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RECENT DEVELOPMENTS IN ALLENE CHEMISTRY

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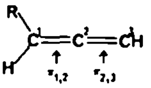
INTRODUCTION

The most recent comprehensive review of the chemistry of allenes appeared in 1966.[1] Shorter reviews of specific aspects of allene chemistry have appeared more recently. During the past five years, however, there has been renewed interest in the study of the reactions of substituted allenes, and their use in the synthesis of complex molecules.

In this short review the author has attempted to provide highlights and some of the more interesting aspects centering around addition reactions, focusing attention on possible intermediates and the factors governing chemoselectivities, stereospecificities and relative reactivities. Due to the brevity of this review the author could not incorporate results from all of the recently reported studies. The author apologizes to those authors whose results for one reason or another have not been incorporated in this review.

In order to facilitate various aspects of the discussion, substituted-allene nomenclature will be used instead of the substituted-1,2-diene convention. The two π systems of a substituted allene will be referred to as $\pi_{1,2}$ and $\pi_{2,3}$ where the substituent is attached to C_1.



Structure and electronic properties of substituted allenes. The central sp-hybridized C atom in the allene chromophore causes only slight changes in the C=C and C–H bond lengths. For example, in allene the C=C and C–H bond lengths are 1.309 and 1.061 A[2] compared to 1.337 and 1.086 Å in ethene.[3] These changes, however, do not result in significant changes in the electronic properties compared to those of ethene. Allene possesses an absorption maximum at 1710 Å[4], while ethene displays a maximum at 1750 Å.[5] The PES ionization potentials of allene and ethene are 10.07 and 10.64 eV (Jahn-Teller splitting),[6] and 10.51 eV,[7] respectively. Finally, the calculated HOMO and LUMO energies (4–31G basis) are very similar; − 10.13 and + 5.01 eV for allene, and − 10.19 and + 5.05 eV for ethene.[8] Thus, the two orthogonal π systems of an allene are virtually identical with the π systems of simple alkenes.

The introduction of an alkyl group onto the allene chromophore results not only in a change in the energy of the π-system to which it is attached, but also affects the energy of the "remote" $\pi_{2,3}$ system. This is illustrated by the PES data given in Table 1.[6] These changes in energy are readily understandable in terms of the mixing of lower-lying π-type group orbitals of the alkyl group with the π MO's. The introduction of a methyl group onto allene lifts the degeneracy of the π MO's of allene, and, on the average, raises the energy of the π MO to which it is attached by ~ 0.40 eV, and that of the $\pi_{2,3}$ system by ~ 0.23 eV. In the former, the elevation in energy arises from mixing of the π-CH_3 group orbital with the π orbital, identical with that observed with substituted alkenes. In the latter case, the $\pi_{2,3}$ orbital mixes with the in-plane, π-type group orbital of the $CH_3CH=$ moiety. The elevation in energy arises from the fact that the $CH_3CH=$ π-type group orbital is higher in energy than the $H_2C=$ π-type orbital, thus the former interacts more strongly with the $\pi_{2,3}$ MO than the latter does with the $\pi_{2,3}$ MO.

The introduction of a heterofunctional group onto the allene chromophore causes more dramatic changes in orbital energies. Table 2 gives the calculated energies (STO-3G) for the occupied (OMO) and unoccupied (UMO) molecular orbitals for a variety of substituted allenes. Electron donating groups (alkyl, –OH, –F) raise the energy of $\pi_{1,2}$ and lower the energies of the $\pi_{1,2^*}$, $\pi_{2,3}$ and $\pi_{2,3^*}$ MO's. Such groups act as remote electron withdrawing groups on the $\pi_{2,3}$ system. Resonance withdrawing groups (–CHO, –CN) lower the energies of all the π-type MO's.

Table 1. PES ionization potential of substituted allenes[a]

Allene	IP_1	IP_2	Δ
Allene	10.07	10.64	0.57[b]
1-Methyl-	9.33	10.06	0.75
1,3-Dimethyl-	9.13	9.65	0.52[b]
1,1-Dimethyl-	8.95	9.86	0.91
1,1-Di-t-butyl-	8.55	9.30	0.75
1,1,3-Trimethyl-	8.69	9.24	0.55
1,1,3,3-Tetramethyl-	8.47	8.96	0.49

[a] From reference 6.

[b] Jahn-Teller splitting.

Table 2. Calculated orbital energies and coefficients for substituted allenes[b]

Orbital Energies (Ev)

Substituent(s)	$\pi_{1,2}$	$\pi^*_{1,2}$	$\pi_{2,3}$	$\pi^*_{2,3}$
(Allene)	-8.80	+8.66	-8.80	+8.66
1-Methyl-	-8.30	+8.79	-8.59	+8.75
1,1-Dimethyl-	-7.95	+8.85	-8.42	+8.81
1,3-Dimethyl-	-6.88	+7.51	-6.88	+7.51
1,1,3-Trimethyl-	-7.79	+8.91	-7.98	+8.92
Tetramethyl-	-7.66	+8.95	-7.66	+8.95
1-Hydroxy-	-7.57	+8.69	-9.01	+8.12
1-Fluoro-	-8.21	+8.55	-9.27	+7.91
1,1-Difluoro-	-7.97	+8.45	-9.67	+7.29
1-Formyl-	-8.49	+7.84	-8.69	+8.21
1-Cyano-	-8.96	+6.32	-9.88	+7.39

[a] From reference 9.

Coefficients

Substituent(s)		$\pi_{1,2}$		$\pi_{2,3}$	
		c_1	c_2	c_2	c_3
(Allene)	OMO	0.655	0.556	0.556	0.655
	UMO	0.770	0.777	0.777	0.770
1-Methyl-	OMO	0.625	0.569	0.545	0.652
	UMO	0.765	0.762	0.767	0.765
1,1-Dimethyl-	OMO	0.606	0.580	0.534	0.647
	UMO	0.754	0.750	0.760	0.762
1,3-Dimethyl-	OMO	0.623	0.559	0.559	0.623
	UMO	0.761	0.752	0.752	0.761
1,1,3-Trimethyl	OMO	0.605	0.571	0.549	0.621
	UMO	0.751	0.740	0.745	0.757
Tetramethyl-	OMO	0.603	0.561	0.561	0.603
	UMO	0.747	0.733	0.733	0.747
1-Hydroxy-	OMO	0.495	0.574	0.565	0.642
	UMO	0.791	0.744	0.727	0.767
1-Fluoro-	OMO	0.549	0.573	0.581	0.639
	UMO	0.782	0.758	0.722	0.773
1,1-Difluoro-	OMO	0.495	0.604	0.600	0.625
	UMO	0.795	0.736	0.680	0.779
1-Formyl-	OMO	0.589	0.523	0.392	0.490
	UMO	0.419	0.626	0.766	0.774
1-Cyano-	OMO	0.554	0.491	0.579	0.636
	UMO	0.562	0.730	0.719	0.755

[a] Calculations were carried out in the author's laboratories at the STO-3G level using the Gaussian 76 and 80 programs. Partial geometry optimization was carried out on most structures.

The orbital interactions described above also have a pronounced effect on the relative magnitudes of the 2p A0 coefficients (Table 2). In allene the largest coefficient is at c_1 (c_3). The effects caused by the introduction of a substituent can be summarized as the following:

Alkylsubstituents

$$\pi_{1,2}\ c_1 > c_2 \text{ in OMO and UMO}$$

$$\pi_{2,3}\ c_3 > c_2 \text{ in OMO and UMO}$$

Resonance donating substituents

$$\pi_{1,2}\ c_2 > c_1 \text{ in OMO, } c_2 < c_1 \text{ in UMO}$$

$$\pi_{2,3}\ c_3 > c_2 \text{ in OMO and UMO}$$

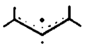
Resonance withdrawing substituents

$$\pi_{1,2}\ c_1 > c_2 \text{ in OMO, } c_2 > c_1 \text{ in UMO}$$

$$\pi_{2,3}\ c_3 > c_2 \text{ in OMO and UMO.}$$

These changes in orbital energies and coefficients play a dominant role in determining the chemoselectivity and reactivity in the reactions of substituted allenes, numerous examples of which will be pointed out later in this article.

A number of reactive intermediates can be formed in reactions with substituted allenes. Substituted allenes undergo anodic oxidation in acetonitrile. [10] The oxidation potentials change little with the degree of substitution, averaging 1.85–2.10 V for mono-, di-, and trialkylallenes. The loss of the first electron produces a radical cation whose structure has not been studied. MO calculations indicate that the radical cation possesses the structure **1**.[9] Substituted allenes also appear to undergo an electron transfer with certain Ni(0) complexes to form a radical anion whose structure is indicated to be **2**.[9] Free radical and cationic intermediates are readily formed in many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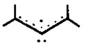
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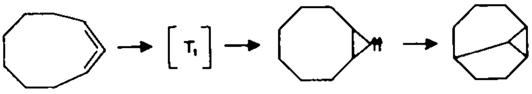
reactions which will be discussed in greater detail later in this article.

