

Electrophilic Addition to Allenic Derivatives: Chemo-, Regio-, and Stereochemistry and Mechanisms[†]

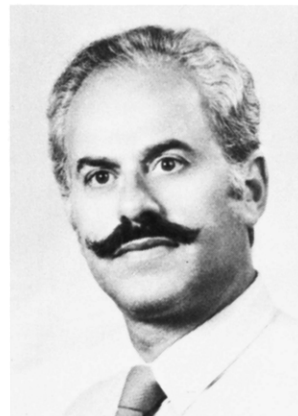
WILLIAM SMADJA

Laboratoire de Cinétique et Mécanisme de Réactions Organiques, ER 84 du CNRS, Université Pierre et Marie Curie, F-75230 Paris Cedex 05, France

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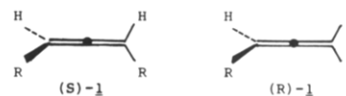
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William Smadja was born in Tunis (Tunisia) in 1936. While a research worker in "Centre National de la Recherche Scientifique", he received the Doctorat-es-Sciences degree from the University of Paris with the late Prof. Ch. Prevost in 1965. After 2 postdoctoral years at University College of London with the late Prof. F. Sondheimer, he joined the group of Dr. C. Georgoulis at the Pierre et Marie Curie University in 1972. His research interests include the carbanionic acetylene-allene-diene isomerization and the structure and reactivity of vinylic chlorides. More recently he turned his attention toward the catalytic stereoselectivity of the isomerization and phenylation of allylic alcohols using transition metals.

I. Introduction

Substituted allenes of the RCH=C=CHR type possess two double bonds which lie in different planes at right angles to each other. This cumulated alkadiene is a chiral molecule, the axial dissymmetry resulting from restricted rotation about the double bond. One cumulated alkadiene can then exist in two stereoisomeric forms, the enantiomers (S)-1 and (R)-1, neither being

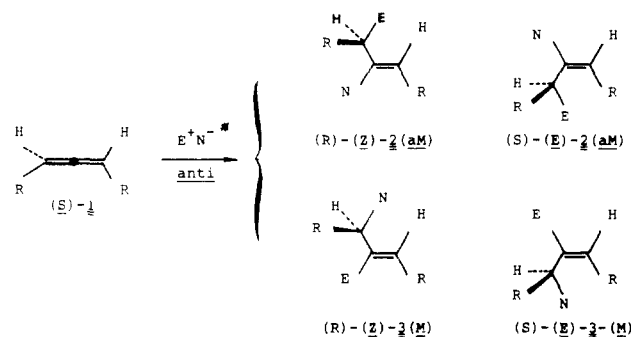


superimposable on the other.

This substance is a very interesting substrate for the synthesis of valuable optically active compounds, such as furanones, γ - and δ -lactones, functionalized dihydrofurans and -pyrans, cyclopentenones and -hexanones, etc., obtained by a transfer of chirality. Finally and importantly, a cumulated diene is a material of choice to study the addition reaction mechanism on the carbon-carbon double bond.

[†]Dedicated to the memory of Professor Charles Prévost, deceased July 11, 1983.

SCHEME I



The electrophilic addition of a reagent EN (E^+ and N^- being respectively the electrophile and nucleophile) to allenic derivatives can occur, as it does for simple olefins,^{196,202} stereospecifically syn (suprafacial) or anti (antarafacial) and regioselectively with Markovnikov (M) or anti-Markovnikov (aM) orientation. The cis-trans isomerism of the remaining double bond contained in the monoadducts 2 and 3 (Scheme I) could be useful to determine the direction of the entering reagent EN. Thus, electrophilic addition to allenes will occur stereoselectively leading to products with *E* or *Z* configuration by reaction of the less or the more hindered π bond, respectively.

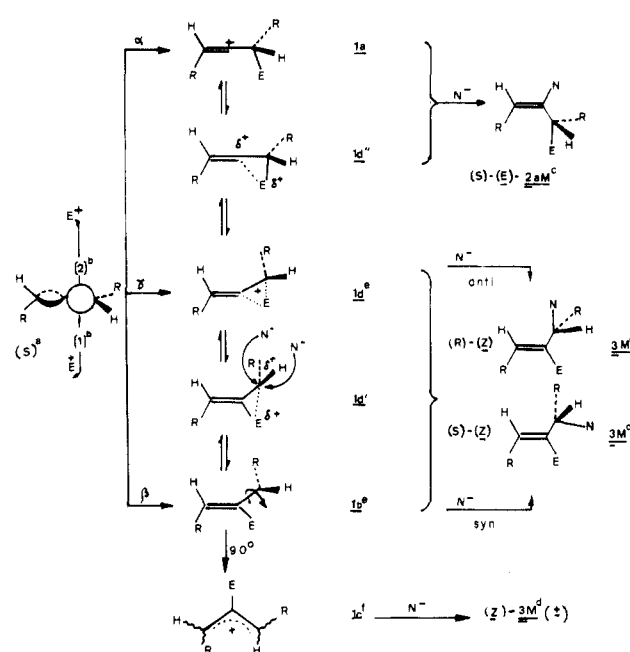
Thus, the electrophilic addition of this reagent to allenic derivatives¹⁻⁸ can follow one of the three different pathways depicted in Chart I: α , electrophilic attack on the terminal carbon atom leading to a vinylic carbocation 1a,⁹⁻¹⁶ which subsequently provides the product 2 with anti-Markovnikov orientation; β , electrophilic attack on the central carbon atom leading to a nonplanar α,β -ethylenic carbocation 1b that is able to isomerize to the delocalized allylic carbocation 1c after a 90° rotation around the single carbon-carbon bond to form the product 3 of M type; γ , electrophilic attack of the double bond producing an "onium" species 1d from which the attack of nucleophile must occur from the backside and the mechanism must be anti.

Although the allylic cation 1c is the most stable intermediate (vide infra), these three pathways can occur according to the nature of reagent, solvent, and unsaturated substrate. (There is probably a spectrum of mechanism between complete onium ion 1d (no rotation) formation and complete open ions 1a or 1b (free rotation) formation with partially bridged onium species 1d' or 1d'' (restricted rotation) in between.) The only type of species that is able to explain formation of chiral product starting from optically active allene should be a nonplanar intermediate such as 1d.

This review covers the literature from 1970 to 1983 (*Chemical Abstracts*, Vol. 98, No. 17) and always refers to the excellent work of Caserio.⁶ The electrophiles treated in this paper are H^+ , X^+ , $-Se^+$, $-S^+$, " HO^+ ", R_3C^+ , and $M_nX_{n-1}^+$. Hydroboration, addition of carbenes,¹⁷ and 1,3-dipolar addition have not been included in this work, since classic electrophilic species are not likely to be involved.

Definitions

Chemoselectivity will be related to the preference for attack of the one double bond of the cumulated dienes. *Regioselectivity* is related to the relative positions of nucleophile and electrophile on the reacting double

CHART I. Electrophilic Addition to Allenic Derivatives^a

^a (a) The out-of-plane and the in-plane π electrons for allenic derivatives are represented by



(b) Sense of electrophile approach leading to the products with *Z* (1) and *E* (2) stereochemistries. For clarity, only path affording the *Z* products has been drawn. (c) The product 2aM is always followed by the formation of the bisadduct 4 (Figure 1). ^d The product (Z)-3 is of M type. (e) Nonplanar species. (f) Planar entity.

bond: the Markovnikov-oriented product will have the electrophile fixed on the central carbon atom of the unsaturated link whereas the anti-Markovnikov product will correspond to the product with the nucleophile at this carbon. *E/Z* Stereoselectivities refer to the geometrical isomerism of the ethylenic adduct. The reaction leading to one major chemo-, regio-, or *E/Z* stereoisomer is chemo-, regio-, or *E/Z* stereoselective whereas the formation affording exclusively one chemo-, regio-, or *E/Z* stereoisomer will be 100% or completely chemo-, regio-, or *E/Z* stereoselective.

Abbreviations

Unless otherwise stated, the following abbreviations have generally been used: R, alkyl; Ph, phenyl; Ar, aryl; M, Markovnikov orientation product; aM, anti-Markovnikov orientation product; RT, room temperature; DNBSC, 2,4-dinitrobenzenesulfonyl chloride; BSC, benzenesulfonyl chloride; PCBSC, *p*-chlorobenzenesulfonyl chloride; BSeB, benzeneselenyl bromide; TMBSelB, 2,4,6-trimethylbenzeneselenyl bromide; BSeC, benzeneselenyl chloride; MCPBA, *m*-chloroperbenzoic acid; PAA, peracetic acid; PFA, performic acid; PNPBA, *p*-nitroperbenzoic acid; ONs, 1-naphthalenesulfonate (nosylate); OTs, *p*-toluenesulfonate (tosylate); OBs, *p*-bromobenzenesulfonate (brosylate); DNB, 3,5-dinitrobenzoate; OAc, acetate; TFA, trifluoroacetic acid.

II. Protonation ($E = H$) (Table I)

The regioselectivity of protonation of allene derivatives is simply related to electron-donating effects of

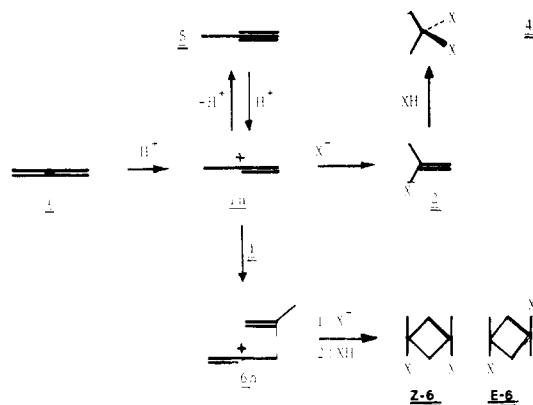


Figure 1. References 2 and 21.

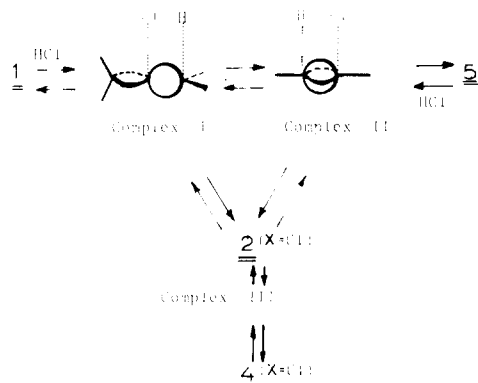


Figure 2. Reference 22. For arabic numerals representing substrates and products see Figure 1. The HCl bond is in the plane. The ^1H NMR showed that the hydrogens of allene 1 are shifted upfield by 2 ± 1 Hz in the presence of HCl whereas the proton of HCl was deshielded by 8 Hz in the presence of 1.

substituents of allenic substrate. When the twisted ethylenic cation **1b** is not stabilized by releasing effect, allenes are attacked at the terminal carbon and the product **2** with anti-Markovnikov orientation is formed via vinyl cation **1a** (see Chart I with $\text{E} = \text{H}$).

A. Vinylic Carbocation **1a**⁹⁻¹⁶

Hydrohalogenation of the propadiene **1** produces mainly the halopropene **2** and the bisadduct **4**. The cyclobutene derivatives **6** are obtained by reaction of another molecule of allene during hydrochlorination and hydrobromination probably because Cl^- and Br^- are weak nucleophiles (see footnote in Scheme I) (entries 1-9 and Figure 1).²⁰³ The hydroiodination does not afford cyclic products (entry 10). (References concerning the works cited in this review appear most often in the corresponding quoted entries) from the Tables I-XIII.) When DCl is used, the deuterium is incorporated exclusively on terminal carbons of the chlorinated products **2** and **4** and this addition is 100% regioselective with exclusive anti-Markovnikov orientation (entry 5). In the absence of Lewis acid catalyst the more stable and the less reactive propyne **5** is formed very probably by loss of proton from vinyl cation **1a** (entries 7,8 and Figure 1). In the gas phase, addition of HCl to the allene **1** affords the same chlorinated compounds **2** and **4** that could be formed through the nonpolar complexes I and II (Figure 2). It has been suggested²² that in solution the overall hydrochlorination of allene has also to take into account the formation of these complexes. Again, protonation of

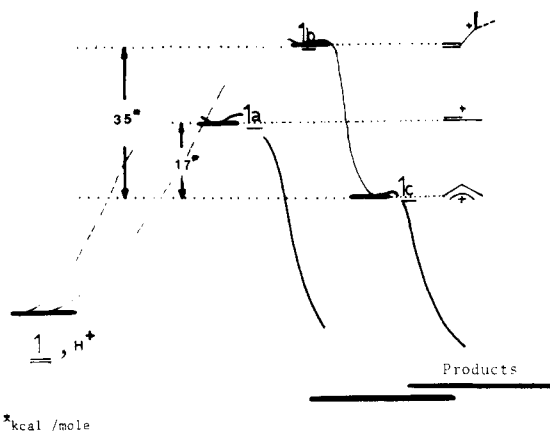
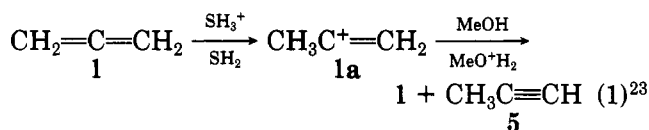


Figure 3. Reference 24.

allene in the gas phase²³ led to the conclusion that formation of the 2-propenyl cation **1a** is the main reaction because this species exchanges its proton with methanol whereas allyl cation **1c** is too stable to allow the same reaction



Theoretical calculations²⁴ are highly revealing, the linear vinyl cation **1a** was shown to be more stable than the twisted olefinic cation **1b** by 18 kcal/mol, thus the protonation of allene will proceed preferentially through the vinyl cation **1a** (Figure 3). Recently,^{31b} the kinetics of the conversion of allene to acetone has been shown to be consistent with rate-limiting protonation leading to the 2-propenyl cation **1a**.

Addition of acid to the 1,2-alkadiene **7** also occurs on the nonsubstituted double bond through the 2-alken-2-yl cation (entries 11-14). When the anion of the reagent (Cl^- , CF_3COO^-) is a weak nucleophile the long-lived 2-buten-2-yl cation loses a proton giving the more stable 2-butyne **9** (entries 11, 12). Addition of trifluoroacetic acid to the 1,2-butadiene **7a** affords a kinetically controlled ratio of stereoisomers that is surprisingly high ((Z) -**8**: (E) -**8** = 3.3), the corresponding ratio obtained under thermodynamic control being only of 2.3, whereas the 1,2-hexadiene gives, under the same conditions (75 °C), the same value 2.3 for the equilibrium mixture and the ratio (Z) : (E) = 1.3 in kinetically controlled protonation (entries 12, 13, see footnotes *i*, *j* of Table I). Interestingly the stereoselectivity is reversed in the hydrobromination of the 1,2-heptadiene **7c** and the stereoisomer (E) -**8c** becomes predominant. The change in stereoselectivity between the 1,2-butadiene and other 1,2-alkadienes could be interpreted by hyperconjugation of methyl groups (vide infra). Since the vinyl cation **7a** is linear, the predominant formation of the isomer **8Z** will correspond to the nucleophile Cl^- or CF_3COO^- entering by the more hindered face of the double bond (Figure 4).

It is noteworthy that addition of $\text{CF}_3\text{CO}_2\text{H}$ to the allene **10** affords the ketone **11**, through the corresponding enol trifluoroacetate and vinyl cation in the rate-determining step with a primary isotope effect $k_{\text{CF}_3\text{COOH}}/k_{\text{CH}_3\text{COOH}} = 7.4$ (entry 15).

Addition regioselectivity of HX to the 1,3-disubstituted alkylallenes **12** is strongly dependent of the nature

TABLE I. Protonation of Allenic Derivatives

entry	allenic derivatives	reagent	solvent	T, °C	yields, %	(c) ¹	(d) ²	product composition, %	ref
1									
2	1	HF ^b		-76				5	18
3	2	HCl/BiCl ₃ ^c		-78	22			3	19
4	3	HCl/TiCl ₄ /O ₂			80			2	20
5	4	HCl/FeBr ₃ /O ₂			58 ^d			2	20
6	5	DCl/BiCl ₃ /O ₂		-78	0.83 ^c			2	20
7	6	HCl		-70	12			8	21
8	7	HCl ^f		-70	71			38	22
9	8	HCl ^f		100				38	22
10	9	HBr ^c		-70	42			44	21
	10	HI		-70	71			R —≡—	21
11		HCl/BiCl ₃							
12	7a, R = Me	HCOOCF ₃		-78	20			9	19
13	7a, R = Me	HCOOCF ₃		75				38.5 ^h	25
14	7b, R = n-Pr	HCOOCF ₃		75				63.2	25
	7c, R = n-Bu	HBr		0	81			62.0	37a
				RT	66			75	37a
15		HCOOCF ₃		75	85 ⁿ				36
16	12	HX							
17	12a, R = Me	HBr		RT				14 ^t	37b
18	12a, R = Me	HBr ^b		RT	90			80	44, 46
19	12b, R = Et	HCl/BiCl ₃		-78	50			75	44, 46
		HBr		RT	90			80	44, 46
20		HBr			86				37a,c
21	17, (n = 10)	HX							
22	20 (n = 6)	HBr ^c		RT	70			<i>cis</i> -19	37f
23	20 (n = 6)	HBr ^c		RT	74			55	37a,e,f
24	20 (n = 6)	DBr ^c		RT	47			100 (2-d)	37f
25	22 (n = 7)	HCl/BiCl ₃		-70	75			100 ^t	45
		HBr ^c		RT				100	37f



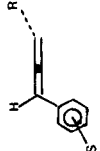

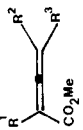
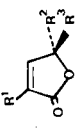
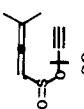
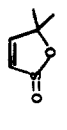
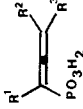
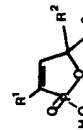
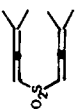
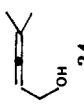
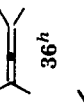
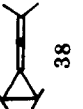
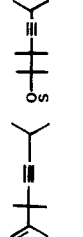
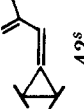
26	20 ($n = 6$)	HBr	HOAc/ether	RT	high	100	37a,d
27		DCl	D ₂ O		high		39c
28	21 	H ₂ SO ₄	H ₂ O		high		39e
29	23 						
30	24a (S = R = H) 24b (S = H, R = Me)	HCl (0.995 M) ^o HCl (0.198 M) ^p	HOAc HOAc	30.4 14.7	98 100		40, 41 42
31							
32	26a Me Et Ph	H ₂ SO ₄	EtOH/H ₂ O	RT	60	27a-d	49
33	26b Me Me Ph				62		
34	26c Et Et Ph				32		
35	26d Ph Ph Ph				93		
36	26e H Ph Me	HOCOFC ₃	HOCOFC ₃	RT	80	27e-l	51
37	(-)-26f H Ph Et				71		
38	(+)-26g Et Ph H				76		
39	(-)-26h Et Ph Me				62		
40	(+)-26i Et Ph Et				84		
41	(-)-26j Me Ph Et				66		
42	(+)-26k Me Ph Me				68	27m-p	52
43	26l Ph Ph naphthyl	17% HCl or H ₂ SO ₄	H ₂ O or DME/CCl ₄	reflux or RT	65		
44	26e H Ph Et				53		
45	26mH o-C ₆ H ₄ (CH ₂) ₃						
46	26n H i-Pr Me						
47	(S)-26e H Ph Me						
48	(R)-26o H Me Ph						
49	(R)-26p H Et Ph						
50		H ₂ SO ₄	EtOH/H ₂ O	RT			50
	27 						
	(R)-27e (O. Y. = 100%) ^u (S)-27o (O. Y. = 100%) (S)-27p (O. Y. = 100%)						
	(R)-27e (O. Y. ?)						

TABLE I (Continued)

entry	allenic derivatives	reagent	solvent	T, °C	yields, %	product composition, %	ref
51	(S)-28p H Et Ph	H ₂ SO ₄	EtOH/H ₂ O	RT		(S)-27p (O. Y. ?)	50
52	(R)-28e H Et Ph	H ₂ SO ₄	DME/CCl ₄	RT		(R)-27e (O. Y. = 83%)	52
53	(S)-28p H Et Ph	17% HCl	H ₂ O	reflux		(S)-27p (O. Y. = 83%)	52
54	 29	HOCOFCF ₃	HOCOFCF ₃	RT	100		53
55	 31a-d	HCl	H ₂ O	67	85		54
56	31a	HOCOFCF ₃		60	100	32a	36
57	31b	HOCOFCF ₃			100	30	53
58	31c						
59	31d						
60	31a						
61	 33						
62	 34	H ₃ PO ₄			45	35	198
63	 36 ^h	HBr ^b		-20		37	44
64	 38	HN	SOH				
65		HN				40	
66		HOTs			64	39	56, 57
67		BF ₃ ·OEt ₂		RT	70	87	56, 57
68		TFA		RT	79	94	56, 57
69		H ₂ SO ₄		reflux		37	56, 57
70		H ₂ SO ₄		reflux		37	55, 57
71	 42 ^s	H ₂ O/THF		reflux		11	57
		HOTs	HOAc	RT	100	22	57
			HOAc	RT	85	40	201
			C ₆ H ₆	RT		100	57

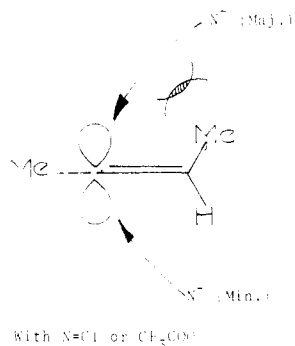
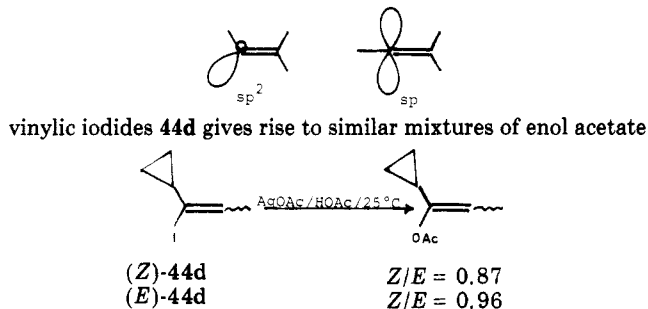
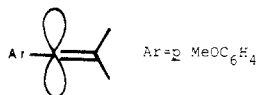


Figure 4. Reference 25. The linearity of vinyl cations⁹⁻¹⁶ has been established by three different ways: Theoretical calculations have shown that the linear cation was energetically more favorable than the bent structure by 45–65 kcal/mol.²⁵ Acetolysis of both



stereoisomers.²⁶ 1H and ^{13}C NMR spectroscopy allows direct observation of stabilized vinyl cation, which confirms this linearity



by the magnetic equivalence of the gem methyl group protons.^{27,28}

of the solvent. In acetic acid–ether solution, the 2,3-pentadiene **12a** reacts with HBr to give mainly one geometrical isomer of vinylic bromide **13** probably with (*E*) configuration (entry 16) whereas up to 80% of allylic bromide **14**, with unknown configuration, is formed in acetic acid medium (entries 17–19). The same trend is observed with strained and large-ring cyclic allenes, thus the solvent might have a profound effect on the addition of hydrogen bromide to allenes (entries 20–26).

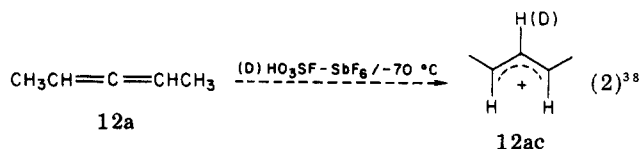
Ketones are generally obtained by acid-catalyzed hydration of allene,³¹ alkylallene,^{29,30,32,33} and 1,3-dialkylallene^{34,35} very probably with a vinylic cation as an intermediate.

B. α,β -Ethylenic Carbocation **1b** and Allylic Carbocation **1c**

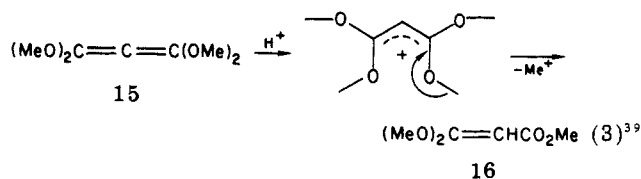
When highly electron-donating substituents such as RO,³⁹ F,⁶⁴ and Ph⁴⁰⁻⁴² are attached to the carbons of allene, protonation occurs exclusively on the central carbon and products with Markovnikov orientation are formed. However, at low temperatures, the 2,3-pentadiene **12a** already affords the allyl cation **12ac** exclusively when fluorosulfuric acid HO_3SF is added. This species has been observed by 1H NMR, because of the weak nucleophilicity of FSO_3^- , and was found to have trans-trans configuration ($^3J = 13.8$ Hz). The exclusive protonation at central carbon was shown using the deuterated acid DO_3SF :

1. Releasing Mesomeric Effect (+M)

Another allylic cation is observable by 1H NMR when the tetramethoxyallene is protonated; the enol ether of of

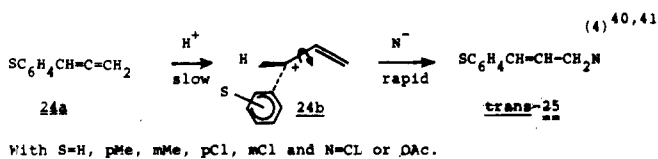


malonic ester is observed after loss of the methyl cation.



