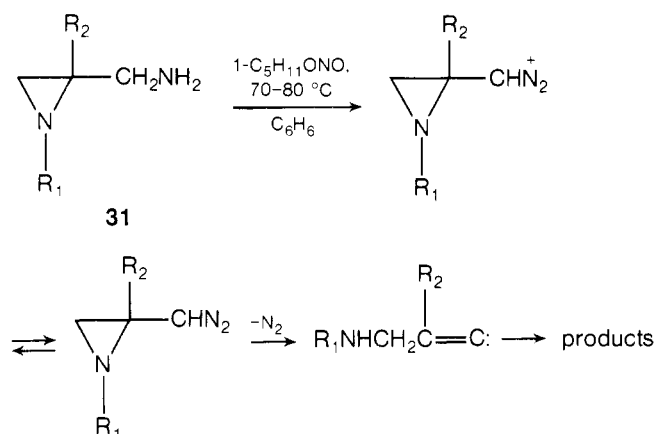
Since alkylvinylamines are not generally available, such deamination reactions are restricted to arylvinylamines. A more general process involving diazonium ions is lithium alkoxide initiated decomposition of *N*-nitrosooxazolidones **27**, developed by Newman and co-workers.²⁴



Although the exact mechanism of carbene formation from **27** is not clearly understood,²⁵ the process is general for 5,5-disubstituted oxazolidones **27**, yielding 40–60% of carbene-derived products along with 40–60% of diols **29**. Diols **29** presumably arise via **28**.²⁴ To avoid such side products *N*-nitrosoacetyl amino alcohols **30** were developed as carbene **1** progenitors.²⁶ Up to 83% of carbene-derived products have been obtained by reaction of **30** with NaOH under phase-transfer conditions.²⁶



Diazonium ions and diazo compounds have been invoked as intermediates, along with alkylidene carbenes **1** in the deamination of certain 2-(aminomethyl)aziridines **31**:^{27a}



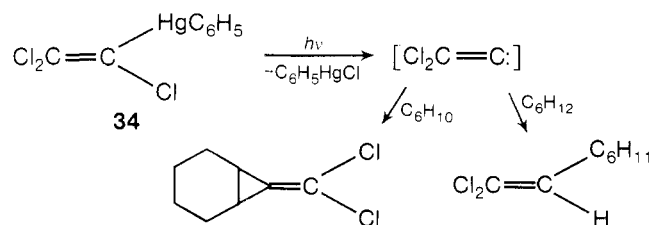
C. Thermal and Photochemical Methods

Unfortunately there is no simple, general method for either the photochemical or thermal generation of unsaturated carbenes **1** or **2**. The ideal progenitors for such photochemical alkylidene carbene generation would be diazoalkenes **32** or methylenediazirines **33**. Neither of these two classes of com-

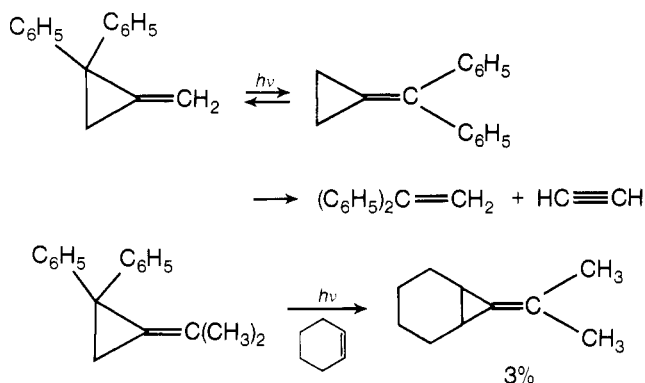


pounds has been isolated or reported,^{27b} although as mentioned in the preceding section diazoethylenes have been invoked as unstable intermediates in some alkylidene carbene formations.

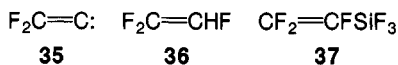
A wide variety of precursors have been employed in the thermal and photochemical generation of alkylidene carbenes. The organomercurial **34** gave 20–25% of carbene derived products upon photolysis in cyclohexene or cyclohexane.²⁸



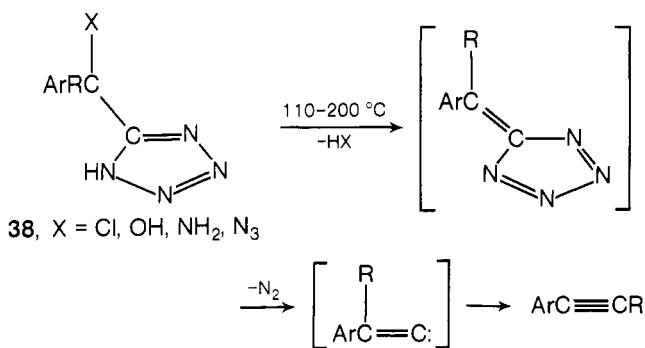
Photolysis of methylenecyclopropanes gave a methylenecyclopropane rearrangement reaction,²⁹ and a cheletropic fragmentation with formation of small amounts of carbene derived products:³⁰



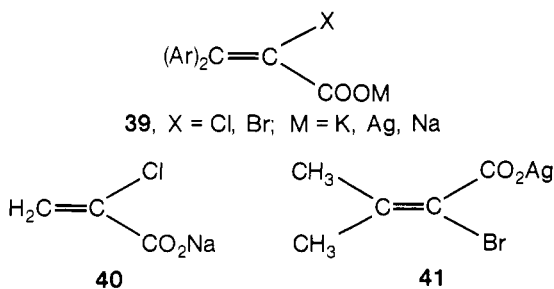
Methylenecyclopropane itself gave ethylene and acetylene via mercury-sensitized photofragmentation.³¹ Difluorocarbene (**35**) has been generated by mercury-sensitized photolysis of either trifluoroethylene³² (**36**) or perfluorovinylsilane³³ (**37**).



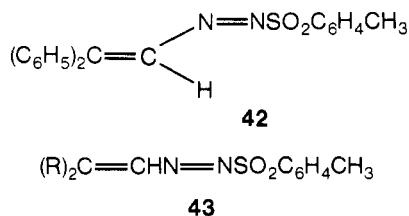
Alkynes, presumably via **1** (see section IV.A), were obtained in the thermolysis of a series of substituted tetrazoles **38**:³⁴



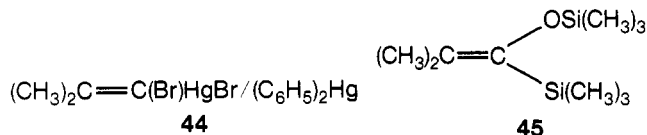
Similarly, alkynes were observed in the thermal decomposition of aryl-substituted α -haloacrylate salts **39**.³⁵⁻³⁷ The parent acrylate **40** gave acetylene and CO₂ as volatile products.³⁶ However, no carbene adduct was observed in the thermal reaction of **41** with diphenylethylene.³⁷



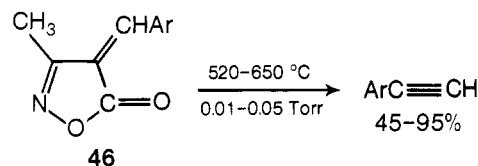
Azoethylene **42** gave N₂, CH₃C₆H₄SO₂H, and diphenylacetylene in CCl₄ at room temperature.³⁸ Tosylazoalkenes **43** also gave N₂ and sulfonic acid along with 25–40% of carbene-derived adducts when reacted with olefins at room temperature.¹⁸



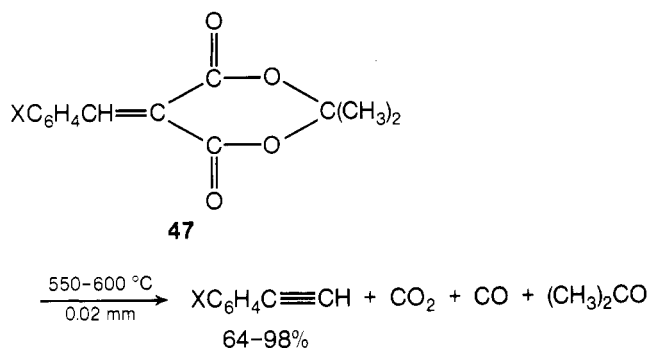
Carbene adducts were also obtained by thermolysis of organomercurial **44**³⁹ at 150 °C or silylsiloxyalkene¹⁸ **45** at 275 °C. The latter reaction presumably proceeds by deoxysilyla-



tion.⁴⁰ Excellent yields of arylacetylenes were obtained⁴¹ in the flash pyrolysis of isoxalones **46**:

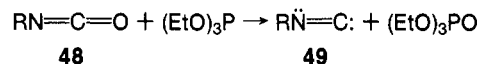


Arylacetylenes were also formed in the flash pyrolysis of a series of ring-substituted isopropylidene malonates **47**:⁴²

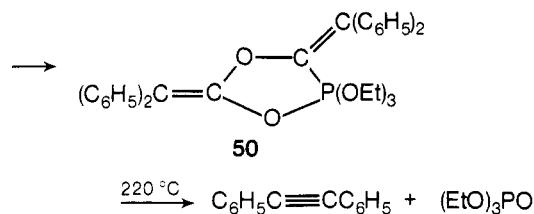
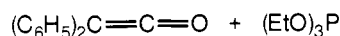


D. Miscellaneous Methods of Generation

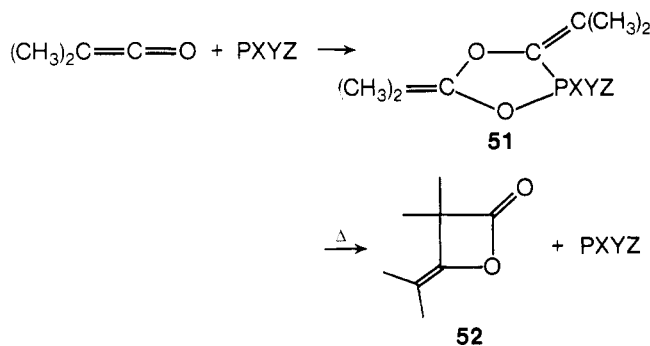
New routes to alkyldene carbenes will undoubtedly be forthcoming. An interesting possibility on paper that does not seem to work in practice is deoxygenation of ketenes. Deoxygenation of isocyanates **48** to isonitriles **49**, the chemical cousins of alkyldene carbenes, is a known process:⁴³



Yet reaction of diphenylketene with triethyl phosphite gives a stable crystalline adduct **50**, which decomposes to diphenyl-



acetylene and triethyl phosphate only upon heating above 220 °C.^{44,45} Although **1** has been suggested as an intermediate in this reaction,⁴⁵ its actual involvement is uncertain in light of



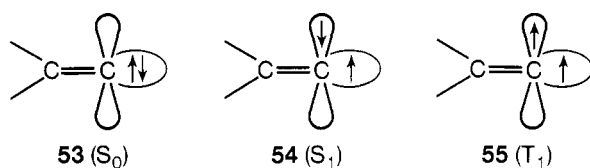
results with dimethylketene.⁴⁶ Dimethylketene formed similar 2:1 phosphorane adducts **51** with a variety of trivalent phosphorus nucleophiles including $(\text{CH}_3\text{O})_3\text{P}$. These adducts decomposed to lactone dimer **52** at various temperatures. No deoxygenation and no carbene products were observed.⁴⁶

III. Nature of Alkylidene Carbenes

One of the more interesting questions regarding any reactive intermediate is its exact nature. The nature of alkylidene carbenes may be defined in terms of spin multiplicity, free carbene or carbenoid character, electrophilicity or nucleophilicity, and steric factors involved in its reactions.

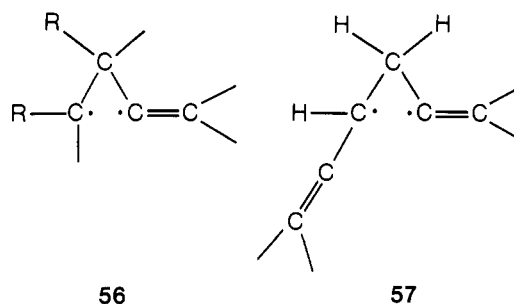
A. Spin Multiplicity

A priori, any carbene, including **1** and **2**, may be in one of three low-energy states: a singlet state (S_0) in which one carbon orbital is empty and the second contains two unshared spin-paired electrons, **53**; a singlet (S_1) with two singly occupied orbitals,



54; and the triplet state (T_1) in which two electrons with parallel spins singly occupy two carbon orbitals, **55**. Methylene has been shown⁴⁷ to possess a triplet ground state, 3B_1 , in agreement with theoretical calculations.⁴⁸ An energy vs. HCH bond angle profile for methylene shows⁴⁹ that the triplet state is 41.5 kcal/mol below the singlet state for a bond angle of 180° , 20.8 kcal/mol below that for an angle of 135° (the experimentally and theoretically predicted bond angle),^{47,48} and nearly degenerate for $\sim 100^\circ$; for an HCH angle of $<90^\circ$, the singlet is more stable than the triplet. Since one can look upon **1** as a methylene with a very small bond angle, this analogy would predict the singlet to be the ground state for alkylidene **1**, and for that matter vinylidene, **2**, carbenes. Theoretical calculations of the Hückel type,⁵⁰ MINDO/2 procedures,⁵¹ and most recently ab initio methods⁵² all predict a singlet ground state, **53**, for alkylidene carbenes with a singlet-triplet splitting of 20–46 kcal/mol. The next excited state of **1** ($R = \text{H}$) is calculated to be the 3A_2 state with an excitation energy of about 75 kcal/mol.⁵² Ab initio calculations also predict a dipole moment of 2.23 D for the 1A_1 (ground) state of **1** ($R = \text{H}$) in the direction of the lone pair electrons, a carbon-carbon bond dissociation energy of 162 kcal/mol (compared with a dissociation energy at 169.9 kcal/mol for ethylene), and a $\Delta H_f^{298}(\text{H}_2\text{CC}:) = 100$ kcal/mol.⁵² The $\text{C}=\text{C}$ bond lengths are calculated to be 1.35 and 1.36 Å for the 1A_1 singlet ground state and 3B_2 triplet state, respectively. The ionization potential for singlet **1** ($R = \text{H}$) is calculated to be 10.8 eV (out of the π orbital); only 0.3 eV above the corresponding IP of ethylene.⁵²

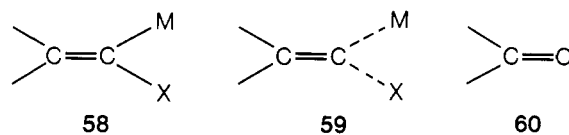
Experimentally, neither the ESR nor CINDP techniques commonly employed⁵³ to probe spin multiplicities of intermediates are compatible with the current methods of unsaturated carbene generation. The alternative technique, first proposed by Skell,⁵⁴ of examining the stereochemistry of carbene addition to olefins⁵⁵ has been employed. Reaction of isopropylidene-carbene (**1**, $R = \text{CH}_3$) with *cis*-2-butene was found to be $>99.5\%$ stereoselective and stereospecific with *trans*-2-butene, and more than 98% stereoselective with each of the 2-methoxy-2-butenes.⁵⁶ Since the vinyl triflate produced carbene is known to be "free" rather than a carbenoid (vide infra), this datum suggests, with the usual caveat^{55,57} about relative life times of rotamer equilibration and spin relaxation in the triplet produced biradical **56**, that the nascent carbene **1** is a singlet. The use of



an inert diluent⁵⁸ ($\text{C-C}_4\text{F}_8$) did not alter this stereoselectivity, strongly suggesting⁵⁶ that the ground state for alkylidene carbene is the singlet, in accord with theoretical calculations.^{50–52} The slower reactivity⁵⁹ of 1,3-butadiene compared to 2-butene (see Table III) provides additional experimental evidence for the singlet nature of **1**. With a triplet ground state, the diradical resulting from the stepwise addition to 1,3-butadiene **57** should be more stable and more readily accessible than the simple diradical **56** resulting from an olefin. Stereospecific addition of **1** ($R = \text{CH}_3$), as generated from the nitrosooxazolidone **27**, to *cis*- and *trans*-4-methyl-2-pentene has also been observed.⁶⁰ There is little doubt that alkylidene carbenes **1** are singlets with a fairly sizable singlet-triplet energy difference.