Optically active 1,3-dialkyl-substituted allenes undergo thermally-induced racemization with activation energies of 46–47 kcal/mole.[11] Extensive calculations on possible transition state structures for the racemization process have been carried out indicating that the lowest energy singlet allene has a planar, bent structure ($\angle$CCC estimated to be 135.4°) which lies 50.1 kcal/mole above the D_{2d} ground state structure and 5.7 kcal/mole below that of a linear, planar (D_{2h}) structure.[12] The lowest energy triplet also possesses a bent, planar (C_{2v}) structure, and lies 47.7 kcal/mole above the ground state singlet.[12,13] The triplet excited state has been implicated in the photochemical transformation of 1,2-cyclononadiene to tricyclo[3.3.0.0^{2,9}]nonane (**4**) *via* a possible triplet cyclopropylidene (**3**).[13,14]



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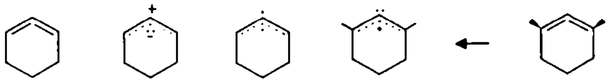
Recent interest has focused on attempts to prepare and study the properties of highly strained, cyclic allenes such as 1,2-cyclohexadiene (**5**).[15] Of particular interest is the electronic structure of such highly strained allenes, which might exist in the diradical or dipolar forms **6**–**8**. The


5 6 7 8 9

base-catalyzed dehydrobromination of 1-bromocyclohexene results in the formation of **5** which is proposed to exist as the asymmetric, bent, nonplanar structure **9**. At ~ 80°, however, **9** is converted to a symmetric structure best represented as **8**.

Methods of preparation of substituted allenes

The high degree of reactivity of the allene function in a wide variety of reactions has led to the use of substituted allenes as intermediates in a number of synthetic pathways leading to highly complex structures. During the past decade numerous new and highly useful methods have been developed for the synthesis of substituted allenes, which has been the subject of three recent reviews. In "Synthesis of Acetylenes, Allenes and Cumulenes" Brandsma and Verkruijsee provide tested procedures for the synthesis of substituted allenes.[16] Hopf has written an extensive review on the methods of preparation of allenes and cumulenes.[17] The synthesis and reactions of α-allenic ketones is covered in a recent Tetrahedron Report.[18] In this review only a general description of selected reactions for the synthesis of substituted allenes will be given.

(1) *Rearrangement of propargyl derivatives.* Certain propargyl derivatives undergo base-catalyzed isomerization to heterosubstituted allenes.[19,20] The yields, and further isomerization to alkynyl derivatives is critically dependent on the solvent and the base used.

$$HC{\equiv}CCH_2{-}X \xrightarrow{base} H_2C{=}C{=}CHX \longrightarrow H_3CC{\equiv}C{-}X$$

$$X = OR,\ SR$$

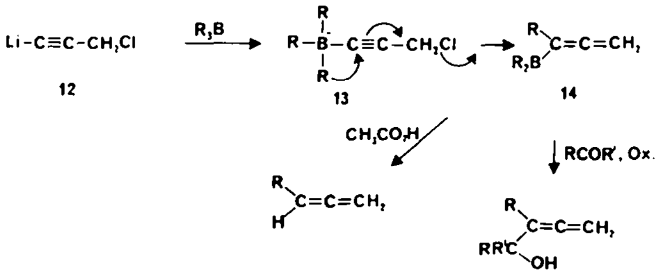
(2) *Via allenyl anions.* The allenyl anion **10** derived by abstraction of an allenyl proton is computed to be 6.6 kcal/mole more stable than the propargyl anion structure **11**.[21] It is possible

$$H_2C{=}C{=}CH_2 \xrightarrow[c\text{-}C_6H_{12},\,THF \quad -60]{R\text{-}Li} \underset{\mathbf{10}}{H\bar{C}{=}C{=}CH_2} \longleftrightarrow \underset{\mathbf{11}}{H{-}C{\equiv}C{-}\ddot{C}H_2} \xleftarrow{R\text{-}Li} H_3CC{\equiv}CH$$

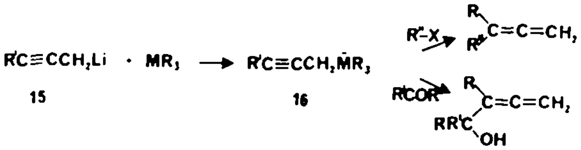
to prepare substituted allenyl anions from either substituted allenes or alkynes, numerous cases of which have been reported.[16] Monoalkylallenes undergo deprotonation predominantly at the terminal methylene, while heterosubstituted allenes react at the substituted carbon. The allenyl anions react smoothly with a variety of electrophilic reagents to give predominantly substituted allenes. With carbonyl compounds, either allene or alkyne may be formed depending on the nature of the carbonyl compound.[22] Slow isomerization of **10**–**11** to an acetylide anion occurs at temperatures above – 60°.

(3) *Reduction of propargyl halides.* Low molecular-weight substituted allenes are efficiently prepared by the reduction of propargyl halides with lithium aluminum hydride (LAH) in refluxing THF.[23] If the allene is not removed as formed, over-reduction occurs to form alkenes.[24]

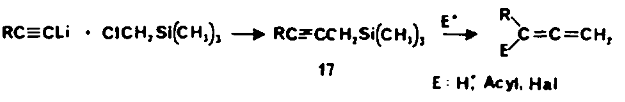
(4) *From lithium acetylides and propargylides.* Lithium chloropropargylide[25a] (**12**) and acetoxypropargylide[25b] react with trialkylboranes at low temperatures to form an intermediate borate **13** which rearranges to the allenylborane **14**. Protonolysis with acetic acid yields the monoalkylborane. Attempts to react **14** with carbonyl compounds to form α-allenic alcohols met with little success. Higher yields of substituted allenes can be obtained from the intermediate allanates or borates **16** derived by reaction of **15** with triisobutylallane or *tri*-sec-butylborane



followed by reaction with an electrophile.[26] In a very similar type of reaction, a wide variety of



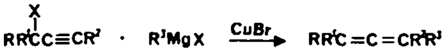
substituted allenes can be prepared from the intermediate silane **17**.[27]



$$RC{\equiv}CLi + ClCH_2Si(CH_3)_3 \longrightarrow \underset{\mathbf{17}}{RC{\equiv}CCH_2Si(CH_3)_3} \xrightarrow{E^+} (R)(E)C{=}C{=}CH_2 \qquad E: H^+, Acyl, Hal$$

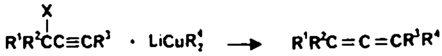
(5) *From Grignard reagents and propargyl derivatives.* Numerous early articles suggested that substituted allenes could be prepared from propargyl halides and Grignard reagents.[28] However,

it has been demonstrated that the formation of substituted allenes occurs via a transition metal (Fe, Co, Ni, Co) catalyzed process.[29] More recently, Grignard reagents have been shown to react with propargyl ethers, sulfonates and epoxides to produce substituted allenes, with cuprous bromide or iodide being the most effective catalysts.[16] In many cases, however, mixtures of allenes and alkyne are formed.



$$RR^1C(X)C{\equiv}CR^2 \cdot R^3MgX \xrightarrow{CuBr} RR^1C{=}C{=}CR^2R^3$$

(6) *From cuprates and propargyl derivatives.* Lithium and magnesium organocuprates react with a variety of propargyl derivatives to produce substituted allenes; including halides,[30,31] acetates,[32]

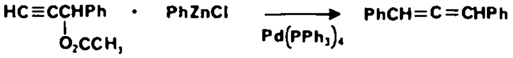


$$R^1R^2C(X)C{\equiv}CR^3 \cdot LiCuR^4_2 \longrightarrow R^1R^2C{=}C{=}CR^3R^4$$

benzoates,[33] carbamates,[34] sulfonates,[34,35] and sulfinates.[36] In general, only the substituted allene is formed.[37] This general procedure has proved to be exceptionally useful for the synthesis of complex structures which have been used as intermediates in the synthesis of retinoids[38a,b] and steroidal compounds related to the vitamin D series.[38c]

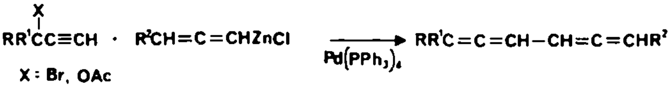
Interestingly, although substituted allenes can be prepared by the reactions of alkyl-, vinyl- and arylcuprates with propargyl derivatives, they cannot be prepared by the reaction of allenylcuprates with alkyl, vinyl or aryl derivatives.[31] The allenyl group when bonded to Cu resembles the alkynyl group in being non-reactive in the transfer reaction. In the reaction of cuprates with propargyl derivatives it appears that a Cu(III) intermediate is formed.[31,35]

In a somewhat similar reaction organozinc compounds have been shown to react with propargylic esters in the presence of a Pd(0) catalyst to form allenes.[39]



$$HC{\equiv}CCH(O_2CCH_3)Ph \cdot PhZnCl \xrightarrow[Pd(PPh_3)_4]{} PhCH{=}C{=}CHPh$$

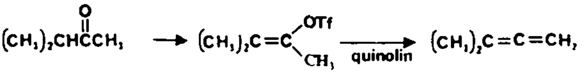
(7) *Allenyl metal compounds with organic halides.* Although allenylcuprates do not react with organic halides to form allenes, allenylzinc[39] (catalyzed by Pd(0) complexes) and silver compounds undergo facile reactions with electrophiles. The reactions of allenylzinc compounds with propargyl derivatives results in the formation of bisallenes, a class of compounds not easily prepared by other methods.