Deuterolysis of allenyl ethers with DCl affords α,β -unsaturated aldehydes (entry 27). It has been shown that in acid catalyzed hydrolysis of ethoxypropadiene the proton is transferred to the β -carbon atom of the substrate in the rate-determining step ($k_{H_3O^+}/k_{D_3O^+} = 3.05$).^{39d} The same behavior is found for the acid catalyzed hydrolysis of allenyl acetates with a smaller solvent isotope effect $k_{H_2O}/k_{D_2O} = 1.46$ (entry 28).^{39e}

The correlation with σ^+ ⁴³ in the kinetics of HCl addition to arylallenes in acetic acid established the Ad_B2 pathway followed by the reaction. The high value of ρ^+ (-4.2) and the increasing rate caused by methyl substitution of allene are in agreement with the existence of a benzylic cation intermediate formed in rate-limiting protonation at the central carbon⁴⁰⁻⁴² (entries 29, 30). (The rate constant is increased by a factor of 4000 and 20 when the allene **24** is methyl substituted in the α - and γ -position respectively.)



A kinetic study of the addition of HCl to cumulated and conjugated phenylbutadienes permitted the determination of relative thermodynamic stabilities of the phenylbutenyl cation **24'** (Figure 5). It has been found that the energy barrier to go from the *cis*-allyl cation to the corresponding *trans* cation through the twisted cation was 7.6 kcal/mol whereas the reversed path re-

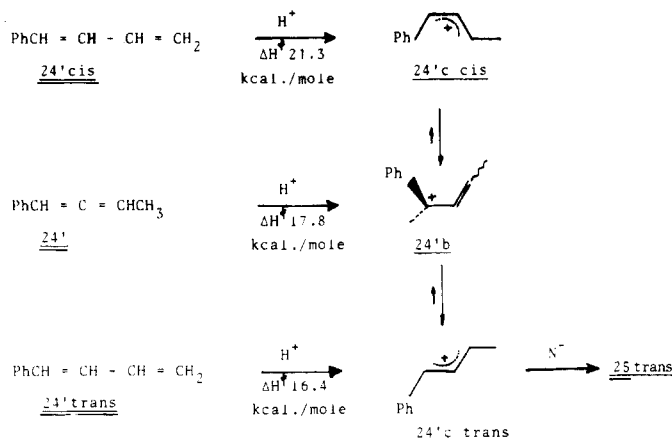


Figure 5. Reference 42.

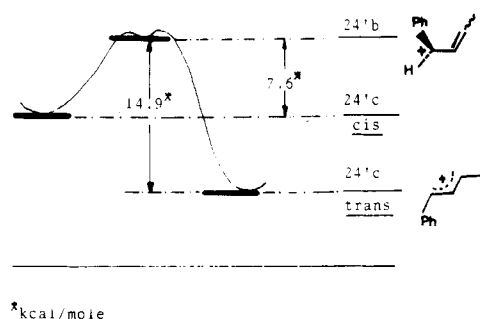


Figure 6. Reference 42.

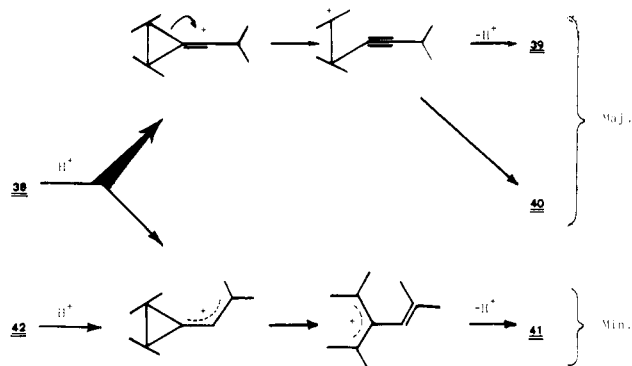
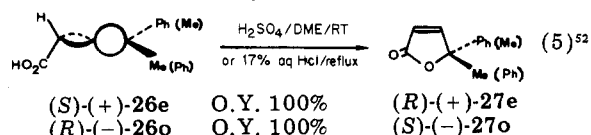


Figure 7. References 55-57.

quires up to 14.9 kcal/mol (Figure 6).

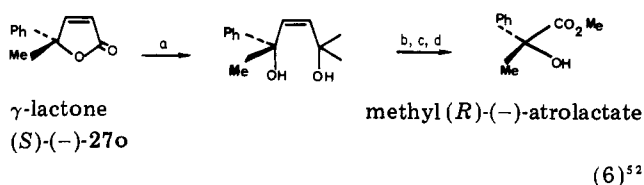
Anti Stereospecific Lactonization. The formation of stabilized benzylic cation by addition of acid to arylallenes has been widely exploited for the lactonization of arylated allenic acids and esters leading to butenolides (entries 31-49). The reaction was shown to be stereospecific from optically active allenic acids **26f-k** (entries 36-41). (*Stereoselective and stereospecific reactions*.^{111a,193,194} Any reaction in which only one of a set of stereoisomers is formed predominantly or exclusively is called stereoselective whereas when a given stereoisomer leads to one product while another stereoisomer leads to the opposite product is called stereospecific. A good example of a complete stereospecific addition to allenic derivatives, say selenylation, is given by the eq 21 and 22, in which one diastereoisomer (*R,S*) of α -allenic alcohol **112** affords the geometrical *Z* isomer of the 3-selenodihydrofuran **113**, whereas the other diastereoisomer, the (*S,S*)-**112** gives the other product (*E*)-**113** with opposite configuration. Moreover, the reaction of optically active substrate is stereospecific if it mainly proceeds by one particular stereochemical course to give optically active product. When the reaction occurs with 100% of optical yield, the reaction is said to be 100% or completely stereospecific.) Later on, the complete stereospecificity of this acidic catalyzed lactonization, which proceeds by an anti mechanism, was established starting from the acids (*R*)-**26e** and (*S*)-**26o** leading, respectively, to the lactones



(*S*)-**27e** and (*R*)-**27o** with 100% of optical yield (o.y.) (entries 47-48).

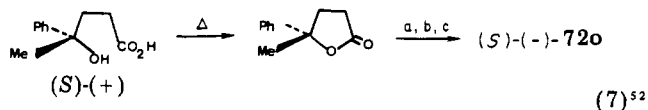
The reaction is 100% stereospecific with the ethyl-substituted acid (*R*)-**26p** (entry 49). Configuration and

specific rotation of γ lactones have been determined by the following correlations



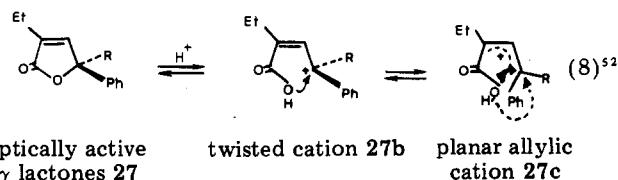
(a) 2 MeMgBr/aq NH₄Cl. (b) O₃/Me₂S.

(c) AgO/NaOH. (d) CH₂N₂.



(a) Base. (b) PhSeBr. (c) O₂/ Δ .

Finally, the enantiomeric stability of the γ -lactones **27g-i** under reaction conditions was shown to be related to the bulkiness of alkyl substituent gem to the phenyl group: H < Me < Et. This phenomenon has been attributed to free rotation of carbon-carbon single bond in the perpendicular cation **27b**⁵¹ (entries 37-39) (see footnote *q* of the Table I).



2. Releasing Inductive Effect (+I)

As with the mesomeric effect (+M), the donating inductive effect (+I) of *gem*-dimethyl groups allows the exclusive protonation of allene on the central carbon and affords the formation of the stabilized tertiary allylic cation. This stabilization has been used for the synthesis of carbo- and heterocyclic esters formed by protonation of allenic esters followed by intramolecular nucleophilic participation. The γ lactones **27**, oxaphospholenes **32**, and γ -sultines **30** were formed by acid-catalyzed cyclization of the corresponding esters and sulfones (entries 46, 50-61). The 2,5-dihydrofuran **35** is formed during the acid-catalyzed cyclization of α -allenic alcohol **34** while tetramethylallene **36** gives rise to the corresponding allylic bromide **37** (entries 62, 63).

3. Alkenylidenecyclopropane

The reaction of acids with the permethylated alkenylidenecyclopropane **38** affords a good example for the study of competition between two stabilizing effects of a positive charge: the inductive effect of *gem*-dimethyl groups and the participation of the cyclopropylidene group that occurs by ring opening during protonation. Depending on reaction conditions, the allene **38** affords various amount of three different compounds all of which are acyclic. Whatever the conditions, the predominant mixture of the enyne **39** and the homopropargylic product **40** has been formed through vinyl cation and participation of cyclopropane ring whereas the minor product **41** came from an allylic species stabilized by the *gem*-dimethyl groups (entries 64-70).

This latter evolution becomes the exclusive one starting with the conjugated diene **42** (entry 71, see also Figure 7).

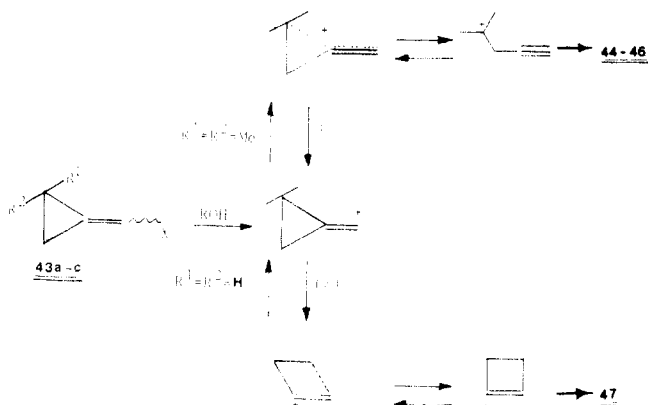
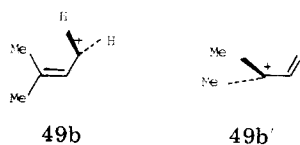


Figure 8. References 60–62.

It is interesting to note that the addition of acid to the nonsubstituted cyclopropylidene allene follows a different route. Some enol acetate of cyclobutene is formed with the expected homopropargylic product (entry 75). This result could be compared with those obtained by solvolysis of the methylated cyclopropylidene halides **43** affording the vinylic cation. The cyclobutene derivative **47** has been formed by rearrangement of vinyl cation mainly when the cyclopropane ring of the halide **43b** is not substituted (entry 73 and path β of Figure 8). The mixture of products **44–46** that are formed through the unique homopropargyl cation occurs by solvolysis of the *gem*-dimethyl substrate **43a** (entry 72 and path α of Figure 8). Finally, the solvolysis is no longer unequivocal with the monomethylated bromide **43c** (entry 74).

4. 1,1-Dimethylallene **49**

Special attention should be paid to the hydrochlorination of allene **49**. This kinetically controlled addition affords a mixture of primary and tertiary chloride (36%:64%) whereas the same reaction under the same conditions with the conjugated diene **50** affords the same mixture in a different ratio (17%:83%) (entries 76, 77). This means that the majority of the primary chloride has been obtained from the allene, because of the higher rate of conjugated diene protonation. This result is difficult to understand in terms of free ionic twisted species in which the primary should be more reactive than the tertiary (*vide infra*).



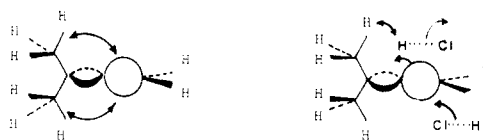
C. Discussion

The regioselectivity of acid addition to allenes is related to the substituent releasing effect.

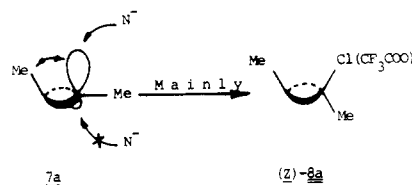
Pathway α in Chart I via vinyl cation is followed when the protonation of allenes occurs on the unsubstituted double bond because of higher stability of vinyl cation vs. twisted olefinic cation (entries 1–14).

Interestingly and surprisingly in ether–acetic acid solution, the hydrobromination of acyclic and nine-membered cyclic allenes affords vinylic bromides whereas in the absence of ether the reaction gives allylic bromides (*cf.* entries 16 and 17 and 22 and 26). If an

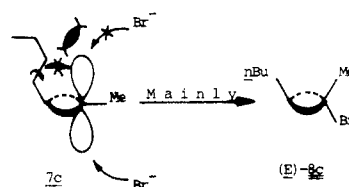
SCHEME II^{19,218}



SCHEME III



SCHEME IV



ionic mechanism is involved vinyl cation must be favored over twisted olefinic cation in the presence of added ether.

A vinyl cation stabilized by ring opening of permethylated cyclopropane is also found to be favorable over allyl cation (entries 64–70 and Figure 7). The evolution of cyclopropylidenevinyl cation is greatly dependent on the three-membered-ring methyl substitution whereas phenyl substitution is not efficient (entries 72–74, see also ref 201).

Allylic products are exclusively obtained by protonation of the central carbon atom of allene substrates bearing highly electron-donating substituents, e.g., ether, acetate, phenyl, or *gem*-dimethyl groups (entries 27–63).

The preferential formation of primary allylic chloride by addition of HCl on the nonsubstituted double bond of the 1,1-dimethylallene **49** could be rationalized by a concerted process in which no positive charge was developed on the allene **49**.²¹⁸

The reactivity of the external double bond has been attributed to the existence of homohyperconjugation of methyl groups (Scheme II).¹⁰⁰

The *Z* vs. *E* stereochemistry observed in acid addition to acyclic allenes **7** is not easy to rationalize. However, if the products (*Z*)-**8** and (*E*)-**8** are formed through linear vinyl cation, the reversal in stereochemistry observed starting from 1,2-butadiene and 1,2-heptadiene could be due to steric and electronic reasons (entries 11–14).

Some in-plane homohyperconjugation of the methyl group in the 2-buten-2-yl cations **7a** (Scheme III) may occur in a through-space interaction; this stabilization overcomes the steric repulsion leading to the *Z* stereoisomer **8a**.

On the other hand, we can admit that homohyperconjugation stabilization of positive charge by methylene group is less effective in the 2-hepten-2-yl cation **7c** and steric hindrance of the *n*-propyl chain is more severe (Scheme IV).

The stereochemistry in strained cyclic allenes is always *cis*, the proton enters from the less crowded face

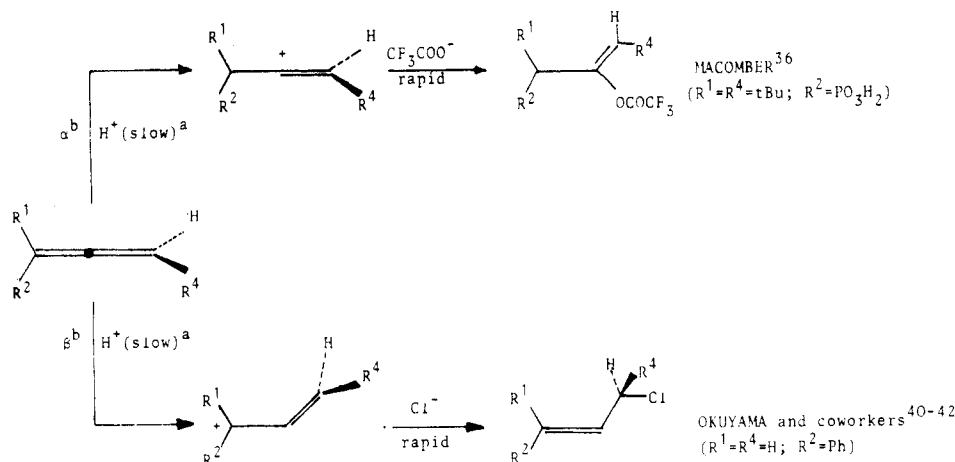
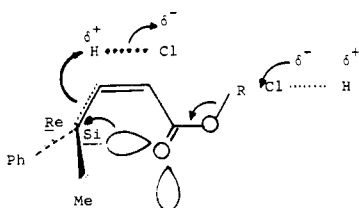
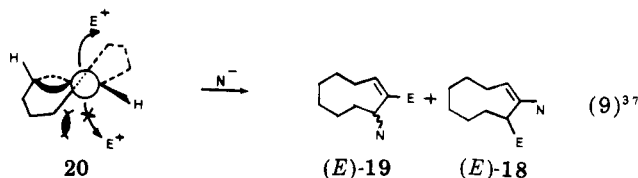


Figure 9. (a) The reaction is second order. (b) Pathways of Chart I.

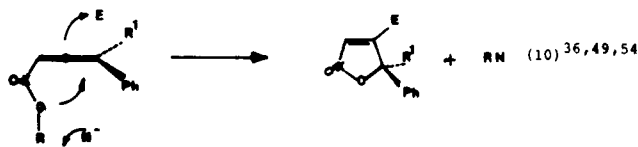
SCHEME V^a

^a Acid (*R*)-26e with R = H; ester (*R*)-28e with R = Me.

of the reacting double bond (entries 22,26 and eq 9 for E = H).



The same *E* stereochemistry is found in acid-catalyzed cyclization of allenecarboxylic and heterocyclic acids and esters because of the intramolecular nucleophilic participation of the carboxyl group (entries 31–60 and eq 10 for E = H).



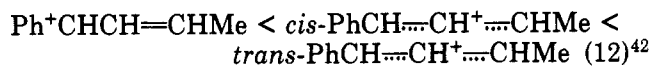
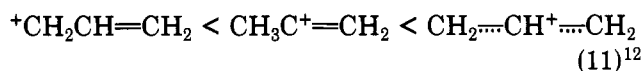
An anti mechanism has been perfectly demonstrated in the stereospecific cyclization of allenecarboxylic acids (eq 5). A bridged species, or more likely, a concerted process involving neighboring-group participation, which occurs by the *si* face of the *pro*-chiral benzylic carbon of the (*R*)-26e enantiomer, could account for the observed stereospecificity (Scheme V).

The lactonization of methyl- and ethyl-substituted acids (*S*)-26e and (*R*)-26p is 100% stereospecific, whereas the reaction with corresponding methyl esters (*S*)-28e and (*R*)-28p is only 83% stereospecific. This difference in stereospecificity of acid-catalyzed cyclization of the derivatives 26 and 28 could be due to the higher energy of bond breaking in O–Me vs. O–H (*vide supra*). These processes are in fact of the S_N2 (R = Me) and E₂ (R = H) type attack by Cl[–]. With ester some

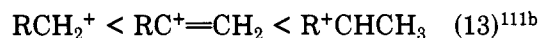
partial racemization may occur by the pathway depicted in eq 8, due to the lowered reaction rate which allows the free rotation of the C–C bond (cf. entries 47 and 49 with 52 and 53).

Protonation of allene can be followed by isomerization to acetylene and to conjugated diene; both are more stable than allene. The acetylene is less reactive than allene and leads to the same vinyl cation. The accumulation of acetylene byproduct leaves no difficulty for interpretation of the mechanism of protonation of allene. However, when more reactive conjugated diene is involved, the study must be done simultaneously on allene and the corresponding conjugated diene under the same conditions.¹⁹

Protonation of allenes offers the best way to study the relative stabilities of vinylic, allylic, and olefinic carbonium ions for which the sequences 11 and 12 were established:



The stabilities of saturated and vinyl cations was already known to follow sequence 13:



Finally, kinetic studies have established that the transfer of proton to allene leading to vinylic and twisted olefinic benzylic cations occurs at the rate-determining step (Figure 9).

III. Halogenation (E = X) Table II


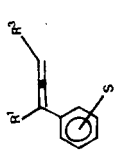
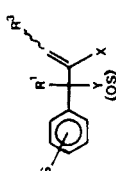
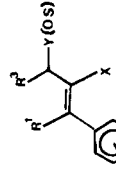
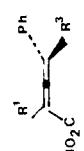
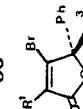
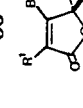
In order to assess the stereochemistry of allene halogenation using XY as reagent variously substituted substrates have been studied. It is already known⁶ that in kinetically controlled halogenation, the monoadduct 3 is formed with Markovnikov orientation (Chart I, E = X). But when the nucleophile is a good leaving group and/or the intermediate formed has stabilized carbonium ion behavior, an allylic rearrangement can occur and all information gathered from these thermodynamically controlled products will not be of any help for this stereochemical study. This mainly happens

TABLE II. Halogenation of Allenic Derivatives

entry	allenic derivatives	reagents	solvent	T, °C	yield, %	product composition, %	ref
		X ⁺ Y ⁻					
1		Cl ₂	HOAc				
2		Cl ₂	CH ₂ Cl ₂ ^a			51	
3		Cl ₂	<i>b</i>			100 (SO = AcO)	65
4		Cl ₂ /O ₂	<i>c</i>	420		40	66
5		PhICl ₂		-30		90	66, 67
6		BrCl	CHCl ₃ ^d	-30		23	68
7		Br ₂	HOAc ^e			46	69
8		BrCl	CCl ₄			100	65
9		BrOH ^f					65
	55			RT	20	56 45.4 ^g 43.5 ^h	70
		XY					
	59						
10	59a (R = CO ₂ Et) ^{i,j}	Cl ₂	CCl ₄	0		50 (45) ^m	73
11		BrCl	CCl ₄	RT	<i>k, l</i>	24	73
12		ICl	CCl ₄	RT	<i>k, l</i>	11	73
13		IBr	CCl ₄	RT	<i>k, l</i>	13	73
14	59b (R = CN)	Br ₂	CCl ₄			100	73, 74
15	59c (R = R)	Br ₂	CCl ₄			minor	75, 74
16		Br ₂	CCl ₄			1	29
17	59d (R = Me)	PhICl ₂	CHCl ₃ ⁿ	-20		73	63, 75
18	59e (R = Et)	ClOH			70	10	69
19	59f (R = <i>n</i> -Pr)	ClOH			70	8	81
20	59g (R = <i>n</i> -Bu)	IOCOPh	C ₆ H ₆	RT		100 { X = I Y = OCOPh	81
		XY					
	12					(Z)	
21	12a (R = Me)	BrY	CCl ₄ ^{p,q}			72 ^r	78
22	(<i>R</i>)-12a α _D	BrCl	CCl ₄ ^{p,q}			(<i>S</i>) 83	77
23	12a α _D	Br ₂	MeOH			(<i>S</i>) 83	77
	12a	Br ₂ or BrCl				(Z)	
24	(<i>R</i>)-12a α _D	IY	MeOH	RT		64 ^{u,l}	77
25	(<i>R</i>)-12a α _D	I ₂	MeOH	RT		α _D -4.1°	78
26	(<i>R</i>)-12a α _D	ICl ^w	MeOH	RT		α _D -13.4°	78
27	(<i>R</i>)-12a α _D	IBr	MeOH	RT		α _D -7.8°	78
28	(<i>R</i>)-12a α _D	I ₂ ^{v,x}	MeOH	RT		α _D -5.5°	78
	12a	I ₂ -MgI ₂ ^{a,l}	ether	RT	51	82 (SO = HO) ^y	79

29	12a	ClY		65	81
30	(R) ¹ -12a $\alpha_D - 11.3^\circ$	ClOH	CHCl ₃	100	69
31	12b (R = Et)	Cl ₂ /O ₂	C ₆ H ₆	66	76b
		IOcOPh			
		XY			
				(Z)	(E)
				85 $\alpha_D - 1.3^\circ$	15 $\alpha_D - 5.2^\circ$
				(Z) (80)	(E) (20)
32	12c (R ¹ = Me, R ² = Et)	ClOH	C ₆ H ₆	67	81
33	12d (R ¹ = Me, R ² = n-Pr)	IOcOPh		50	76b
		XY		5	5
				(Z)	(E)
				45	45
				70	71
				2	13
				28	56 ^{ah}
				100	
34	69a (R ¹ = Me, R ² = H)	Cl ₂ /O ₂	C ₂ F ₃ Cl ₃	72	67
35		PhICl ₂	CHCl ₃ ^{ag}	85	69
36		ClOH	ether		81
37		I ₂ -MgI ₂ ^{al}	CHCl ₃	100 ^{am}	79
38		I ₂		100	181a
39	69b (R ¹ = R ² = Me)	ClOH		100	81
40	69c (R ¹ = Et, R ² = Me)	I ₂	CHCl ₃	100	181a
		XY			
				(Z)	(E)
				74	75
41	R ¹ R ² R ³				
42	73a Me H Me	I ₂ -MgI ₂ ^{al}	ether	100	79
43	73b Me H i-Pr	I ₂ -MgI ₂ ^{al}	ether	85	79
44	73c Me H t-Bu	I ₂ -MgI ₂ ^{al}	ether	ar 34.5	79
45	73d (CH ₂) ₄ Me	I ₂ -MgI ₂ ^{al}	ether	100	79
	73a Me H Me	ClOH	ether	100	81
		XY			
				(Z)	(E)
				76	77
46		I ₂ -MgI ₂ ^{al}	ether	100	79
47		Cl ₂ /O ₂	C ₂ F ₃ Cl ₃	100	67
48		PhICl ₂		100	69
49		ClOH		100	81
				100	
				78	79
				100	
				100	
				100	
50		Cl ₂ /O ₂	CCl ₄		57
51		Br ₂	MeOH	100	57
				minor	major
				80-85	
				-78	
				25	

TABLE II (Continued)

entry	allenic derivatives	reagents	solvent	T, °C	yield, %	product composition, %	ref
							