B. Encumbrance

In discussions of carbene encumbrance one must consider three major species: organometallic reagents **58**, carbenoids



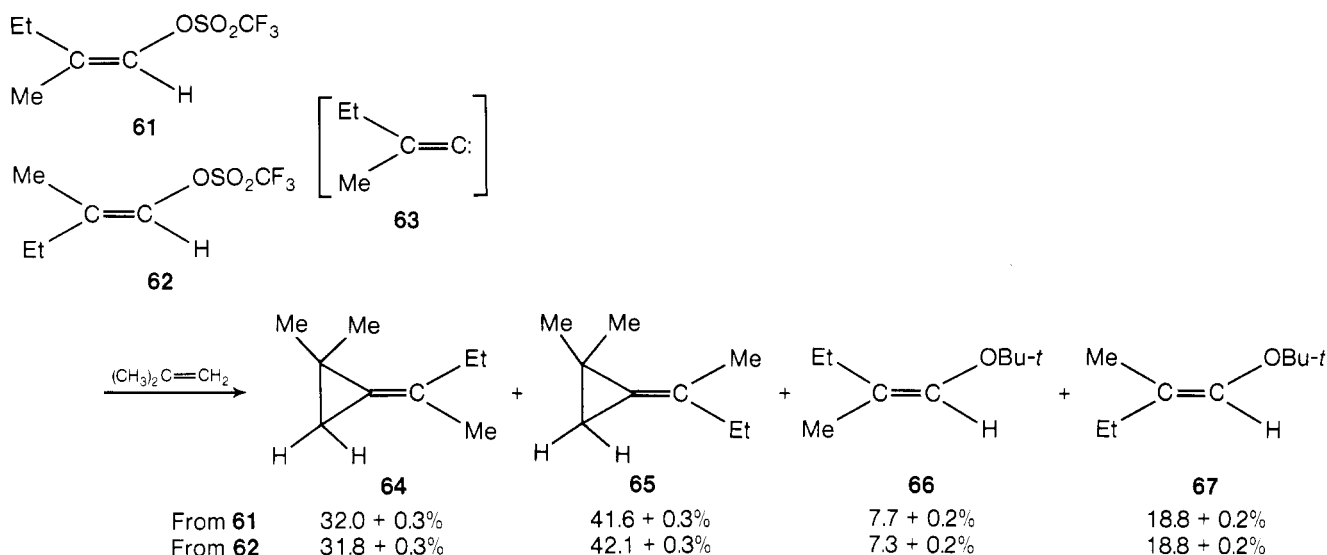
59, and "free" carbenes **60**. Species **58** is basically an organometallic compound where the metal and halogen are essentially covalently bound to carbon, whereas in a carbenoid⁶¹ either the leaving group or the metal of the base used, or both, is associated with the carbene intermediate **59**. A free carbene, **60**, is not burdened by any such encumbrance and is usually encountered only under dilute gas-phase conditions. An entire spectrum of intermediates, with a concomitantly wide range of chemical behavior, is possible between the two extremes of **58** and **60**.

Experimentally, intermediate **58** may be distinguished from **59** and **60** by its anion-like nucleophilic behavior in contrast to the usual electrophilic properties of carbenes. The degree of encumbrance and the distinction between **59** and **60** in turn is generally accomplished by examination of the chemical behavior, usually stereochemistry and selectivity, of a particular carbene generated from as many different progenitors and by as many different processes as possible. Identical chemical behavior under a wide variety of conditions implies an unencumbered species **60**.

From the extensive and elegant work of Köbrich and co-workers,⁶² there is no doubt that use of vinyl halides and alkyllithium and similar bases results in an organometallic species **58**, which by α -elimination of LiX converts to **59**. A large number of organometallic intermediates of type **58** have been formed and characterized at low temperature in THF.⁶³ These species undergo nucleophilic reactions typical of organometallic compounds and can be readily trapped with CO_2 , CH_3I , COCl_2 , Br_2 , and other nucleophiles as well as salts of metals less electropositive than the alkali metals.^{63,64} Upon warming, these species, **58**, readily react with olefins and other electrophiles presumably via carbenoids **59**.

In contrast, the behavior of the species generated from primary vinyl triflates, **14**, strongly suggests the intermediacy of

SCHEME I. Reaction of an Unsymmetrical Carbene with an Unsymmetrical Olefin

TABLE I. Selectivity of $(\text{CH}_3)_2\text{C}=\text{C}:$ toward Styrenes ($\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$)

Substrate X	Reaction conditions, reference, and k_{rel} (substrate/styrene)			
	$(\text{CH}_3)_2\text{C}=\text{CHOSO}_2\text{CF}_3$ <i>t</i> -BuOK, -20 °C, ref 65	$(\text{CH}_3)_2\text{C}=\text{CHOTf} + 18\text{-crown-6}$ <i>t</i> -BuOK, -20 °C, ref 65	$(\text{CH}_3)_2\text{C}=\text{CHN}=\text{NAr}$, 0 °C 43, R = CH ₃ , ref 66	$(\text{CH}_3)_2\text{C}=\text{COTfSi}(\text{CH}_3)_3$, 0 °C 17, R = CH ₃ , ref 66, R ₄ N ⁺ F ⁻
<i>p</i> -CH ₃ O	1.51	1.50	1.51	1.44
<i>p</i> -CH ₃	1.28	1.26	1.31	1.18
H	1.00	1.00	1.00	1.00
<i>p</i> -Cl	0.63	0.62	0.67 (<i>p</i> -Br)	0.85 (<i>p</i> -Br)
Cyclohexene/styrene	1.74	1.78	1.84	2.6
	$(\text{CH}_3)_2\text{C}=\text{CBr}_2$, -40 °C CH ₃ Li, ref 67	$(\text{CH}_3)_2\text{C}=\text{CHBr}$, -10 °C <i>t</i> -BuOK, ref 67, 68	Oxazolidone, 40 °C (27, R = CH ₃), LiOCH ₂ CH ₂ OEt, ref 60	
<i>p</i> -CH ₃ O		21.0	19.0	12.0
<i>p</i> -CH ₃		1.0	1.0	1.0
<i>p</i> -Cl		0.34	0.32	0.42
Cyclohexene/styrene				0.16

an unencumbered carbene, **60**. Specifically, the degree of encumbrance of alkylidene carbenes with the leaving group, presumably through the empty p orbital, has been determined by the following method. Addition of an unsymmetrical carbene **63** to an unsymmetrical olefin such as isobutylene results in two distinct adducts **64** and **65**, as well as, in the case of the vinyl triflate derived carbene, in two distinct insertion products **66** and **67**, as shown in Scheme I. It is then a necessary, albeit not sufficient, condition for the intermediacy of the free carbene (free of association with the leaving group) that both pure isomeric starting triflates **61** and **62** give an identical ratio of adducts and insertion products. To put it differently, if there is any association with the leaving group there should be a memory effect that reflects itself in the product ratio as a function of the stereochemistry of the isomeric carbene progenitors. As the data¹⁴ in Scheme I indicate within experimental error, the product ratios were identical in accord with an intermediate free of association with the leaving group.

Association with the metal may be established by selectivity studies under diverse conditions and with different precursors. This has been accomplished for alkylidene carbenes with the results summarized in Table I. The close agreement (probably the same within experimental error) in the selectivities of $(\text{CH}_3)_2\text{C}=\text{C}:$ as derived from **14**, **17**, and **43** (R = CH₃) strongly suggests an unencumbered carbene **60** as the intermediate in these reactions.⁶⁹ The results with the crown ether as well as with precursor **43** (columns 2 and 3 of Table I, respectively) are

particularly significant. In the case of crown ethers one would expect the 18-crown-6 to be a much more effective complexing agent with K⁺ than with a carbene. In fact, Moss and co-workers⁷⁰ have shown crown ethers to be an effective means of generating unencumbered carbenes, identical in their selectivities with the species derived from thermal or photochemical decomposition of diazo precursors and greatly differing from the carbenoid selectivities. With precursor **43** (R = CH₃) no metal or base as well as a different leaving group is involved in the alkylidene carbene generation, precluding the possibility of any such associations, yet the selectivities are identical with the triflate **14** derived results with or without crown ethers. In contrast the alkyl halide derived carbene selectivities differ markedly⁶⁸ from the others, perhaps suggesting the involvement of a carbenoid, **59**, rather than the free carbene, **60**. The oxazolidone **27** derived species seems to be between the vinyl halide and vinyl triflate **14** derived carbene selectivities.

The difference in behavior and the different nature of the intermediates as derived from vinyl halides (carbenoids **59**) and vinyl triflates (unencumbered carbenes **60**) may be accounted for by the vastly superior leaving ability of CF₃SO₃⁻ compared to X⁻.^{13,71,72} The 10⁸-10⁹ times greater reactivity of CF₃SO₃⁻ compared to halogens would suggest that α-elimination of CF₃SO₃H from vinyl triflates **14** by any base is a concerted process proceeding directly to a free carbene, **60**, whereas HX elimination from vinyl halides is a stepwise process first forming **58** then **59** and perhaps in special cases **60**. This hypothesis is

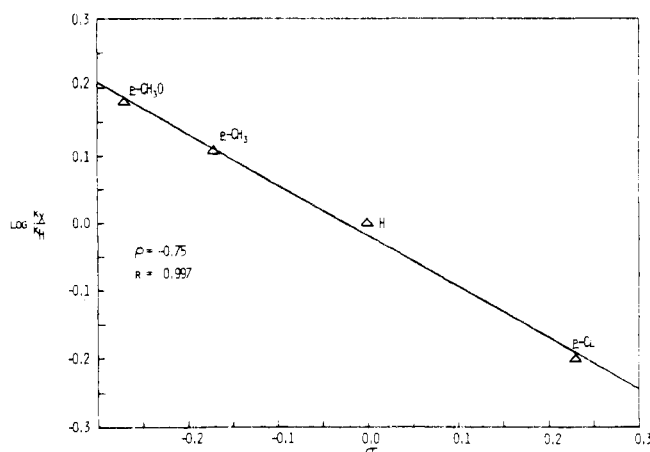


Figure 1. Hammett σ - ρ plot of $(\text{CH}_3)_2\text{C}=\text{C}:$ addition to $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$.

supported by the existence⁷³ of an anionic equilibrium and re-isolation of deuterated starting vinyl halides in *t*-BuOD with $(\text{C}_6\text{H}_5)_2\text{C}=\text{CHBr}$ and the lack¹⁴ of such equilibrium in the presence of base and *t*-BuOD with vinyl triflates **14**.

Hence, analogous to normal carbenes,⁴ there is an entire spectrum of alkylidene carbene intermediates ranging from organometallic species **58** through carbenoids **59** to less encumbered if not "free" carbenes **60**.

C. Electrophilicity

Alkylidene carbenes, like any carbene, being electron deficient would be expected to be electrophilic. A Hammett plot of the vinyl triflate data in Table I gives a good correlation with a $\rho = -0.75$ as shown in Figure 1. Other relevant carbene selectivities toward styrenes are summarized in Table II. It is evident from these data that alkylidene carbenes **1** are electrophilic, as are most carbenes, with the exception of cycloheptatrienyliene,⁷⁸ and initially interact with olefin π systems via their empty p orbitals. It is also obvious from the data in Table II that the vinyl halide **5** and oxazolidone **27** derived species **1** are much more⁶⁸ electrophilic than the vinyl triflate derived carbene. It is possible that these large differences in selectivities⁶⁸ reflect differences in the nature of the intermediates with the halide and oxazolidone derived species being carbenoids **59** and the vinyl triflate derived species **60** being unencumbered. However, even considering such differences, the ρ values reported for the vinyl halide and oxazolidone derived species are the largest for any known carbenic additions to styrenes and suggest an unusually highly polarized transition state for such reactions. These ρ values are comparable to the values observed for bromination⁷⁹ ($\rho = -4.3$) and hydration⁸⁰ ($\rho = -4.0$) of styrenes with a nearly fully developed charge in the transition state. It is true that alkylidene carbenes **1** are isoelectronic with the corresponding vinyl cations but so are normal carbenes isoelectronic with carbanion ions. Yet saturated carbenes, including the $:\text{CH}_2$ carbenoid, seem to be much less selective ($\rho = -1.6$) than the species derived from **5** and **27**. An interesting rationalization has been provided for the high selectivity of these alkylidene carbenoids by invoking a less effective back-donation of electron density by the lone pair carbenic electrons into the empty olefin π^* orbital from alkylidene carbenes than from saturated carbenes.⁸¹

The selectivity of the vinyl triflate **14** derived carbene implies that unencumbered alkylidene carbenes **60** are mildly electrophilic with a concerted addition to olefins with but a slightly polar transition state. As the data in Table II indicate, **60** seems about as electrophilic as the halocarbenes or cyclopentadienyliene. As Seyferth and co-workers⁷⁴ have pointed out, singlet-state divalent carbon species (carbenes) are also isoelectronic with

Table II. Carbene Selectivities toward Styrenes





Carbene	Reaction conditions	ρ	Ref
$(\text{CH}_3)_2\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}=\text{CHOSO}_2\text{CF}_3$, <i>t</i> -BuOK, -20°C	-0.75 (σ)	65
$(\text{CH}_3)_2\text{C}=\text{C}:$	<i>N</i> -Nitrosooxazolidone, 27 , $+40^\circ\text{C}$	-3.4 (σ^+)	60
$(\text{CH}_3)_2\text{C}=\text{C}:$	$(\text{CH}_3)_2\text{C}=\text{CHBr}$, <i>t</i> -BuOK, -10°C	-4.3 (σ^+)	67
$\text{Cl}_2\text{C}:$	$\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$, C_6H_6 , 80°C	-0.62 (σ^+)	74
$\text{F}_2\text{C}:$	$\text{C}_6\text{H}_5\text{HgCF}_3$, C_6H_6 , 80°C	-0.57 (σ^+)	75
	 , <i>h\nu</i> , RT	-0.76 (σ)	76
$\text{H}_2\text{C}:$	$(\text{Et})_2\text{Zn} + \text{CH}_2\text{I}_2$, C_6H_6 , 78.6°C	-1.6 (σ)	77
	 , <i>h\nu</i> , THF	$+1.0$ (σ)	78

TABLE III. Relative Reactivity of $(\text{CH}_3)_2\text{C}=\text{C}:$ with Olefins

Substrate	Reaction cond., k_{rel}^a (ref)	
	$(\text{CH}_3)_2\text{C}=\text{CHOSO}_2\text{CF}_3$, <i>t</i> -BuOK, -20°C (59)	Oxazolidone, 27 , $\text{R} = \text{CH}_3$, LiOR, 40°C (60)
Styrene	0.49	6.2
Ethyl vinyl ether	2.53	
Cyclopentene		1.1
Cyclohexene	1.00	1.00
<i>cis</i> -2-Butene	0.96	
Tetramethylallene		0.9
Cyclooctene	0.88	0.7
Cycloheptene		0.6
Norbornylene	0.54	
<i>cis</i> -4-Methyl-2-pentene		0.5
<i>tert</i> -Butoxyethylene		0.4
2-Methyl-2-butene	0.30	
1,3-Butadiene	0.30	
1-Methylcyclopentene		0.3
1-Octene	0.22	0.1
<i>trans</i> -2-Butene	0.18	
1-Butene	0.17	
Isobutylene	0.11	
<i>trans</i> -4-Methyl-2-pentene		0.07
2,3-Dimethyl-2-butene	0.027	0.02
Tetrachloroethylene		0.0

^a Relative to cyclohexene.

trigonal boron compounds that have been shown to react with styrenes⁸² and other olefins⁸³ by means of relatively nonpolar π -complex-like transition states.

Finally, organometallic intermediates **58** that can serve as precursors to carbenoids **59** display nucleophilic behavior typical of anions^{65,64} (see section III B).

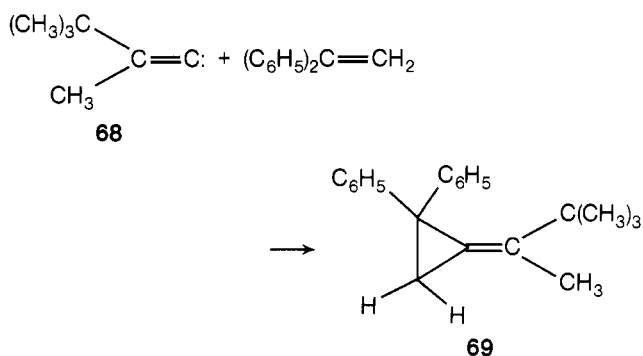
D. Steric and Other Factors

Further insight into the nature of alkylidene carbenes has been gained by studies of the relative reactivity and regioselectivity of these species toward various olefins. Relative reactivities are summarized in Table III.