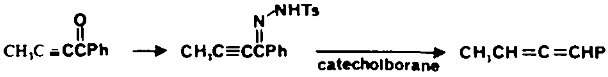
$$RR^1C(X)C{\equiv}CH \cdot R^2CH{=}C{=}CHZnCl \xrightarrow[Pd(PPh_3)_4]{} RR^1C{=}C{=}CH{-}CH{=}C{=}CHR^2$$

$$X = Br,\ OAc$$

(8) *Miscellaneous methods.* Substituted allenes can also be prepared from carbonyl compounds via the enol triflate,[42] tosyl hydrazone,[43] and formaldehyde[44] as illustrated in the following equations.



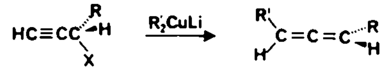
$$(CH_3)_2CHC(O)CH_3 \longrightarrow (CH_3)_2C{=}C(OTf)CH_3 \xrightarrow[quinolin]{} (CH_3)_2C{=}C{=}CH_2$$



$$CH_3C{\equiv}CC(O)Ph \longrightarrow CH_3C{\equiv}CC({=}NNHTs)Ph \xrightarrow[catecholborane]{} CH_3CH{=}C{=}CHPh$$

$$RC{\equiv}CH \cdot H_2C{=}O \xrightarrow[(i\text{-}Pr)_2NH,\ CuBr]{} RCH{=}C{=}CH_2$$

(9) *Synthesis of chiral allenes.* Organocuprates react with chiral propargylic derivatives to form chiral allenes. Stereochemical studies have shown that the displacement occurs in a predominantly *anti* manner;[45-47] i.e.



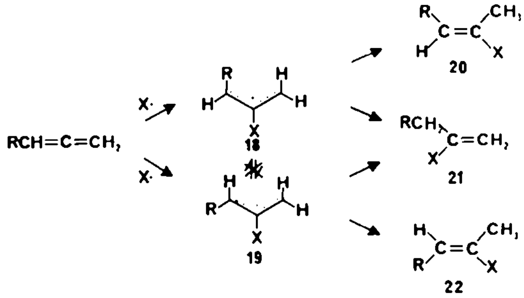
The Pd(0) catalyzed displacement with organozinc compounds also occurs in an *anti* manner.[48] The recent report that propargyl alcohols of high enantiomeric purity can be prepared by the asymmetric reduction of α,β-acetylenic ketones[49] provides for a facile method of synthesis of chiral allenes.

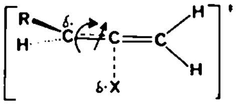
Radical chain addition reactions

Substituted allenes undergo rather facile radical chain addition reactions. Attack by a radical species can occur either at the central or a terminal C atom. Interestingly, C-based free radicals (e.g. $\cdot CH_3$, $\cdot CF_3$, and $\cdot CCl_3$)[50] add almost exclusively to a terminal C atom, while heteroatom-based free radicals (e.g. $Br\cdot$[51], $RS\cdot$[52], $ArSO_2\cdot$[50] and $R_3Sn\cdot$[53]) add preferentially to the central C atom. In the latter case, the degree of selectively depends on the extent of substitution on the allene chromophore; for example, mono- and trialkylallenes undergo ~ 10–15% attack at the least substituted terminal C atom, while 1,1-dialkylallenes undergo reaction only at the central C atom. The reason(s) for this selectivity is(are) not obvious.[50] Attempts by this author to correlate this selectivity with the MO properties of the allenes and free radicals using the FMO approach thus far has not been successful.

Attack at the central C atom results in the formation of a planar resonance stabilized allyl radical intermediate. Although it has been suggested that the intermediate "may be initially nonallylic",[54] recent kinetic isotope effect (KIE) measurements indicate that rotation (and probably translation or bending) of the incipient radical center is occurring in the transition state,[52b] resulting in the direct formation of the planar allyl radical intermediate. In addition, the KIE results indicate that in unsymmetrically substituted allenes the attacking radical adds to the 2p AO of the more highly substituted π bond.[52b] In most reactions the attack at the central C atom is irreversible.

The addition to the central C atom of a monosubstituted allene results in the formation of the two stereoisomeric radicals **18** and **19**. Results of a stereochemical study of the cycloaddition of substituted allenes with 1,1-dichloro-2,2-difluoroethene[55] (1122), which proceeds via a diradical intermediate containing an allyl radical center as in **18** and **19** (see later discussion), indicate that **18** is preferentially formed despite the fact that **18** is less thermodynamically stable than **19**. In the transition state for the formation of **18**, the R group rotates *away* from the approaching reagent (X·), while in the formation of **19** the R group rotates *toward* the approaching reagent as illustrated in **23** and **24**. When R is t-Bu, only **18** is formed. As the interconversion of **18** and **19** possesses a higher energy barrier than those of the final abstraction steps, the stereochemistry of **18** and **19** is maintained in the final product, and **20** will be the dominant product. As an example, the radical-chain addition of trimethyltin hydride to 1,2-butadiene produces **25** and **26** ($R{=}CH_3$, $X{=}R_3Sn$) in a 38.6:16.3 ratio.[53] However, the radical-chain addition of hydrogen bromide produces **25** and **26** ($R{=}CH_3$, $X{=}Br$) in a 10.5:83 ratio,[51] and the addition of benzenethiol to 1,2-pentadiene

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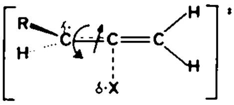
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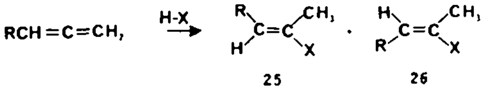
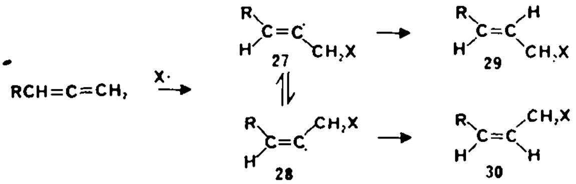
produces **25** and **26** (R-C_2H_5, X=C_6H_5S) in a 32:49 ratio.[52a] In the latter case it has been shown



that **25** and **26** (X=C_6H_5S) undergo benzenethiyl induced equilibration under the reaction conditions, and thus the final product ratio does not reflect the original ratio of **18** and **19** formed in the reaction. In the case of the addition of hydrogen bromide, Br atom catalyzed equilibration[56] must also have occurred.

Attack at a terminal C atom appears to be reversible, and produces a pair of rapidly inverting, non-linear, vinyl radical intermediates **27** and **28**.[57] H-atom abstraction appears to occur to form the more stable product **29**.[53]



The relative reactivities of substituted allenes toward benzenethiyl have been measured (Table 3).[52] The reactivity of the monosubstituted allenes decreases as the size of the R group increases. This decrease in rate arises primarily from a decrease in the rate of formation of **19** due to increasing

Table 3. Total and partial relative reactivities for phenylthiyl radical addition to substituted allenes[526]

Substituents	k_{rel}(total)	k_{rel}(C_2)	k_{rel}(C_3)
Ethyl	1.00	0.83	0.17
Butyl	0.95	0.79	0.16
Isobutyl	0.95	0.79	0.16
Isopropyl	0.69	0.58	0.11
tert-Butyl	0.54	0.34	0.20
1,1-Dimethyl	12.5 (1.00)[a]	12.5	b
1-Ethyl-1-methyl	11.6 (0.93)	11.6	b
1-*tert*-butyl-1-methyl	6.4 (0.51)	6.4	b
3-Ethyl-1,1-dimethyl	19.8	16.3	3.5
1,1,3,3-Tetramethyl	9.5	9.5	b

[a] Numbers in parentheses are relative rates within the 1,1-dialkylallene series. [b] No C_3 attack product detected by NMR.