52	20 (n = 6)	PhICl ₂	THF	-5	84	90 ^{af}	69
53	20	I ₂ -MgI ₂ ^{al}	ether	RT		100	79
54	20	Br ₂				60	82, 88
55	(R)-(+)-20	Br ₂	CCl ₄	z	78	61 (R)-(+)-f,aa,ab	80
56	(R)-(+)-20 α _D 23.4°	Br ₂ ^{ae}	MeOH	0	85	32 (R)-(+)-f,ad	80
57	(S)-(-)-20	Br ₂	MeOH			(S)-(-)	90
58	22 (n = 7)		MeOH			100	89
59	82 (n = 5)		MeOH			100	89
60	20 (n = 6)	IN ₃				100	191
61	17 (n = 10)	IN ₃				100 (Z)	191
		XY					
							
							
62	84a H H H	Br ₂	MeOH	0		84 (SO = MeO)	87
63	84b H H H	Br ₂	MeOH	0		89 (SO = MeO)	87
64	84c H H H	Br ₂	MeOH	0		78 (SO = MeO)	87
65	84d Me H H	Br ₂	MeOH	0		54 (SO = MeO)	87
66	84a H H H	Br ₂	CS ₂	0		2	87
67	84a H H H	IBr	CS ₂	0		20	87
68	84a H H H	Br ₂	CS ₂	-70		25	87
69	84a H H H	Cl ₂	MeOH	0		70 (SO = MeO)	87
70	84a H H H	Br ₂	MeOH	0		84 (SO = MeO)	87
71	84a H H H	Br ₂	MeOH	-70		100 (SO = MeO)	87
72	84a H H H	IBr	MeOH	0		100 (SO = MeO)	82
73	84c H Me H	I ₂ /MgI ₂	ether	RT	43	20 (E) (SO = HO)	79
74	84f Me Me H	I ₂ /MgI ₂	ether	RT	28	80 (E) (SO = OH)	79
							
							
							

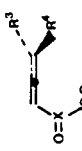
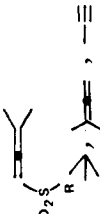
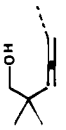
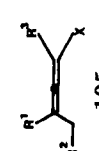
75	R^1	R^3	(S)-(+)-91a-d			70-90		85
76	H	H	91a	Br_2	CCl_4	(S)-(+)-92a-d (O.Y. = 100%)	85	
77	H	Me	91b	Br_2	CCl_4	(S)-(+)-92a-d (O.Y. = 100%)	85	
78	H	<i>i</i> -Pr	91c	Br_2	CCl_4	(S)-(+)-92a-d (O.Y. = 100%)	51	
79	H	<i>t</i> -Bu	91d	Br_2	CCl_4	(S)-(+)-92a-d (O.Y. = 100%)	51	
80	H	Et	91e	Br_2	CCl_4	(S)-(+)-92a-d (O.Y. = 100%)	51	
81	Et	H	91f	Br_2	CCl_4	(S)-(-)-92e (O.Y. = 100%)	51	
82	Et	Me	91g	Br_2	CCl_4	(+)-92g	51	
83	Et	Et	91h	Br_2	CCl_4	(-)-92h	51	
	Me	Et	91i	Br_2	CCl_4	(+)-92i	51	
	H	H	91j	Br_2	CCl_4	(-)-92j	51	
	H	Et	91k	Br_2	CCl_4	92k	51	
	Ph	naphthyl	91l	Br_2	CCl_4	92l	51	
								
84			93 (X = C) allenecarboxylate ⁱ	Br_2	CCl_4	94 γ -lactone	83	
85			95 (X = S) allenesulfinate ⁱ	Br_2	CCl_4	96 γ -sultine	53, 83	
86			97 (X = PPh) allenephosphinate ⁱ	Br_2	CCl_4	98 phospholene oxide	53, 83	
87			99 (X = POEt ₂) allenephosphonate	Br_2	CCl_4	100 phospholene oxide	83	
88			101 (X = POH) (R)(-)-allenephosphonic acid (R = R ³ = H, R ⁴ = <i>t</i> -Bu)	Br_2	CCl_4	100 (R)(+) (O.Y. = 42%)	86	
89				Br_2	CCl_4	96 γ -sultine	53, 83	
90				Br_2	CCl_4		84	
			103 (α_D 9.3°)	I_2 -MgI ₂ ether		104 (α_D 0°)	79	
						(Z) 106 (E)		
						(Z) 107 (E)		
91	H	H	105a			27	100	
92	Me	H	105b			24	54 ^{ao} 18	
93	Me	H	105c			31	48 ^{ao} 9	
94	Me	H	105d			80	62 6	
95	(CH ₂) ₄	H	105e			61	100 8	
96	Me	H	105f			90	100	
97	H	CH ₂ Ph	105g			37	55	
98	Ph	H	105h			70	14.6	

TABLE II (Continued)

^a The presence of $\text{BF}_3 \cdot \text{OEt}_2$ does not change the ratio 40:60 of the mixture 51:52. ^b Ionic medium made by eutectic mixture of NaAlCl_4 - KAlCl_4 salts. ^c 4.3% of 2-chlorohex-1-en-5-yne (53) and 1.5% of 2,5-dichloro-1,5-hexadiene (54) are also formed. ^d PhICl_2 is used for ionic conditions. ^e In all solvents only the dibromide 51 is formed. ^f The brominated allylic alcohols 56 and 57 are stable under reaction conditions. ^g The kinetic secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.83$ (for two deuterium) or $k_{\text{H}}/k_{\text{D}} = 0.91$ (for one deuterium) has been established by ^1H NMR by the ratio of the unsaturated allylic alcohols 56:57. ^h The thermodynamic secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.77$ (for two deuterium) or $k_{\text{H}}/k_{\text{D}} = 0.88$ (for one deuterium) has been determined from the 56:57 ratio after acid equilibration. ⁱ The halogens used are $\text{XY} = \text{Cl}_2, \text{BrCl}, \text{ICl}, \text{IBr}$, and I_2 . ^j The reaction is conducted in the presence of NaHCO_3 to avoid the nucleophilic addition of Y^- that is catalyzed by HBr . ^k CH_2Cl_2 and ether are also used. ^l The complement to 100% is constituted by the nucleophilic adducts (see footnote *j*). ^m Composition of the stereoisomers *E* and *Z* in CH_2Cl_2 . ⁿ The reaction is conducted with 5% of CF_3COOH . ^o PREVOST reagent ($\text{PhCOO})_2\text{Ag}^+ \text{I}^-$ is used. ^p The $\text{E}2$ elimination of dibromide 63 by some known reverse process. ^q The first reaction leads to the conjugated diene and not to the starting chiral 2,3-pentadiene 12a and the second affords the enyne and not the bromomethoxy 63. ^r By means of silver-assisted methanolysis the mixture of chiral dibromides 63Z:63E = 83:17 with $\alpha_{\text{D}} - 7.35^\circ$ is transformed into a chiral mixture of bromo ethers 63Z:63E = 95:5 with $\alpha_{\text{D}} + 0.6^\circ$. ^s 5% of dibromide is also present. ^t The structure has been determined by methoxymercuration and bromodemercuration. ^u α_{D} of the iodo ethers is corrected to take into account the presence of the dihalides. ^v The methoxyiodination of (*R*)-(-)-12a in the presence of four-fold excess of NaI affords optically inactive iodo ether. ^w In pyridine the iodochlorination of allene 12a gives the (*Z* + *E*) mixture 64(85:15) of iodo chlorides. ^x In CCl_4 the diiodo adduct from the reaction of iodine and the 2,3-pentadiene is unstable. ^y 18% of $\text{O}(\text{CHMeCl}=\text{CHMe})_2$ with *Z* configuration is also formed, the iodo alcohol 64Z is a product of aqueous workup. ^z The composition of normal and transannular dibromides is nearly stable between -75 and 30°C . ^{aa} The dibromides 80-81 lose HBr during the gas-liquid chromatography. ^{ab} Ag-assisted methanolysis of dibromides 80-81 with $\alpha_{\text{D}} + 2.38^\circ$ affords a bromomethoxy mixture with $\alpha_{\text{D}} + 1.00$ and roughly the same geometrical isomerism for the product. ^{ac} The reduction of the bromomethoxy 81 with $\alpha_{\text{D}} + 6.26^\circ$ by Na in liq. NH_3 affords the *cis*-4-methoxycyclohexene with $\alpha_{\text{D}} + 2.95^\circ$ and unknown configuration. ^{ad} The same reaction of bromomethoxy (*E*)-80 gives rise to the (*R*)-*cis*-3-methoxycyclohexene. ^{ae} The optical rotation ($\alpha_{\text{D}} + 12.92^\circ$) of the dibromides formed in methanol solution is 5 times higher than in CCl_4 . ^{af} 10% of unknown product is also formed. ^{ag} 5% of CF_3COOH is present. ^{ah} 16% of unknown compound is also formed. ^{ai} $\text{R} = \text{R}^2 = \text{R}^3 = \text{Me}$. ^{aj} With pyridine. ^{ak} NaHCO_3 is present. ^{al} Excess of I_2 and MgI_2 . ^{am} Probably formed after 1,3-allylic migration of iodide. ^{ao} Initially a transhalogenation occurs. ^{ap} Hydrolysis of the triiodo product occurs during the workup. ^{aq} The addition takes place on the iodinated double bond. ^{ar} 9% of $\text{Me}_2\text{C}=\text{C}(\text{CHOH})\text{Bu}-t$ (89) is also formed.

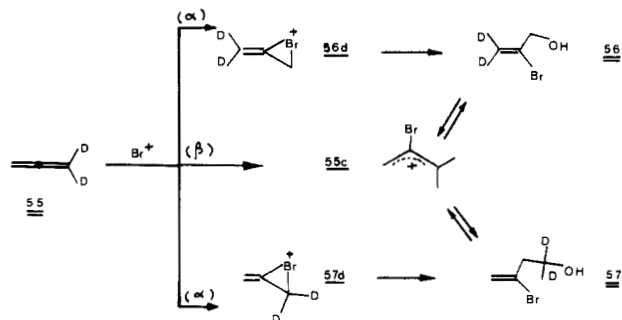


Figure 10. Reference 70. Secondary isotopic effect of deuterium $k_{\text{H}}/k_{\text{D}} = 0.71$ is generally attributed to the change of the out-of-plane C-H vibration (800 cm^{-1} to 1350 cm^{-1}) which derives from the change of carbon hybridization (sp^2 to sp^3) as it occurs during addition to a double bond.⁷¹

when halogenation takes place in CCl_4 and $\text{C}_2\text{F}_3\text{Cl}_3$.

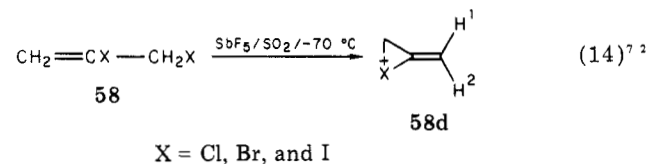
A. Acyclic Derivatives

1. Allene and Halonium Species

In acetic acid the chlorination of allene 1 provides the α -chloroallylic acetate 51 exclusively, whereas in chloroform and methylene chloride the reaction forms up to 60% propargyl chloride 52 (entries 1-5). At a lower temperature and in ionic conditions some unsaturated chlorinated dimers have been isolated (entry 4) (See footnote *c* of Table II.) No propargyl bromide was obtained by bromination of allene 1 (entries 6-8).²⁰³

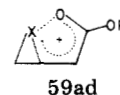
Addition of hypobromous acid to the 1,1-dideuterio-propadiene 55 affords a mixture of allylic alcohols 56 and 57 through the bromonium species 56d and 57d that occurs with a kinetic α -secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.83$. It has been found that this value was higher than the corresponding thermodynamic isotope effect obtained during acid equilibration of the allylic alcohols 56-57 $k'_{\text{H}}/k'_{\text{D}} = 0.77$ via the allylic entity 55c (entry 9, Figure 10).

In the presence of a weak nucleophile, the direct observation of these halonium entities has been possible and the ^1H NMR spectroscopy shows the magnetic nonequivalence of their vinylic protons H^1 and H^2 .



2. Monosubstituted Allenes

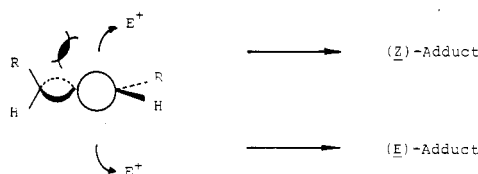
Halogenation of the allenic ester 59a occurs exclusively on the external double bond affording crotonic esters dihalides 61. Except for chlorides, the kinetic ratio *Z/E*, always higher than the thermodynamic one, has been attributed to the existence of delocalized species 59ad with neighboring participation of carb-



ethoxy group (entries 10-13) (vide infra).

The bromination of the nitrile 59b also takes place on the more nucleophilic double bond because of the

SCHEME VI



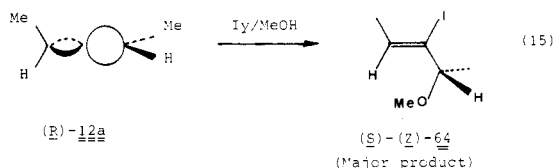
highly electron-withdrawing effect of the cyano group (entry 14).

The halogenation of 1,2-dienes occurs mainly (Cl, Br) if not exclusively (I) on the more substituted double bond (entries 15–20, except 17) although the chlorination using iodobenzene dichloride under ionic conditions leads up to 74% of external attack (entry 17).

3. 1,3-Disubstituted Allenes

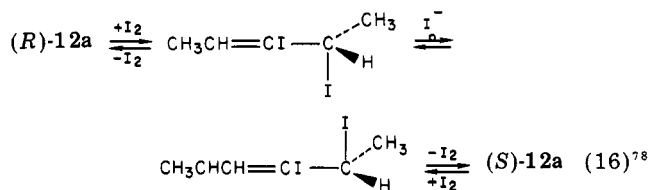
(a) **Z Stereoselectivity.**^{76b,81} Whatever the halogens and the solvent, the halogenation of 1,3-dialkylated allene **12a–d** Scheme VI is always stereoselective. The ratio of geometrical isomers of vinylic halides **64** (*Z*:*E*) is always greater than 1 and varies from 72:28 to 96:4 (entries 21–33). This stereoselectivity could correspond to the entry of the electrophile on the more hindered face of the double bond (vide infra).

(b) **Anti Stereospecificity.**^{77,78} The stereospecificity of the methoxyiodination of acyclic allenes is anti, since the chiral 2,3-pentadiene (*R*)-(-)-**12a** provides the op-



tically active iodo ether **64Z** with an (*S*) configuration (entries 25–27) very probably via an iodonium species **12ad** (see Chart I with E = I).

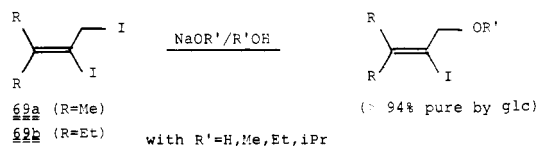
The degree of this anti stereospecificity, measured by the rotation of optically active ether **64Z**, will decrease with increasing nucleophilicity of the counter ion Y: $\text{Cl}^- < \text{Br}^- < \text{I}^-$ (entries 25–27). The product **64Z** is found to be inactive when methoxyiodination of chiral allene **12a** is conducted with a large excess of iodide. The unreacted starting material has been found to be racemized to the extent of 39% after 50% conversion. This racemization has been attributed to the nucleophilic substitution of the *vic*-diiodides by the excess of iodide, which occurs with inversion ($\text{S}_{\text{N}}2$). Elimination mechanism of I_2 is assumed to be anti.



The chlorination of allene (*R*)-(-)-**12a** (entry 30) affords optically active dichlorides **65**, when the reaction is conducted under ionic conditions (low temperature and presence of oxygen).

With unsymmetrical allenes **12d**, the benzoyloxyiodination, using Prévost reagent,^{76a} is still regioselective and stereoselective with formation of four products all of them being of M type, *Z*-isomers being predominant (entry 33).

SCHEME VII



4. 1,1-Disubstituted Allenes

Addition of hypochlorous acid to *gem*-disubstituted allenes is 100% chemo- and regioselective. The reaction occurs in the internal double bond, the more nucleophilic one, and affords the adduct **70** with Markovnikov orientation (entries 36,39). The iodination of allenes **69** gives exclusively the more stable primary allylic bisiodide **71**, after an allylic rearrangement of I^- in the nonisolated tertiary product **70** (entries 37,38,40). Nucleophilic substitution of the compound **71** affords good yields of a corresponding α -iodo allylic ethers (Scheme VII).

In nonpolar solvents, the chlorination of 1,1-dimethylallene is no longer regio- and chemoselective, products of allylic transposition **71** and elimination **72** are predominant. The latter is due to loss of a proton from the intermediate with strong carbonium ion behavior (entries 34, 35).

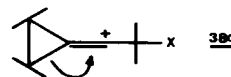
5. Trisubstituted Allenes

Again, halogenation of the alkyl trisubstituted allenes **73** is regio- and chemoselective. The reaction is also 100% *Z* stereoselective, HY being lost in the product **75** (entries 41,42,44,45). A reverse 100% *E* stereoselectivity is observed when the substituent R^3 borne by the unreacted double bond is the *tert*-butyl group (entry 43).

6. Tetrasubstituted Allenes

Halogenation of tetramethylallene is 100% regioselective with Markovnikov orientation, the diene **77** is the expected product obtained after dehydrohalogenation although the chlorhydrin **76** is stable (entries 46–49).

Halogenation of permethylcyclopropylideneallene affords the acyclic enyne **78** and homopropargylic ether **79** as major products. These products were formed, similar to the protonation reaction, through the incipient vinyl cation **38a** (entries 50, 51, for the evolution



of **38a** see Figure 7).

B. Cyclic Derivatives

1. 1,2-Cyclononadiene

(a) **E Stereoselectivity.** In nonpolar solvents chlorination and iodination of 1,2-cyclononadiene afford the 2,3-dihalocyclononene (*E*-**80**) as normal addition product, whereas the bromination in CCl_4 of the same allene is contaminated by up to 39% of transannular compound (*E*-**81**) formed by a 1,5-hydrogen shift. The amount of the latter product increases to 68% when bromination is conducted in methanol solution (entries

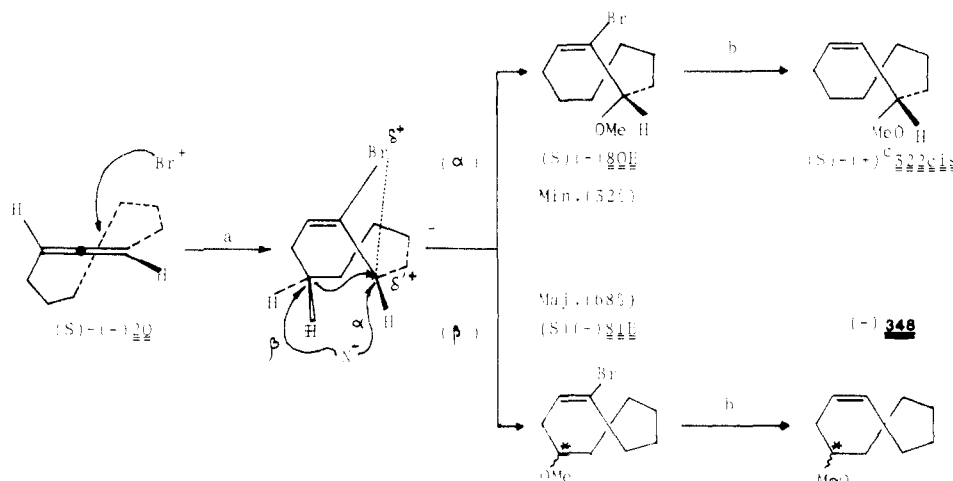


Figure 11. References 80 and 90. (a) Br₂, MeOH. (α) Pathway to the normal adduct 80. (β) Pathway to the transannular product 81. (b) Na-liquid NH₃. (c) See footnotes *ac* and *ad* of Table II.

52–56). Previously considered as *Z*-stereoisomer,⁸² the structure of the dibromo compound 80 was subsequently corrected and shown to have the *E* configuration.⁸⁸ There are no such transannular products in the bromination of 8- and 13-membered ring allenes (entries 58, 59). The strained 1,2-cyclononadiene 20 affords the 3-azido-2-iodocyclononene with *E* configuration whereas the normal addition product 80 is obtained with *Z* configuration starting from the large ring allene 17 (entries 60, 61).

It has been shown, that the transannular product was formed through a species with strong carbonium ion behavior. Thus, the S_N1 process which occurs during methanolysis of the allylic iodo sulfone (*E*)-80 (X = PhSO₂, Y = I, *n* = 6) is responsible for the formation of 18% of the transannular 4-methoxy-1-(phenylsulfonyl)cyclononene (*E*)-81 (X = PhSO₂, SO = MeO, *n* = 6)⁸⁰.

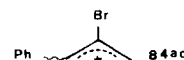
(b) **Anti Stereospecificity.** The syn-anti stereochemistry of the bromination of 1,2-cyclononadiene 20 has been simultaneously studied by Caserio⁸⁰ and Bach⁹⁰ using (*R*)-(+)- and (*S*)-(–) enantiomers of the chiral substrate, respectively. In polar solvent (MeOH), the bromomethoxy 80 formed in both experiments is optically active (entries 56, 57). The structure of the asymmetry carbon C-3 has been established by correlation with that of (*R*)-*cis*-3-methoxycyclononene which is levorotatory (see footnotes *ac*, *ad*, of Table II). Methoxybromination of the allene 20 is then stereospecific. Then, the electrophilic methoxybromination of the (*R*)-1,2-cyclononadiene 20 providing the product 80 (normal addition with *R* structure) proceeds by an anti mechanism, the degree of this stereochemistry being unknown (Figure 11). Bromination of allene 20 in CCl₄ was also shown to be anti stereospecific, the structure of the dibromide has been correlated to the bromomethoxy compound obtained by silver-assisted methanolysis (see footnote *ab* of Table II) (entry 55).

Very interestingly, the mixture of dibromides obtained by bromination in methanol of chiral cyclic allene 20 has been formed by an anti process, which is at least 5.5 times more stereospecific than the same mixture formed in carbon tetrachloride (see footnote *ae* of Table II). This result is in agreement with the known stabilization of carbocationic species, in polar solvent, observed in the bromination of olefins.^{94,180}

C. Aromatic Derivatives

1. Regioselectivity: I⁺ > Br⁺ > Cl⁺

At low temperature the methoxybromination and iodination of phenylallene is 100% chemo- and regioselective (entries 71, 72). The halobenzyl ether 85 with Markovnikov orientation was formed by attack of the internal double bond. A solvent change from protic (MeOH) to aprotic (CS₂) affords reversal in chemoselectivity of phenylallene bromination (entries 62, 66). The formation of the product 86 is probably due to the intervention of allylic species 84ac because of the la-



bility of benzylic halide 85 that increases with increasing temperature (entries 66, 68, 70, 71).

When R¹ = Me, the benzylic intermediate becomes tertiary and some loss of proton can occur in nonprotic solvent, leading to a certain amount of iodinated conjugated diene with *Z* configuration (cf. entry 74 to 65).

The observed regio- and chemoselectivities have been attributed to the existence of halonium species 84ad in

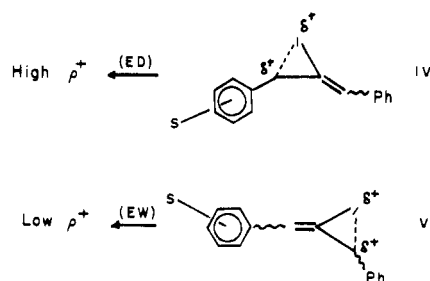


which the carbocationic character varies mainly with the polarity of the solvent (entries 62, 66) and the donating effect of the substituents (entries 62, 65, 73, 74); the stability of this intermediate increases with the size of the electrophile as I⁺ > Br⁺ > Cl⁺ (entries 69, 70, 72).

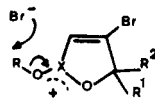
2. Kinetics

Kinetic study of the iodination of 12 1,3-diaryllallenes in 1,2-dichloroethane is consistent with the linear free energy relationship of Brown–Okamoto with a ρ⁺ value, high enough to imply a carbocationic intermediate (–3.2) but not sufficiently high to be a benzylic localized one (–4 to –5). Then this charge can be spread over an allylic moiety. An iodonium intermediate, if any, should give, by analogy with the bromination of monosubstituted *trans*-stilbenes in methanol, two ρ⁺ constant values, one high and the other low, corresponding to the species IV and V (Scheme VIII) respectively and the relationship log *k* vs. ρ⁺ will then be curved.^{94,199}

SCHEME VIII



SCHEME IX



This has not been observed and the transition state of iodination of monosubstituted 1,3-diphenylallenes is very similar to a planar diphenylallyl cation. Equal values for racemization and addition rates are in agreement with a symmetrical intermediate formed in a slow step common to both reactions.