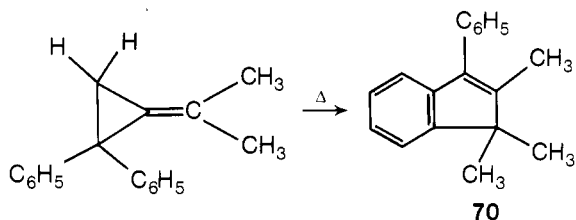
The relative reactivity data in Table III indicate the considerable steric requirements of alkylidene carbene-olefin interactions. Unlike most saturated carbenes that react⁸⁴ faster with electron-rich olefins like tetramethylethylene than with less substituted alkenes, alkylidene carbenes react slower. It was to account for these steric effects as well as the observation of the thermodynamically less stable adduct **69** in the addition of carbene **68** to 1,1-diphenylethylene that Newman and Patrick^{60,85} initially postulated a two-step carbene addition with zwitterionic intermediates. Subsequently, it was recognized⁸⁶

TABLE IV. Regioselectivity of R(CH₃)C=C: Olefin Additions

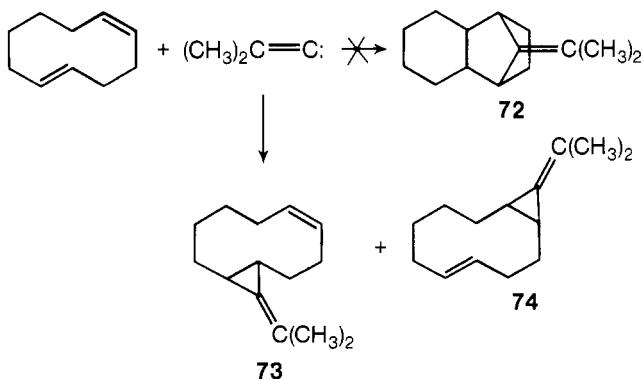
R	R ₁ = R ₂ = CH ₃	%	%
Et		43	57
<i>i</i> -Pr		40	60
<i>t</i> -Bu		33	67
	R ₁ = H, R ₂ = <i>t</i> -Bu		
Et		33	67
<i>i</i> -Pr		25	75
<i>t</i> -Bu		6	94



that the stereochemical assignment of **69** was complicated by the known⁸⁷ thermal rearrangement of such methylenecyclopropanes to indenenes **70**. The Newman-Patrick pathway would



also require 1,1-disubstituted olefins to be more reactive than 1,2-disubstituted alkenes, contrary to recent experimental observations.⁵⁹ Such a sequential reaction would also suggest the formation of a bicyclic product **72** from the addition of such carbenes to *cis,trans*-1,5-cyclodecadiene (**71**), but only normal 1,2-addition products **73** and **74** were observed.⁸⁸



As Newman and Patrick^{60,85} recognized, the initial approach of the electrophilic carbene to the olefin π system occurs via the empty p orbital of the carbene, which is constrained to be in the same plane as the β -alkyl substituents, thereby causing steric congestion with the substituents on the olefin. However, this itself does not require sequential bond formation and zwitterionic intermediates.

The reactivities in Table III are the result of opposing effects of the electronic and steric factors in the olefin in its interaction

with the carbene. Electron-rich unhindered alkenes like ethyl vinyl ether react faster than alkyl-substituted olefins. More electron-rich disubstituted olefins react faster than unsubstituted olefins. The extra electron density of additional substituents is outweighed by steric factors and tri- and tetrasubstituted olefins react slower than 1,2-disubstituted ones. Deactivated alkenes such as tetrachloroethylene do not react at all.

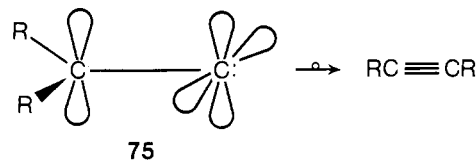
These steric effects are reaffirmed by the regioselectivity data⁸⁸ summarized in Table IV. There is a definite regioselectivity for addition of an unsymmetrical carbene to an unsymmetrical olefin with a preference for the thermodynamically more stable antiadducts. This preference is a function of both the structure of the carbenes as well as that of the olefin. Furthermore with large steric interactions such as in the addition of (*t*-Bu)MeC=C: to *tert*-butylethylene, a significant amount of intramolecular alkyl migration and (CH₃)₃CC=CCH₃ formation is observed as well.⁸⁸

It is obvious from the foregoing that alkylidene carbenes are singlets in their ground state, they are encumbered to various degrees depending upon their mode of generation, are electrophilic, and have definite steric requirements in their interactions with substrates. In the next section their reactions will be discussed with by and large little regard for their origin or nature.

IV. Reactions of Alkylidene Carbenes

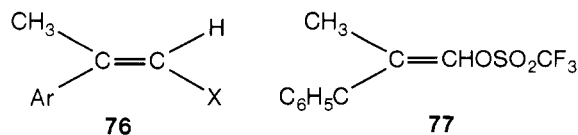
A. Intramolecular Reactions

The fact that the β -substituents in alkylidene carbenes are constrained to lie in the same plane as the empty p orbital of the carbenic carbon (see **75**) coupled with the shorter bond length



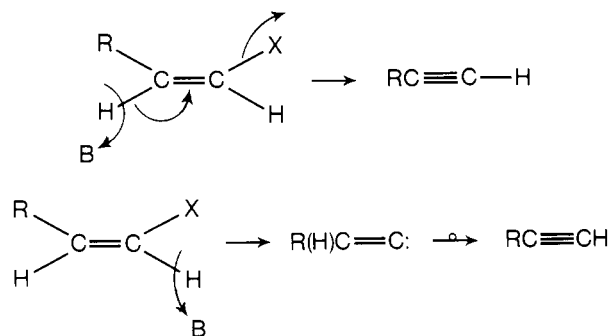
of the C_{sp}2-C_{sp} bond and the electron deficiency of divalent carbon makes intramolecular rearrangement and acetylene formation a particularly facile process for such species. As noted in section II.A the Fritsch-Buttenberg-Wiechell rearrangement⁸⁹ of β,β -diarylvinyll halides upon treatment with base has been known since the 1890s, with rearrangement occurring under a variety of conditions.⁹⁰ The elegant labeling studies of Bothner-By⁹¹ and Curtin and co-workers^{92a} established that the rearrangement is stereospecifically *trans*, thereby ruling out the involvement of the free carbene **60** and implicating an organometallic, **58**, or perhaps carbenoid, **59**, intermediate.^{92b}

Similar aryl migration and exclusive acetylene formation occurs in the base treatment of 1,1-dihalo-2,2-diarylethylenes,⁹³ 5,5-diaryl-*N*-nitrosooxazolones⁹⁴ (**27**, R = C₆H₅), as well as diarylvinyll triflates¹⁴ (**14**, R = C₆H₅).



Exclusive rearrangement occurs even with one β -aryl group such as in 1-halo-2-arylpropene⁹⁵ (**76**) and the corresponding triflates **77**. Once again Köbrich and co-workers⁹⁶ have by means of stereochemical studies and low-temperature isolation established that the halides **76** react through organolithium or carbenoid intermediates. In contrast, the completely nonstereospecific rearrangement of the triflate **77** strongly suggests, but does not absolutely prove, the involvement of the free carbene **60** rather than a carbenoid **59** in this intramolecular reaction.⁹⁷

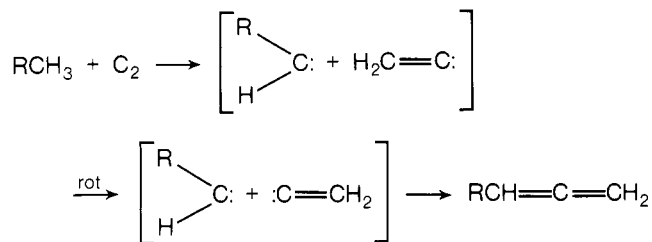
Acetylene formation in monosubstituted vinyl compounds can occur by one of two ways:



a classical bimolecular β -elimination or α -elimination, alkylidene carbene formation, and hydrogen migration. Calculations^{52,98} indicate that $\text{HC}\equiv\text{CH}$ is some 38–46 kcal/mol more stable than $\text{H}_2\text{C}=\text{C}:$, hence the rearrangements

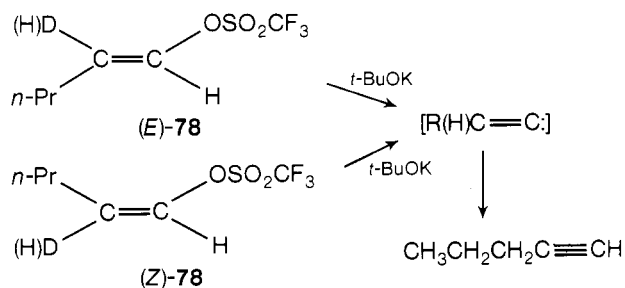


should occur rapidly with little or no activation energy. Indeed, $\text{H}_2\text{C}=\text{C}:$ has only been trapped intermolecularly, at the expense of exclusive acetylene formation, by special techniques.^{2a,99} C_2 (**3**) was allowed to react with a mixture of C_3H_8 and C_3D_8 to yield allenes by 1,1-diabstraction of hydrogen by C_2 to produce alkylcarbene and vinylidene:

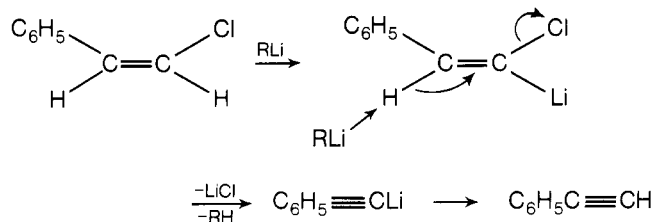


The vinylidene so formed could rearrange to acetylene or rotate through 180° (estimated rate $\sim 10^{11}$ s) and couple with the $\text{R}\dot{\text{C}}\text{H}$ to produce the observed allenes.⁹⁹ On the other hand, $\text{F}_2\text{C}=\text{C}:$ has been calculated to have a minimum $E_a = 59$ kcal/mol for rearrangement to $\text{FC}\equiv\text{CF}$ although the latter is some 36 kcal/mol more stable than the carbene.⁹⁸

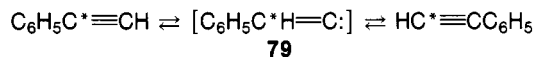
The complete absence of a deuterium isotope effect as well as a lack of stereochemical preference in the reaction of (*E*)-**78** and (*Z*)-**78** vinyl triflates with *t*-BuOK established an α -elimination and alkylidene carbene and hydrogen migration as the most likely reaction pathway.¹⁰⁰



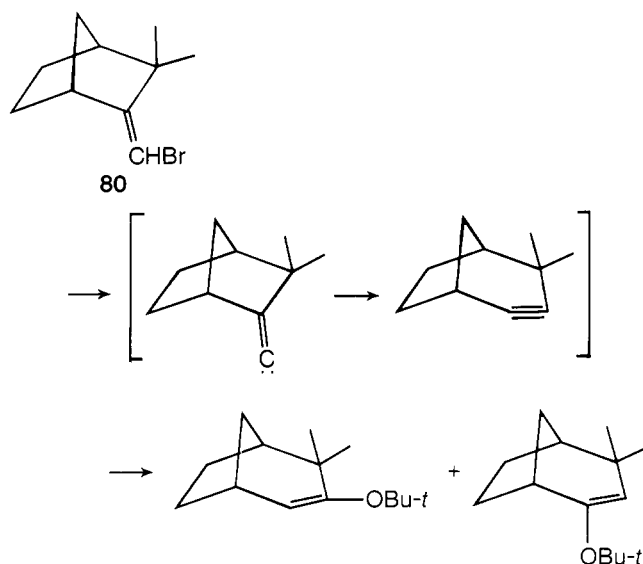
An alkylidene carbene has also been suggested as an intermediate¹⁰¹ in the formation of phenylacetylene from β -styryl bromide and $\text{C}_6\text{H}_5\text{Li}$, a reaction first observed by Wittig and co-workers.¹⁰² However, more detailed stereochemical and deuterium isotope effect studies of Schlosser and Ladenberger¹⁰³ on the reaction of alkyllithiums with styryl chloride rule out the involvement of a free alkylidene carbene and suggest an E-2 type mechanism:



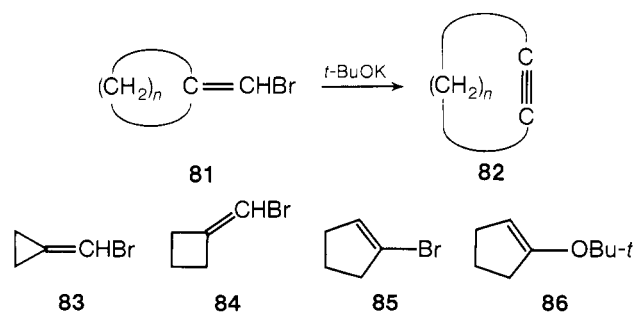
An alkylidene carbene **79** has also been suggested as an intermediate in the thermal scrambling of labeled phenylacetylene at 550–700 °C:¹⁰⁴



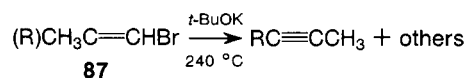
Intramolecular alkyl migrations in alkylidene carbenes or carbenoids can also occur, but only under more vigorous conditions and in the absence of olefin or other traps. Intramolecular alkyl migration and acetylene formation was postulated in the reaction of bromocamphene (**80**) with *t*-BuOK in refluxing toluene.¹⁰⁵



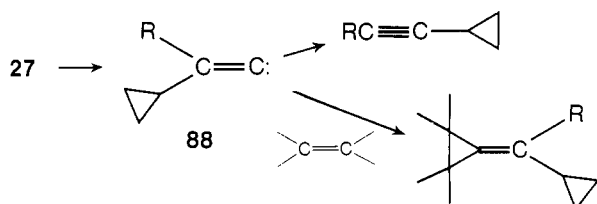
ene.¹⁰⁵ Similarly, alkylidene carbenes followed by alkyl migration has been invoked in the formation of cycloalkynes **82** from bromomethylenecycloalkanes **81** upon reaction with *t*-BuOK. The smaller ring C_5 and C_6 cycloalkyne intermediate could be trapped as Diels–Alder adducts with 1,3-diphenylisobenzofuran. With C_8 and larger rings the acetylenes were isolated.¹⁰⁶ No alkylidenes are involved in the reaction of **83** with bases or the formation of **85** and **86** from **84** and *t*-BuOK.¹⁰⁷



Alkynes were also observed (besides insertion products) presumably via alkylidene carbenes in the reaction of acyclic vinyl halides **87**, with *t*-BuOK at 240 °C:¹⁰⁸



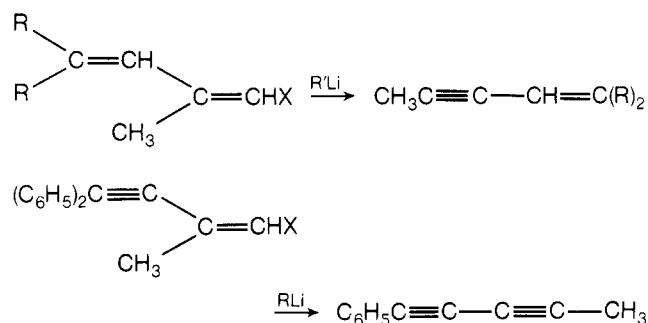
Alkyl migration and acetylene formation compete with intermolecular trapping by olefin in the case of cyclopropyl-sub-



stituted alkylidene carbenes **88** as derived from the corresponding oxazolidone **27**.¹⁰⁹ Dicyclopropylcarbenes (**89**) gave only acetylene products (**90**) and could not be intermolecularly trapped.^{109,110}



Rearrangement and alkyne formation also occurred on base treatment of 1-halo-1,3-dienes^{111a} and 1-halo-1-ene-3-alkynes.^{111b}

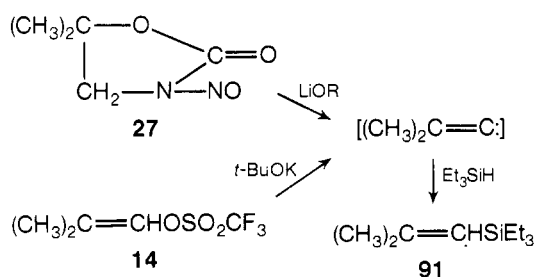


It is obvious that alkylidene carbenes or carbenoids are involved in many if not all of the alkyne forming reactions mentioned in section II even if the intermediates could not be intermolecularly trapped. It is also evident that intermolecular reactions with substrates can only be carried out with β -dialkyl substituted (and perhaps heteroatom substituted) alkylidene carbenes and not with aryl or hydrogen substituted ones.