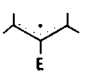
steric effects. The rate of formation of **18** does not appear to be affected by the size of the R group. 1,1-Dialkylallenes react slightly more than ten times faster than the monoalkylallenes. The introduction of a third alkyl group causes only a slight increase in reactivity, while the introduction of a fourth alkyl group results in a reduction in reactivity which is probably due to increased steric congestion in the transition state. Much smaller differences in relative reactivities have been reported for the hydrogen bromide addition to methyl-substituted allenes.[51] The increase in reactivity with increasing substitution has been attributed to increased hyperconjugative stabilization in the allyl radical intermediate.[51] More recently, however, the changes in reactivity and position selectivity have been interpreted in terms of FMO theory.[52b] The introduction of an alkyl group raises the energy of the $\pi_{1,2}$ HOMO (Table 2) which reduces the energy difference between the π HOMO and the SOMO of the benzenethiyl. The increase in the position selectivity with 1,1-dialkylallenes arises from the greater difference in the magnitude of the c_i's at the terminal and central C atoms.

In the product forming steps, the allyl radical can undergo reaction at either end. It appears that steric effects play a dominant role, with abstraction occurring at the least substituted end to form predominantly **20** and **22**.[52]

Electrophilic addition reactions

Many electrophilic addition reactions with substituted allenes have been investigated. Several reviews have appeared in the past few years,[58] and no attempt will be made to cover this area in detail in this review. A few features of these reactions will be discussed, however, as they relate to free radical and cycloaddition reactions, such as the structures of intermediates and stereochemical aspects.

The addition of an electrophile to an allene to generate an open cationic intermediate can occur at either the central or a terminal C atom. Attack at the central C atom ultimately results in the formation of a planar allyl cation (**31**). However, bent-orthogonal allyl cations (**32**) have been implicated as transitory intermediates.[59] Theoretical calculations indicate that **32** (R=R^1 = E=H) lies



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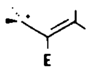

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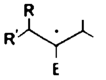

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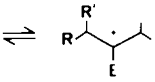

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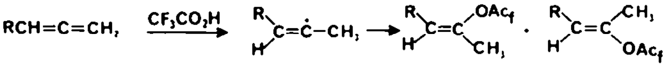
34.8 kcal/mole (6–31G* basis set) above **31**,[60] and corresponds to the barrier to nonconcerted rotation of one CH_2 in **31** (R=R^1=E=H); i.e. the transition state for the stereoisomerization **33**$\rightleftarrows$**35** (R=R^1=H). (NMR studies indicate that the barriers to rotation in methyl-substituted allyl cations are > 18 kcal/mole).[61] Thus, it seems very doubtful that bent-orthogonal allyl cations such as **32** are discrete intermediates. In all probability bending *and* rotation have occurred to some extent in the transition state, similar to that observed in radical addition and cycloaddition reactions (see later discussion). Similar steric effects should govern the direction of rotation in unsymmetrically substituted systems resulting in the preferential formation of **33** when R is larger than R′. There appears to be no information available concerning the stereochemical aspects of these reactions.

Electrophilic attack at a terminal C atom is reversible[62a] and results in the formation of a non-resonance stabilized vinyl cation **35**. Subsequent reaction with a nucleophile results in the predominant formation of the *Z*-isomer **36**.[63]



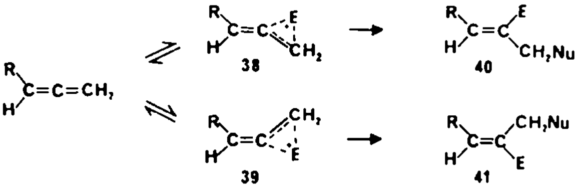
$$RCH{=}C{=}CH_2 \xrightarrow{CF_3CO_2H} (R)(H)C{=}\dot{C}{-}CH_3 \longrightarrow (R)(H)C{=}C(OAc_f)(CH_3) \cdot (R)(H)C{=}C(CH_3)(OAc_f)$$

35 36 37

Allene and monoalkylallenes undergo electrophilic attack at the least substituted terminal C atom, while 1,1-dialkylallenes undergo attack at the central C atom. In the gas phase allene undergoes predominant protonation (78%) at a terminal C atom with mild protonating agents; however, when higher-energy protonating agents are used attack at the central C dominates (65%).[62b] This at first seems somewhat surprising in that the allyl cation is calculated to be

17 kcal/mole lower in energy than the Z-propenyl cation,[60] while experimental heats of formation give a value of 11 kcal/mole.[62] Apparently the transition state for electrophilic attack occurs very early along the reaction coordinate in which little bending or rotation has occurred in the transition state for electrophilic attack at the central C which is necessary to gain the stabilization of the planar allyl cation. With 1,1-dialkylallenes the alkyl groups must provide sufficient stabilization of the incipient cationic center to lower the energy of the transition state for attack at the central C atom below that for attack at a terminal C atom.

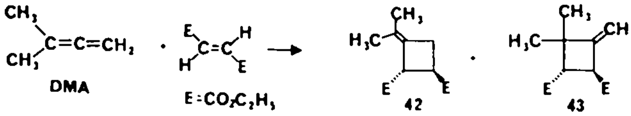
The reactions of substituted allenes with large polarizable electrophiles (halogens, mercuric salts, benzenesulfenyl and -selenenyl halides, etc.) proceed *via* the reversible formation of cyclic onium ion intermediates (**38** and **39**).[64] Nucleophilic attack occurs only at the non-vinyl C atom to produce **40** and **41**. Nucleophilic attack on **38** is less sterically hindered and results in the predominant formation of **40**.



Cycloaddition reactions

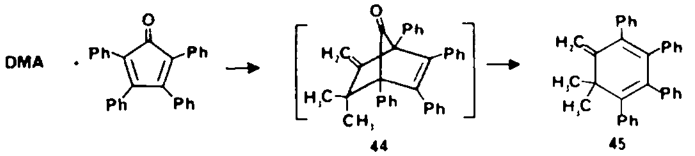
Substituted allenes undergo a variety of cycloaddition reactions including carbene additions, (2 + 2) cycloadditions with alkenes, allenes (cyclodimerization) and ketenes, (4 + 2) cycloadditions with dienes, and dipolar (2 + 2) cycloadditions. Of these, the (2 + 2) cycloaddition reaction has attracted much interest, directed particularly toward determination of the mechanism(s) of these reactions. Recent results from the author's laboratories have provided much useful information concerning not only the details of the (2 + 2) processes, but also for the other types of reactions mentioned above.

Early studies showed that both the (2 + 2) cycloaddition and -dimerization reactions proceed with a very high degree of stereospecificity. For example, the reaction of 1,1-dimethylallene (DMA) with diethyl fumarate (DEF) was reported to occur with at least 99% stereospecificity to form **42** and **43** (with the former predominating)[65] while optically active 1,2-cyclononadiene undergoes cyclodimerization with an estimated 100% stereospecificity.[66] These results were originally interpreted in terms of a stereospecific, concerted (${}_\pi2_s + {}_\pi2_a$) processes, although later studies on the generation and reactions of 2,2′-bis(1,1-dimethylallyl) diradical led to the conclusion that the DMA cyclodimerization process was not concerted.[67] The cycloaddition of optically 2,3-pentadiene with acrylonitrile is reported to produce a mixture of four cycloadducts, all of which were optically active.[68] A two-step, diradical intermediate process was proposed involving certain restrictions on the mode of formation and reactions of the intermediates. A comparison of isotope effects determined in allene (4 + 2) and (2 + 2) cycloaddition reactions resulted in the suggestion that allene (2 + 2) cycloadditions do not proceed via concerted reaction pathways.[69]

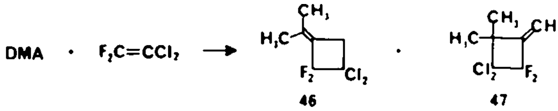


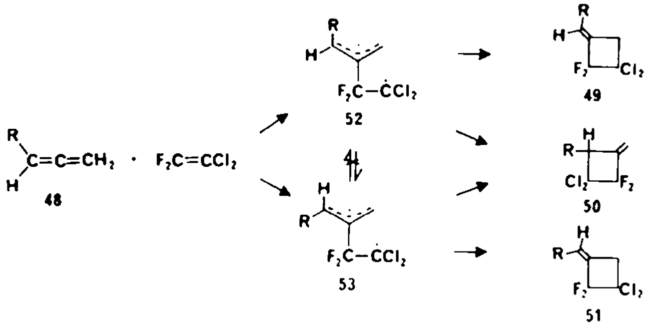
Mechanistic studies in the author's laboratories on the cycloaddition reactions of substituted alkenylidenecyclopropanes[70] suggested that both π-systems of an allene could be involved in bonding in the cycloaddition transition states via a [${}_\pi2_s + ({}_\pi2_s + {}_\pi2_a$] process. The results of a theoretical study suggested that this process should be more favorable than the (${}_\pi2_s + {}_\pi2_a$) process.[71] Furthermore, different chemoselectivities were predicted. For example, DMA is predicted to undergo cycloaddition across the $\pi_{1,2}$ bond in (${}_\pi2_s + {}_\pi2_a$) and (${}_\pi2_s + {}_\pi4_s$) processes, while in the [${}_\pi2_s$ + (${}_\pi2_s$ + ${}_\pi2_s$)] process cycloaddition should occur across the $\pi_{2,3}$ bond. The latter prediction was consistent with the results observed in the reaction of DMA with DEF. Finally, the $[{}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_{\pi}2_s)]$ model predicted a dominant Z-stereochemistry about the exocyclic double bond in cycloaddition reactions with unsymmetrical 1,1-disubstituted allenes, and in allene cyclodimerization reactions. Experimental information was not available on the former, while the available data on the latter were consistent with the predictions for the $[{}_{\pi}2_s + ({}_{p}2_s + {}_{\pi}2_s)]$ process.