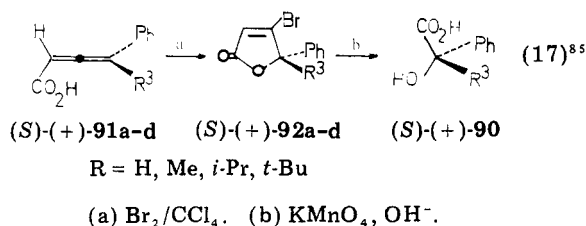
D. Functional Derivatives

1. Mechanism of Bromolactonization

Halogenation of functional allenic derivatives provides cyclic bromo esters because of neighboring-group participation of the nucleophilic function. γ -Bromo lactones **92a–l** are then formed from carboxylic acids and esters, γ -bromo sultines **96** from sulfinic acids **95** and sulfones **102**, finally, bromooxaphospholones **98** and **100** are obtained from phosphonic esters **97** and **99** (entries 75–89). The cyclic bromination of various esters (Scheme IX, X = C, S, P) has been established to proceed through an S_N2 attack of bromide ion on the methyl substituent; whereas with the sulfone **107**, the corresponding 4-bromo- γ -sultine is only obtained when the alkyl substituent can afford a stabilized carbonium ion, e.g., *tert*-butyl, allenyl, and propargyl. The S_N1 process is necessary to agree with the decreasing rate of nucleophilic attack due to the steric hindrance of the α - SO_2 group.⁹¹ A bromo dienic sulfone is then formed by an elimination process when sulfone bears an alkyl group (Figure 12).

2. Anti Stereospecificity

Early in 1967, the 100% anti stereospecificity of the bromolactonization of the trisubstituted allenic acid has been settled⁸⁵ (entries 75, 76), the (*S*)-(+)-enantiomer of chiral acid **91a–d** leading to the 4-bromo- γ -lactone



92a–d with the same configuration and 100% optical yield. The structure and the optical purity have been

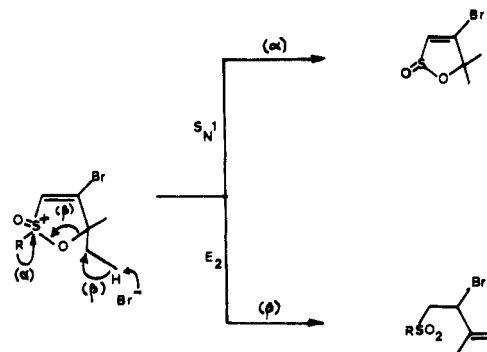


Figure 12. References 83 and 91.

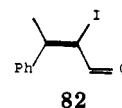
correlated to the known α -hydroxy acid.

Bromolactonization of tetrasubstituted allenic carboxylic acids is stereospecific⁵¹ (entries 78–81), unfortunately the configuration and the optical purities of the 3-alkylated-4-bromo- γ -lactones **92g–j** are not yet known. Whereas bromophospholenation of the monosubstituted allenic phosphonic acid (*R*)-(-)-**101** is 42% anti stereospecific (entry 88).

Surprisingly, bromination of the chiral allenic alcohol **103** furnishes the racemic β -bromodihydropyran **104** (entry 90) whereas the corresponding sulfenylation is stereospecific (*vide infra*).

3. Iodination of Haloallene

Iodination of the trisubstituted haloallenes **105d–g** occurs on the nonhalogenated double bond leading to the *vic*-diiodo conjugated dienes **106** obtained after a loss of HI (entries 94,97). This *vic*-diiodo compound is still formed even when the starting material is chlorinated **105b** or brominated **105c**, probably because the reaction is preceded by a transiodination (entries 92, 93). The iodhydrin **107** is formed exclusively during iodination and aqueous workup of the unsubstituted 1-iodo-1,2-butadiene **105a** (entry 91). When a phenyl group is present, iodination of the 1-phenyl-3-iodoallene **105h** affords predominantly (85.6%) the (*E*)- α -iodo- β -methylcinnamaldehyde (**82**), through iodination of the



double bond bearing the iodine (entry 98).

Finally, the trisubstituted allene bearing a *tert*-butyl group such as compounds **73i** and **105i** are unreactive



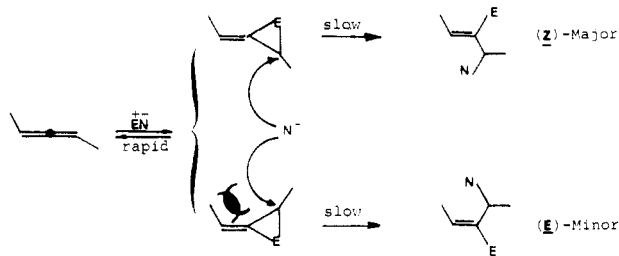
in the presence of excess of I_2 - MgI_2 in ether solution.

E. Discussion

In kinetically controlled halogenation, the electrophilic addition to allenic derivatives is chemoselective. The reaction occurs exclusively on the more nucleophilic double bond (entries 10, 14, 20, 36, 39, 45, 49, 75, 97).

The halogenation reaction is regioselective leading to central attack of the allene linkage by the electrophile X^+ with the formation of Markovnikov-orientated products. The exception of the allene **38** is due to the participation of the cyclopropylidene ring that is in-

SCHEME X



involved during the halogenation reaction.

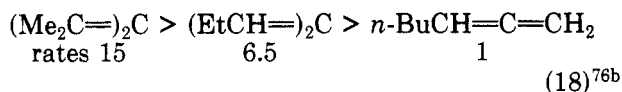
The *Z* stereoselectivity observed in the bromination and iodination reactions could be reasonably explained by reversible formation of halonium ion, with nucleophilic attack by Y^- being rate controlling and occurring from the least hindered side of the double bond, leading predominantly to the *Z* adduct **61** (entries 11–13, 21–33, 44, 45, 61, 74).

The 100% *E* stereoselectivity encountered in halogenation of strained cyclic allenes is consistent with the electrophile entering on the less crowded face of the reacting double bond (entries 52–60 and eq 9 with $E = X$).

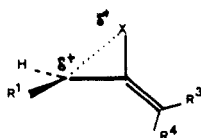
Solvents play a very important role in the steric course of the reaction. The replacement of a nonpolar solvent by a protic one increases the amount of transannular product **81** during the bromination of 1,2-cyclonadiene and in this latter solvent the optical purity of the bromides **80** and **81** is 5 times higher than in CCl_4 (entries 55, 56). This change of solvent can also reverse the chemoselectivity of the reaction (entries 62, 66).

Chemo- and stereoselectivity of allenic derivative halogenation is dependent upon the lifetime of the intermediate and varies in the order $I^+ > Br^+ > Cl^+$.

A competitive iodination of variously substituted aliphatic allenes using Prévost reagent^{76a} shows the electrophilic nature of this addition.



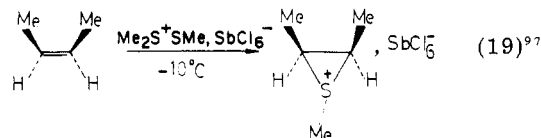
The variation in the character of the transition state, in going from the stereospecific anti addition to 1,3-dialkylallenes^{77,78} to the nonstereospecific iodination of 1,3-diaryllallenes⁹² via symmetrical intermediates, is quite similar to that found for addition to olefins,^{93–95} the former proceeding with the occurrence of bridged halonium ions as intermediates.



- 20, $R^3 = H$, $R^1 + R^4 = (CH_2)_6$ (entries 55–57)
 12a, $R^1 = R^3 = Me$, $R^4 = H$ (entries 22, 23)
 84a, $R^1 = Ph$, $R^3 = R^4 = H$ (entries 71, 72, 75, 76, 88)

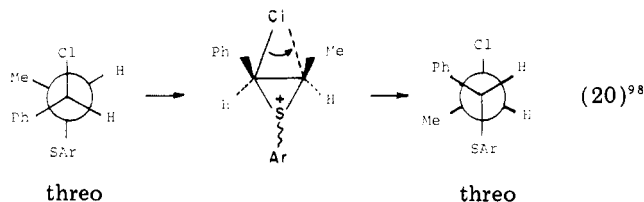
IV. Sulfenylation ($E = S-$) and Selenylation ($E = Se-$) (Table III)

Electrophilic addition of reagent $ArSX$ on olefins¹¹⁰ and unsaturated substrates has been reviewed recently.⁹⁶ It has been shown that from *cis*-2-butene an



episulfonium salt can be isolated in the absence of any nucleophile. The structure of this bridged species has been determined by 1H NMR spectroscopy and was shown to have *E* configuration.

Stereochemistry of the arenensulfonyl chloride addition on *cis*-methylstyrene has been shown to be anti.



The kinetically controlled threo adduct $PhCHClCH-(ArS)Me$ with Markovnikov orientation will isomerize to give the thermodynamically controlled threo adduct $PhCH(SAr)CHClMe$ with anti-Markovnikov orientation. This stereospecificity can be explained by the same bridged species.

Sulfenylation and selenylation of variously substituted allenic derivative reagents are now discussed.

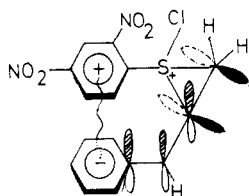
A. Allene²⁰³

Sulfonyl chlorides ($RSCl$) add to allene itself leading mainly (entries 1–4), if not exclusively (entry 5), to a monoadduct **108** with Markovnikov orientation in which the sulfur is bound to the central carbon. The kinetically controlled product **108** is stable only when the substituent on the reagent is electron withdrawing (thioacetyl and 2,4-dinitrophenyl). Some thermodynamic control occurs with the formation of prototropic rearranged product **110** and a mixture of stereoisomers is formed when the sulfenylation is performed with $MeSCl$ and $PhSCl$. The stability of the product **108** with an allylic chlorine will then depend on the nature of reagent substituents in $RSCl$ as in the following sequence: $Me \approx Ph \approx AcS \approx 2,4$ -dinitrophenyl. On standing at room temperature, the major product **108** affords the bisadduct **109** (entry 5). The amount of compound **111** obtained by hydrochlorination of rearranged product **110** is also increased on standing (entries 2–4).

B. Monosubstituted Derivatives

Sulfenylation of an aliphatic 1,2-diene using 2,4-dinitrobenzenesulfonyl chloride (DNBSC) is 100% chemoselective; the addition occurs only on the more substituted double bond. The reaction has also been shown to be 100% regioselective with Markovnikov orientation for the product **114** (entries 6–8). In contrast, 29% of the attack on the external double bond of the 1,2-butadiene **59d** leads to a mixture of stereoisomers **115** ($Z/E = 1.66$) when the reagent is benzenesulfonyl chloride (BSC) (entry 12).

Sulfenylation of allenic esters **59a** occurs on the two double bonds, the sulfur being always fixed on the central carbon of the allenic system. With allene **1** some olefin isomerization of the product **114** can take place affording a mixture of more stable stereoisomers ($Z +$

SCHEME XI¹⁰⁴

E)-EtOCCCCl=C(SR')Me 116 (entries 10,11).

The reaction with the phosphonic ester **59i** shows complete regio- and chemoselective benzenesulfenylation with the formation of Markovnikov orientation product by exclusive addition on the internal double bond (entry 13).

It has been recently found that alkylsulfenyl chlorides add to the cumulated diene of vinylallenephosphonic esters **59j** with different chemoselectivity leading to a mixture of five-membered heterocyclic compounds of sulfur and phosphorus. The former predominates at low temperature and has been obtained by nucleophilic participation of the isolated double bond whereas the latter is formed at higher temperature with nucleophilic participation of the phosphonic acid (entry 14).

The most interesting features are the chemoselectivity and the *Z* stereoselectivity observed in the sulfenylation of the phenylallene **59h** providing predominantly the product **115** by addition on the nonsubstituted double bond (entry 9). It has been proved that the external attack was a kinetically controlled reaction and took place through an episulfonium ion formed during the rate-determining step. All of this is strongly supported by an α -secondary isotope effect $k_H/k_D = 0.92$ (for one deuterium) observed in the sulfenylation of γ,γ -dideuterated phenylallene PhCH=C=CD₂ using DNBS as reagent; under the same conditions no isotopic effect is found with PhCD=C=CH₂ ($k_H/k_D = 1.01$).¹⁰⁴ This chemoselectivity offers the advantage of retaining conjugation of the α,β -double bond of phenylallene. The chemoselectivity observed in sulfenylation of phenylallene contrasts with the one shown during protonation and halogenation of this substrate (vide supra).

The *Z* stereochemistry has been attributed to the existence of a charge-transfer complex between the two aryl groups of allene and reagent; these aryl groups will be retained on the same side of the unreacted double bond. Then, only the essentially nonconjugated double bond of phenylallene, the "orthogonal π -bond", is reactive toward DNBS (Scheme XI). A very similar trend was obtained during the sulfenylation of 1-phenylpropyne.¹⁰⁵

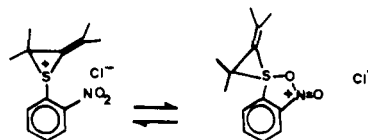
C. Disubstituted Derivatives

1. 1,3-Disubstituted Acyclic Allenes

(a) **Sulfenylation.** The reaction of DNBS with acyclic symmetric alkyl 1,3-disubstituted allenes is completely regioselective with Markovnikov orientation, the sulfur being linked to the central carbon atom (entries 15–18).

The reaction was also shown to be *E* stereoselective, the kinetically controlled ratio of stereoisomers *E/Z* was shown to increase with the bulkiness of alkyl substituent cis to the arylthio group (entries 14–16). This steric course was confirmed with variously substituted are-

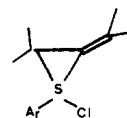
SCHEME XII



nesulfenyl chlorides (Table IV).

It was important to determine the cationic character of the sulfur in the intermediate and to see what stabilization of this positive charge was offered by the *o*-nitro group via neighboring group participation during the sulfenylation reaction (Scheme XII).¹⁸⁴

The reaction of various *o*-nitroarenesulfenyl chlorides shows no special ortho effect by electrophilic addition to 1,3-disubstituted allenes (Table IV). The intermediate of the thiiranium type will then be a covalent entity and not an ion pair.



The role of steric and electronic effects during the rate- and product-determining steps for the addition of arenesulfenyl chlorides to 1,3-disubstituted allenes has been examined and they showed little effect on the rate-determining step (Tables IV, V, and VII).

A kinetic study of the addition of *p*-chlorobenzenesulfenyl chloride (PCBSC) to the five methyl-substituted allenes and to ethylene has recently¹⁰¹ given similar results. These surprising results support the view that substituent effects are transmitted across both the double bonds in sulfenylation of allenes. The electrophilic character of this addition is shown by the increasing rate observed when the hydrogens of allene are substituted by methyl groups and by the fact that the para chlorinated reagent adds 3.8 times faster than the benzenesulfenyl chloride on the five methyl-substituted allenes (except for 1,2-butadiene, which reacts 8.9 times faster).

(b) **Selenylation.** Very recently the reactions of benzeneselenenyl bromide (BSeB) and 2,4,6-trimethylbenzeneselenenyl bromide (TMBSSeB) with 1,3-disubstituted allenes have been fully investigated.¹⁸⁵

In all cases the phenylseleno moiety of benzeneselenenyl chloride (BSeC) attacks regioselectively the central carbon atom with *Z* preference under kinetic control. This stereochemistry is reversed with the crowded selenenyl reagent TMBSSeB independent of which allene is used; perhaps "steric approach control" is an explanation (Table VI).

Whereas benzenesulfenyl chloride shows only minor variation in the second-order kinetics when 1,3-alkyl substituents of allenes are changed, the corresponding selenenyl reagent exhibits very large fluctuations (Table VII). In contrast to the corresponding sulfur reagent,¹⁰¹ the rates of BSeC addition to allene and ethylene and their five methyl-substituted derivatives show a greater effect on the addition rate for the methyl substituted derivatives.¹⁸⁸

2. Cyclic Allenes

The exclusive formation of the *E* adduct from the reaction of DNBS with 1,2-cyclononadiene **20** can be rationalized in terms of steric hindrance. The *Z* isomer

22		112 a-q (17 examples)	70-98	113 a-q 	182
23		49	PhSeCl		120
24		DNBSC		Major	100
25		DNBSC		40	109
26		Me ₂ S ⁺ SMe BF ₄ ⁻		100 (N = SMe ₂) ⁿ	101
		PhSeCl		20	
27		73a	CH ₂ Cl ₂		101
		36	R'SCl		122
28		AcSSCl	80		124
29		DNBSC ^b	55	100	99
30		PhSeCl	75	55 ^m	103
			RT	75	101
				25	
					123
				Z (40)	
				E (32)	

^a Values in brackets are ratios after isomerization. ^b 2,4-Dinitrobenzenesulfonyl chloride. ^c 6% of the anti-Markovnikov product is also present. ^d The structure of the major product has been confirmed by Jacobs.¹⁰³ ^e On standing at 25 °C, the major product 108 gives the bisadduct 109. ^f The exclusive product 114 is stable under reaction conditions. ^g PhCHClC(SR)=CH₂ and (Z + E)-PhCCl=C(SR)CH₃, 125 are also present in small quantities. ^h The product of external attack is the kinetically controlled compound. ⁱ These products are unstable; an isomerization occurs leading to a mixture of the stereoisomers Z and E. C₂H₅OCOC(=C(SR)CH₃), 130. ^j The monoadduct (Z)-117 with Markovnikov orientation was previously attributed to the anti-Markovnikov orientation product 118. ^k Conjugated diene CH₂=C(CH₃)-C(SAr)=CH₂ (60%) is also formed with Ar = 2,4-(NO₂)₂C₆H₃. ^l Conjugated diene 138 CH₂=C(CH₃)-C(SPh)=CH₂ (6%) is also formed. ^m Unidentified oil (30%) is also obtained. ⁿ MeS⁺ is the electrophile and Me₂S the nucleophile. ^o Conjugated dienes (13%) are also formed.

TABLE IV. Kinetically Controlled Product Distributions for the Reaction of Arenesulfonyl Chlorides with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR^{18,7}

	E/Z composition, %			
	C ₆ H ₅ S	Me ₃ C ₆ H ₄ S	2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ S	2-NO ₂ -4-XC ₆ H ₃ S ^a
Me	55/45	60/40	76/24	60/40
Et	72/28	83/17	98/2	78/28
<i>i</i> -Pr	80/20	100/0	100/0	90/10
<i>t</i> -Bu	97/3	100/0	100/0	100/0

^a The ratio is independent of X; X = NO₂, Cl, MeO.

TABLE V. Relative Rate of the Addition of Various Arenesulfonyl Chlorides to 1,3-Dimethylallene.^{18,7}

arenesulfonyl chloride substituents	<i>k</i> ₂ rel.
none	1
4-Me	0.86
2-Me	0.56
2,4,6-Me ₃	0.24

Table VI. Kinetically Controlled Product Distributions for the Reaction of PhSeBr(BSeB) and 2,4,6-Me₃C₆H₂Br-(TMBSeB) with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR¹⁸⁵

R	<i>E/Z</i> composition, %	
	BSeB ^a	TMBSeB
Me	28:72	55:45
<i>i</i> -Pr	30:70	80:20
<i>t</i> -Bu	0:100	100:0
(CH ₂) ₁₀ ^b	32:68	100:0

^a BSeC and BSeB give very similar results. ^b With 1,2-cyclononadiene the selenylation is 100% stereoselective affording exclusively the *E* seleno derivatives whatever the selenyl bromide used is BSeB or TMBSeB.

Table VII. Relative Rates of Addition for the Reaction of PhSeCl(BSeC) and PhSeCl(BSeC) with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR¹⁸⁵

R	<i>k</i> rel.	
	BSeC	BSeC
Me	1.00	1.00
Et	0.83	0.34
<i>i</i> -Pr	0.54	0.095

would involve attack from the inside of the ring. The formation of both *E* and *Z* alkenes from 1,2-cyclotridecadiene 17 is indicative of the greater conformational flexibility of the 13-carbon ring. The mixture (*E*:*Z* = 86:13) is very similar to the one (80:20) obtained from the open chain (entries 16, 20).

These results are in agreement with the sulfenylation of cyclic allene 20 using Me₂S⁺SMe BF₄⁻ as a reagent,¹⁰⁸ but are in contrast to those previously obtained in which cyclononadiene 20 and cyclodecadiene 22 give rise to adducts with anti-Markovnikov orientation when the vinylic chloride is formed with 70^{100,107} and 82%¹⁰⁷ yield, respectively, using DNBSC as reagent.

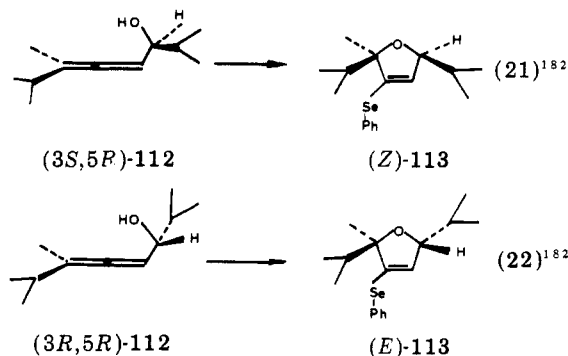
3. Anti Stereospecificity

(a) **Sulfenylation.** Early in 1967, the optically active β -allenic alcohol 103 has been shown to react stereospecifically with DNBSC reagent to afford an optically active 3-(arylthio)-3,4-dihydropyran 104, through neighboring-group participation of hydroxy group. This steric course indicates that a bridged cation 103d (Chart I, with E = SAr) is very likely to be an intermediate. Unfortunately, neither specific rotation nor configuration of both organic substrate and product are known. Thus, it is not possible to determine the syn-anti nature and the degree of the stereospecificity observed by Jacobs⁸⁴ (entry 21).

Very recently, an analogous reaction with α -allenic alcohols affording excellent yields in racemic 3-(phenylthio)-2,5-dihydrofuran has been reported.¹⁸²

(b) **Selenylation.** The same group, in the synthesis of various configurationally well-defined 2,5-dihydrofurans by selenylation-induced cyclization of α -allenic alcohols, has established the anti stereospecificity of the addition. One diastereoisomer (3*S*,5*R*) of the allenic alcohol 112 affords the (*Z*)-3-selenodihydrofuran 113, whereas the other stereoisomer (3*R*,5*R*)-112 of the alcohol gives the opposite isomer (*E*)-113 of the furan (eq 21,22 and entry 22).¹⁸²

The kinetics are shown to be second order; these data are indicative of the existence of cyclic intermediate 112d or a nonplanar carbenium-ion 112b that collapses



to the product before bond rotation to the planar and stabilized entity 112c (Chart I, with E = SeAr).¹⁸²

4. 1,1-Disubstituted Allenes

It has been shown surprisingly that 3-methyl-1,2-butadiene 49 adds the reagents DNBSC and Me₂S⁺SMe BF₄⁻ predominantly, if not exclusively, on the nonsubstituted double bond, leading to the Markovnikov-orientated product. However, a normal addition occurs predominantly on the more substituted double bond when the reagent is BSC (entries 23,25 and entries 24,26).

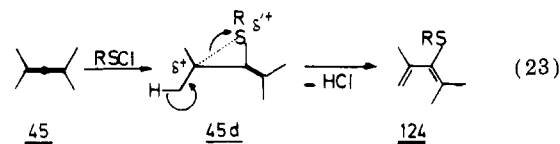
The unexpected chemoselectivity has been attributed to the existence of the homohyperconjugation of the methyl substituents that may increase the nucleophilicity of the external double bond. The ¹H NMR of the 1,1-dimethylallene 49 shows an upfield shift of 0.2 ppm for the methylenic hydrogens compares with those of the propadiene (Scheme II).

D. Trimethylallene

The addition of benzenesulfonyl chloride to the trimethylallene 73a occurs mainly (72%) on the more substituted double bond leading exclusively to the Markovnikov-orientation products (entry 27).

E. Tetramethylallene

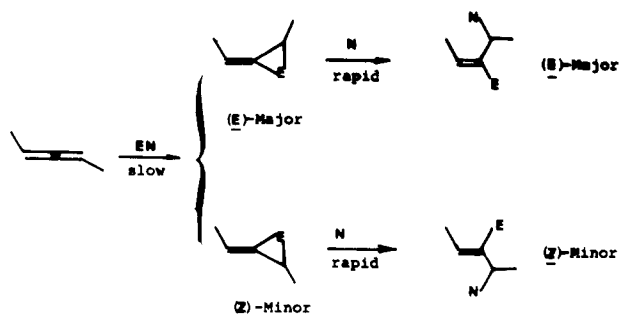
Except for PhSeCl, which leads to 25% of M-oriented monoadduct 123 (entry 30), the tetramethylallene 45 affords mainly the conjugated dienic thioethers 124 when the sulfur of the electrophile bears withdrawing inductive effect substituents (entries 28,29). This result is consistent with the carbocationic character of the intermediate; the charge on the sulfur δ^+ is directly dependent upon the nature of the R' substituent ($\delta' \gg \delta$ when R' is an electron-donating substituent, $\delta' \ll \delta$ when R' is an electron-withdrawing substituent such as R = AcS and 2,4-(NO₂)₂C₆H₃). In the case of the electron-withdrawing substituent some conjugated dienes can be formed by deprotonation of the intermediate when the nucleophilic attack is retarded (eq 23).