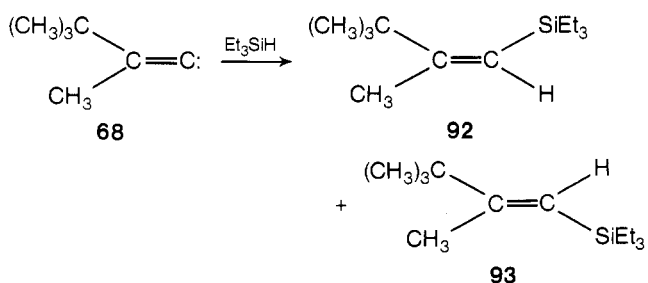
B. Intermolecular Reactions

1. Insertions

Alkylidene carbenes readily insert into Si-H and O-H bonds. Both vinyl triflate **14** and oxazolidone **27** derived carbenes gave high yields of vinylsilanes **91** by reaction with triethylsilane.^{14,112}

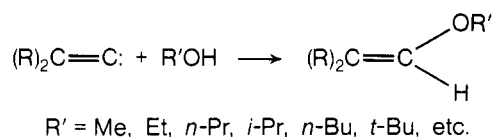


The carbene **68** from oxazolidone⁸⁵ or vinyl triflate¹¹³ gave

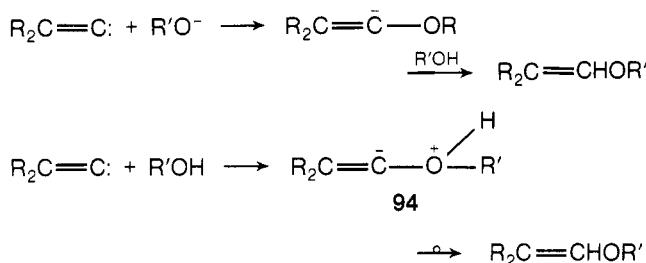


predominantly the thermodynamically less stable isomer **92**, with only small amounts of **93** as product. A stepwise hydride removal, rather than a concerted insertion, has been postulated⁸⁵ to account for such contrathermodynamic behavior.

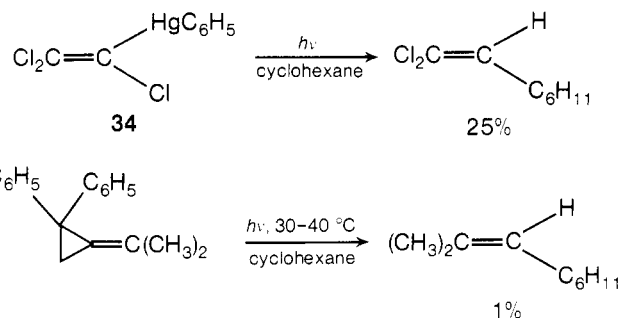
A large number of alkylidene carbenes from diverse progenitors have been observed to give vinyl ether products. Newman and Okorodudu^{24b} have investigated the interaction of a number of oxazolidone derived alkylidene carbenes with a variety of alcohols and found 60–90% yields of vinyl ether products:



The exact mechanism of formation of these vinyl ether products remains to be elucidated. It is not clear if reaction occurs by capture of the carbene by RO^- , usually present, by ylide **94** formation followed by a hydrogen shift, direct insertion, or by yet a different pathway.



Unlike "insertion" into Si-H and O-H bonds by alkylidene carbenes and in contrast to the behavior of alkylcarbenes,⁴ intermolecular insertion into C-H bonds occurs much less readily. Only in special circumstances have C-H insertions by alkylidene carbenes been observed. Intermolecular C-H insertions have been observed only with photogenerated^{28,30} carbenes with but modest yields. No other alkylidene carbenes or carbenoids have

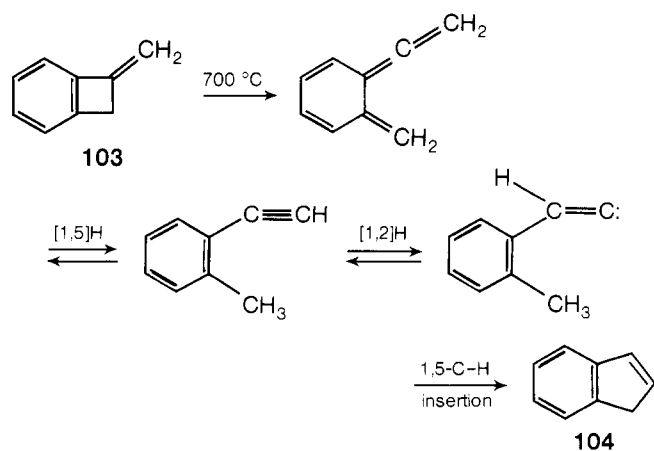
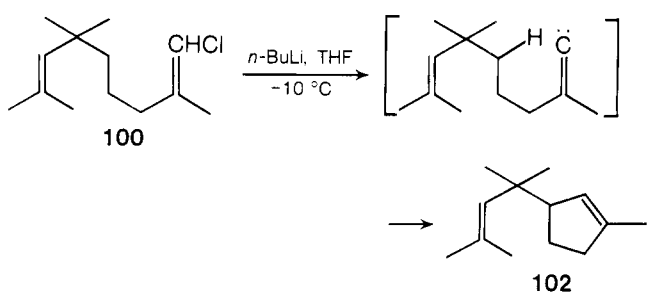
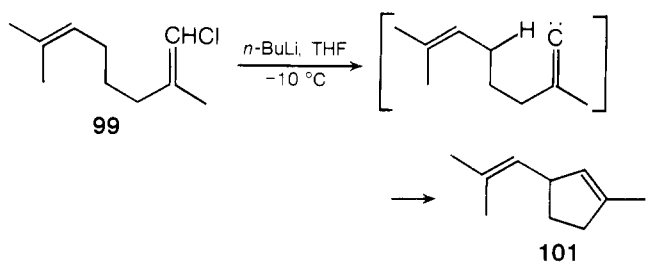
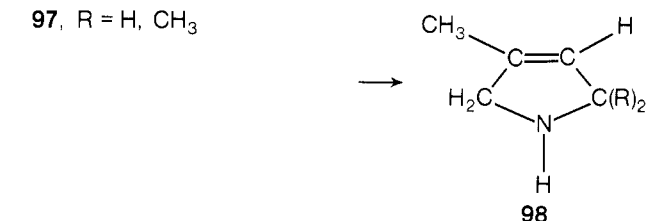
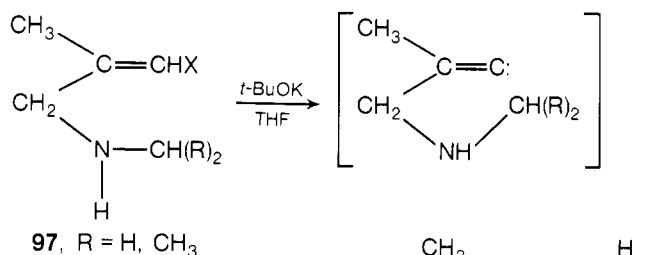
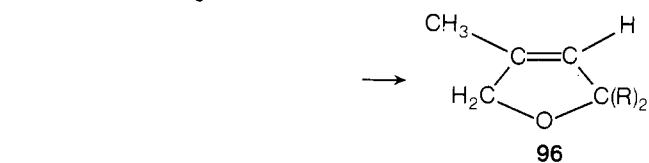
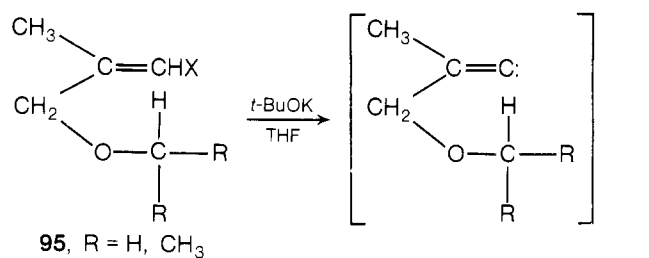


been reported to undergo intermolecular C-H insertions. It is possible that normal C-H bonds do not possess sufficient electron density to be attractive substrates for weakly electrophilic unsaturated carbenes.

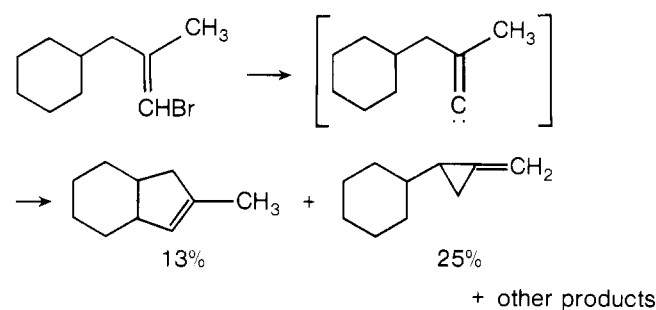
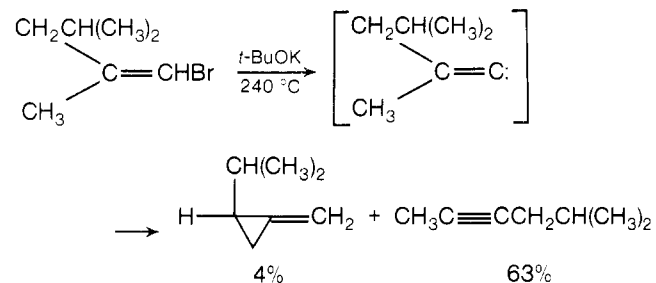
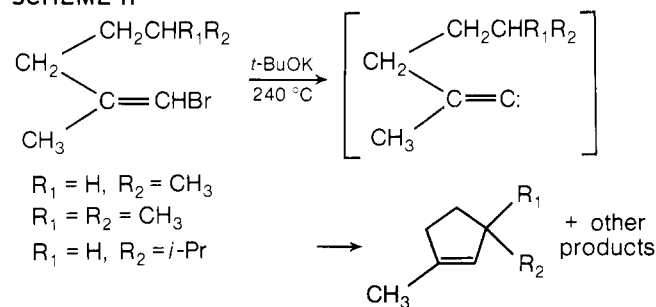
A number of intramolecular C-H alkylidene carbene insertions have been reported. Walsh and Bottini¹¹⁴ reported the formation of dihydrofurans **96** and 3-pyrrolines **98** via intramolecular alkylidene carbene insertion, from halopropenyl ethers **95** and amines, **97**, respectively.

Insertion to give cyclopentenes **101** and **102** was observed upon treatment of chlorodienes **99** and **100** with n -BuLi in THF, respectively.¹¹⁵

In a recent study,¹⁰⁸ 1,5-carbon-hydrogen as well as 1,3-carbon-hydrogen insertion was observed upon treatment of acyclic terminal vinyl bromides with t -BuOK, neat at 240 °C (see Scheme II). The reason for the preference for 1,5 and to some extent 1,3 insertion over 1,4 or 1,6 insertion is not clear. The



SCHEME II



relative amount of 1,5-C-H insertion followed the order tertiary > secondary, benzylic >> primary.¹⁰⁸

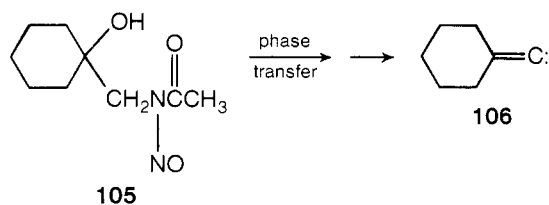
1,5-C-H alkyldiene carbene insertion was postulated to account for the formation of indene (**104**) from **103** upon flash pyrolysis at 700 °C.⁴²

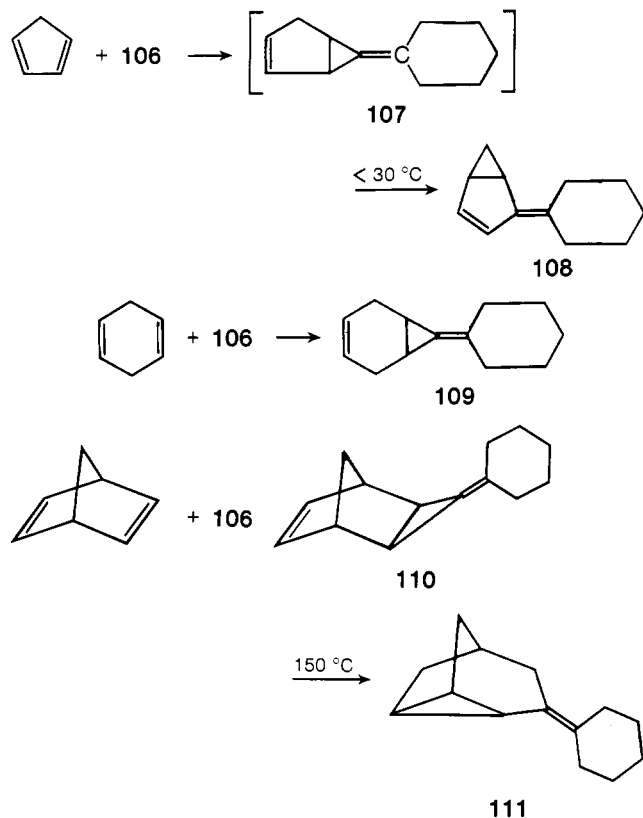
No data are available on the mechanism of any of these alkyldiene carbene C-H "insertions". It is not known if they occur by a concerted or a stepwise process nor are the stereochemical requirements of the reaction known.

2. Addition to Double Bonds

The preferred intermolecular reaction of alkyldiene carbenes is methylenecyclopropane formation via addition to olefins. Such addition is commonly used to establish the intermediacy of alkyldiene carbenes or carbenoids in a particular reaction; hence they were largely discussed in sections II and III. This part will treat unusual additions to C=C bonds not previously mentioned, and interactions of alkyldiene carbenes with heteroatom double bonds such as C=O and N=N.

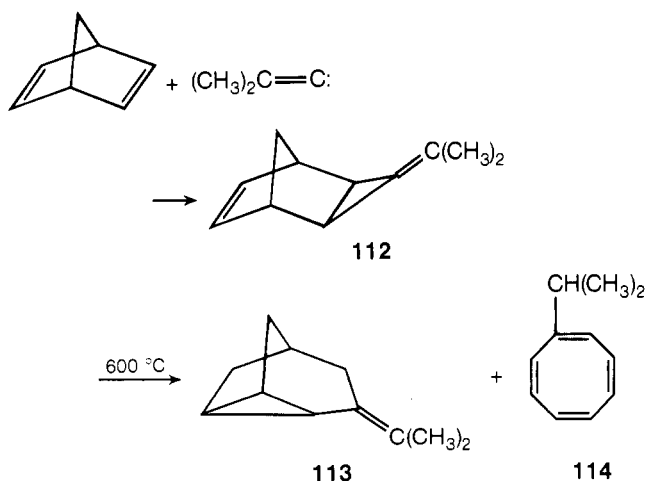
Alkyldiene carbene **106**, derived from **105**, has been added to several cyclic dienes.¹¹⁶ Addition to cyclopentadiene gave adduct **108** via the intermediacy of **107** and a trimethylene-methane-type rearrangement.¹¹⁷ With cyclopentadiene only 1,2-adduct **107** was observed with no 1,4-alkyldiene carbene addition products being observed. Since 1,4-alkylcarbene ad-