The prediction of the chemoselectivity for $({}_{\pi}2_s + {}_{\pi}2_a)$ and $({}_{\pi}2_s + {}_{\pi}4_s)$ allene-HOMO, alkene- or diene-LUMO controlled cycloadditions were tested using the cycloaddition reaction of tetraphenylcyclopentadienone (TPCP) with DMA. The cycloaddition occurs *only* across the $\pi_{1,2}$ bond to produce the thermally labile adduct **44** which undergoes decarbonylation to give **45**.[72]



(1) (2 + 2) *Cycloaddition reactions*. In order to determine the chemoselectivity, stereospecificity and relative reactivities in a two-step, diradical-intermediate process the cycloaddition reaction of 1,1-dichloro-2,2-difluoroethene (**1122**) with substituted allenes was investigated; **1122** cycloaddition reactions with alkenes and dienes being known to occur via diradical intermediates.[73] DMA reacts with **1122** to produce a mixture of the adducts **46** and **47**, with **46** being the major product. The reaction of **1122** with monoalkylallenes produces a mixture of **49–51** in which **49** is formed in greater





amounts than **50**, and the sum of **49** and **50** is greater than the amount of **51** formed (Table 4). It should be noted that with *t*-butylallene cycloadduct **50** is not formed, indicating that only one diradical intermediate (**52**) is formed in that reaction. The dominant stereospecificity observed in the formation of **49** and **51** is opposite that predicted for the concerted $[{}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$ process.

The relative reactivities of DMA and monoalkylallenes with **1122** are also given in Table 4. For comparison purposes the relative reactivities for attack by benzenethiyl radical are also included. It should be noted that the relative reactivities are all very similar. The stereospecificities, chemoselectivities, and relative reactivities observed in the cycloaddition reactions with **1122** are considered to be diagnostic for a two-step, diradical-intermediate cycloaddition reaction with substituted allenes.

The above criteria have been applied to the results derived from the cycloaddition reactions of substituted allenes with N-phenylmaleimide (NPMI).[74] In this case, however, the reaction is more complicated. In addition to the four expected cycloadducts, **54–57**, ene products were also formed which underwent further cycloaddition to form **58**, and with monoalkylallenes some attach was observed to occur at the least substituted, terminal C atom. (Attack at the least substituted, terminal C atom was also observed in the radical-chain addition of benzenethiol to monoalkylallenes).[52] The relative yields and reactivities are given in Table 5. The chemoselectivities,

Table 4. Relative yields and reactivities in the cycloaddition of 1122 with monoalkylallenes

R	Relative Yields 49	50	51	Relative Reactivities 1122	$C_6H_5S\cdot$
C_2H_5-	50.5	23.7	15.4	1.00	1.00
$(CH_3)_2CHCH_2$-	48.2	27.1	24.7	0.97	0.95
$(CH_3)_2CH$-	55.0	20.0	25.0	0.72	0.69
$(CH_3)_3C$-	55.0	-	35.3	0.53	0.54
DMA	85.9		14.1	11.6	12.5

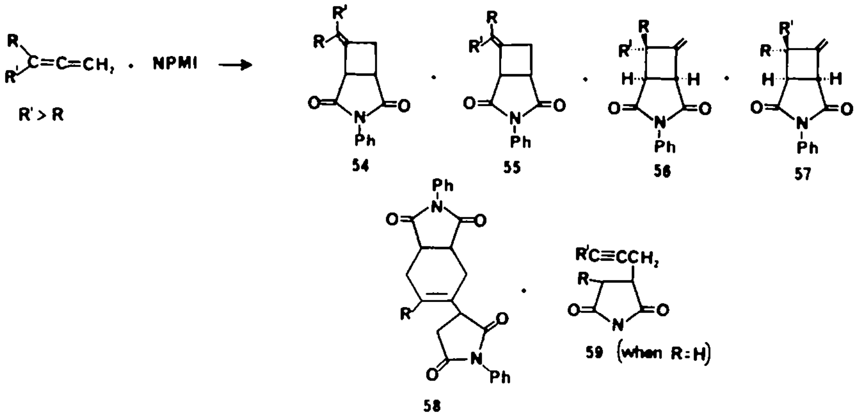


Table 5. Relative yields and reactivities in the cycloaddition of substituted allenes with N-phenylmoleimide

R	R'	Relative Yields 54	55	56	57	58	59	Relative Reactivities
C_2H_5-	H	33.3	20.8	8.7	9.1	23.9[a]	4.0	1.0
$(CH_3)_2CHCH_2$-	H	26.7	16.6	6.1	17.9	26.0[a]	6.8	0.86
$(CH_3)_2CH$-	H	24.7	15.3	8.0	20.7	4.7	26.6	0.64
$(CH_3)_3C$-	H	45.6	-	8.3	16.8	-	29.3	0.72
CH_3-	CH_3-	57.2		9.1		33.7	-	2.8

[a] Mixture of two diastereoisomers.

stereospecificities, and relative reactivities strongly imply that **54–57** are formed via two-step, diradical-intermediate processes. The formation of **58** and **59** is also believed to occur via diradical intermediates (see original paper for details).[74]

In the cycloaddition reactions with **1122** and NPMI information concerning the possible reversible formation of the diradical intermediates and the occurrence of internal rotation prior to ring closure was not available. Such information became available from the results of studies on the cycloaddition reactions with diethyl fumarate (DEF) and maleate (DEM).[75] The reaction of DEF with DMA produces adducts **60–62**, *all containing the* trans-*diester stereochemistry*. (Adduct **62** is derived from isoprene formed by a [1.3]sigmatropic rearrangement of DMA). The characteristics of the cycloaddition reactions of DEF with monoalkylallenes are consistent with a two-step, diradical-intermediate process.[75] In the reaction of DEM with DMA, however, in addition to the *cis*-diester adducts **63–65**, the *trans*-diester adducts **60–62** are also formed. Most interestingly, the ratios of **60**:**61** derived from DEF and DEM are different, but become similar at higher temperatures (Table 6), indicating different pathways for the formation of **60** and **61** in the reactions with DEF and DEM. In addition, isomerization of DEM to DEF occurs, which does not happen in the absence of DMA. These results can be accommodated only if internal rotation and cleavage occurs competitively with ring closure in the intermediates (**68** and **69**) derived from DEM. In the intermediates derived from DEF (**66** and **67**) internal rotation does not occur, and cleavage cannot be detected. In **68** and **69** the ester functions are initially eclipsed and may rotationally relax to a synclinal conformation. In **66** and **67** the ester functions are initially antiperiplanar, and probably remain so. The steric repulsion between the ester functions in **68** and **69** raise the energies of the intermediates, in effect lowering the barriers to rotation and cleavage

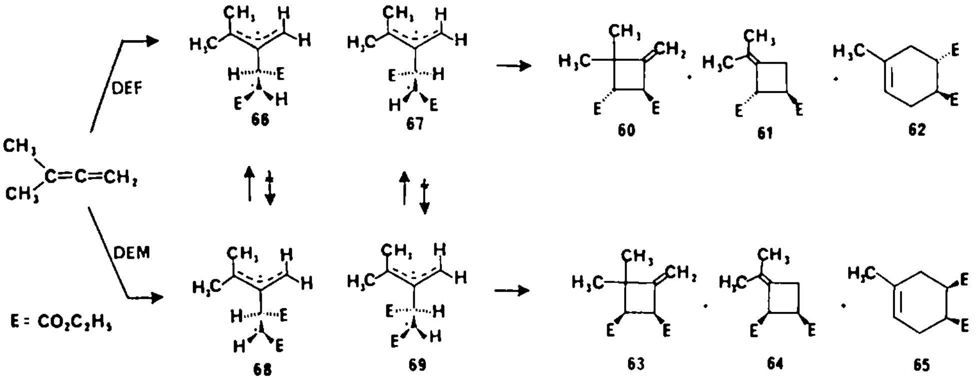


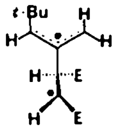
Table 6. Ratios of 60:61 as a function of dienophile and reaction temperature[a]

Temperature (°C)	DEF		DEM	
	60	**61**	**60**	**61**
160	86.2	11.5	52.0	48.0
180	86.8	13.2	75.7	24.3
200	88.1	11.9	86.4	13.6

[a] In toluene solution.

but *not* ring closure, and both rotation and cleavage become competitive with ring closure. In **66** and **67** the barriers for ring closure must be at least 2.0–2.5 kcal per mole lower than those for rotation resulting in the preservation of the original stereochemistry present in the dienophile.