F. Discussion

Second-order kinetics, α -secondary isotope effect of deuterium, *E* stereoselectivity, and reaction with optically active β -allenic alcohol have clearly established

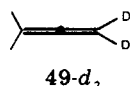
SCHEME XIII



that the sulfenylation of allenes follows an Ad_E2 mechanism. The first step appears to be rate-determining formation of the less crowded episulfonium species due to steric approach control during attack on sulfur and subsequent nucleophilic attack of halide in a fast step (Scheme XIII, $E = ArS$ and $N = Cl$).^{84,101,107}

Benzeneselenyl chloride (BSeC) and benzenesulfonyl chloride (BSC) react differently with 1,3-disubstituted allenes with respect to E,Z stereoselectivity (Tables IV and VI), relative rates (Table VII), and chemoselectivity; BSeC adds to the least substituted double bond whereas BSC adds to the most substituted one. However, the sulfur and the selenium are always bound to the central carbon atom of 2,3-pentadiene and 3-methyl 1,2-butadiene leading to the same Markovnikov regioselectivity.¹⁸⁸

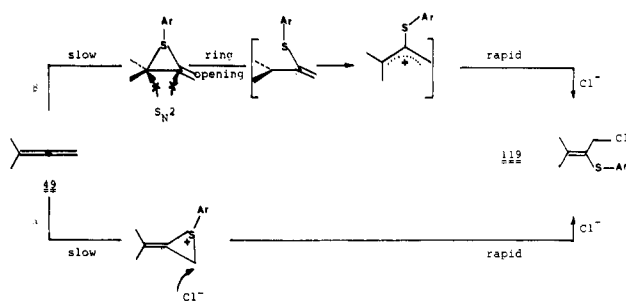
The kinetically controlled selenylation follows an Ad_E2 mechanism and may go via a seleniranium intermediate, which, in the product-determining step, undergoes an anti stereospecific attack by Cl^- to give predominantly the Z isomers¹⁸⁶ (Scheme X with $E = SeAr$ and $N = Cl$). These data indicate that the structure of the rate-determining and the product-determining transition states are different for benzenesulfonyl chloride (BSC) and benzeneselenyl chloride (BSeC).¹⁸⁸ These differences are very similar to those observed in the electrophilic addition of arenesulfonyl and areneselenyl chlorides to alkenes in which, unlike the addition of 4-chlorobenzenesulfonyl chloride (CB-SC), the addition of benzeneselenyl chloride (BSeC) is not cumulative when the six methyl-substituted ethylenes are kinetically studied. Furthermore, the selenium adduct is preferentially Markovnikov orientated whereas the sulfur derivative gives predominantly anti-Markovnikov orientation.¹⁸⁹ If steric approach control, leading irreversibly to thiuranium intermediates during sulfenylation of both double bonds for the allene 49, is assumed (vide supra), the fast reaction of the nucleophile Cl^- would afford the product 119 either directly (path α of the Scheme XIV) or subsequently after ring opening of the bridged entity formed across the substituted double bond affording an allyl cation (path β of Scheme XIV). The former route could be supported by a possible α -secondary isotope effect starting from the allene 49- d_2 .



V. Epoxidation ($E = "HO"$) (Table VIII)

It is well-known that the epoxidation reaction of olefins is of the electrophilic type.^{111c,112,113} We will now

SCHEME XIV

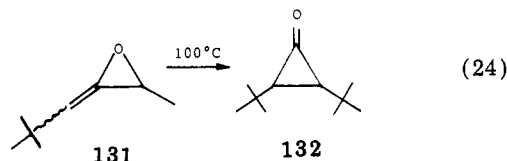


discuss this reaction with allenic compounds¹¹⁴ and their α - and β -functional derivatives.

A. Allenic Hydrocarbons

Epoxidation of allenes affords the monoadduct, the allene oxide 126,¹⁶¹ which is stable only when cumulated dienes are hindered (entries 1,3,6,7). The addition is chemoselective and occurs only on the more substituted double bond (entry 3,6). The epoxidation of allenes is E stereoselective, only the less hindered face of the molecule is reactive (entry 7).

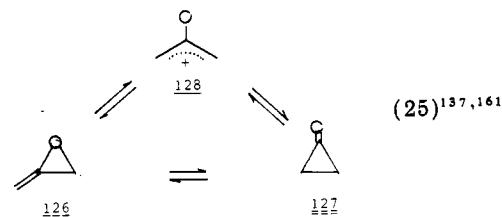
At a higher temperature or with ozone, the cyclopropanone 127, a valence isomer of the allene oxide, is predominantly obtained from the 1,1-*tert*-butylallene 133 (entries 2,4). The corresponding thermally more stable cyclopropanone 132 is also obtained when the



allene oxide 131 is heated.¹¹⁵

It is noteworthy that an additional *tert*-butyl group in the substrate increases the stability of the monoadduct allene oxide 145 against the valence isomer cyclopropanone 134¹³⁶ (entries 2,7).

Allene oxide 126 and cyclopropanone 127 are, along with the oxallyl 128, members of valence tautomerism.



Some interconversion can occur either directly $126 \rightleftharpoons 127$ or through the zwitterionic species 128.¹⁶¹

With excess of peracid a bisadduct, the spiro dioxide 129, is afforded and can be isolated from reaction with crowded allenes. The epoxidation was shown to be 100% E stereoselective (entries 5,8).

The oxidation of nonhindered acyclic, cyclic, and aromatic allenes affords unstable mono- and bisadducts that react under the reaction conditions leading to other products, mainly α -keto esters, α -ketols, and β -lactones (entries 9-18).

Results of acidic reaction with nonisolated allene oxide 126 and cyclopropanone 127, leading on the one hand to the α keto esters and with the spiro-dioxacyclopentane 129, leading on the other hand to

TABLE VIII. Epoxidation of Allenic Derivatives






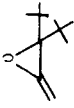







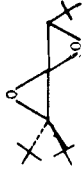

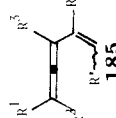
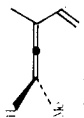
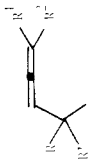
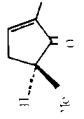
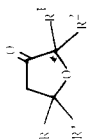
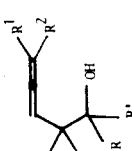
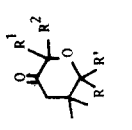
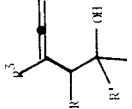
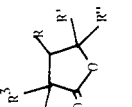
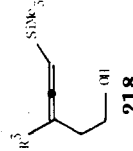
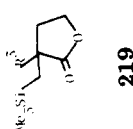
entry	allenic derivatives	reagents	solvent	T, °C	yield, %	product composition, %	ref
1		MCPBA ^a	Hexane				115
2	130 	PAA ^c	CH ₂ Cl ₂	RT	90		116, 117
3	133 	PNPBA ^b		-30	80		117
4		O ₃					123
5	137 	2 PAA ^c	CH ₂ Cl ₂	RT	100		117, 118
6	148 	PNPBA ^b	CH ₂ Cl ₂	RT			117
7	140 	MCPBA ^{a,e}	CH ₂ Cl ₂	reflux	91		117, 119
8		O ₃					123

TABLE VIII (Continued)

entry	allenic derivatives	reagents	solvent	T, °C	yield, %	product composition, %	ref
							
20	38	PAA ^c	CH ₂ Cl ₂	0	91	179	55
21		MCPBA ^a	CH ₂ Cl ₂	0	84	180	57
							
22	a	PNPBA ^b	CH ₂ Cl ₂		80	100	129-131
23	b	PNPBA ^b	CH ₂ Cl ₂		60	100	129-131
24	c	PNPBA ^b	CH ₂ Cl ₂		55	95	129-131
25	d	PNPBA ^b	CH ₂ Cl ₂		60	65	129-131
26	e	PNPBA ^b	CH ₂ Cl ₂		65	100	132
27	f	PNPBA ^b	CH ₂ Cl ₂		80	100	132
28	g	PNPBA ^b	CH ₂ Cl ₂		45	100	133
29	h	PNPBA ^b	CH ₂ Cl ₂		70	100	133
30	i	PNPBA ^b	CH ₂ Cl ₂	0	45	100	140
31	j	PNPBA ^b	CH ₂ Cl ₂	0	49	100	140
32	k	PNPBA ^b	CH ₂ Cl ₂	0	58	100	140
33	l	O ₂ /hν	CH ₂ Cl ₂		57	100	138
34	m	O ₂ /hν	CH ₂ Cl ₂			60	139
							
35		MCPBA ^a					134a
36		Payne (H ₂ O ₂ , PhCN)					
							
37	a	Payne					10
38	b	Payne					60
39	c	Payne					100
40		MCPBA ^a					
41							
							
35							134a
36							
							
37	a	Payne					10
38	b	Payne					60
39	c	Payne					100
40		MCPBA ^a					
41							

43	190		190	191		192		134b
44	190a (R = H) 190b (R = Me)		72 63	24		100		
45	193		193	62	194a	160		
46			75	75	194b	25		
47	(R)-193b $\alpha_D -2.59^\circ$			50	(S)-194b $\alpha_D^{20} -0.20^\circ$ (O.Y. 100%)	25	141	
48	31b		206	100				
49	31b		75	50	PAA ^c	209	210	
50			75	50	MCPBA ^a	208	209	
51				0	PNPBA ^e	208	210	
52						208	210	
53						209	210	
54						209	210	
55						209	210	
56						209	210	
57						209	210	
58						209	210	
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241						209	210	
242						209	210	

TABLE VIII (Continued)

entry	allenic derivatives	reagents	yield, %	product composition, %	ref
					
	212			213	
60	R' Me R ² H R H R'	Payne	10		142, 143
61	Me Me Me H H Me	Payne	60		142, 143
62	Me Et Me Me Me	Payne	100		142, 143
63	(+)-212c $\alpha_D = 2.76^\circ$	Payne		(-)-213 $\alpha_D = 1.76^\circ$ (O.Y.?)	134
64	(+)-212c $\alpha_D = 2.76^\circ$	MCPBA ^a		(-)-213 $\alpha_D = 1.25^\circ$ (O.Y.?)	134
					
	216	Payne		217	
65	R'' H R' H R ³ Me			217a	142, 143
66	H H Me H Me Me			217b	142, 143
67	H H Me Me Me Me			217c	142, 143
68	Me Me Me H Me			217d	142, 143
69	H H (CH ₂) ₄ Me(cis-216e)			cis-217e	135
70	H H (CH ₂) ₄ Me(trans-216e)			trans-217e	135
71	Me H (CH ₂) ₄ (CH ₂) ₄ (threo-216f)			cis-217f (70)	135
72	H H Me (CH ₂) ₄ (erythro-216g)			cis-217f (100)	135
					
	218	Payne		219	
74	Me ₃ Si R' R ¹ = H	Payne	quantitative	221a	192
75	(S)-(+)-220b (R ¹ = Et)		quantitative	(+)-221b	

^a *m*-Chloroperbenzoic. ^b *p*-Nitroperbenzoic acid. ^c Peracetic acid. ^d Performic acid. ^e Excess of allene. ^f *n* equiv of reagents for 1 equiv of allenic substrate. ^g Stereochemistry of the allene oxide 131 is not given. ^h 20% of starting allene 133 was recovered. ⁱ One equiv of PAA reacts with allene 137 and affords also 8% of keto ester 136 (2,2,5-trimethyl-2-acetoxy-3-pentanone). ^k R = H. ^l R = *p*-ClC₆H₄. ^m The Payne reagent¹⁷ (=50% H₂O₂, PhCN, MeOH) does not afford the Baeyer-Villiger reaction with cyclopropane intermediate whereas the peroxy acids do. ⁿ When NaHCO₃ (aq 0.5 M) is present some epoxidation of olefinic double bond also occurs. ^o 5% of the corresponding epoxide 141 is also isolated. ^p 5% of α -keto *p*-nitrobenzoate is also formed. ^q The peroxy acid is added to the allene (reverse addition). ^r The 4-oxo-1,2-oxaphospholane was isolated as a dicyclohexyl ammonium salt. ^s C₆H₉ = CH₃(CH₂)₂C \equiv C-OH.

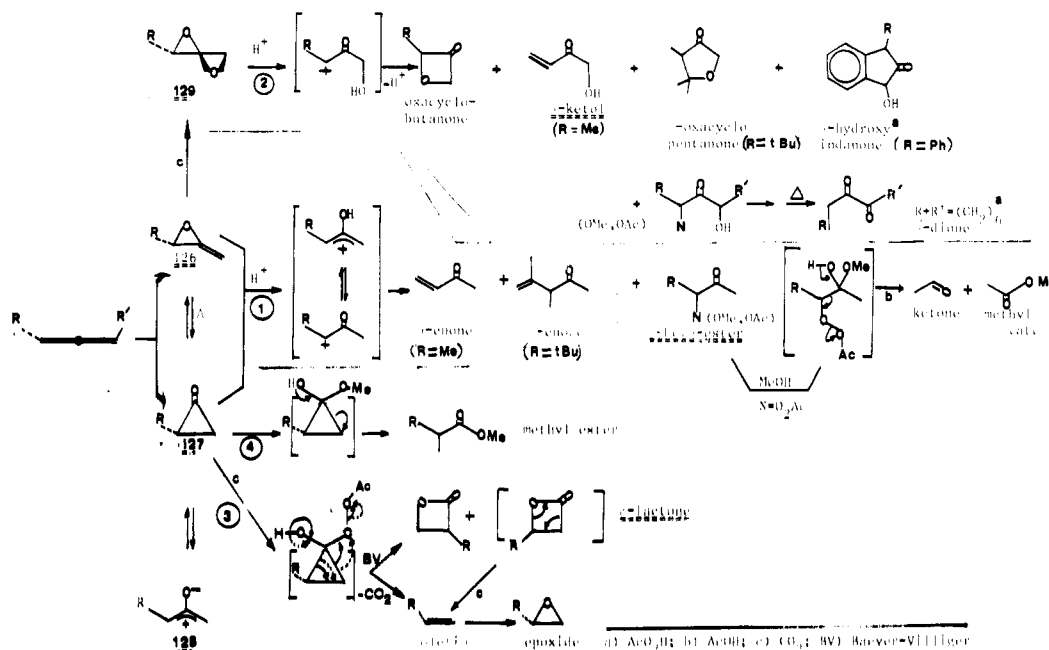
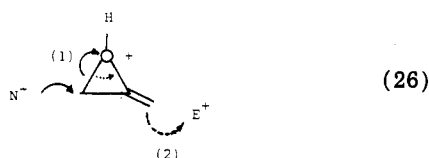


Figure 13. (a) For clarity the alkyl substituent R' of the starting allene has been drawn in the product only when it is necessary for the comprehension of the process. (b) Main products are doubly underlined. (c) Peracetic acid. BV = Baeyer-Villiger.

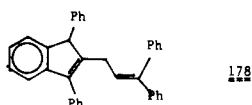
α -ketols, have been illustrated, respectively, by the paths 1 and 2 of the Figure 13. The Baeyer-Villiger reaction with the cyclopropanone 127, giving β -lactones, can compete with precedent evolutions, and is illustrated by the path 3. This route can be prevented if the Payne reagent¹²⁷ (H_2O_2 , PhCN, MeOH) is used.

Predominant α -keto esters and α -keto ethers are formed more likely by a concerted nucleophilic attack of the protonated monoadduct than on the unstable α -acyl carbonium ion (path 1 of Figure 13).



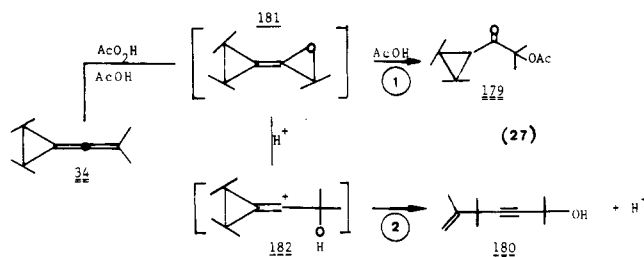
When the nucleophilic attack is prevented by steric hindrance of the ring in strained cyclic allenes α -keto esters are not formed, the reaction follows the pathway 2 and/or 3 leading, respectively, to α -dione, olefin, and subsequent oxirane (entries 11-14).

The acid-sensitive triphenylallene 177 affords the indene 178¹²⁶



whereas the tetraphenylallene 175 gives up to 83% of hydroxyindanone 176 (entry 19). This fused ring formation could be well rationalized by electrophilic aromatic substitution from the corresponding spiro dioxide via a carbonium ion with $R' = Ph$. This species is also responsible for the methyl-rearranged β -oxacyclopentanone formed by the same route when $R = t-Bu$ (path 2 of Figure 13). Carbonyl compounds formed during epoxidation, such as benzaldehyde (entries 15-18), di-*tert*-butyl ketone (entry 4), and acetone (entries 10,48,49) could be conveniently assigned to the oxidative cleavage of α -keto perester as shown in path 1 of Figure 13.

Finally, epoxidation of cyclopropylideneallene 34 affords mainly the expected α -keto ester product 179,



via the allene oxide 181, some concerted ring-opening also occurs with peracetic acid leading to the unsaturated alcohol 180 (entry 20).

B. α -Functional Derivatives

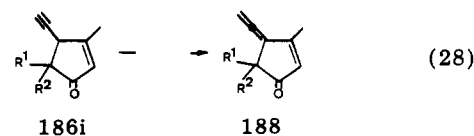
Nucleophilic groups on allenes can participate during epoxidation; cyclic products will then be obtained.

1. Vinylallenes

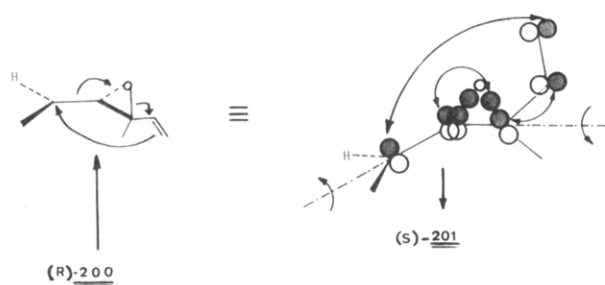
With the 1,2,4-trienes 185 the epoxidation reaction mainly affords the conjugated cyclopentenone 186 by electrophilic attack on the cumulated double bond. But when the olefin is methyl substituted, up to 35% of the epoxidation occurs on this double bond with formation of the allenyl epoxide 187 (entries 22-25,34).

This unequivocal oxidative cyclization has been applied to the synthesis of dihydrojasmane 186e and dehydrojasmane 186g (entries 26,28).

When a triple bond is conjugated with the 1,2,4-triene, as in the compound 185i, the epoxidation reaction affords the expected 4-ethynylcyclopent-2-ene-1-one 186i, which gives the corresponding allenylidene de-



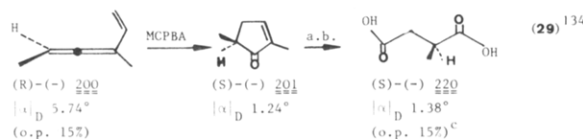
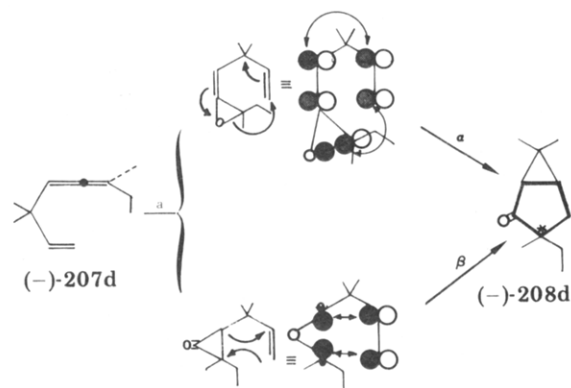
SCHEME XV



relative 188 by a mild isomerization with Na_2CO_3 (entries 30–32).

Some cyclopentenone (1861 and 186m) have also been obtained by photochemical oxidation (entries 33, 34).

Recently, it has been shown that the epoxidation of (*R*)-(-)-4-methyl-1,2,4 hexatriene **200** is 100% stereo-

SCHEME XVI^a

^a (a) $\text{RCO}_3\text{H}/\text{MeOH}$; (α) $\pi^2 + \pi^2 + \sigma^2$; (β) $\pi^2_s + \sigma^2_a$.

(a) $\text{O}_3/\text{CH}_2\text{Cl}_2$. (b) H_2O . (c) The rotation for optically pure α -methylsuccinic acid is 9.2° .

specific (entry 35). The structure and the optical purity of the (-)-2,5-dimethylcyclopent-2-enone **201** obtained have been correlated to that of α -methylsuccinic acid **220** and shown to be *S*.

This transfer of chirality prevents the exclusive formation of the planar zwitterionic oxallyl species **129** as the valence isomerism of the intermediate allene oxide **200d** in which the attack by oxygen occurs through the less hindered face of the external double bond. A thermally allowed pericyclic process from this chiral epoxide with an aromatic transition state of six π electrons ($\pi^2_s + \sigma^2_s + \pi^2_s$) or ($\pi^2_s + \sigma^2_a + \pi^2_a$) would then occur and provide the optically active cyclopentenone **201** (Scheme XV).

2. α -Allenic Alcohols

The α -allenic alcohols **202** provide the oxacyclopentanones **203** by epoxidation reaction using the PAYNE reagent¹²⁷ (50% H_2O_2 , PhCN, MeOH) (entries 37–41). Addition occurs on the external double bond when a *gem*-dialkyl group is present on the terminal carbon of the allenic system. Furthermore the yield of oxacyclopentanone **203** increases from primary to tertiary alcohols and becomes quantitative with the tertiary alcohols **202c** (entry 39). The reaction has been shown to be stereospecific, since chiral α -allenic alcohol **204** gives optically active β -oxacyclopentanone **205**, through an unstable allene oxide intermediate. Unfortunately the structure of both allene **204** and 3-oxacyclopentanone **205** are not known, thus nature and degree of the observed stereospecificity cannot be estimated (entries 40,41).

Very recently, it has been shown that epoxidation reaction of the corresponding α -allenic acetate **190** affords the conjugated dienones **191** and **192**. α -Allenic trimethylsilyl ethers **193** gives rise to silyl ethers of unsaturated α -ketols (entries 43–46). In both reactions a 1,4-migration of the functional group is involved. It was shown that from optically active silyl derivatives

a complete transfer of chirality occurs by a concerted pericyclic process that is thermally allowed (entry 47). This epoxidation takes place on the more substituted double bond by the less hindered face of the remaining double bond. The reaction is then 100% chemo- and 100% *E* stereoselective.

3. α -Allenyl Phosphonic Acid

The phosphonic acid function has recently been shown to be able to participate intramolecularly during the epoxidation of the allenic derivative **31b** affording a good yield of the β -oxoxaphospholane **206** that has been isolated as its dicyclohexylammonium salt. Surprisingly, the α -allenyl phosphonic acid 1,3-substituted by two *tert*-butyl groups remains intact, whereas under the same conditions the corresponding hydrocarbons **140** and **148** yield the epoxidation products (entries 6,7 and 48, 49).

C. β -Functional Derivatives

Structure of products formed by epoxidation of allylallenes and β -allenic alcohols are directly related to the substitution of cumulated double bonds.

1. Allylallenes

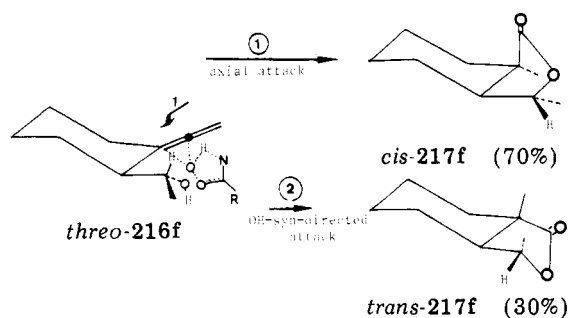
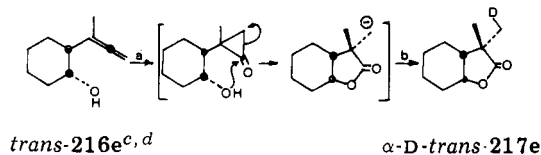
1,2,5-Triene **207** epoxidation is very complex. The bicyclic ketone **208**, a product of neighboring group participation, is obtained when the allene **207** is *gem* disubstituted (entries 53–56). This product is formed exclusively in methanol (entry 53). α -Ketols **209**, β -lactone **210**, and γ -enones **211** are formed without participation, the former being obtained through the spiro dioxide of allene **207** (path 1 of Figure 13) (entries 50–56).

The formation of the bicyclic ketone **208** (Scheme XVI) was shown to be stereospecific and may occur by concerted processes, through allene oxide or cyclopropanone, both being thermally allowed (entries 58, 59).

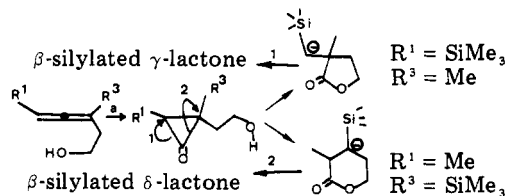
2. β -Allenic Alcohols

The epoxidation of β -hydroxyallenes affords 3-oxacyclohexanones when the terminal carbon of the allene is fully substituted and the yield becomes quantitative with tertiary alcohols (entries 60–63). The reaction was shown to be stereospecific (entries 63–64). The evolution is different with nonsubstituted terminal allene;

SCHEME XVII

SCHEME XVIII^a

^a (a) H₂O₂, PhCN. (b) MeOD. (c) See also entries 69, 70. (d) The alcohol *cis*-216e affords the other deuterated stereoisomer β -D-*cis*-217e.

SCHEME XIX^a

^a (a) Payne reagent.

the epoxidation of β -allenic alcohols affords γ -lactones and the reaction was shown to be general (entries 65–70) and stereospecific (entries 71,72). The main or the exclusive *cis*- γ -lactone **217f** (Scheme XVII)¹⁸⁵ has been formed by attack of the reagent by the less crowded face of the internal double bond, an axial approach, whereas the minor *trans*-**217f** was obtained because of syn-orientating effect of the hydroxy group that occurs on the more hindered face of the same double bond (entry 29).