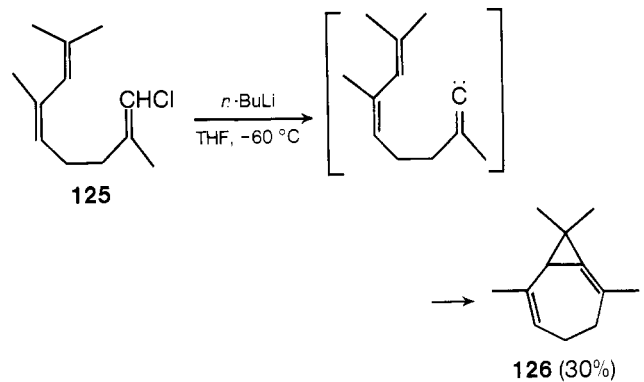
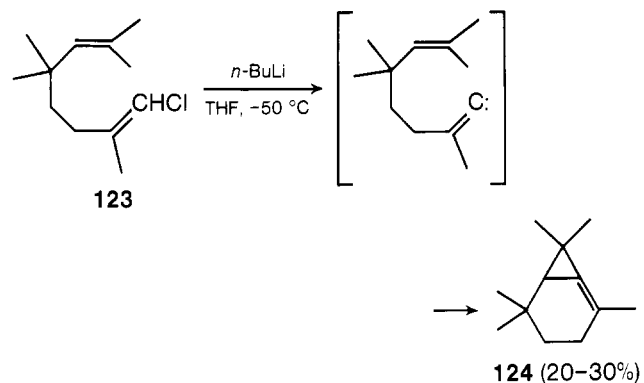
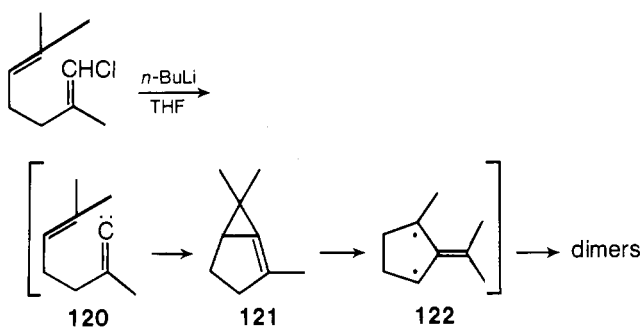
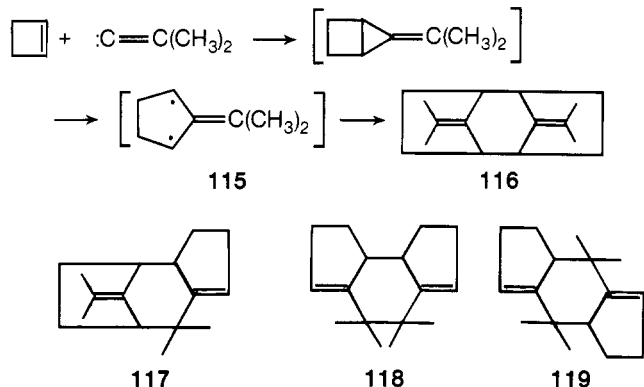


ditions¹¹⁸ are rare, this is not too surprising. Addition of **106** to 1,4-cyclohexadiene gave the expected adduct **109**. Interaction of **106** with norbornadiene also resulted in a 1,2-addition product **110**, which upon heating at $150\text{ }^\circ\text{C}$ converted to **111** by a trimethylenemethane diradical path. The alternative cycloaddition process is symmetry forbidden.¹¹⁹

Similarly isopropylidenecarbene has been added¹²⁰ to norbornadiene to give **112** which upon flash thermolysis gave **113** at $400\text{ }^\circ\text{C}$ and a mixture of **113** and **114** at $600\text{ }^\circ\text{C}$. Rearrangements giving **110** and **111** have been observed.¹²¹

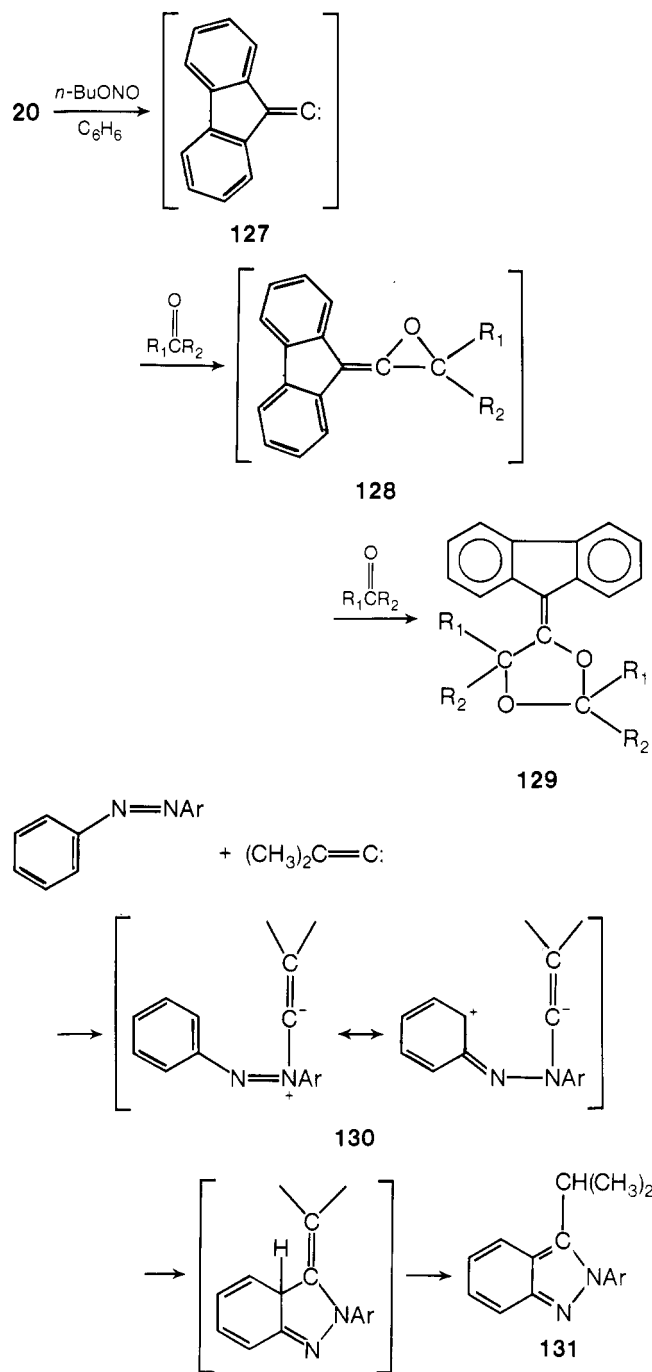


A trimethylenemethane-type diradical, **115**, was involved in the addition of isopropylidenecarbene to cyclobutene. The actual products observed consisted of dimers of **115**, namely **116**–**119**.¹²² Trimethylenemethane **115** was an intermediate in the thermolysis or photolysis of appropriate azo precursors and was extensively investigated by Berson and collaborators.¹²³ An analogous diradical, **122**, was involved in an intramolecular addition of an unsaturated carbene, **120**, and dimer formation.¹²⁴ Adducts **124** and **126**, analogous to **121**, were isolated as stable compounds from the reactions of **123** and **125** via intramolecular carbene additions.^{125,126}



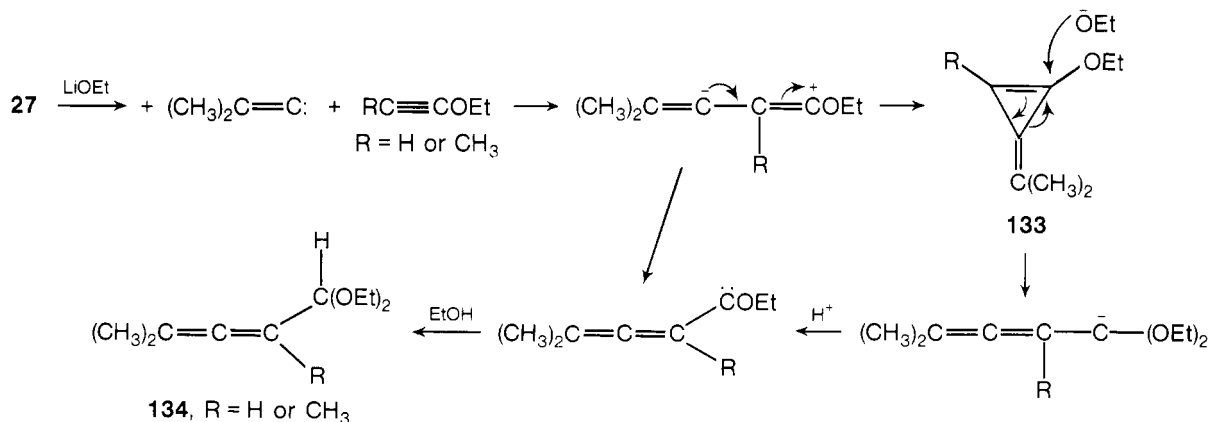
Alkylidene carbenes have also been added to carbonyls.¹²⁷ Carbene **127** from the deamination of **20** in the presence of ketones and aldehydes gave diadducts **129**, presumably via the intermediacy of allene epoxides **128**, although no such allene oxides¹²⁸ could actually be isolated.

Alkylidene carbenes have been reacted with azoarenes.¹²⁹ Good yields of 2-indazoles **131** were obtained, representing a simple, single step entry into this 10- π -electron heterocyclic system. A number of mechanisms are possible for the formation of **131**, but interaction of the carbene with the nitrogen lone pair to give ylide **130** and subsequent ring closure followed by hydrogen migration seem most reasonable. Analogous addition



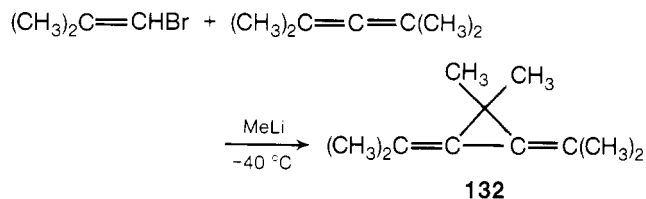
of alkylcarbenes to azoarenes resulting in dihydroindazoles are known.¹³⁰

SCHEME III

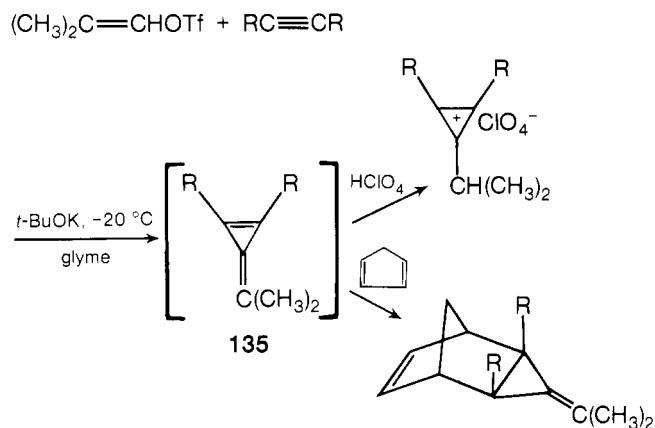


3. Addition to Allenes, Alkynes, and Cumulenes

As first observed by Shechter,¹³¹ alkylidene carbenes readily add to allenes to give 1:1 adducts **132**. The identical product was observed via the oxazolidone **27** route.⁶⁰



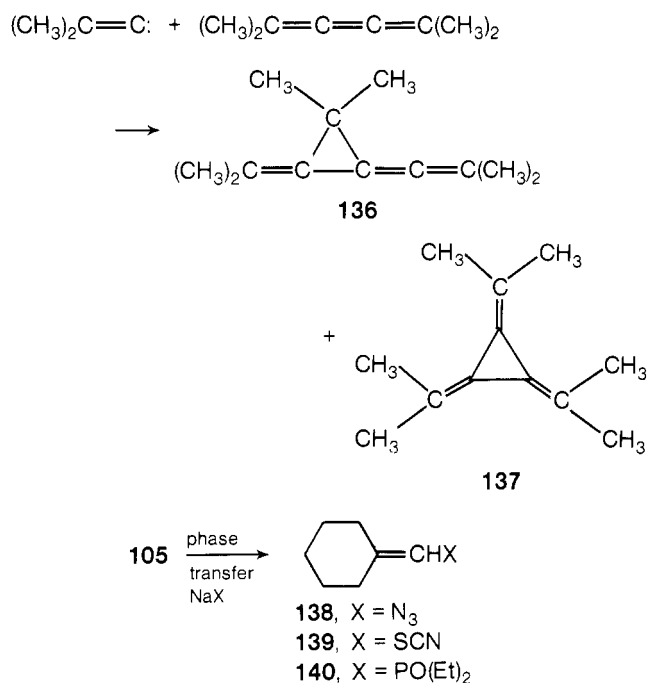
Interaction of **27** derived carbene with ethoxyacetylene and ethoxypropyne, respectively, gave adducts **134** via the mechanism postulated in Scheme III.¹³² No methylenecyclopropene **133** could be isolated. Addition of vinyl triflate **14** derived carbene to 2-butyne or 3-hexyne has provided a ready route¹³⁴ into the in situ preparation of simple¹³⁵ alkyltrifluvenes **135**, as shown by trapping with cyclopentadiene or HClO₄. Although triafulvenes **135**, could not be isolated, evidence¹³⁶ indicates that the difficulty is reaction with oxygen rather than just thermal sensitivity.



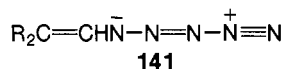
Alkylidene carbenes gave both expected 1:1 adducts **136** and **137** with butatriene as well as some diaddition products.¹³⁷ Compound **137** is an interesting member of a class of strained¹³⁸ organic molecules known as radialenes. The parent radialene, **137**, is known as well.¹³⁹

4. Miscellaneous Reactions

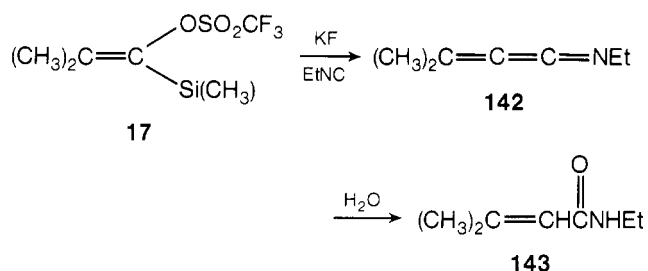
Reaction of **105** under phase-transfer conditions in the presence of NaN₃ and NaSCN yielded **138** and **139**, respectively, and reaction with (EtO)₃P gave **140**.¹⁴⁰ The involvement of alkylidene carbenes in these reactions has not been established except in the reaction with N₃. Kirmse and Schnurr¹⁴¹ have



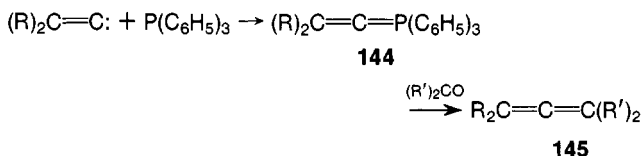
shown that the reaction of **105** derived diazonium ions with NaN_3 involves vinyl cations and alkylidene carbenes as well as pentazenes **141**. Similar intermediates may be involved in the other reactions as well.



Reaction of isonitriles with **17** derived alkylidene carbene gave amide **143** as product.^{142a} Such an amide could arise via the reaction of the initially formed alkylideneketeneimine^{142b} adduct, **142**, with water.



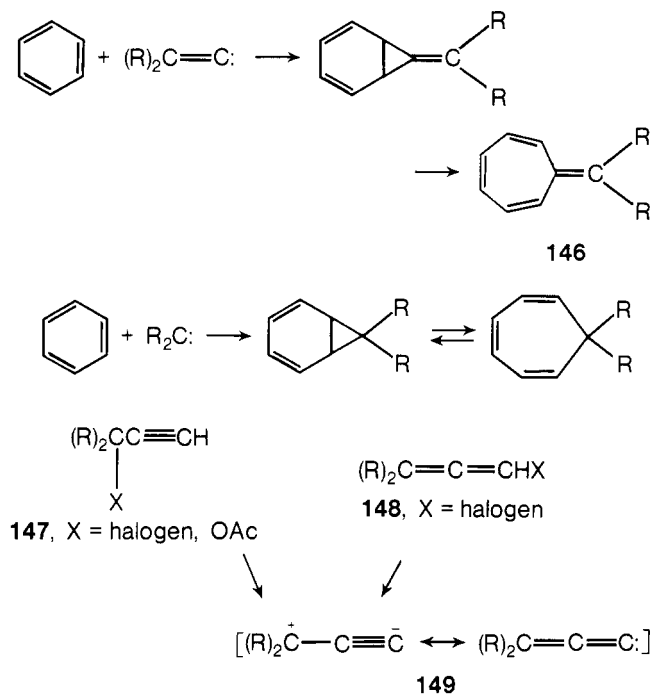
Several potentially interesting reactions of alkylidene carbenes such as interaction with phosphines to form ylides **144**, then allenes **145**, have not been reported. Such a reaction would



represent an alternative entry into the novel cumulated phosphorus ylides investigated by Bestmann and co-workers.^{142b} Neither have interactions of alkylidene carbenes with aromatic substrates nor the formation of heptafulvenes **146** via this route been reported, although the analogous addition of alkyl carbenes to aromatics and formation of norcadienes are well known.⁴

V. Generation of Vinylidene Carbenes

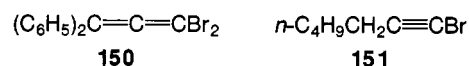
Vinylidene carbenes have mostly been generated by interaction of base with propargyl derivatives **147** or haloallenes **148**. It was to account for the slow reactivity in aqueous ethanol



(compared to *tert*-amyl chloride) and kinetic dependence on added NaOH of 1-chloro-3-methyl-1,2-butadiene and 3-chloro-3-methyl-1-butyne that such a carbene was first proposed by Hennion and Maloney.¹⁴³ A simple $\text{S}_{\text{N}}1$ reaction was ruled out by the effect of added NaOH on the reactivity of the terminal alkyne **147** and the lack of any effect on the methyl-substituted (2-pentyne analogue) halide.¹⁴⁴ Initially, Hennion and Maloney proposed a slow loss of H^+ and rapid subsequent loss of halide. Subsequent work of Shiner and co-workers¹⁴⁵ showing rapid deuterium exchange in deuterated solvent as well as common ion rate depression by added halide established that reaction occurs via a rapid preequilibrium and anion formation followed by a rate-determining loss of halide and carbene **149** formation (Scheme IV).