In the reaction of *t*-butylallene with DEF *and* DEM *only* trans-diester products are formed, and extensive isomerization of DEM to DEF occurs. Only diradical intermediates **70** and **71** are formed in the reaction *t*-butylallene with DEM. The strain energy in the allyl radical portion of **71** further elevates the total energy of the intermediate thus leading to more extensive internal rotation and cleavage.



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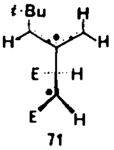

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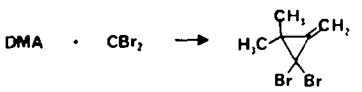
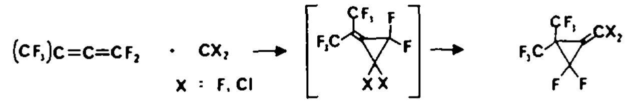
These data suggest that the relative rates of ring closure, internal rotation, and cleavage are a sensitive function of the relative energies of the diradical intermediates. Raising the energy of the intermediate by introducing strain into either the allyl or aliphatic radical portions results in more extensive internal rotation *and* cleavage relative to ring closure. On the other hand, stabilization of either radical center should result in increased reactivity, and should reduce the relative rates of cleavage and ring closure and allow for more extensive rotational equilibration. Preliminary evidence indicates that this is the case. The cycloaddition of methoxyallene proceeds at ~ 100 times the rate of that of DEF with DMA, and produces *only* trans-diester cycloadducts.[76] In contrast, methoxyallene reacts with DEM to produce *mostly* (~ 75%) trans-diester cycloadducts, with *no* isomerization of DEM to DEF being detectable. Continued studies in this area should provide a wealth of information on the factors affecting the relative rates of ring closure, internal rotation and cleavage in such diradical intermediates which has not been previously available.

In the following portions of this section other cycloaddition reactions of allenes will be reviewed, including comparisons of chemoselectivities and stereospecificities in order to clarify the possible mechanisms of the reactions.

(2) *Carbene additions*. Dibromocarbene, generated from bromoform and *t*-butoxide, readily adds to substituted allenes to produce methylenedibromocyclopropanes.[77] With DMA, the addition occurs across the $\pi_{1,2}$ bond. This chemoselectivity is that expected for a concerted (${}_\pi 2_s + {}_\omega 0_s$) process.



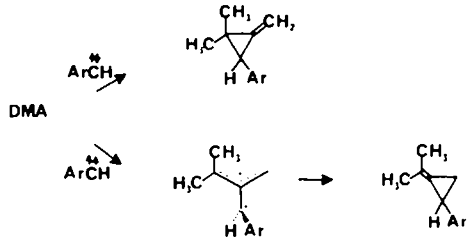
The addition of difluoro- and dichlorocarbene to perfluoro-1,1-dimethylallene in the gas phase results in the formation of the rearranged cyclopropane derivative **73**.[78] Addition to the more



72 **73**

reactive C=CF$_2$ double bond (see the relative MO energies in Table 2) is believed to initially occur to form **72** which then undergoes rearrangement to **73** under the reaction conditions.

A number of phenyl-substituted carbenes have been added to DMA.[79] All singlet carbenes add across the $\pi_{1,2}$ bond, while triplet carbenes add predominantly across the $\pi_{2,3}$ bond. The addition of triplet carbene to DMA results in the formation of the trimethylenemethane diradical **74**. The selectivity in the ring closure of **74** is the same as that observed in the ring closure of the



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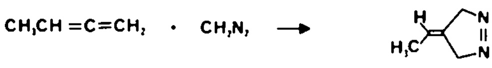
intermediates formed in the cycloaddition of DMA with **1122**. The difference in chemoselectivity between singlet and triplet carbene additions is a very useful probe for the multiplicity of a carbene.[79]

(3) [4 + 2(*Allene*)] *cycloaddition reactions*. Based on FMO theory [4 + 2(allene)] cycloaddition reactions should occur across both the $\pi_{1,2}$ and $\pi_{2,3}$ bonds depending on the electronic properties of any substituent attached to the allene chromophore. In an allene containing an electron donating group the $\pi_{1,2}$ HOMO [HOMO(1,2)] is higher in energy than the OMO(2,3) (Table 2). Thus, any cycloaddition with an electron poor diene will be expected to occur across the $\pi_{1,2}$ bond. Cycloaddition with a sufficiently electron rich diene is expected to occur across the $\pi_{2,3}$ bond. When an allene contains an electron withdrawing group, however, the energies of the UMO(1,2) and OMO(1,2) lie *below* the UMO(2,3) and OMO(2,3), and cycloaddition with an electron-rich diene is expected to occur across the $\pi_{1,2}$ bond. Examples of all three types of cycloaddition reactions are known.

In an electron-rich allene—electron-poor diene cycloaddition reaction, tetraphenylcyclopentadienone (TPCP) adds exclusively across the $\pi_{1,2}$ bond of DMA, to produce **45**, and adds preferentially across the $\pi_{1,2}$ bond of monoalkylallenes.[72] The relative reactivities of DMA and monoalkylallenes do not follow the same trend as observed in the radical-chain addition of benzenethiyl and cycloaddition with **1122**.[80] Steric factors play a dominant role in determining the relative reactivities.[80]

An example of the cycloaddition of an electron-rich allene with a sufficiently electron rich (high-lying HOMO) four π-electron component is exemplified by the cycloaddition reaction of substituted allenes with diazoalkanes. Diazomethane adds exclusively across the $\pi_{2,3}$ bond of methyl- and 1,1-dimethylallene to produce the 4-alkylidenepyrazolines **75** and **76** respectively.[81] In a very interesting stereochemical experiment, the reaction of diazomethane-d$_2$ with methylallene produced only **77**, while the cycloaddition of 3,3-dideuteriomethylallene with diazomethane produced only **78**; both reactions are *totally* stereo- and regiospecific.[81] These results are consistent



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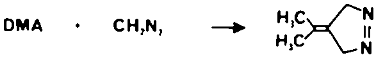

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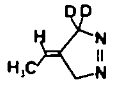

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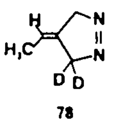

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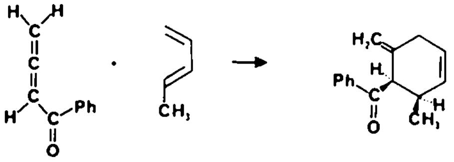
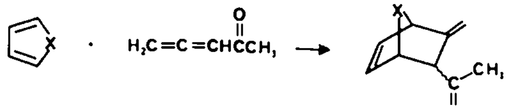
only with a concerted cycloaddition process in which the diazomethane approaches the $\pi_{2,3}$ bond from the least hindered direction. The total stereospecificity observed would not be expected from a two-step, nonconcerted process. The chemoselectivity for cycloaddition across the $\pi_{2,3}$ bond is consistent with the dominant interaction being between an allene LUMO and the diazomethane HOMO. The regioselectivity is also that expected, C$_3$ of the allene and the terminal nitrogen of diazomethane having the largest coefficients in their respective FMO's.[82]

Examples of the cycloaddition of electron-poor allenes with four π-electron components is exemplified by the reactions with dienes and diazoalkanes. Allenic ketones undergo highly regio- and stereoselective cycloaddition reactions with alkyl-substituted 1,3-butadienes as illustrated in the following reaction.[83] Again, the chemo- and regioselectivity are consistent with predictions from

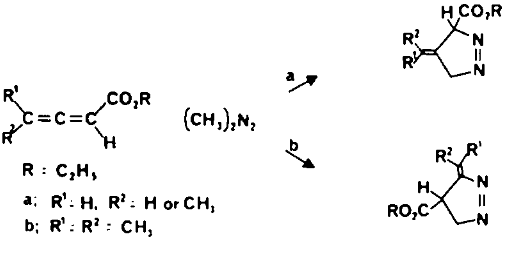


FMO theory. Allenyl methyl ketone undergoes cycloaddition with cyclopentadiene and furan to produce a mixture of *endo* and *exo* isomers.[84]

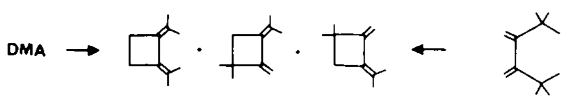


	endo	exo
X : CH₂	65	35
X : O	90	10

Allenic esters undero cycloaddition reactions across the $\pi_{1,2}$ bond with diazoalkanes.[85] Interestingly, however, although the chemoselectivities are very high, the regioselectivities depend on the degree of substitution at C_3.