The γ -lactone **217** (Scheme XVIII) was shown to be formed through the cyclopropanone by intramolecular nucleophilic attack of the hydroxy group. The product was found to be stereospecifically monodeuterated only on one methyl group when the reaction is conducted in MeOD.^{142,143}

Silylated γ -lactone **219** (Scheme XIX)¹⁹² is prepared by epoxidation of allene that bears a trimethylsilyl group on the C-1 carbon of the allene **218**, which occurs by the expected route (entry 73). Whereas if the silicon is bound to the C-3 carbon, a different course is followed and silylated δ -lactone **221** is formed with excellent yield (entry 74).

These reactions were shown to proceed through cyclopropanone and the evolution of the ring opening by nucleophilic attack of hydroxy is dependant on the nature of substituents R¹ and R³ as shown.

The formation of the δ -lactone **221b** was shown to occur by a concerted mechanism. The chiral β -allenic alcohol (*S*)-(+)-**220b** when submitted to epoxidation affords a mixture of two diastereoisomers one of which is optically active (entry 75). This stereospecificity

excludes the zwitterionic oxallyl **129**, a planar species, as an exclusive intermediate for epoxidation of functional allenes.

D. Discussion

Monoadducts, allene oxide and cyclopropanone, and the bisadducts spirodioxide can be isolated only when allenes bears bulky substituents such as the *tert*-butyl group (entries 1–8). Otherwise only acidic decomposition products with ring opening of oxirane are stable (entries 9–21). The epoxidation of allenes is chemoselective, only the more substituted double bond is reactive. The epoxidation of allenes is *E* stereoselective, the peracid reacts on the less hindered face of the remaining double bond. The epoxidation of the vinylallene (*R*)-(-)-**200** was shown to be 100% stereospecific, the consecutive cyclization occurring by a concerted process that is thermally allowed. The epoxidation of α -allenic alcohol, its silyl ether, allyllallene, and β -allenic alcohol proceed stereospecifically.

VI. Allenic Participation In Solvolysis (*E* = *C* <) (Table IX)

In a functional allenic derivative >C(X)—(CH₂)_{*n*}—C(=C=C<)-, in which X is a leaving group; ionization of carbon-halogen bond during a solvolysis affords a partial positive charge on the carbon atom and some intramolecular participation of the cumulated double bond on this carbocationic species can occur. This can account for the formation of the cyclic products. We wish to report recent results and mechanistic study of this cyclization concerning β (*n* = 1), γ (*n* = 2), and δ (*n* = 3) functional allenic substrates.

A. β -Allenic Carbocations

Results that appeared before 1969 have been rationalized by Modena¹⁰ in a review that showed that homoallenic participation during the solvolysis of β -allenic ester affords three- and four-membered-ring products. These compounds obtained by participation of the unsaturated linkage can be well explained if we assume the formation of a nonclassical carbocationic species such as the methylenecyclobutonium **223d** (Also rapidly equilibrating classical carbonium ions such as the vinylcyclopropyl **223a** and the allylcyclobutenyl **223b** could explain the results. Of course, the entity **223d** which could be only a transition state must lie on the reaction path connecting the two open ions.) (Figure 14). Evolution of this cyclic entity is directly dependent upon methyl substitution of the allenic system.

Thus, a methyl group bound to the carbon atom C-3 (R³ = Me) enhances the formation of methylenecyclobutane products through the allylic species **223b** (path a) whereas a nonsubstituted substrate affords mainly the enol ether of cyclopropyl ketone via a vinylic cation **223a** (path b). A terminal methyl substitution yields the more stable cyclopropylacetylene hydrocarbon probably after loss of proton from the intermediate **223d** (path c), an elimination of H⁺ from the species **223a** being also able to account for the acetylenic product formation (path d). Finally some rearrangement occurs during solvolysis of the primary β -allenic derivatives bearing a *gem*-dimethyl group on the carbon atom C-4 (R = Me).

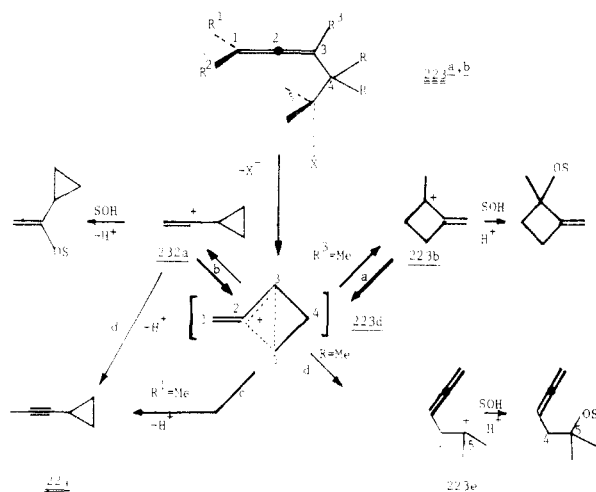
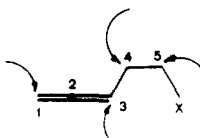


Figure 14. Rationalization of product formation during solvolysis of acyclic β -allenic esters.¹⁰ (a) X = Br, ONs, OTs, OBs, and DNB. (b) The alkyl substituents R¹, R², R³, and R will be mentioned in the species **223a–e** only when they are different from hydrogen.

Rearranged products have been obtained from the more stable tertiary carbocation **223e** after an exchange between C-4 and C-5 positions (path e). It has also been shown,¹⁰ that methyl substitution of an allenic unsaturated double bond increases the solvolysis reaction rate by a factor that depends upon the location of this substituent. The enhancement observed is illustrated by the following scheme:



1. Acyclic Derivatives

Whatever the position of methyl substituents, reductive acetolysis (acetolysis followed by reduction with LiAlH₄. Alcohols that are formed can then be compared with those obtained by hydrolysis of the same allenic tosylate.) (SOH = AcOH) and hydrolysis (SOH = H₂O) of various methyl-substituted acyclic β -allenic tosylates **225–228** afford up to 81% of cyclic products which, are formed with participation of the allenic system (entries 1–12).

E and *Z* stereoisomers of the cyclopropyl ketones **230** are mainly obtained during solvolysis when allenic substrate is not substituted on cumulated double bonds, whereas the methylenecyclobutanols **233**, **234** and their allylic isomers, the cyclobutenyl methanols **235**, **236**, become predominant when the allenic system of the derivatives, **226–228** is methyl substituted on the carbon atom C-3 (entries 1–3; 6–12, respectively).

Stereospecificity of this cycloaddition has been studied by hydrolysis of the chiral tosylate (*S*)-**225** and reductive acetolysis of *R* enantiomers of the tosylates **225** and **228**. Inversion of configuration observed in the cyclopropyl ketones (1*R*,2*R*)- and (1*S*,2*R*)-(*E*)-**230** formed, respectively, from the *S* and *R* tosylates **225** on the one hand and the 4*S* structure of the methylenecyclobutanol (*Z* + *E*)-**234** on the other hand is in agreement with an S_N2 attack, on the carbon-atom bearing the positive charge, by the allenyl system (entries 4, 5, and 12 respectively). For acetolysis of the tosylate (*R*)-**225** (Figure 15), the rate constant observed

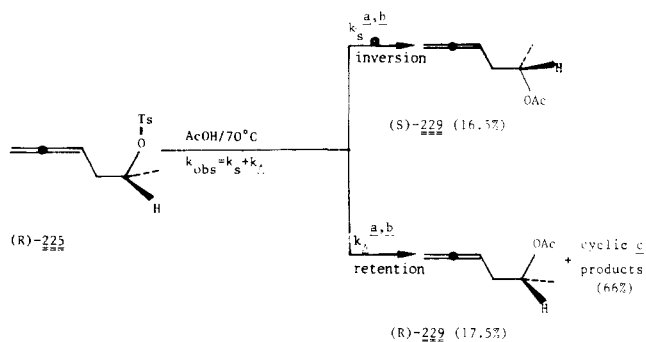


Figure 15. Kinetics and stereochemistry of the acetolysis of the tosylate (*R*)-**225**. (a) $k_s = 0.46 \times 10^{-5}$ and $k_\Delta = 2.32 \times 10^{-5}$ are respectively, the rate constant without and with participation of the allenic system. (b) $k_\Delta/k_s = 5.04$. (c) For the structure and the composition of the cyclic products see entry 3 of Table IX.

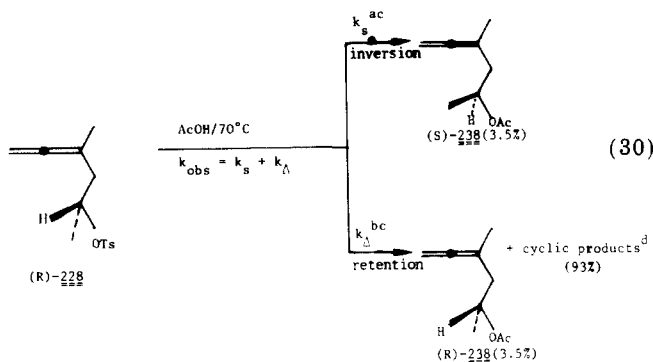


Figure 16. Kinetics and stereochemistry of the acetolysis of the tosylate (*R*)-**228**. (a) $k_s = 0.50 \times 10^{-5}$. (b) $k_\Delta = 13.8 \times 10^{-5}$. (c) $k_\Delta/k_s = 27.6$. (d) See entry 12 in Table IX.

(k_{obs}) can be considered as the sum of the rate constant of the (*S*)-acetate **229** formed by an S_N2 process without participation of the allenic system (k_s) and the one obtained with neighboring group participation (k_Δ) leading to the formation of cyclic products and to the (*R*)-acetate **229** formed with retention of configuration. If k'_s is the rate constant of the corresponding saturated tosylate of 2-hexanol ($k'_s = 4.17 \cdot 10^{-5}$), the relationship $k_s/k'_s = 9$ obtained, implies that the decreasing rate observed with the unsaturated tosylate **225** may be attributed to the electron-withdrawing effect (–I) of the β -allenyl group.

The kinetics of acetolysis of 3-methyl-substituted tosylate (*R*)-**228** (Figure 16) shows that the methyl substitution on carbon C-3 does not change the rate constants without participation k_s , enhances the rate constant with participation k_Δ by a factor of 6, increases the ratio of cyclized products from 66% to 93%, and finally produces rate constants k_Δ always greater than k_s (entries 1,10; footnotes of Figures 15,16).

When the carbon atoms C-4 and C-5 carry different substituents such as in the tosylates **227** and **228** (entries 8–12) an apparent exchange of position occurs during the cyclization. Up to 33.5% of α -methyl-disubstituted products **233** and **235** have been found from the hydrolysis of β -dimethyl-substituted tosylate **228** (entry 10). While the hydrolysis of primary α -dimethyl-substituted tosylate **227** affords 16.5% of β -dimethyl derivatives **234** and **236** (entry 8). It has been assumed that these rearranged products are formed through a common cyclopropylvinyl cation **227a** or **228a** in which the more nucleophilic σ bond of the cyclopropane ring affords 5 times more β -dimethylated

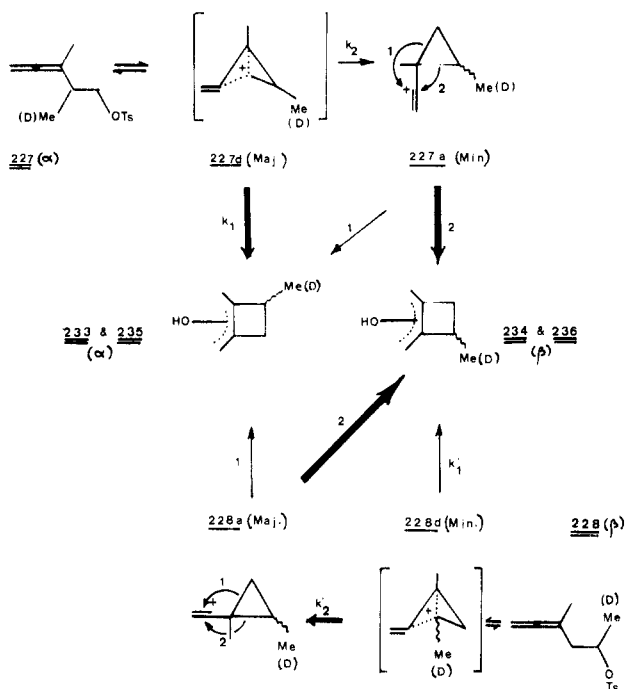


Figure 17.

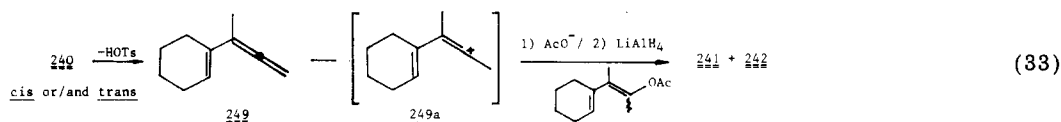
cyclobutene derivatives **234**, **236** than α -dimethylated ones **233** and **235** (Figure 17). Besides, the same ratios of α - and β -dimethyl-substituted cyclobutenes have been found in hydrolysis of the chloride **237** very probably through a vinyl carbocation identical to the species **227a** and **228a**.



Taking into account results obtained during hydrolysis of the two different methylated tosylates **227** and **228**, we must admit that hydrolysis of the primary tosylates **227** goes directly to the products **232-236** mainly ($k_1 \gg k_2$) through the methylenecyclobutonium species **227d** whereas this reaction from the secondary tosylate **228** leads to the same products with different composition via the cyclopropylvinyl cation **228a** ($k_2' \gg k_1'$) after isomerization of the corresponding species **228d** (entries 8,10 and Figure 17). This apparent exchange has been also observed when the tosylates are deuterium labeled on the carbon atoms C-4 or C-5 (see footnote o of Table IX). It has been similarly established by kinetics and product distribution study,¹²⁸ that acetolyses of monomethylated β -allenic tosylates **225** and **222** involved the vinylcyclopropyl tosylate **239** and that all three compounds react *via* the same vinylcyclopropylcarbanyl ion **225a**^{26b,c} (Figure 18).

2. Cyclohexanol Derivatives

Reductive acetolysis of the *cis*- and *trans*-tosylates **240** leads, respectively, to the *trans* and *cis* fused derivatives of 6-methylenebicyclo[4.2.0]octan-7-ol



(33)

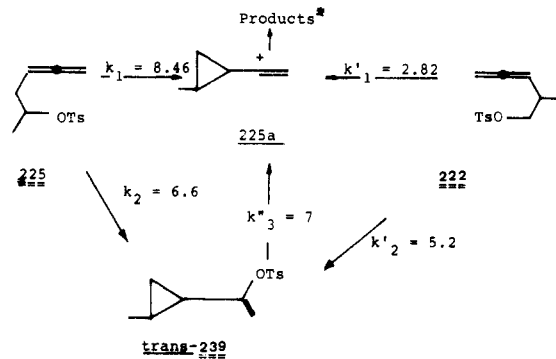
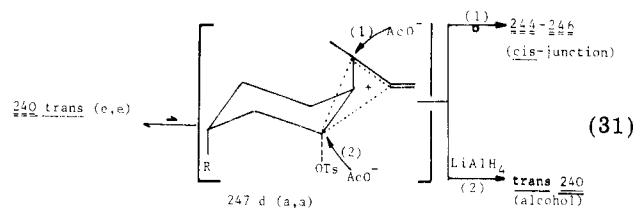
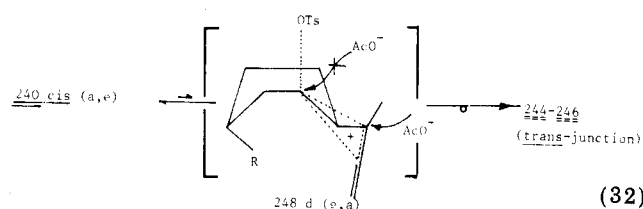


Figure 18. Reference 128. * $k \times 10^5$ s at 85 °C; $k_3 = 6.6$ and $k'_3 = 8.2$ with $k_1 > k_3$ and $k'_1 < k'_3$.

(**244-246**) with inversion of configuration (entries 13, 14, path 1 of eq 31 and 32). 4.5% of *trans*- β -allenic



(31)



(32)

alcohol is formed with retention of configuration from the corresponding *trans*-tosylate **240**, by a nucleophilic substitution (S_Ni) on the carbon atom bearing the leaving group because of the anchimeric effect of allenic system in a *diaxial* conformer of a methylenecyclobutonium entity **247d** (path 2 of eq 31).

The *cis*-tosylate **240** gives the *trans*-fused products through a very strained boat conformer of the non-classical carbocation **248d**, especially when $R = Me$. The minor products **241** and **242** that are common to the *cis* and *trans* substrates were probably formed after reduction of enol acetate of the ketone **240**. Addition of acetic acid to the vinylallene **249** obtained by elimination must occur exclusively on the terminal carbon atom of the allenic system leading to the vinyl cation **249a** and subsequently to enol acetate and its corresponding ketone **241**. (See entries 13 and 14.)

It has been shown that only the acetate **244** was kinetically controlled. The products **245** and **246** were obtained after isomerization of this acetate under the reaction conditions; the nucleophilic substitution of the *trans*-tosylate **240** using AcO^- in DMSO affords, in fact exclusively, the acetate **244** with *cis* junction.

The acetolysis rate constant of the nonmethylated tosylate **240** is twice that of the corresponding methylated one. This is in accordance with the axial position of this substituent in both intermediates **247d** and **248d**

TABLE IX. Solvolysis of β -, γ -, and δ -Allenic Esters

entry	allenic derivatives	reagent and solvent	T, °C	yield	products composition, %					ref		
β-Allenic Esters												
	225				(E)	230 (Z)	(E)	231 (Z)				
1		hydrolysis ^{a,b,p}	100		44.5	22.5				147		
2		hydrolysis ^{a,c,r}	55		48	33				147		
3		acetolysis ^{n,d}	80		25	18.4	8.5	6.5		147		
4	(S)-(-)	hydrolysis ⁿ			(1R,2R)-(-)	(1S,2R)-(+)				148		
5	(R)-(+)	acetolysis ⁿ			(1S,2R)-(+)	(1R,2S)-(-)				148		
	226 (R = H)^x				(Z)	232 (E)	(Z)	233 (E)	234 (E)	235	236	147
6		hydrolysis ^{a,e,o,p}										
7		acetolysis ^{a,e,o,q}										
8		hydrolysis ^{a,f}	10	1	36.5	19	4.5	10	38	6.5	2	
9		acetolysis ^{a,h}			15	23	8	15	30		10	
	227 (R = Me)^x											
10		hydrolysis ^{a,g}	3.1	1	16	13.5	15	33	4.1		63	
11		acetolysis ^{a,i}			8.1	12.4	14.4	24.5	14		19	
	228 (R = Me)^x											
12	(R)-(+)	reductive acetolysis ^s			20.5	39		14	19			
					(3S)-(+)	(4S)-(+)		(3S)	(?)			
13	<i>cis</i> -240 (R = H)	reductive acetolysis ^s			241	242	243	244 ^t	245 ^t	246 ^t	150	
14	<i>trans</i> -240 (R = H)				3	4	10	16 (trans)	33 (trans)	34 (trans)		
					3.5	5		20 (cis)	50 (cis)	17 (cis)		
15	<i>threo</i> -250	hydrolysis ^p	100		251 (4)	252 (34)	253 (22)	254 (12)	255 (28)		151	
		[H ₂ O:dioxane (3:1)]										
16	<i>erythro</i> 250	hydrolysis ^p	100		251 (4)	256 (41)	257 (11)	<i>erythro</i> -258 (44)			151	
		[H ₂ O:dioxane (3:1)]										
γ-Allenic Esters												
	270 (X = OTs)				271	272	273 (OH)	274 (OAc)	275			
17		hydrolysis	80		24	12	44.5 ^u		0.5		152	
18		acetolysis ^w	30		72	5.5		22.5				
19		acetolysis ^w	70		63	18		13	1			
20	276 (X = ONs)^x	acetolysis ^w	60		70.5	13		11	0.5			
21	277^w	HCO ₂ H		70							153	
22	279^w	CF ₃ COOH/(CF ₃) ₂ O		74							153	

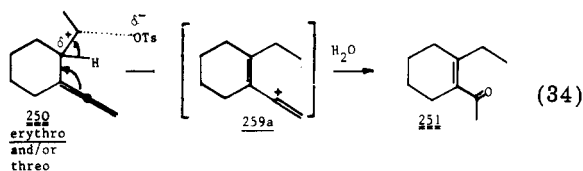
TABLE IX (Continued)

entry	allenic derivatives	reagent and solvent	T, °C	yield	products composition, %	ref
δ-Allenic Esters						
23		CF ₃ CH ₂ OH ^u	60	65	 285 (45) 286 (45)	154
<p>^a β-Allenic alcohols or acetates are also present. ^b 27%. ^c 19%. ^d 34%. ^e 25%. ^f 3.5%. ^g 8%. ^h 2.5%. ⁱ 7.5%. ^j 20.5%. ^k 45%. ^l 7.5%. ^m 4.5%. ⁿ From chiral tosylate 225, the corresponding β-allenic alcohol obtained is optically inactive during hydrolysis, whereas reductive acetolysis affords the same β-allenic alcohol with 3% of optical purity. ^o The C-4 or C-5 monodeuterated tosylates afford cyclic products with only 60% of the deuterium at the expected position; the remaining is found in the α-carbon. ^p The hydrolysis is performed with H₂O and CaCO₃. ^q NaOAc in acetic acid is used for the acetolysis. ^r H₂O in acetone is also used for hydrolysis. ^s In the reductive acetolysis, the products of the acetolysis reaction are subsequently treated by LiAlH₄. ^t The cis and trans configuration of the products 224–246 concern the junction of the bicyclic products. ^u 15% of an equimolecular mixture of the cis and trans α,α'-disubstituted tetrahydrofurans 281 and 282 has been formed from the alcohol 273 by protonation of the cumulated double bond and intramolecular participation of the hydroxy group. ^v 5% of uncyclized material and 5% of unidentified product are also obtained. ^w 5% of unidentified product is also present. ^x This substituent is present in the products.</p>						

postulated for the ring products formation (eq 31, 32). Surprisingly, rate constants for the *cis*- and *trans*-tosylate 240 are of same value. It seems that this high reactivity of the *cis* isomer is due to destabilization of the ground state by the allenic system. The activation energy leading to the products from the *cis* substrate with R = Me should then be lowered.

3. Cyclohexylidene Derivatives

The minor product 251, which is common to the *erythro*- and *threo*-tosylates 250 has been probably



formed by hydrolysis of the unsaturated vinyl cation 259a obtained after a 1,2 hydride shift from ionization of the substrates 250 (entries 15,16).

Hydrolysis of *threo*-tosylate 250 gives rise to the products 252–255 whereas the *erythro* diastereoisomer affords the compounds 256–258 (entries 15,16). These products arise from homoallenic participation with inversion of configuration at the carbon bearing the positive charge. The allenic alcohol *erythro*-258 was formed with double inversion. The vinyl cations 261a and 261a' or the methylenecyclobutonium cations 260d and 260d' that are probably involved in the hydrolysis of the tosylates 250 must have different reactivities mainly because they are diastereoisomers (Figures 19 and 20).

Concerted ring expansion of cyclopropane affords seven-membered ring products 254–256 from the vinylic species 261a and 261a', without formation of a positive charge at the bridgehead. The latter entity is less strained and also gives 11% of bicyclic ketone 257 whereas the former does not (Figure 20).

The rearranged methylenebicyclooctanols 252 and 253 have been formed by hydration of the nonclassical cation 260d directly for the former (path 1) and by a

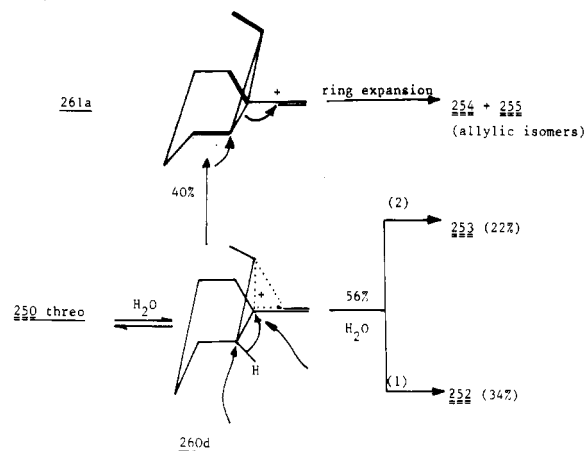


Figure 19. Hydrolysis of the secondary *threo*-tosylate 250.

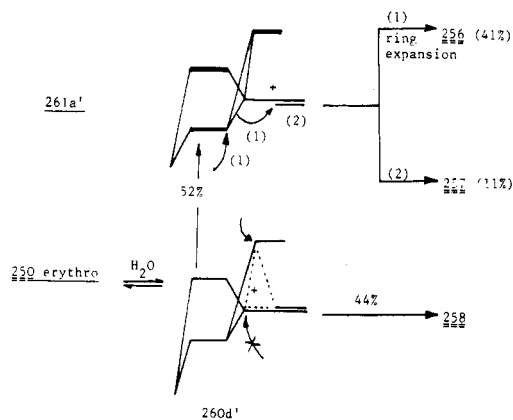


Figure 20. Hydrolysis of the secondary *erythro*-tosylate 250.

previous 1,2 hydride shift for the latter (path 2 of Figure 19).