Carbene **149** can also be generated in aprotic hydrocarbon media from either **147**¹⁴⁶ or **148**^{147,148} and base, usually *t*-BuOK. Generally better yields of carbene-derived products are observed if the more recent phase transfer¹⁴⁹⁻¹⁵¹ or crown ether¹⁵² procedures are employed with either **147** or **148** for the generation of **149**.

Dihaloallenes **150**^{153,154} and bromoalkyne¹⁵⁵ **151** have also been employed as carbene **149** progenitors. Cyclopropane¹⁵⁶

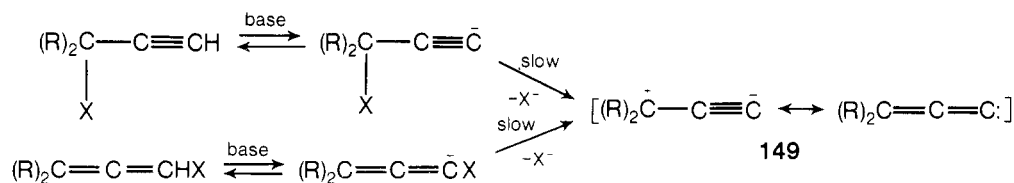


152 as well as bis(nitrosourethane)¹⁵⁷ **153** have been shown to give carbene-derived products (Scheme V). This latter reaction is the only one that might involve a diazoallene, **155**, in the generation of a vinylidene carbene. Unfortunately, the yields of carbene derived products are very low because of competing diphenyldiazopropanone (**157**) formation presumably via intermediates **154** and **156**. Vinylidene carbenes have also been implicated in the isomerization¹⁵⁸ of thioalkyne **158**, as well as in the reaction¹⁵⁹ of carbamate **159**.

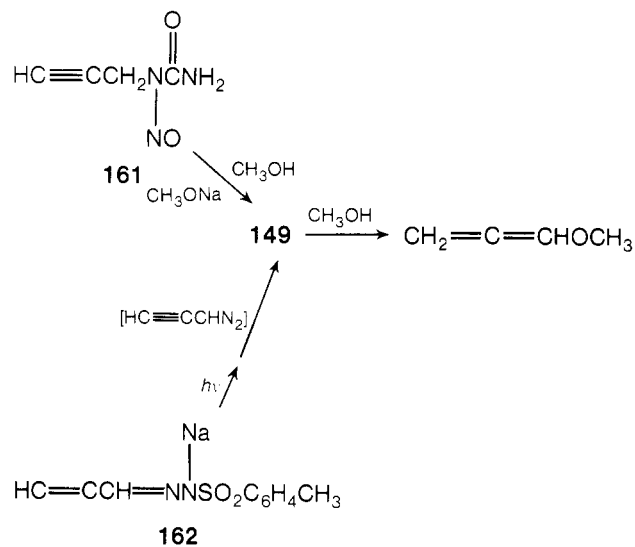
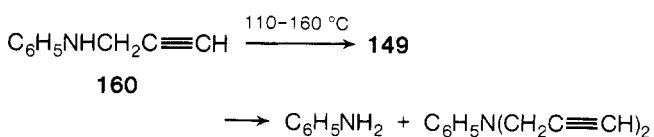
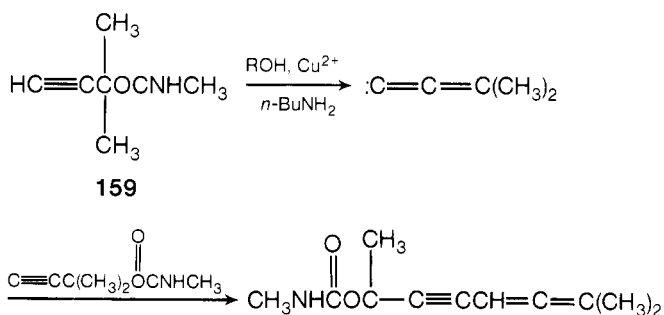
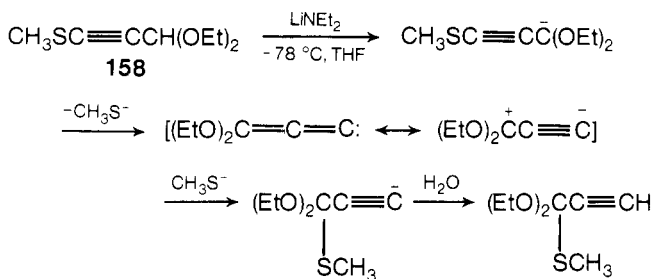
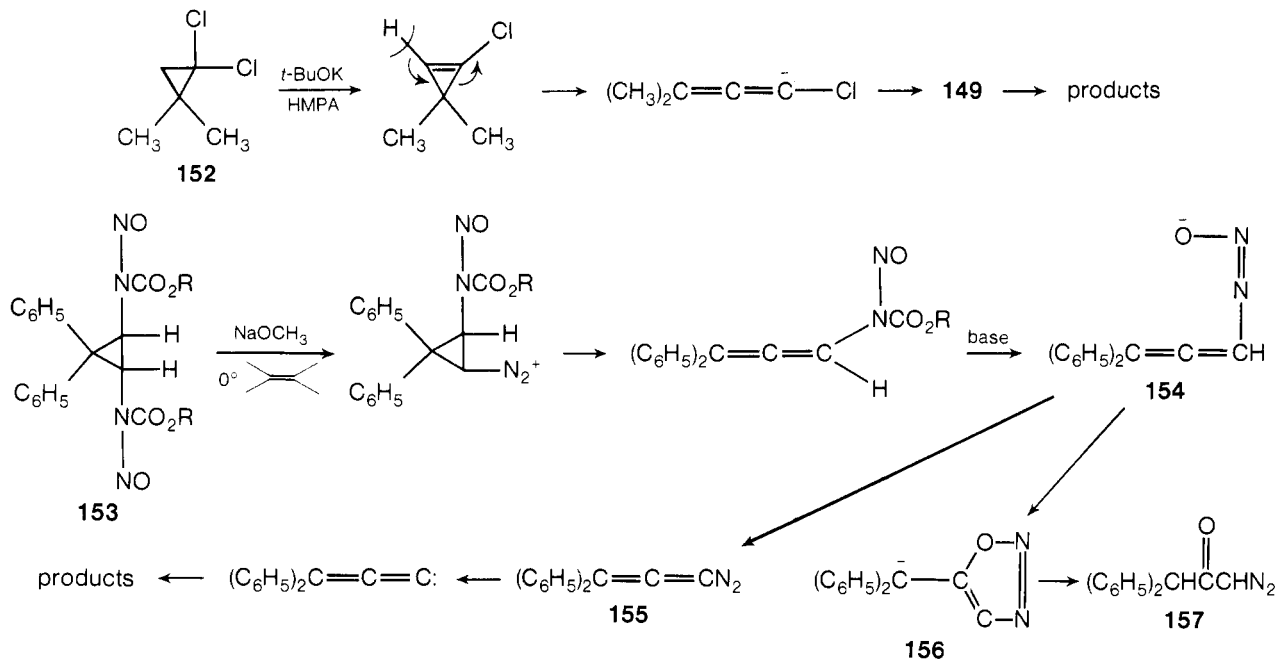
Vinylidene carbenes are probably intermediates in the thermalolysis of propynylaniline¹⁶⁰ (**160**) and the alkaline methanolic cleavage of propargylnitrosourea (**161**) and photolysis of tosylhydrazone¹⁶¹ **162**.

Other than the reactions of **162**, to date no procedures have been reported for the generation of vinylidene carbenes that do not involve some type of base initiated elimination. Other than

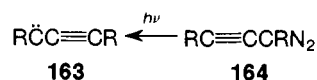
SCHEME IV



SCHEME V



Species which are isomeric with vinylidene carbenes, namely alkynyl carbenes or propargylenes, **163**, should be briefly mentioned. The parent as well as substituted propargylenes



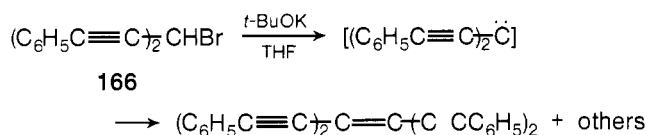
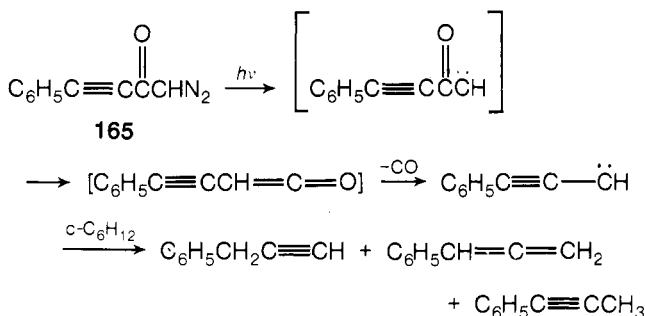
have been prepared¹⁶² by photolysis of the appropriate diazalkynes **164**, and shown¹⁶³ to be triplets in accord with expectations.¹⁶⁴ Substituted propargylenes have also been produced by photolysis¹⁶⁵ of **165** and via the reaction¹⁶⁶ of **166** with *t*-BuOK.

Finally C₂O (**168**) has also been generated¹⁶⁷ by photolysis

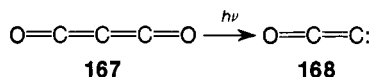
the photolysis of **162** there are also no photochemical processes known for the generation of **149**.

TABLE V. Relative Reactivity of (R)₂C=C=C: toward Olefins

Olefin	Reaction conditions, <i>k</i> _{rel} (ref)		
	(CH ₃) ₂ C(Cl)C≡CH, -10 °C <i>t</i> -BuOK (170a)	(CH ₃) ₂ C=C=CHCl, -10 °C <i>t</i> -BuOK (147)	(<i>t</i> -Bu) ₂ C(OAc)C≡CH, <i>t</i> -BuOK + 30 °C (171)
(CH ₃) ₂ C=C(CH ₃) ₂	20.0	16.0	16.0
(CH ₃) ₂ C=CHCH ₃	4.7	4.9	4.9
(CH ₃)C ₂ H ₅ C=CH ₂	5.1	4.2	2.0
Cyclohexene	1.0	1.0	1.0
CH ₃ (CH ₂) ₃ CH=CH ₂	0.25	0.23	0.20
	(C ₆ H ₅) ₂ C(OAc)C≡CH, 0 °C <i>t</i> -BuOK (157)	Nitrosourethane 153 , 0 °C CH ₃ ONa (157)	(CH ₃) ₂ C=C=CHBr, 0-5 °C <i>t</i> -BuOK, 18-crown-6 (170b)
(CH ₃) ₂ C=C(CH ₃) ₂	9.0	8.0	16.9
(CH ₃) ₂ C=CHCH ₃			7.6
(CH ₃)C ₂ H ₅ C=CH ₂			
Cyclohexene	1.0	1.0	1.0
CH ₃ (CH ₂) ₃ CH=CH ₂	0.61	0.70	0.1

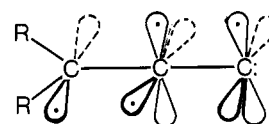


of carbon suboxide (**167**) and its chemistry investigated.¹⁶⁸



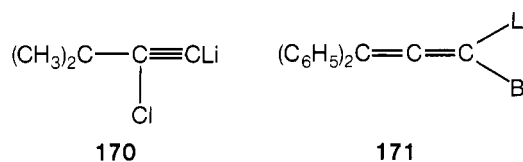
VI. Nature of Vinylidene Carbenes

Unlike alkylidene carbenes (**1**), vinylidene carbenes (**2**) are hybrids of a zwitterionic and a neutral resonance form, **149**. The relative importance of the two resonance forms is strongly affected by the structure as well as the environment of the particular species. Electron-donating substituents such as alkyl and aryl groups should enhance the contribution of the zwitterionic form as should polar solvents such as aqueous ethanol and ethers capable of strong solvation. In contrast nonpolar solvents like hydrocarbons should favor the neutral carbenic resonance form. There is also good evidence from measurement of activation volumes that in aqueous protic solvents the intermediate from reaction of either **147** or **148** (R = CH₃) is a halide associated ion pair rather than the free carbene.¹⁶⁹ In contrast, relative reactivity data summarized in Table V strongly suggest that there is very little carbene encumbrance in the transition states of olefin additions. The similarity in olefin selectivity of vinylidene carbenes **149** regardless of progenitor not only suggests a free carbene but also shows very little steric requirement for reaction. The dimethyl-, di-*tert*-butyl-, and diphenylcarbenes react similarly with each olefin. This is as expected since in vinylidene carbenes, unlike alkylidene carbenes **75**, the substituents are perpendicular and one carbon removed from the reactive site at the empty carbenic orbital in **169**. Faster reaction with more substituted, and hence electron-rich olefins, further indicates that vinylidene carbenes like alkylidene carbenes are electrophilic. This conclusion is supported by the ρ value of -0.95 observed in the interaction of (CH₃)₂C=C=C: with various ring-substituted styrenes.⁶⁷



169

At low temperatures in THF, both organolithium compounds **170**¹⁷² and **171**¹⁷³ were stable and exhibited nucleophilic behavior characteristic of such species.^{172,173} This suggests that



perhaps a rapid equilibrium exists between carbenoid and free carbene, even in nonsolvating solvents like olefins, with the free carbene reacting faster than the carbenoid. Such an equilibrium would account for all of the behavior of vinylidene carbenes **149**, both in protic polar solvents and in nonpolar olefin solvents (i.e., the similar selectivity of Table V).

By arguments similar to those applied to alkylidene carbenes in section III.A, vinylidene carbenes would be expected to be singlets. The addition of (CH₃)₂C=C=C: to *cis*- and *trans*-2-butene was found to be stereospecific.¹⁷⁰ This implies that at least the nascent carbene is a singlet. Recent theoretical calculations¹⁷⁴ indicate that vinylidene carbenes **2** possess a singlet ground state, with a singlet triplet splitting of about 50 kcal/mol.

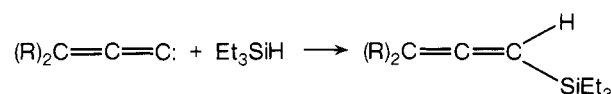
Vinylidene carbenes **2**, like their alkylidene counterparts **1**, are singlets and electrophilic. They exhibit behavior characteristic of both carbenoids and free carbenes. Unlike alkylidene carbenes there is very little steric requirement for addition to olefins, but there are definite steric requirements for reaction with nucleophiles (vide infra).

VII. Reactions of Vinylidene Carbenes

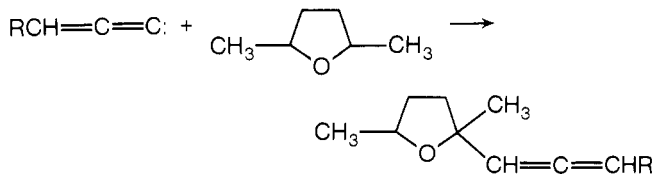
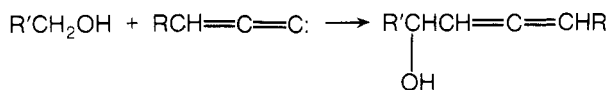
Unlike alkylidene carbenes the substituents in vinylidene carbenes are not predisposed to migration by virtue of their location as shown in **169** and hence no intramolecular rearrangements are possible or known.