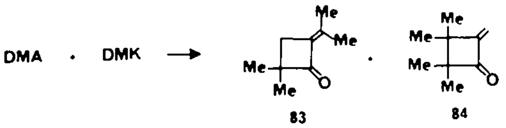
(4) *Cyclodimerization of allenes*. A number of substituted allenes undergo cyclodimerization to form 1,2-bisalkylidenecyclobutanes. For example, DMA undergoes cyclodimerization at 151° to form a mixture of the dimers **79–81** in a ratio of 48:35:17.[67] Thermolysis of the cyclic azo compound **82** also produces **79–81** in ratio identical with that from the cyclodimerization of



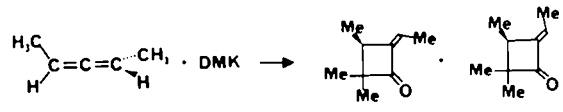
79 **80** **81** **82**

DMA.[67] These results strongly implicate the 2,2-bis(1,1-dimethylallyl) diradical as an intermediate in the cycloadimerization process. The results derived from the cyclodimerization of other substituted allenes are also consistent with a two-step, diradical-intermediate process.

(5) *Cycloadditions of allenes with ketenes*. Substituted allenes undergo cycloaddition with dimethylketene (DMK) to produce 2-alkylidenecyclobutanones as is exemplified by the reaction of DMA with DMK which produces **83** and **84** in a ratio of 71:29.[86] Optically active 1,3-dimethylallene produces **85** and **86** (75:29 ratio) which are optically active and possess the configurations shown.[87] Several possible mechanisms were briefly discussed, but no firm conclusions



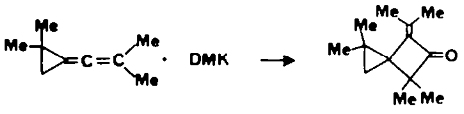
83 **84**



85 86

could be drawn. The chemoselectivity observed in the reaction of DMA with DMK strongly implicates a two-step, diradical-intermediate mechanism.

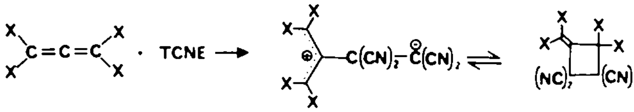
Allene **87** reacts with DMK to produce **88**.[86] This chemoselectivity is the same as that observed in diradical-intermediate cycloaddition reactions of such compounds.[88] Although dipolar intermediates are possible in ketene cycloaddition reactions, the reactions of compounds such as **87** with



87 88

typical dipolar-intermediate forming reagents (e.g. chlorosulfonylisocyanate) result in opening of the 3-membered ring[89] (see later discussion), which suggests that the reaction of **87** with DMK does not proceed via a dipolar intermediate.

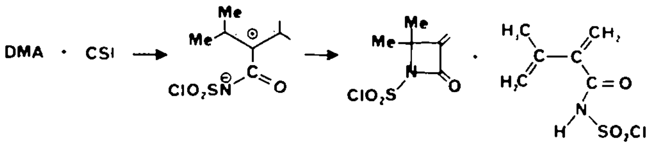
(6) *Dipolar-intermediate cycloaddition reactions.* The very electron rich tetramethoxyallene (**89a**) reacts with tetracyanoethylene (TCNE) to produce an equilibrium mixture of the dipolar intermediate **90a** and the cycloadduct **91a**.[90] Tetraethylthioallene (**89b**) similarly reacts with TCNE



89 a; X: OCH_3
b; X: SCH_2CH_3
90 91

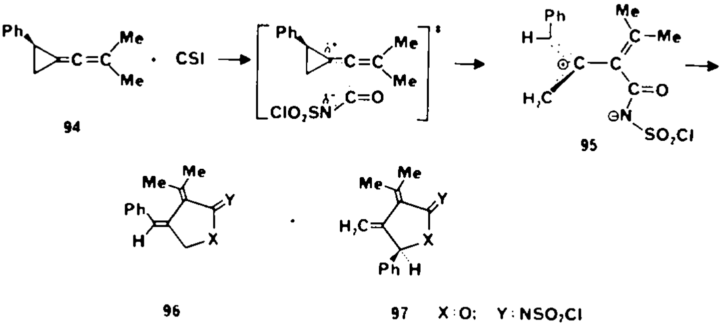
to produce **91b**; however, in this case there is no evidence for **90b** being in equilibrium with **91b**.[91]

Less electron rich allenes such as DMA also appear to react with chlorosulfonyl isocyanate (CSI) via dipolar intermediates. Although CSI reacts with DMA to produce **92** and **93**, only cycloadduct is formed in the reaction with 1,2-cyclononadiene.[92]



92 93

Alkenylidenecyclopropanes react with CSI to form the dipolar intermediate **95** which undergoes ring closure to form **96** and **97**.[89] When optically active **94** is reacted with CSI at temperatures below 0° **96** and **97** are formed in a completely stereoselective manner, while at temperatures above 61° **96** and **97** are obtained racemic.[93] This temperature dependence of the optical purity of **96** and

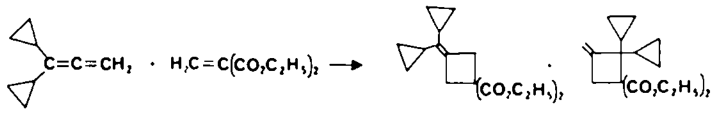


94 95

96 97 X: O; Y: NSO_2Cl
X: NSO_2Cl, Y: O

97 indicates that rotation about the C^2—$C^{1'}$ bond occurs competitively with ring closure, and predominates at higher temperatures.

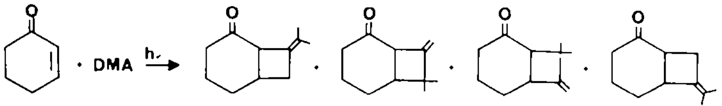
The chemoselectivity of the cycloaddition of 1,1-dicyclopropylallene with diethyl methylenemalonate is markedly influenced by the polarity of the solvent and the presence of a Lewis acid. In benzene solution a mixture of **98** and **99** is formed in a ratio of 83:27, while in acetonitrile the



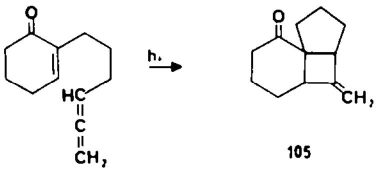
98 **99**

ratio is 8:92! In the presence of aluminum chloride only **99** is formed. It would appear that in benzene solution the reaction proceeds via a diradical-intermediate mechanism, while in acetonitrile, or in the presence of aluminum chloride, a dipolar-intermediate mechanism is operative. Such reversals in chemoselectivity are not observed in the cycloaddition reactions of 1,1-dicyclopropylallene with methyl acrylate, DEF and DEM.

(7) *Photochemical cycloaddition reactions.* Inter- and intramolecular photoinduced cycloadditions of allenes to α,β-unsaturated ketones are known, and have proved to be useful in the construction of complex molecules. Irradiation of a mixture of cyclohexenone with DMA produces a mixture of cycloadducts from which **100–103** have been isolated in a ratio of 71:8:13:8.[95] Cyclohexenone **104** undergoes an intramolecular cycloaddition to produce **105** in high yield.[95]



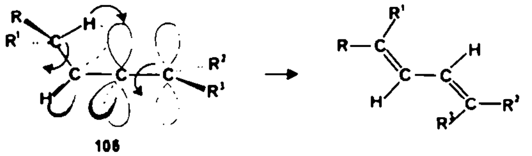
100 **101** **102** **103**



104 **105**

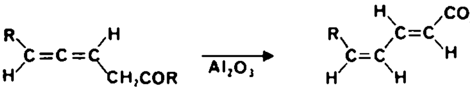
Thermal rearrangement reactions of substituted allenes

(1) *Hydrogen* [1.3]*sigmatropic rearrangements.* In the cycloaddition of DMA with DEF and DEM adducts **62** and **65** derived from isoprene are formed.[75] (In these cycloaddition reactions precautions were taken to avoid acid- and base-catalyzed rearrangements of DMA.) The similar type of adduct is not formed during the cycloaddition of DMA with the more reactive NPMI.[74] It is currently thought that the rearrangement of DMA to isoprene occurs via a concerted process. Instead of migrating the hydrogen atoms to the 2p AO on C_2 of the $\pi_{1,2}$ bond as would occur in the "forbidden" suprafacial rearrangement in simple alkenes, migration to the 2p AO on C_2 of the $\pi_{2,3}$ bond as shown in **106** is conceivable. The rotational motions shown in **106** represent an "allowed" concerted process. Futher studies are required in this area.