B. γ-Allenic Carbocations

Acetolysis of the secondary γ-allenic tosylates 262, 266, and 270 (entries 18, 19) occurs partially with intramolecular participation of the cumulated double

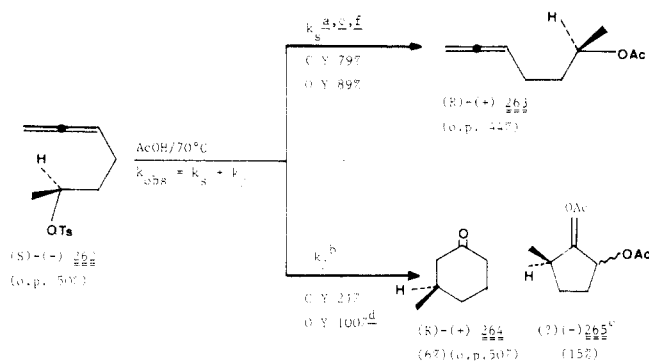


Figure 21. Kinetics and stereochemistry of acetolysis of the nonmethylated γ -allenic tosylate **262**. (a) $k_a = 1.52 \times 10^{-5}$. (b) $k_b = 0.40 \times 10^{-5}$. (c) $k_b/k_a = 0.26$. (d) Optical yield (OY) for **264**. (e) The configuration and the optical purity of the levorotatory acetate **265** are not known. (f) CY for chemical yield and OY for optical yield.

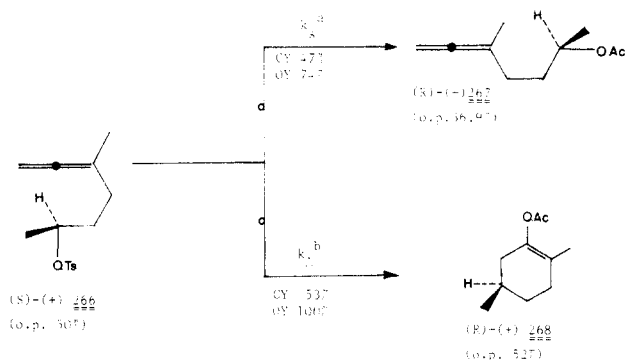


Figure 22. Kinetics and stereochemistry of acetolysis of the monomethylated secondary γ -allenic tosylate **266**. (a) $k_a = 1.31 \times 10^{-5}$. (b) $k_b = 1.47 \times 10^{-5}$. (c) $k_b/k_a = 1.12$. (d) The configuration and the optical purity of the enol acetate **268** have been correlated to the corresponding known ketone (R)-(+)-**269**. (d) CY and OY, respectively, for chemical and optical yield.

bond whereas the corresponding primary derivative does not. The cyclic products **264** and **268**, obtained respectively from the optically active tosylates **262** and **277**, are always formed with 100% inversion of configuration for the carbon atom bearing the leaving group (Figures 21 and 22). The nature of the five- and/or six-membered-ring products is directly dependent on the methyl substitution of the allenic system. The six-membered ring product is mainly (53%) produced from the 3-methyl-substituted tosylate **266**, whereas up to 81% of the cyclopentene derivatives are formed when the substrate is 1,1-dimethylated as in the compound **270** (Figure 23). A partial anchimeric assistance of the cumulated double bond can also be detected on the linear acetates **263** and **267**. These products have been formed by an S_N2 process with, respectively, 6 and 13% retention (Figures 21 and 22).

Very interestingly the neighboring group participation of the γ -allenic system has been used in the unequivocal synthesis of the *cis*-decalone **278** and the *cis*-diketone **280** in which some carbocationic species, involved during a protonation reaction, is added exclusively to the terminal carbon of the allene, leading to a vinylic six-membered ring intermediate of **266a** type. The good overlap of the orthogonal C-1-C-2 π bond and the positive charge of the functional carbon atom C-6 would be in agreement with the absence of the fused cyclopentane product in these reactions (entries 21, 22 and Figure 23).

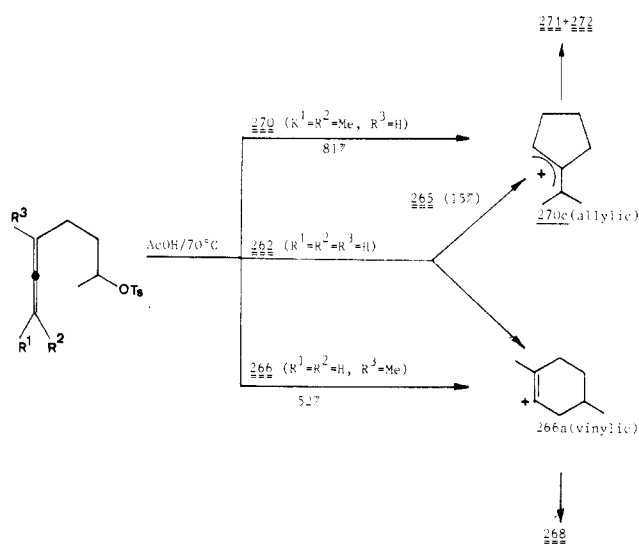
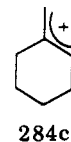


Figure 23. Acetolysis of secondary β -allenic tosylates. Regioselective cyclization.

C. δ -Allenic Carbocations

More than 90% cyclization occurs in solvolysis of the primary δ -allenic tosylate **284** using 2,2,2-trifluoroethanol. An equimolar mixture of allylic ethers **285** and **286** is formed very probably through the allylic carbocation of six-membered ring **284c** (entry 23). Similar



to the β - and γ -tosylates acetolyses the rate constant of this trifluoroethanolysis ($k_{\text{obsd}} = 8.15 \times 10^{-7} \text{ s}^{-1}$) is higher than its corresponding saturated counterpart.

D. Discussion

Acetolysis rate constants without participation (k_s) of β - and γ -allenic tosylates are smaller those of the corresponding 2-hexanol by a factor of 2.7 and 8.7, respectively. This decreasing effect has been attributed to the electron-withdrawing effect of the allenyl group that was found to be independent of the methyl substitution of allenic linkage.

In contrast, monomethylation was shown to increase the rate constant with participation (k_a) by a factor of 5.9 for the β -tosylates **228** vs. **225** and by 3.7 for the γ -tosylates **262** vs. **266**. For the γ -tosylates **266** vs. **279**, it has been observed that an additional exaltation by a factor of 7.9 for the rate occurs during a second methylation. The amount of cyclic products also increases with methylation of allenic system (Table X).

This increasing rate with the increasing nucleophilicity of the cumulated double bond of allenic tosylates, inversion of configuration observed in cyclic products, and retention of configuration observed in noncyclic compounds are in good agreement with a bimolecular nucleophilic substitution on the carbon bearing the leaving group, the nucleophile being one allenic double bond.

Allenic participation reaction that occurs during solvolysis of β -allenic tosylates is chemoselective; only the internal double bond of the allene participates in the formation of cyclic products.

Table X.^a Acetolysis Rate Constants of the Methyl-Substituted Secondary β - and γ -Allenic Tosylates

allenic tosylates	$k_{\text{obsd}} \times 10^5, \text{s}$	$k_s \times 10^5, \text{s}$	$k_{\Delta} \times 10^5, \text{s}$	k_{Δ}/k_s	methylation of substrate	cyclic products, %	ref
225 (β)		0.46	2.32	5.04	no	66	147, 148
228 (β)		0.50	13.8	27.6	3-Me	93	147, 148
262 (γ)	1.93	1.52	0.4	0.26	no	21	152
266 (γ)	2.78	1.31	1.47	1.12	3-Me	53	152
270 (γ)	13.6	1.9	11.7	6.16	1,1-Me ₂	81	152

^a See Figures 15, 16, 21, 22, 23. ^b $k_s' = 4.17 \times 10^5$. ^c $\bar{k}_s(\beta) = 0.48 \pm 0.02$. ^d $\bar{k}_s(\gamma) = 1.55 \pm 0.25$. ^e $k_s' : \bar{k}_s(\beta) = 8.7$. ^f $k_s' : \bar{k}_s(\gamma) = 2.7$.

The reaction is regioselective: *four*-membered-ring products are formed by central attack of the cumulated system through an allylic species when allene is methyl substituted on the carbon C-3 whereas *three*-membered-ring products are obtained via a vinyl ion formed during a terminal attack by the carbonium ion (compare entries 1 and 6).

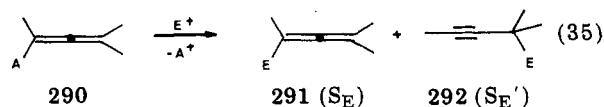
Finally, the reaction of β -allenic tosylates affording cyclic products is stereospecific, the reaction proceeding through an S_N2 pathway taking place on the carbon bearing the leaving group (entries 4,5).

Regioselectivity of the γ -allenic tosylate solvolysis is related to the 1,1-dimethyl substitution of allene and follows the same trend as the β -isomers (Figure 23). Solvolysis of γ -allenic tosylates is 100% stereospecific; the chiral β -methylcyclohexanones 264 and 268 are obtained with 100% inversion of configuration (Figures 21 and 22).

Intramolecular allenic participation during solvolysis of β -, γ -, and δ -allenic tosylates affords syntheses of three-, four-, five-, and six-membered-ring products. Steric and electronic factors, mainly competitive stabilities of vinylic vs. allylic ions, will control the neighboring group assistance of one allenic double bond in ring product formation.

VII. Electrophilic Substitution (S_E) (Table XI)

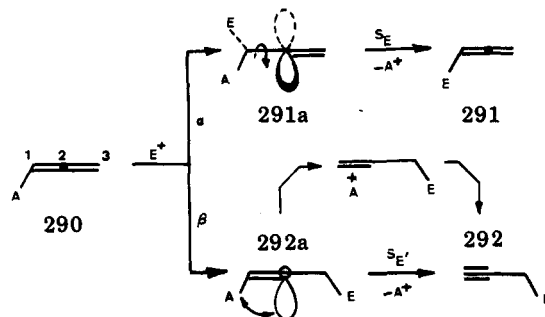
When an electrophile E^+ reacts with an allenic substrate bearing an electropositive substituent A such as a tin or silicon group, a substitution reaction of A by E will take place. This electrophilic substitution can occur either with retention of the allenic linkage (S_E)



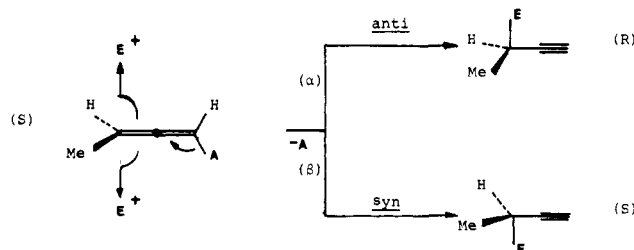
or with allenyl-propargyl isomerization (S_E'). Usually, a mixture of acetylenic and allenic derivatives is formed. Acetylenic and allenic products could arise from two different carbonium ions, which are obtained by attack on terminal carbon atoms of the two double bonds that have different reactivities. Electrophilic addition to the internal one, will afford the new allenic compound 291 via the corresponding vinylic cation 291a only when a 90° rotation around the carbon-carbon single bond takes place. Thus, the C-Sn or C-Si bond and the vacant orbital become coplanar and some elimination of the electrophile A^+ will then be possible (path α of Scheme XX).

In contrast, addition to the external double bond will afford directly the acetylene 292 via the isomeric vinyl cation 292a in which the σ carbon substituent bond C-A is already coplanar with the given orbital. Some cationic rearrangement across the double bond will afford

SCHEME XX



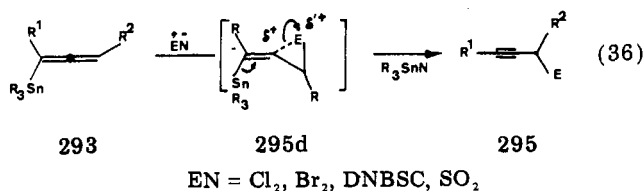
SCHEME XXI



some acetylenic-bridged species 292d that will decompose to give again the acetylene 292 (path β of Scheme XX). Furthermore, the stabilization of the positive charge by a possible through-space interaction of the σ_{C-A} bond will probably favor the formation of acetylenic products that are also thermodynamically more stable (see species 292a in Scheme XX). The latter pathway could be concerted (S_E2') and proceed by a syn or an anti mechanism (Scheme XXI). Electrophilic additions to allenyltin and allenylsilicon compounds is now described.

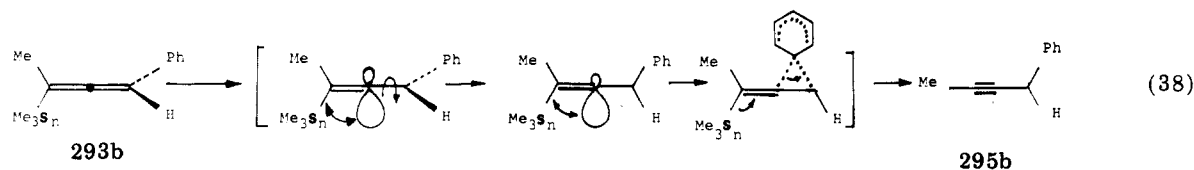
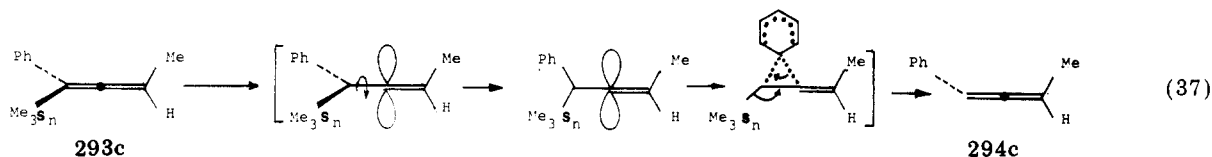
A. Organotin Derivatives

Halogenation, sulfenylation, and addition of sulfur dioxide to the allenyltin derivatives 293 is 100% chemoselective and 100% regioselective. The reaction

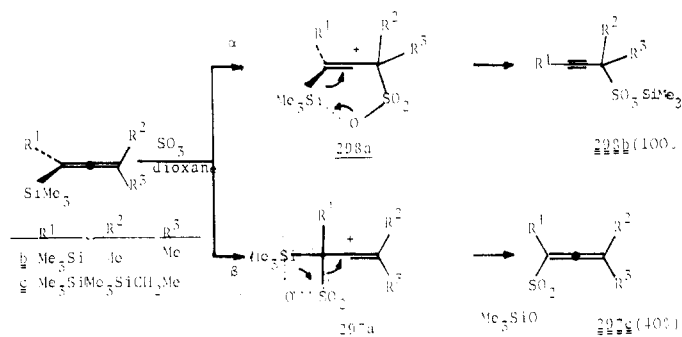


affords exclusively the acetylenic product 295 by attack of the nonfunctionalized C-2-C-3 double bond. A vinyl cation or a bridged species with carbocationic character may account for this complete transposition (entries 1-5).

In contrast, the chemoselectivity of protonation is controlled by steric and electronic factors. Thus, an



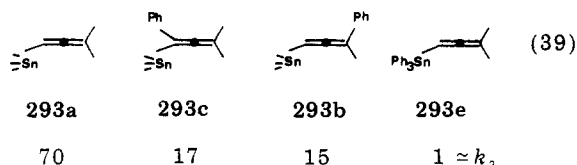
SCHEME XXII



allenic hydrocarbon such as **294a** is slightly predominant during protonation of the (trimethylstannyl)allene **293a** whereas reverse chemoselectivity was observed by reaction with the corresponding triphenyl derivative **293e** that gives up to 85% of acetylenic product. This difference could be attributed to steric hindrance around the tin atom increasing from methyl, to ethyl and phenyl that prevents internal attack of proton, but also to the electron-withdrawing effect of three phenyl substituents transmitted across the heteroatom to the C-1-C-2 double bond (entries 6, 9, 10).

A neighboring group participation of a phenyl group can occur during protonation reaction of allenyltin derivatives bearing this substituent. This cationic stabilizing effect, through the formation of phenonium species, will orientate the chemoselectivity of the protonation towards the double bond bearing the phenyl group. With the allene **293c** ($R^1 = \text{Ph}$), the formation of the isomeric allene **294c** will be favored by attack on the carbon C-1, whereas with the allene **293b** ($R^2 = \text{Ph}$) the protonation will occur on the carbon C-3 and afford predominantly the acetylene **295b** (entries 7 and 8 and eq 37 and 38).

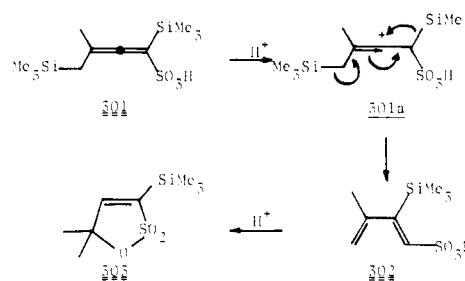
Second-order kinetics was found for protonation of allenyltin derivatives. The reaction rate (k_2) always decreases with the substitution of a methyl group by a phenyl group and this retardation seems to be additive; the decreasing factor being roughly 4.2.



B. Organosilicon Derivatives

Proto- and halodesilylation of alkenylsilanes have been extensively studied and shown to occur often with

SCHEME XXIII



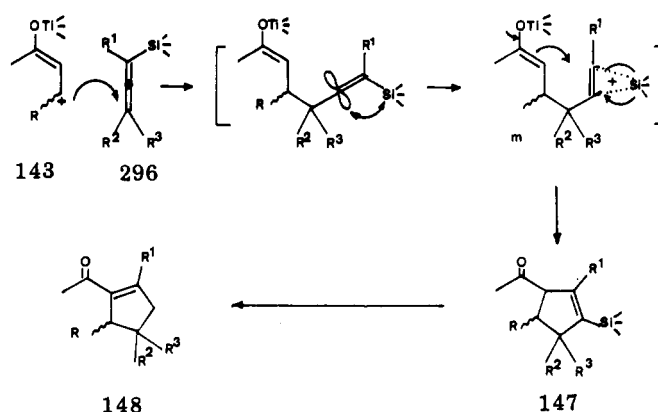
retention of the double bond configuration.¹⁹⁰

Sulfonation of the silylated allenes **296** using SO_3 or $\text{ClSO}_3\text{SiMe}_3$ as electrophilic reagent, affords variously unsaturated silyl esters of sulfonic acid **297-299** with $\text{E} = \text{O}_2\text{SO}_3\text{SiMe}_3$ (entries 11-14 and 17,18).

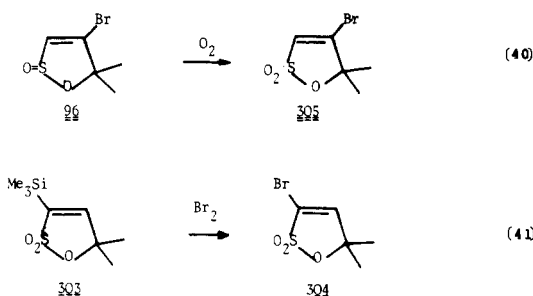
Electrophilic desilylation of (trimethylsilyl)allene takes place either with retention of allenic linkage or, more frequently, by allene-acetylene isomerization that takes place through two different vinylic cations by electrophilic addition on terminal carbon atoms (Scheme XX for $\text{A} = \text{SiMe}_3$). Sulfonation of both monosilylated and *gem*-disilylated allenes **296** is 100% chemoselective leading to propargylic sulfonic esters **298** by addition on the less hindered γ -position of the allenic linkage, the vinylic intermediate **298a** being then desilylated intramolecularly in a twisted dipolar five-membered cyclic species (entries 11,12 and path α of Scheme XXII). However, when terminal carbons of allene are not well differentiated sterically, up to 40% of allenesulfonic ester **297** is formed with retention and SO_3 addition will take place on the α -carbon atom, which is followed by an intramolecular desilylation reaction via a four-membered cyclic transition state (entry 13 and path β of Scheme XXII).

An interesting 1,2-cationic rearrangement of the trimethylsilyl group across the double bond has been observed from a vinylic carbonium intermediate during protonation of the allenesulfonic acid **301** leading to the

SCHEME XXIV



conjugated diene sulfonic acid **302** that is followed by acid-catalyzed cyclization affording the 3-silyl γ -sultone **303** (Scheme XXIII). This product could be a very valuable starting material for synthesis of 3-halo- γ -sultones that are isomeric forms of the corresponding 4-bromo- γ -sultone obtained by bromocyclization of allenyl sulfonic ester followed by oxidation (see entry 85 of Table II and eq 40 and 41).

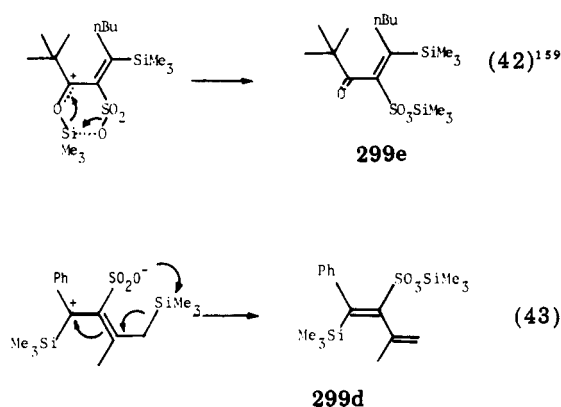


It has been shown, very recently,^{158b} that (trimethylsilyl)allenes **296** can be used, as three-carbon components, for cyclopentannulation (entries 19–24). This reaction affords an alkoxy allylic carbocation by initial complexation of an α,β -unsaturated ketone and TiCl_4 . This cation adds 100% regioselectively on the terminal carbon C-3 of the silylated substrate providing a vinyl cation that is stabilized by the cis-coplanar C–Si bond. Migration of the SiMe_3 group across the vinyl cation double bond affords an isomeric vinyl cation that is intercepted by the titanium enolate to produce a new five-membered ring (Scheme XXIV). Isomerization followed by desilylation transforms the silylated cyclopentene to an α,β -unsaturated ketone.

It is noteworthy that the unsubstituted silylallene **296a** ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$) affords a poor yield of cyclic product because of the relative instability of the primary terminal vinyl cation (entry 19), required in the mechanism proposed^{158b} and depicted in Scheme XXIV, whereas a good yield of δ -ynone is obtained when α,β -enone is replaced by the corresponding more reactive α,β -ethylenic acyl cyanide (entry 27). The (trimethylsilyl)cyclopentene annulation is stereoselective with *trans*-3-penten-2-one and cyclohexenone (entries 25,26).

Finally, when a strongly electron-donating substituent, such as a silyl ether group, is bound to an allenylsilicon derivative, sulfonation affords stabilized allylic carbonium ion, an alkoxonium ion, by electrophilic central attack. Some allene-conjugated diene isomer-

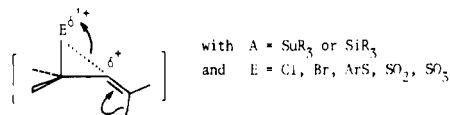
ization will take place during addition reaction, leading to the α -enone **299e** (entry 18 and eq 42). Some con-



jugated diene is also obtained by sulfonation of silylated phenylallene bearing a second silicon atom in the δ -position allowing a 1,4-elimination reaction (entry 17 and eq 43).

C. Discussion

Except for protonation, electrophilic addition to allenyltin and -silicon (halogenation, sulfenylation, sulfonylation, sulfonation) occurs with complete allenyl-propargyl rearrangement. This 100% chemoselective electrophilic substitution with transposition (S_{E}') affords various functional propargyl products very probably through a bridged species with vinylic carbocationic character.



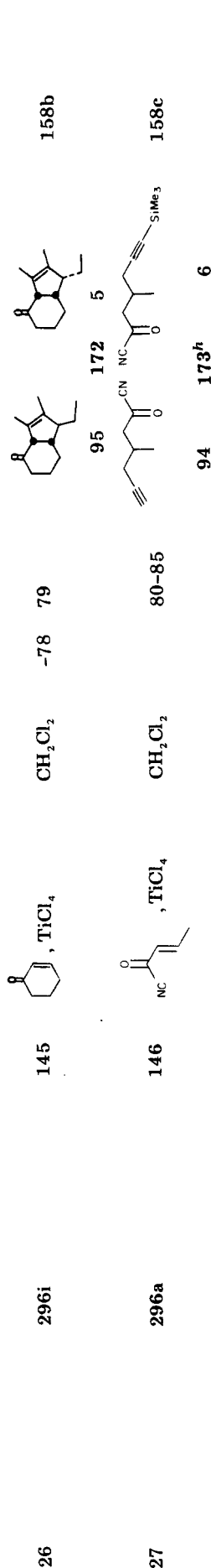
The possible concertedness of this reaction could be accessible by using optically active allenic substrates, and some research has yet to be done. However, an interesting migration of the trimethylsilyl group has been exploited for a one-step cyclopentene annulation and for a synthesis of 3-silylated γ -sultone.