A. Insertions

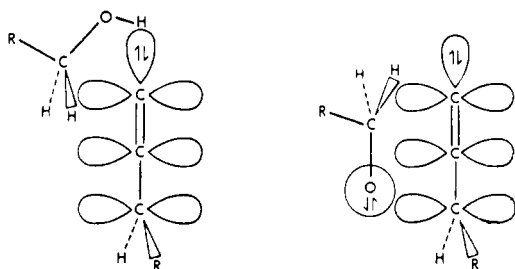
Vinylidene carbenes readily insert into Si-H bonds to give silyllallenes.¹⁷⁵ No data are available on the mechanism of such



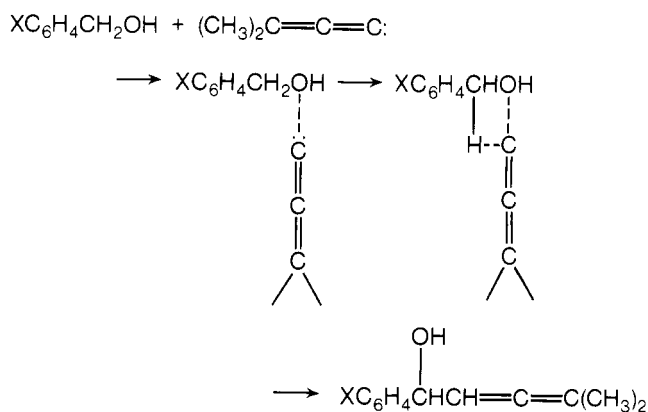
insertions. Insertion into C-H bonds α to oxygen has been observed with alcohols and 2,5-dimethyltetrahydrofuran.^{175,176}



Prior hydrogen bonding between the O-H and the carbene lone pair orienting the empty p orbital in close proximity to the α -C-H bond has been proposed¹⁷⁶ to explain the specificity of C-H insertion. An alternative possibility of an anion carbene pair formed between alkoxide ion and the C-3 orbital was considered less likely.¹⁷⁶ No insertion was observed into cumene, THF, or glyme.



Nucleophilic character was attributed to vinylidene carbenes in their insertion into the benzylic C-H bond in a series of ring-substituted benzyl alcohols, to explain the positive ρ value of 0.52 that was observed.¹⁷⁷ The reaction was considered to proceed by a concerted process due to the small value of ρ , since a full benzyl anion¹⁷⁸ has a Hammett ρ value of 4.0. Hydrogen bonding followed by ylide formation and collapse to product was proposed as a reaction pathway.¹⁷⁷

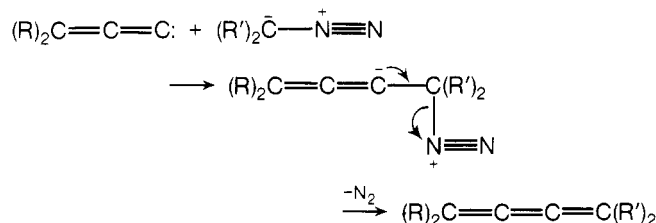
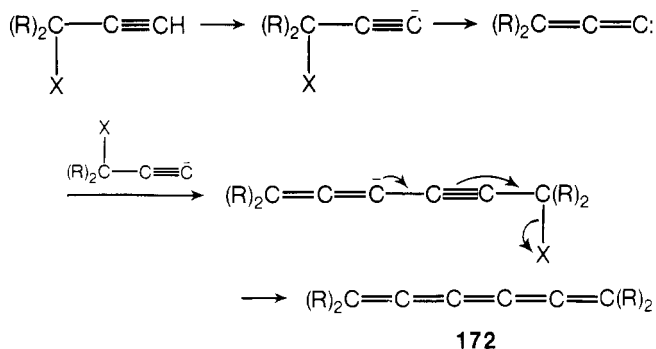


B. Addition Reactions

1. With Nucleophiles

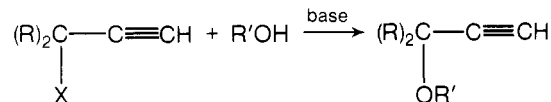
A large number of nucleophiles react with vinylidene carbenes **149**, generally derived from the corresponding propargyl halides. Barring steric complications in protic polar media, reaction generally occurs at the more electrophilic tertiary carbon resulting in propargylic products. Steric factors, solvent effects, and nucleophilicity affect these reactions although in ways not clearly understood.¹⁷⁹

In contrast, in aprotic (hydrocarbon) media, reactions seem to be more straightforward with involvement of the carbene form rather than the zwitterionic form **149**. Hexapentaenes **172** can be formed by interaction of the initially formed acetylide with the



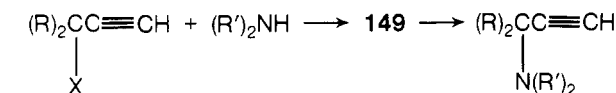
carbene.^{146,154,180-182} Similarly, butatrienes were obtained upon reaction of **149** with diazo compounds.¹⁸³

Alcohols readily react with **149** to give, in the absence of steric hindrance, propargyl ethers.^{143,184} Work of Hennion and

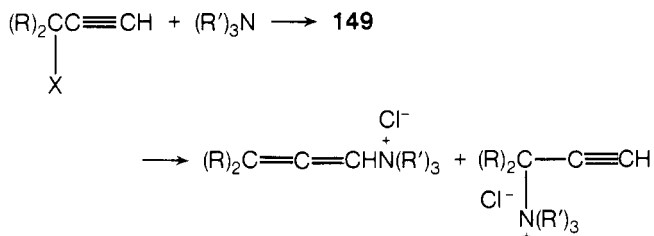


Motier¹⁷⁹ indicates that reaction probably proceeds via the alkoxide rather than the alcohol itself. In *t*-BuOH:H₂O only propargyl alcohol and ene-yne were observed, whereas in aprotic media the *tert*-butoxy propargyl ether was observed.¹⁸⁵ In contrast, with steric hindrance in **149** ($R = t$ -Bu) mixtures of allenyl and propargyl ethers were observed.¹⁸⁶

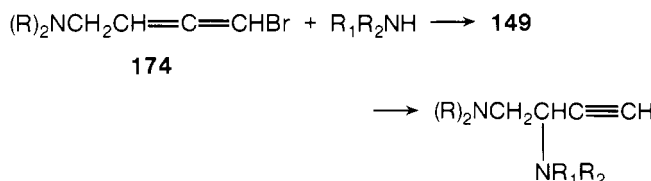
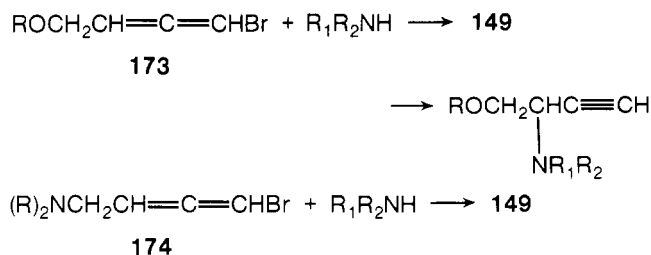
A large variety of amines readily react with propargyl halides via **149** to give propargyl amines.¹⁸⁷⁻¹⁹¹ The reaction appears



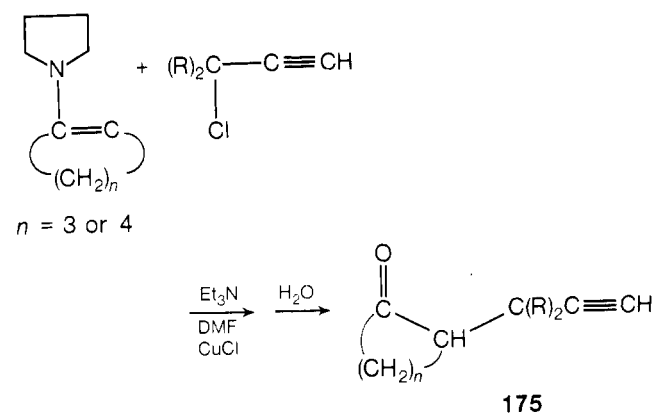
to be catalyzed by trace amounts of cuprous salts¹⁸⁹ and less affected by steric factors than reaction with alcohols. Tertiary amines were found to give mixtures of allenic and alkynyl amine



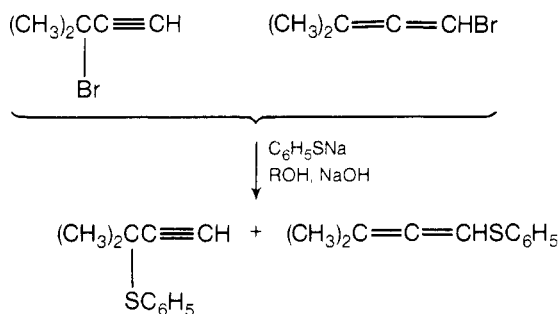
salts.¹⁹² Alkynyl amines were also obtained from allenyl bromides **173** and **174** and amines.¹⁹³



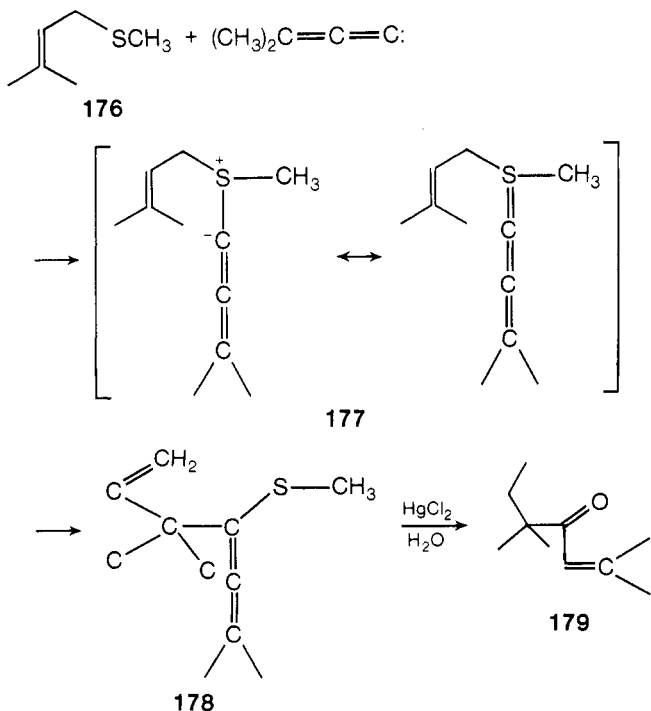
Enamines and propargyl chlorides gave after hydrolysis acetylenic ketones **175**.¹⁹⁴ Reaction presumably occurred via C-alkylation with **149** although the nature of the initial product is unknown.¹⁹⁴



Sulfur nucleophiles such as thiophenoxide gave mixtures of allenyl and acetylenic thioethers with an identical product ratio from either haloallene or acetylene.^{145b} Vinyl sulfide **176** gave

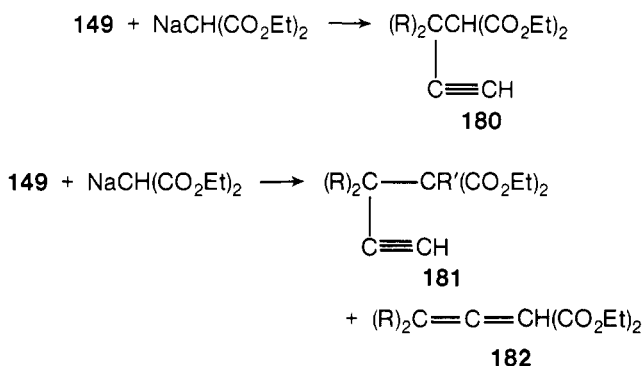


sulfide **178** upon reaction with **149** via a [2,3]-sigmatropic shift of ylide **177**.¹⁹⁵ Such [2,3]-sigmatropic shifts of sulfur ylides are well known.¹⁹⁶ Subsequent hydrolysis of **178** in the presence of HgCl_2 gave artemesia ketone **179** in good yield.¹⁹⁵



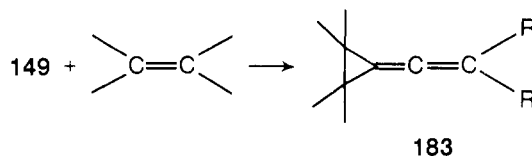
Various substituted diethyl sodiomalonates have also been employed as nucleophilic traps for **149**. Sodio unsubstituted diethyl malonate gave¹⁹⁷ **180** whereas substituted diethyl sodiomalonates such as diethyl sodiomethylmalonate¹⁹⁸ and diethyl

sodioformylaminomalonate¹⁹⁹ gave both acetylenic and allenic products **181** and **182**. Similar products were obtained with sodioacetoacetate as nucleophile.²⁰⁰ Grignard reagents have also been used as nucleophiles.²⁰¹

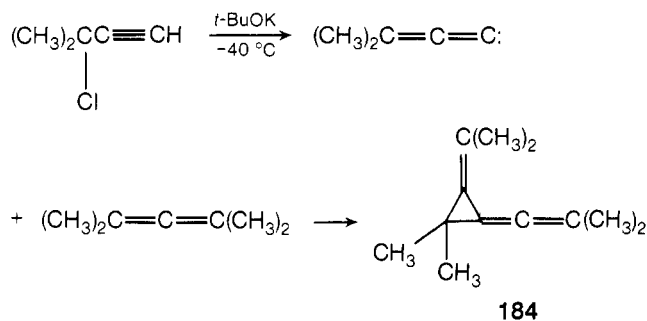


2. With π Bonds

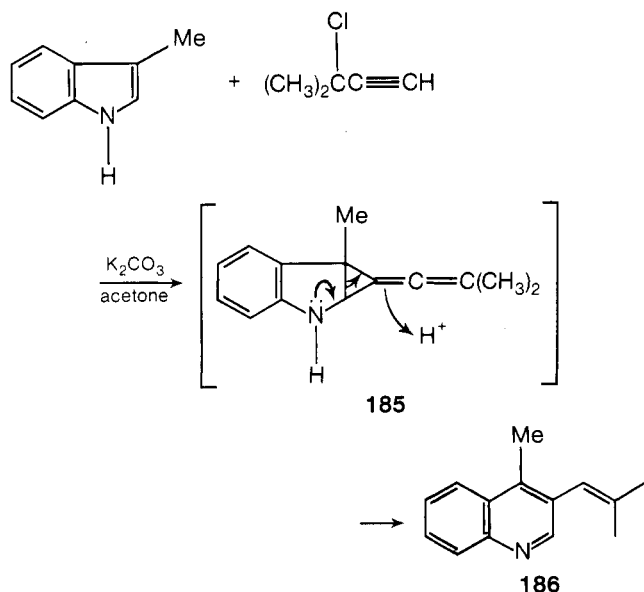
Similar to alkylidene carbenes, the major reaction of vinylidene carbenes with π bonds is addition to olefins, to give alkynylidene cyclopropanes **183**. Alkynylidene cyclopropanes in



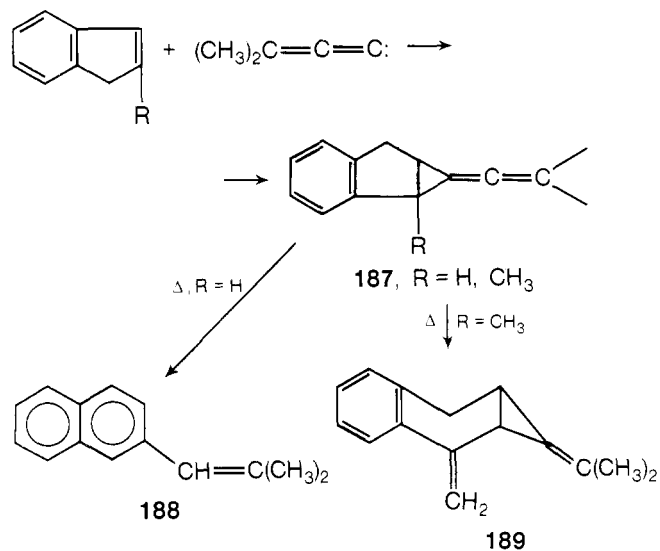
turn have been extensively employed as substrates in cycloaddition reactions²⁰² and in thermolysis.²⁰³ Addition to tetramethylallene gave **184** in 35% yield.¹³¹ Addition to skatole



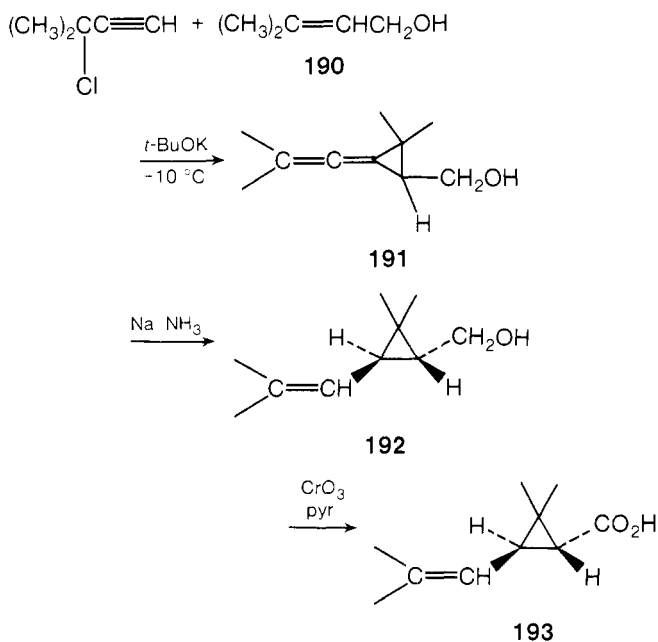
gave **186** via **185**.²⁰⁴ Addition to indene yielded **187** which upon



heating readily underwent rearrangement to **188** whereas the methyldiene addition product resulted in a different rearrangement product, **189**.²⁰⁵ Addition to dihydronaphthalenes



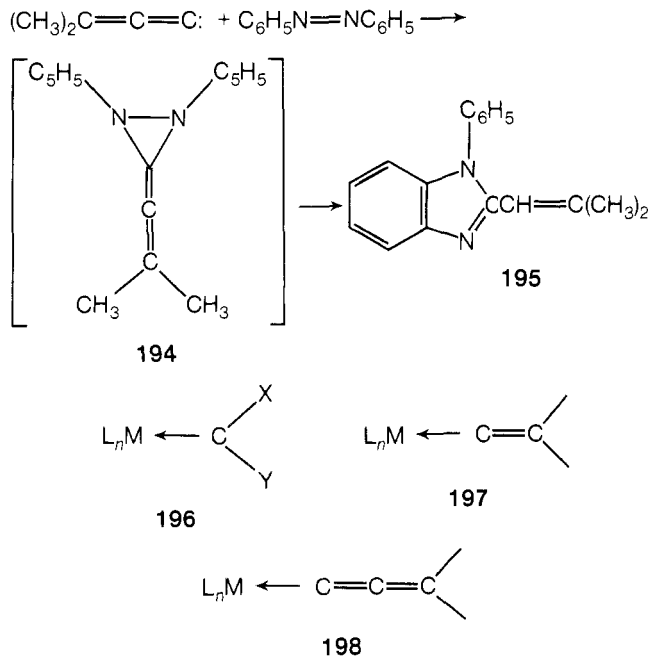
resulted in similar products.²⁰⁵ Vinylidene carbenes have been employed in an elegant synthesis of chrysanthemic acid.²⁰⁶ Addition of dimethylvinylidene carbene to allyl alcohol **190** resulted in a 45% yield of adduct **191**, which upon reduction with Na in liquid ammonia gave a 90% yield of a 3:1 trans:cis chrysanthemyl alcohol **192**, which was readily oxidized to *trans*-chrysanthemic acid **193**.