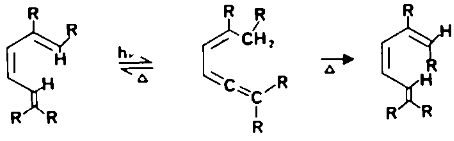
106

β-Allenic esters **107** undergo thermal rearrangements to the (2*E*,4*Z*)-dienoic esters **108** over an alumina catalyst in high yields with 90–100% stereospecificity.[96] The stereochemistry is believed to be controlled by the steric interactions between the groups attached to the allene and the surface of the alumina.[96]



107 **108**

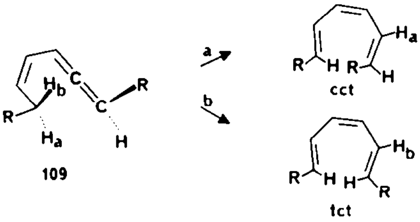
(2) *Hydrogen* [1.5]*sigmatropic rearrangements*. The first reported hydrogen [1.5]sigmatropic arrangement of a 1,2,4-triene appears to be that shown in the following equation.[97] Very shortly



thereafter, 1,2,4-trienes were implicated as intermediates in the base-catalyzed rearrangement of 1-en-4-ynes to a mixture of 1,3,5-trienes.[98]

$$\begin{tikzcd}[column sep=small] -C{\equiv}C{-}CH_2{-}CH{=}CH{-}CH_2{-} \arrow[r, "base"] & -CH{=}C{=}CH{-}CH{=}CH{-}CH_2{-} \arrow[d, "\Delta"] \\ & -CH{=}CH{-}\underset{cis}{CH{=}CH}{-}CH{=}CH{-} \end{tikzcd}$$

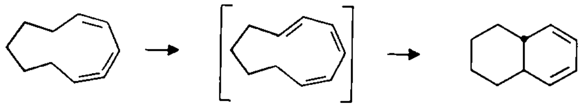
The formation of mixtures of stereoisomeric trienes, in which the central double bond always has the *cis* configuration, is readily understood if one considers the possible conformations of a substituted 1,2,4-triene. In conformation **109**, in which the larger R′ group is oriented in the least sterically crowded direction, migration of H_a in a suprafacial manner produces the *cis,cis,trans*-isomer (*cct*), while migration of H_b produces the *tct*-isomer. Migrations of H_a or H_b



109

in the other two less populated conformations attainable by rotation of the $-CR'H_aH_b$ group result in the formation of the *ccc*- and *tcc*-isomers of the 1,3,5-triene.

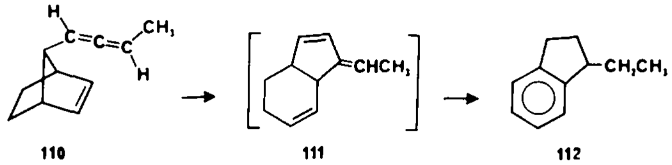
In contrast to the low degree of stereoselectivity encountered in the rearrangement of acyclic 1,2,4-trienes, similar rearrangements in conformationally rigid, cyclic systems are considered to be completely stereospecific as is illustrated in the following equation.[99]



Extensive use has been made of the hydrogen [1.5]sigmatropic rearrangement in the synthesis of retinoids[33b,38,100] and analogs of vitamin D.[33a,101]

Thus far, all of the hydrogen [1,5]sigmatropic rearrangements are considered to occur via allowed, suprafacial, concerted processes. As of the writing of this review, there appears to be no report of a carbon [1.5]sigmatropic rearrangement involving a 1,2,4-triene.

(3) [3.3]*Sigmatropic rearrangements*. The thermolysis of **110** at 250° results in the ultimate formation of ethylindan (**112**).[102a] The triene **111** has been isolated, and on thermolysis does undergo consecutive [1.5]hydrogen sigmatropic rearrangements to product **112**.[102b] The formation

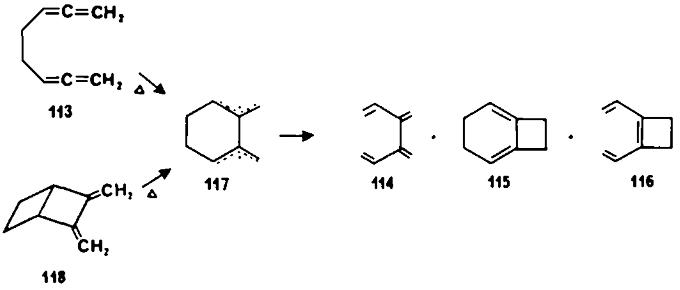


of **111** from **110** is considered to occur via an allowed eight-electron process.

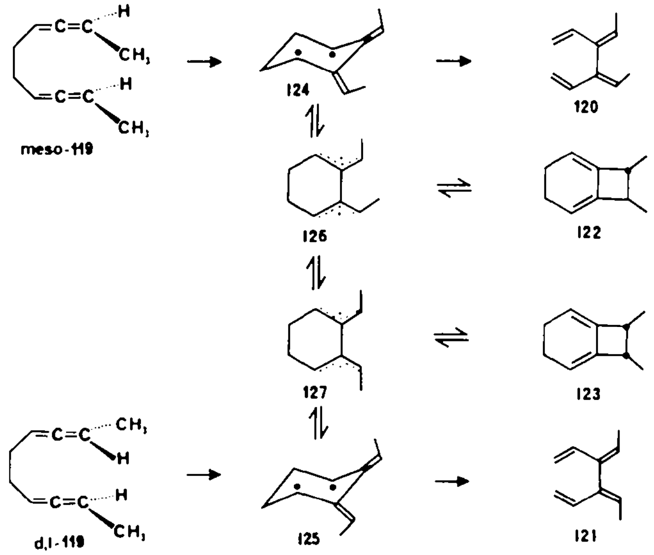
Several other synthetically useful [3.3]sigmatropic rearrangements of heterosubstituted 1,2,6-trienes have been reported.[103]

The thermolysis of 1,2,6,7-octatetraene (**113**) at 310^{c} results in the formation of **114**.[104] At lower temperatures, however, the thermolysis of **113** also produces **115** and **116** in addition to **114**.[105] The diradical intermediate **117** has been proposed as an intermediate in the reaction. In support of this proposal, the thermolysis of **118** has been shown to produce **114**, **115** and **116** in a ratio identical with that derived from the thermolysis of **113**.[106]

In a very interesting stereochemical study, *meso*- and *dl*-**119** have been prepared and subjected to thermolysis, producing rather similar ratios of **120**–**123** (± 4% maximum in relative yields).[107] The mechanism shown in the following scheme was proposed in which non-planar, non-resonance delocalized diradicals **124** and **125** are initially formed, which then either undergo ring closure or



rotational relaxation to the planar bisallyl intermediates **126** and **127**. An isomerization equilibrium between **126** and **127** was also proposed to occur. Results described earlier in this review strongly



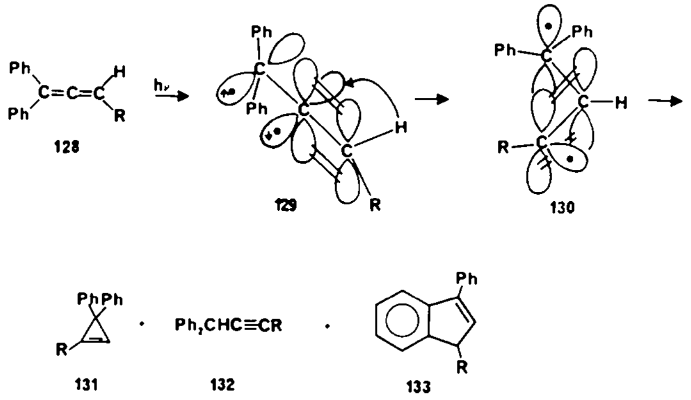
imply that planar, resonance-delocalized allyl radical-containing intermediates are derived directly from a coupling process. Stereochemical considerations would then suggest that **125** should be preferentially derived from both *meso*- and *dl*-**119** (a *Z*,*Z*-diradial intermediate would not be expected to be formed). Thermodynamic and kinetic considerations, and prior experimental results would suggest that the allyl-radical portions of diradical intermediates do not undergo stereoisomerization faster than ring closure and/or cleavage reactions. The situation is further complicated by the fact that conformations of *meso*- and *dl*-**119** other than those depicted many undergo reaction to form **126** and/or **127**. These results are very interesting, but further studies will be required to provide more intimate details of the sigmatropic rearrangement process.

Photochemical reactions of substituted allenes

Relatively little is known concerning the photochemistry of allenes, primarily because simply substituted alkyl-allenes absorb at two short a wavelength to be excited by normal sources of radiation. In the photochemical cycloadditions of substituted allenes with α,β-unsaturated ketones, the latter absorbs the energy resulting in an excited state which then reacts with the allene. For an allene to be photochemically reactive it must bear a substituent which provides a suitably long wave-length absorbing chromophore, or very short wave-length light must be used.

Irradiation of 1,2-cyclononadiene apparently produces a triplet cyclopropylidene derivative (**3**) which undergoes intramolecular insertion to produce **4**.[14]

1,1-Diphenyl-substituted allenes (**128**) undergo photo-induced conversion to the primary products **131–133** via the proposed singlet excited state **129** which undergoes a 1,2-hydrogen shift to form **130**. Further electronic reorganization and/or ring closure results in the formation of **131–133**. This also appears to be an area where further studies are warranted.



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