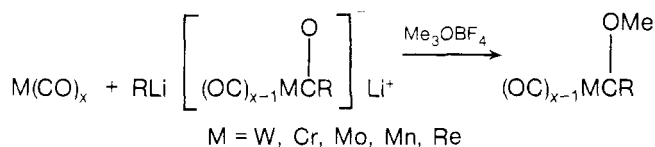
There is only one report on the addition of vinylidene carbenes to heteronuclear bonds. Azobenzene gives benzimidazole **195** via adduct **194**.²⁰⁷

VIII. Transition Metal Complexes of Unsaturated Carbenes

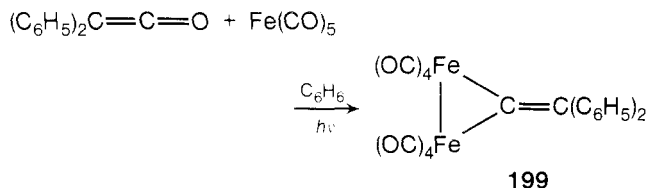
An enormous amount of work has been done on metal-carbene complexes²⁰⁸ of the type **196**. The simplest and most common entry into these complexes is the procedure²⁰⁸ de-



veloped by Fischer and co-workers involving metal carbonyls and alkyllithium:

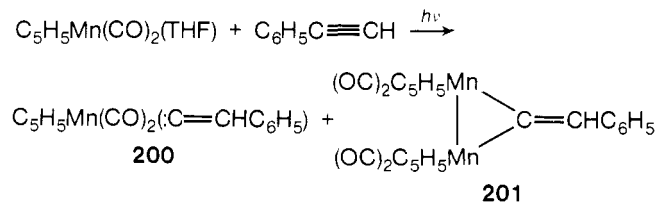


Unfortunately, to date, no such general procedure exists for the preparation of analogous alkylidene **197** or vinylidene **198** complexes, and little is known about these unsaturated carbene complexes. UV irradiation of diphenylketene and $\text{Fe}(\text{CO})_5$ in benzene results in the bridged complex **199**.²⁰⁹ Unambiguous



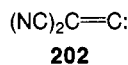
evidence for **199** was obtained by x-ray analysis that indicated a Fe-C (carbene) distance of 1.98 Å, Fe-Fe of 2.64 Å, and a C=C of 1.33 Å with a nearly planar arrangement of the two iron and two double-bonded carbon atoms.²⁰⁹ Complex **199** could also be obtained by treatment of diphenylketene with $\text{Fe}_2(\text{CO})_9$ in the absence of any irradiation, strongly suggesting that it was not formed by direct trapping of the preformed diphenylcarbene.

The manganese complexes **200** and **201** of $\text{C}_6\text{H}_5\text{CH}=\text{C}:$ were obtained in 7 and 2% yields, respectively, by treatment of phenylacetylene with $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{THF})$.²¹⁰ X-ray analysis was employed to unambiguously establish the structures of **200** and **201**. In **200** the Mn-C (carbene) distance was found to be 1.68 Å, which is considerably shorter than the Mn-C alkyl σ bond of 2.16 Å and the Mn-C bond of 1.88 Å in a saturated carbene-Mn complex, indicating double bond character between the carbenic

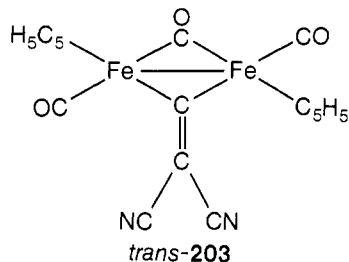
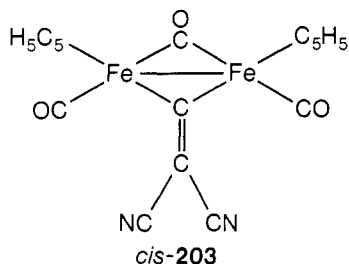


carbon and manganese.²¹⁰ The C=C distance was found to be 1.34 Å. A nearly linear bond angle of 174° was observed around the Mn=C—C moiety. In complex **201**, the Mn—Mn bond was found to be 2.73 Å and the Mn—C (carbene) to be 1.94 Å, respectively, with an Mn—C—Mn angle of 88.0°. At the moment nothing is known about the chemistry of complexes **199–201**.

The only systematic investigation of alkylidene carbene–metal complexes to date has been carried out by King and co-workers²¹¹ on complexes of dicyanovinylidene (**202**). Treatment of 1,1-dichloro-2,2-dicyanoethylene with the highly nucleophilic anion $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ resulted in the bridging cis and trans

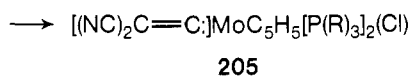
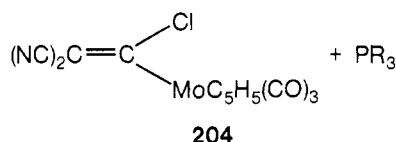


complexes **203**.²¹² Once again x-ray crystallography unambiguously established²¹³ the structure of **203**. The Fe—Fe bond was found to be 2.5 Å and the Fe—C (carbene) 1.87 Å which is

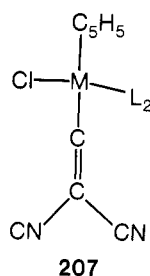
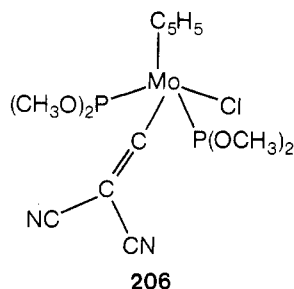


considerably shorter than the Fe—C 1.94 Å for the bridging C=O.²¹³

Subsequently, **202** was also observed as a terminal ligand in complexes of the type **205** obtained by reaction of **204** with various phosphine nucleophiles.²¹⁴ X-ray data on **206** estab-

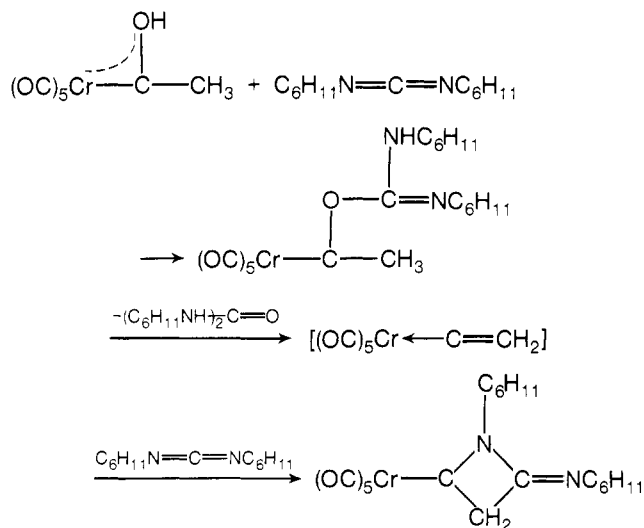


lished²¹⁵ the structure to be a distorted square pyramid around the metal with a Mo—C (carbene) bond of 1.83 Å which is much shorter than the Mo—C of 1.93–2.06 Å for C=O. The shorter M—C (carbene) bond distance in these complexes compared to the analogous M—C(CO) distances along with other spectral data



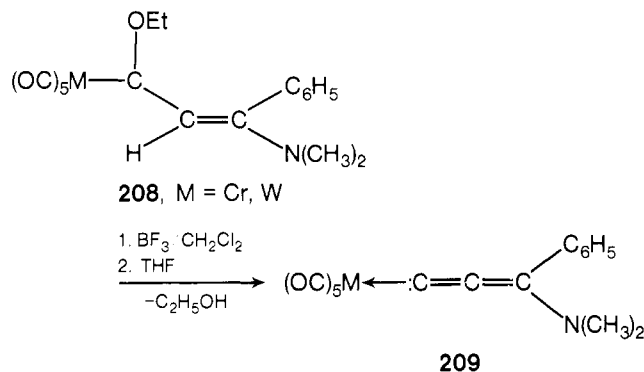
indicate that dicyanovinylidene **202** is a stronger π acceptor than C=O in metal complexes.²¹⁶ A number of related complexes of **202** of the general structure **207** may be prepared by analogous reactions.²¹¹

Finally, although not isolated, the parent carbene ($\text{CH}_2=\text{C}:$) complex has been implicated as an intermediate by Fischer and co-workers:²¹⁷

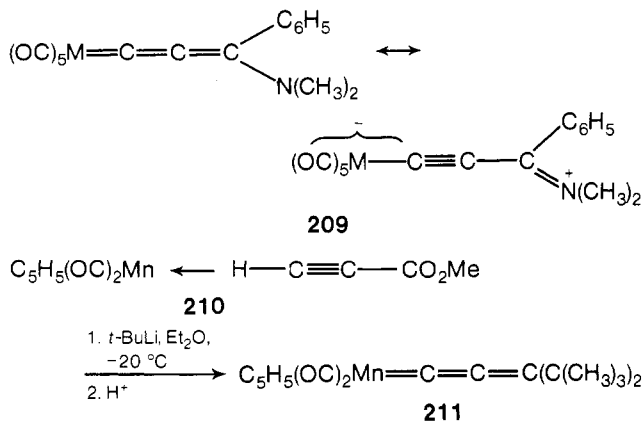


No reports have yet appeared that would indicate that any of the above metal complexes of alkylidene carbenes would serve as progenitor of the carbene itself, or that they might serve as transfer agents of the carbene to olefins or other substrates.

Most recently two reports have appeared on the preparation of vinylidene transition metal complexes. Reaction of carbene complex **208** with a Lewis acid followed by a weak base gave complex **209**.²¹⁸ X-ray analysis established that the heterocu-



mulene moiety in **209** is nearly linear with a M—C (carbene) bond order of between 1 and 2. This, along with the short C₁—C₂ and C₃—N bond lengths and the observation of two distinct CH₃ groups in the proton NMR indicate a considerable contribution



from the mesomeric ionic form in **209**. A similar complex, **211**, was obtained²¹⁹ by treatment of complex **210** with *t*-BuLi. The structure of **211** was assigned by spectral means.²¹⁹ To date no chemistry has been reported with these novel complexes.

IX. Conclusion and Prognosis

There is no doubt that both alkylidene and vinylidene carbenes are viable reactive intermediates. Alkylidene carbenes may be generated by a variety of techniques from diverse progenitors, whereas vinylidene carbenes have been generated by base-initiated eliminations. Both types of unsaturated carbenes are singlets and electrophilic, and their degree of encumbrance varies as a function of media and progenitor. Both types of carbenes readily add to alkenes to give alkylidene and alkenylidene cyclopropanes, respectively. Interaction with a variety of other substrates occurs as well. Transition metal complexes of both alkylidene and vinylidene carbenes have been reported.

Yet, a lot remains to be done. Clearly, better and more general methods of photochemical generation of unsaturated carbenes would be highly desirable. Such a mode of generation might allow matrix isolation and better physical characterization of these novel intermediates.

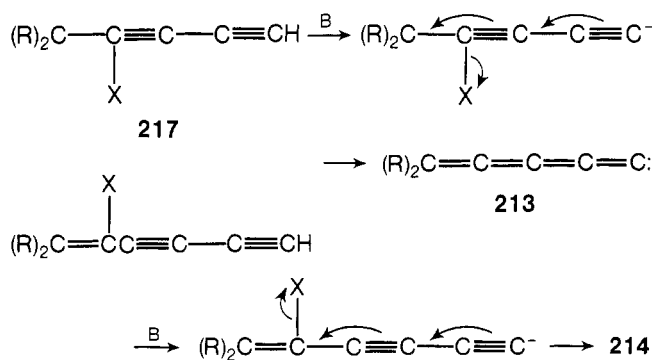
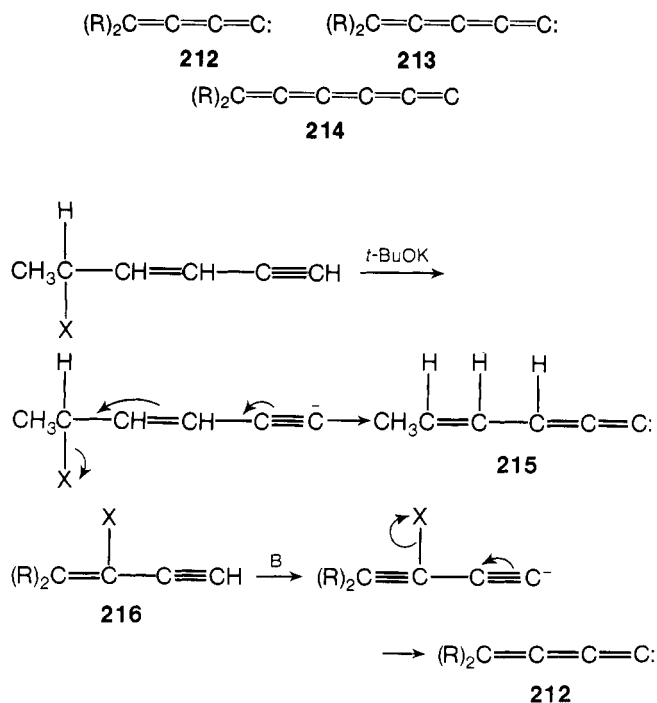
Little is known about heteroatom (O, N, S, Si, halogens, etc.) substituted unsaturated carbenes. These would be of interest not only from a mechanistic point of view and their possible contrasting behavior to their alkyl substituted counterparts, but also from a synthetic point of view. Since they would possess added functionality imparted by the heteroatom, they have the potential for further synthetic manipulation.

There will undoubtedly be more work on the synthetic application and uses of unsaturated carbenes, particularly in the area of small ring and strained compounds.

More work needs to be done in deciphering the nature and mechanism of unsaturated carbene "insertion" reactions, along with elucidating the exact profile of olefin-carbene interactions.

The reported synthesis of the transition metal complexes is but a start. General methods of preparation of unsaturated carbene transition metal complexes need to be developed along with exploring the chemistry of such complexes.

Extended unsaturated carbenes such as **212**, **213**, and **214** might be observed. Such species would be of interest not only



from a mechanistic point of view but also from a synthetic point of view, for they might provide ready entry into some interesting cumulene chemistry. The recent observation²²⁰ of vinylvinylidene (**215**) might serve as a model for the generation of such extended carbenes via **216**, **217**,²²¹ and **218**, respectively.

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X. References and Notes

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