VIII. Solvometalation ($\text{E} = \text{M}_n\text{X}_{n-1}$) (Table XII)

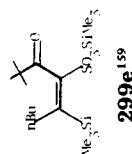
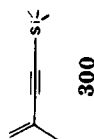
In the last part of this study of electrophilic addition to allenic derivatives, reaction of metallic salts, mercuric (HgX_2), thallic (TlX_3) and plumbic (PbX_4), with various allenes are described. Solvents that are more often

Table XI. Electrophilic Addition to Allenyl Tin and Silicon Derivatives

entry	allenic derivatives	reagents	solvent	T, °C	yields, %	product composition, %	ref
1	R	Cl ₂			77	294(S _E)	155
2	Me	Br ₂			92	295(S _E)	155
3	Me	DNBSC			69		155
4	Me	SO ₂					156, 157
5	H	SO ₂					156, 157
6	Ph	HCl			57		155
7	Me	HCl			40		155
8	Me	HCl			85		155
9	Et	HCl			33		155
10	Ph	HCl			11		155
11	R ¹	"SO ₃ " ^{c,d}			good	297 ^b	158a
12	H	"SO ₃ " ^{c,d}					158a
13	Me ₂ Si	"SO ₃ " ^{c,d}					157, 158a
14	Me ₃ SiCH ₂	MeSO ₃ H			70	(25) ^c 40 ^d	157
15	Me ₂ Si	Br ₂			70	^e	157
16	Me ₃ SiCH ₂	<i>t</i> -BuOCl, AlCl ₃ ⁱ			70	100 ^f	157
17	Me ₃ Si	"SO ₃ " ^{c,d}					158a
18	Ph	"SO ₃ " ^{c,d}					158a, 159
19	R ¹		CH ₂ Cl ₂	-78	17-19	147	158b
20	H	TiCl ₄			48-94		
21	Me	TiCl ₄			69-85		
22	<i>i</i> -Pr	TiCl ₄			68		
23	Me	TiCl ₄			79		
24	Et	TiCl ₄			60-80		
25	Me	TiCl ₄	CH ₂ Cl ₂	-78	69		158b



^a With sulfur dioxide the product 295 is a propargyl sulfinic tin ester with $\text{E} = \text{OSOSnR}_3$ resulting from a six-membered cyclic transition state depicted for the silicon in Scheme XXII. ^b With sulfur trioxide SO_3 the products 297-299 are unsaturated sulfonic silyl esters with $\text{E} = \text{O}_2\text{SOSiMe}_3$, ^c " SO_3 " = $\text{ClSO}_3\text{SiMe}_3$, ^d " SO_3 " = $\text{SO}_3/\text{dioxane}$. ^e The bromination product is the conjugated enyne 300, which has been formed by elimination of BrSiMe_3 from an unstable α -bromo- β -silylated propynylic derivative. ^f $\text{E} = \text{O}-t\text{-Bu}$. ^g The product 299e is an α -enone. ^h The ratio 94:6 has been corrected in order to take into account the 20% of propargylsilane present in the starting material.



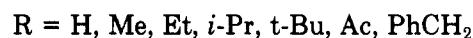
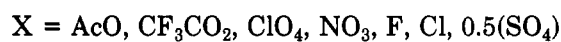
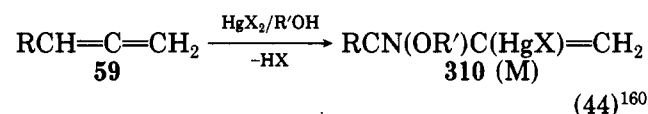
protic play an important role; they participate as a nucleophile in the formation of products and the metalation reaction is then called solvomercuration. Reactivity of these salts are directly dependent upon the nature of their anions X^- (AcO^- , ClO_4^- , NO_3^- , F^- , Cl^- , CF_3COO^- , and $0.5(\text{SO}_4)^{2-}$); it has been shown that mercuration of olefins occurs faster with the increasing ionic character of Hg-X bond as follows: $\text{Hg}(\text{ClO}_4)_2 > \text{Hg}(\text{ClO})_2 \gg \text{HgCl}_2$.¹⁹⁶

A. Solvomercuration ($\text{E} = \text{HgX}$)

Early in 1967, oxymercuration of allenes has been studied simultaneously by Gardner⁴⁵ and Kiefer¹⁶⁰ and aminomercuration was studied by Lattes.¹⁶⁸ Their results were subsequently confirmed and completed by Caserio,⁷⁷ Bach,¹⁶⁴ Devaprabhakara,¹⁷⁸ and Pirkle.¹⁶⁹

1. Solvomercuration of Acyclic Allenes

(a) **Chemo- and Regioselectivity.** Solvomercuration of dissymmetric acyclic allenes is chemo- and regioselective. Addition of mercuric salt occurs predominantly, if not exclusively, on the more substituted double bond leading to the monoadduct 310 with Markovnikov orientation obtained by central attack of the mercuric salt (entries 4, 18-20, 23-29).

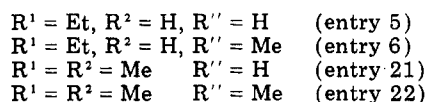
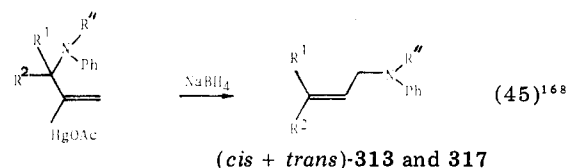


The 100% Markovnikov regioselectivity is retained during *tert*-butoxymercuration of the hindered 1,1-dimethylallene 49 leading to exclusive formation of tertiary allylic derivatives 316 (entries 18-20).

The structure of the Markovnikov chloromercury monoadduct 316 was unequivocally established by ¹H NMR spectroscopy by studying heteronuclear coupling constant ³J_{H-Hg} for nuclei directly attached to the π bond. The relationship ³J_{trans} > ³J_{cis} was used (Table XIII).

Allylic alcohols 316-OH and 350-OH were formed by aqueous workup of the corresponding allylic acetates, which are byproducts obtained by competitive attack of acetoxy ion that increases with steric interaction to the entering of nucleophile (cf. entries 19 and 20, 25 and 26, and 26 and 28).

Formation of the other chemoisomer such as 313, 317, or 351 obtained during aminomercuration of 1,2-allenes



followed by reductive demercuration of the corre-

TABLE XII. Metalation of Allenic Derivatives

entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %	ref
1	1	Hg(OAc) ₂ ^b	MeOH/H ₂ O	RT	95	 307(M)	
2		Hg(OAc) ₂ , NaBH ₄	PhNH ₂ / THF/H ₂ O		10	PhNHCH ₂ CH=CH ₂	(MeO) ₂ C(CH ₂ HgOAc) ₂ ^a 160
3		HgMe ₂ ^c			97		168
4	59d (R = Me)	Hg(OAc) ₂	MeOH	RT	95	 310(M)	(E) 311(aM) (Z)
	59e (R = Et)	Hg(OAc) ₂ , NaBH ₄ ^b	PhNHR''/ THF/H ₂ O			 312	MeCH(HgOAc)C(OMe) ₂ CH ₂ HgOAc ^c 33
5			R'' = H		55	 313	80
6			R'' = Me		30	 314	25
	12					(cis) 313 (trans)	
7	12a (R = Me)	HgCl ₂ ^e	EtOH	RT		 315	100 ^{f,h}
8		Hg(OAc) ₂	MeOH	RT	93		75
9		Hg(OAc) ₂	MeOH	RT	100 ^h		83
10		Hg(OAc) ₂	i-PrOH	RT	95 ^{h,i}		83
11		Hg(OAc) ₂	t-BuOH	RT	75 ^{h,i}		86
12	(R)-12a α _D -15.9 ^{g,z}	Hg(OAc) ₂	MeOH	RT	h		S 83 (op 7.0)
13	(R)-12a α _D -14.5	Hg(OAc) ₂	MeOH	RT	h		S 86 (ee 9.2)
14	(R)-12a α _D -29.6	Hg(OAc) ₂	MeOH	RT	h		S 95 (ee 19.0)
	12b (R = Et)		MeOH	-78			
15	(R)-12b α _D -22.7 ^z	Hg(OAc) ₂	MeOH	-78	h		S 96 (ee 21.6)
16	(S)-12b α _D +33.8	Hg(OAc) ₂	MeOH	-78	h		R 94 (ee 31.1)
17	(R)-12b α _D -26.4	EtHgOAc, BF ₃ ·OEt ₂		0	j		S 95 (ee 25)
	49a (R = Me)					 316 (R = Me)	
						 317	

160
160
160R'O HO AcO
100
50 28 14
10 60 30MeOH
i-PrOH
t-BuOH
PhNHR''/
THF/H₂OHg(OAc)₂
Hg(OAc)₂
Hg(OAc)₂,^b
NaBH₄18
19
20168
168343 100 (R'' = H)
344 50 (R'' = Me)50
4521
22

181a



350

351

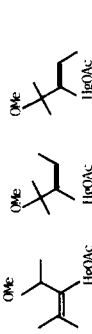
Hg(OAc)₂,
I₂23
24
25
26
27R'O HO
10
4
10
15
25
6 8H₂O
MeOH
EtOH
i-PrOH
H
i-PrOHHg(OAc)₂23
24
25
26
27

49b (R = Et)



29

73a

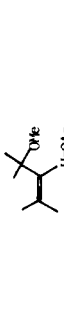
319
18Hg(OAc)₂

29



30

36

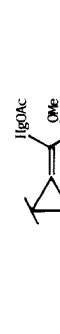
320
72Hg(OAc)₂

30



31

38

195
196 (79a,b)Hg(OAc)₂

31



197 (21)

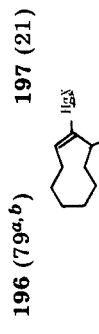
Hg(OAc)₂,
NaBH₄

32



33

20

199 (E) 100
200 (ee 8.4)

AcOH


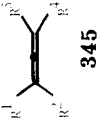

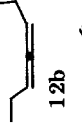
32

(R)-20^z
α_D 18.8°33
34100
(R)-20^z
100 (ee 8.4)EtOH
MeOH33
3445, 178, 179
169

TABLE XII (Continued)

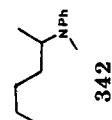
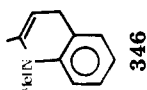
entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %	ref
35	20	HgO/BF ₃ ¹	MeOH		69	 OR (<i>cis</i>)-322	164
36		HgO/BF ₃ ¹	<i>i</i> -PrOH		81	(<i>cis</i>)-322	164
37		HgO/BF ₃ ¹	EtOH (reflux)		80 (71)	(<i>cis</i>)-322	45, 164
38		HgO/BF ₃ ¹	<i>t</i> -BuOH		63	(<i>cis</i>)-322	164
39		HgO/BF ₃ ¹	PhCH ₂ OH		85	(<i>cis</i>)-322	164
40		HgSO ₄ -H ₂ SO ₄	MeOH		75 (56)	(<i>cis</i>)-322	45, 164
41		HgSO ₄ -H ₂ SO ₄	H ₂ O-AcMe(H ₂ O, THF)		78 (30)	(<i>cis</i>)-322	
42	 (<i>S</i>)-20	HgO/BF ₃	EtOH			(<i>S</i>)- <i>cis</i> -322	164
43	(<i>S</i>)-20	HgO/BF ₃	MeOH			α D + 17.7°	164
44	α D - 145.3°	HgO/BF ₃	H ₂ O-Dioxane			α D + 7.3° α D + 8.3°	164
45	α^{25} D - 81.8° (o.p. 36.7%) ¹⁶⁹	EtHgOAc/ BF ₃	EtOH		85	α^{25} D + 15.3°	165
46		PhHgOAc/ BF ₃	EtOH		42	α^{25} D + 13.6°	165
47		Hg(OAc) ₂	EtOH		67	α^{25} D + 12.6°	165
48		Hg(ClO ₄) ₂	EtOH		82	α^{25} D + 12.1°	165
49		HgO/BF ₃	EtOH		73	α^{25} D + 11.1°	165
50		HgSO ₄	EtOH		72	α^{25} D + 10.4°	165
51		Hg(NO ₃) ₂	EtOH		70	α^{25} D + 9.9°	165
52		HgF ₂	EtOH			α^{25} D + 1.4°	165
53	α^{25} D - 14.6° (o.p. 6.5%) ¹⁶⁹	HgCl ₂	EtOH			α^{25} D + 0°	165
54		Hg(OAc) ₂	AcOH			α^{25} D + 1.1°	166
55	 334	HgCl ₂	EtOH			 OR 335	45
56	17	HgSO ₄ /H ₂ SO ₄	MeOH		65	85 (trans) (R = Me)	164, 179
57	17	HgO/BF ₃	EtOH		78	15 (cis) 85 (trans) (R = Et)	164
58	(<i>R</i>)-17 ^z α D + 15.2°	Hg(OAc) ₂ , NaCl	MeOH		86	 OR (<i>S</i>)-(Z)-323	169

TABLE XII (Continued)

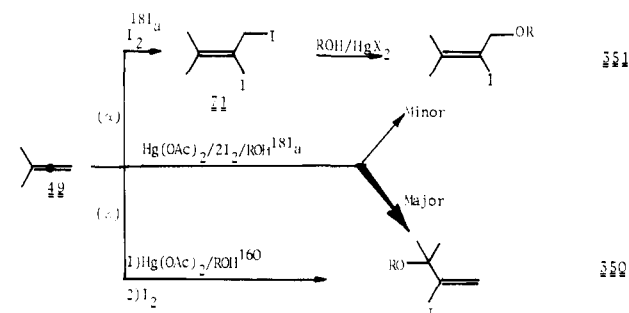
entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %	ref
82	325 (Y = Br)	HgBr ₂	acetone	RT	49	331 Y	171b
83		HgCl ₂	acetone	RT	56	100 (Br)	171b
84		HgCl ₂	aprotic solvents ^s	variable	61-97	0-12 (Cl)	171b
85	325 (Y = Cl)	HgCl ₂	acetone	RT	56	100	171b
86	325 (Y = Cl)	HgBr ₂	acetone	RT	55	100 (Cl)	
87	 (S)-20	Tl(OAc) ₃ /NaBH ₄ /BF ₃	AcOH	RT	(84) ^f 61	(S)-(cis)-322	177
88	$\alpha_D - 15.6^\circ$ (o.p. 7%)	Tl(OAc) ₃ /NaBH ₄ /BF ₃	MeOH	RT	(76) ^f 73	$\alpha_D + 0.9^\circ$	
89		Tl(OAc) ₃ /NaBH ₄ /BF ₃	EtOH	RT		$+ 2.8^\circ$	
90		Tl(NO ₃) ₃ NaBH ₄	MeOH	RT		$+ 4.0^\circ$	
91	$\alpha_D - 22.7^\circ$ (o.p. 10.2%)	Tl(NO ₃) ₃ NaBH ₄	EtOH	RT		$+ 2.2^\circ$	
						$+ 2.7^\circ$	
92	 345	Tl(OAc) ₃ /BF ₃	MeOH				176
93	a				100		
94	b				94		
	c				50		
95	 (S)-12a	Pb(OAc) ₄ ^u	AcOH, THF	RT	41.4 ^u	(S)-347 ^w	175
	$\alpha_D + 22.4^\circ$ (o.p. 12.9%) ^{g, 169}					$\alpha_D + 6.6^\circ$ (o.p. 7.4%) ^w (O.Y. = 57%)	
96	 12b	Pb(OAc) ₄	AcOH	RT		348 (> 75%)	175
97	(S)-20	Pb(OAc) ₄	AcOH			(R)-349 (major)	166
	$\alpha_D - 14.6^\circ$ (o.p. 6.5%) ¹⁶⁹					(R)-322 ^x	
						$\alpha_D + 7.6^\circ$	
						$\alpha_D - 9.3^\circ$ (o.p. ?)	

^a These bisadducts are easily hydrolyzed during aqueous workup affording remarkably stable α, α' -dimercury ketones. ^b Solvomercuration is followed by reductive demercuration reaction using NaBH₄ under basic conditions. ^c This mercurinium ion has been observed in gas phase. ^d 60% of the saturated amine 342 is also obtained (see Scheme XXVI). ^e Methoxymercuration of the optically active 2,3-pentadiene (R)-(-)-12a by using HgCl₂ as mercuric salt affords racemization of the starting allene. ^f The geometrical configuration of the product 314 is not given. ^g Optical purity has been determined according to Brewster¹⁶² and found to be 9.1%. The specific rotation of the 2,3-pentadiene $\alpha_D 17.4^\circ$ is in perfect agreement with the value that has been determined subsequently by Pirkle.¹⁶⁹ ^h Mixture of acetoxymercury adducts (HgX = HgOAc) such

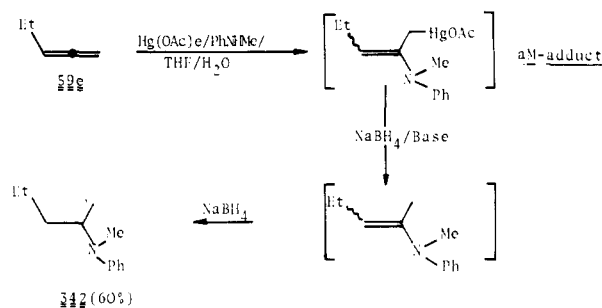
as 314 has been analyzed as stable chloromercury derivative (HgX = HgCl) obtained after an exchange with NaCl. ⁱ 5% and 25% of corresponding allylic acetates are respectively obtained during oxymercuration of the allene 12a by using 2-propanol and 2-methyl-2-propanol. ^j An additional Lewis acid, such as BF₃·OEt₂, is always needed when the anion X⁻ corresponding to the mercuric salt would afford weak acid during oxymercuration (eq 44). In this case, an in-situ protodemercuration occurs and allylic ethers are directly obtained. ^k 50% of the amine 346 is also formed (eq 46). ^l BF₃·OEt₂ is present in a catalytic amount (0.1 molar equiv). ^m HgSO₄ and Hg(OAc)₂ give a similar mixture of the products 337-339. ⁿ The tricyclic compound 339 is unstable in formic acid. ^o For the optically pure oxaphospholene 324, the melting point is 255-257 °C and the specific rotation is α_D 16.6°. ^p The yields between brackets are after treatment with HClO₄. ^q For clarity the phenyl substituents of the products 326-331 are not represented, only the C-C bonds are drawn. ^r 77% of the product 330 was protodemercrated. ^s The solvents used are Me₂CO, *t*-Bu₂CO, THF, OEt₂, CS₂, MeCN, AcOH, and PhOH. ^t The yields in brackets are of thallium adducts. ^u Allene 12a and lead tetraacetate are in stoichiometric amounts. ^v Bis(acetates) are also present in the mixture. ^w The *S* structure and the optical purity (7.4%) for the propargyl acetate 347 have been established by correlation with the (*S*)-(+)-2-pentanol with specific rotation α_D 18.8° after saponification and catalytic hydrogenation of 347; thus the acetate 347 with α_D +6.6° obtained in the reaction leads to the (*S*)-(+)-2-pentanol with α_D 1.36°. ^x Importantly the configuration of the allylic acetate (*R*)-322 is opposite to the one obtained in the corresponding oxymercuration. ^y The acetoxyplumbation of the 1,2-cyclononadiene 20 was shown to be 8 times more stereospecific than the corresponding oxymercuration (compare entries 54 and 97). ^z Interestingly oxymercuration of allenes 12b, 12a, 17, and 20 allows the determination of the specific rotation of these allenes which are, respectively, 104 ± 2°, 175 ± 1°, 195°, and 223°, when chiral solvating agent and ¹H NMR are used (see entries 15, 12, 58, and 34).¹⁶⁹



SCHEME XXV



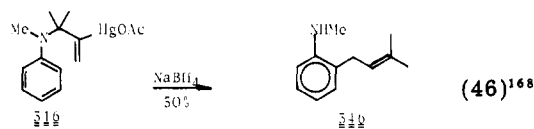
SCHEME XXVI



sponding monoadduct on the one hand, and by oxymercuration followed by in situ iododemercuration of 1,1-dimethylallene on the other, is always due to an allylic rearrangement (entries 5, 6, 21-28).

In the last case, it seems that iodination followed by nucleophilic substitution of primary allylic iodide 71 which is catalyzed by mercuric salts (path α of Scheme XXV) competes with oxymercuration followed by iododemercuration (path β of Scheme XXI) (entries 23-28).

Aminomercuration of the allene 49a, using Hg(OAc)₂ as mercuric salt, water as external ligand, and *N*-methylaniline as entering nucleophile, affords up to 50% of the ortho-substituted *N*-methylaniline 346. This byproduct was probably formed by an amino Claisen rearrangement during the reductive demercuration of the acetoxymercury adduct 316 (entry 22).



Solvomercuration of the nonsubstituted double bond of 1,2-allenes can also take place. This chemoselectivity occurs to the extent of 33% in the methoxymercuration of the 1,2-butadiene 59d (entry 4) and to the extent of 60% in the aminomercuration of 1,2-pentadiene 59e by using the more bulky aniline (entry 6). In those cases, electrophilic attack of the mercury occurs on the terminal carbon atom of the cumulated double bonds. However, the anti-Markovnikov monoadducts that should be formed are reactive entities and a subsequent oxymercuration of the remaining double bond takes place affording the bisadducts 307 and 311 isolable, after aqueous workup, as α,α'-dimercury ketones²⁰³ (entries 1,4).

It is also of interest to note that the predominant saturated amine 342 (Scheme XXVI) obtained by am-

TABLE XIII. NMR Data for 316

316

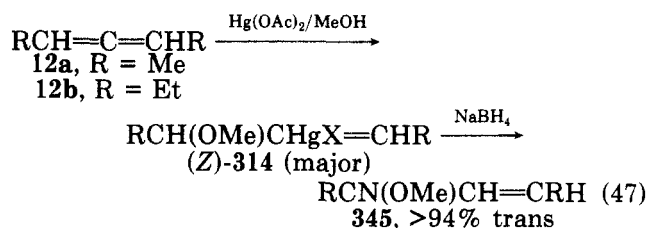
R	N	X	trans, δ Hb, ppm	cis, δ Ha, ppm	trans, 3J Hb, ^{199}Hg , Hz	cis, 3J Ha, ^{199}Hg , Hz	ref
Me	OMe	Cl	5.73	5.35	620	315	160
Me	PhNH	Cl	5.60	5.10	622	312	168
Me	OH	OAc	5.60	5.15	630	320	181b
Et	OH	OAc	5.53	5.23	640	332	181b

inomercuration of the nonsubstituted double bond of the 1,2-pentadiene **59e** with anti-Markovnikov orientation, was due to a full hydrogenation of the double bond during the reductive demercuration (entry 6).

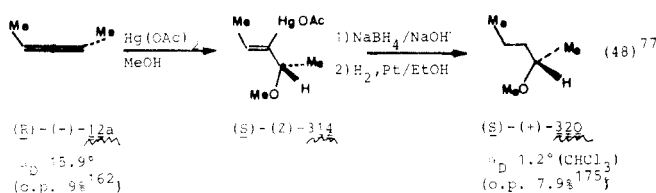
The overcrowded mercury-containing ion, obtained by methoxymercuration of tetramethylallene **36**, undergoes nucleophilic attack leading to the expected Markovnikov monoadduct **320** with excellent yield (entry 30). Methoxymercuration of cyclopropylideneallene **38** occurs on the isopropylidene double bond affording the normal addition product without participation of the cyclopropane ring unless reaction is followed by reductive demercuration (cf. entries 31 and 32).

(b) Z Stereoselectivity. Methoxymercuration of the symmetrically 1,3-disubstituted allenes **12** affords an acetoxymercury adduct with a predominant *Z* configuration. This is a very general process for acyclic allenes (entries 7–17, 29). An electrophile is then introduced on the central carbon atom on the more crowded face of the reactive double bond (see Scheme VI with E = HgX). The *Z* stereochemistry could be explained by reversible formation of mercury-containing ion followed by nucleophilic attack of alcohol, which is the rate- and product-determining step occurring on the least hindered side of the intermediate double bond (see Scheme X with E = HgX).^{160,169}

Oxymercuration of acyclic allenes followed by reductive demercuration either under acidic conditions ($\text{BF}_3 \cdot \text{OEt}_2$, H_2SO_4 , HNO_3) or under basic conditions ($\text{NaBH}_4/\text{base}$) affords a very attractive route to stereoselective synthesis of *trans*-allylic alcohols, ethers, or acetates (entries 14–17). The *Z*:*E* ratio = 4.9 at room temperature and may reach 17 at 0 °C or -78 °C (entries 14–17). The organomercury adduct **314** (HgX = HgCl) has been isolated as a chloromercury product by exchange with NaCl.



(c) Anti Stereospecificity. The stereochemistry of acyclic allenes was established early in 1968 by Caserio.⁷⁷ It was shown that methoxymercuration of the (*R*)-(-)-2,3-pentadiene **12a** followed by reductive demercuration and catalytic hydrogenation affords the dextrorotatory 2-methoxypentane that is known to have the *S* configuration (entry 12).



The *S* structure of the major organomercury adduct (*Z*)-**314** obtained from the allene (*R*)-**12a** implies an anti mechanism for the oxymercuration of acyclic allenes. This anti stereochemistry is in agreement with a back-side solvent approach in the mercury-containing intermediate (see path γ of Chart I and Scheme X with E = HgX).^{77,169}

Pirkle¹⁶⁹ has recently shown that methoxymercuration of the (*R*)- and (*S*)-3,4-pentadiene **12b** using $\text{Hg}(\text{OAc})_2$ as mercuric salt proceeds stereospecifically by an anti mechanism, the reaction occurs with the same stereospecificity when EtHgOAc is used (entries 15–17). Enantiomeric excesses of the major adducts (*Z*)-**314** and (*Z*)-**315** have been determined by proton NMR spectroscopy using the (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol **353** as chiral solvating agent affording the specific rotations of 2,3-pentadiene and 3,4-heptadiene which, are found to be, $175 \pm 1^\circ$ and $104 \pm 1^\circ$, respectively; methoxymercuration of acyclic allenes by the two procedures is considered as 100% stereospecific (entries 13–17).

Finally, attempts made to study the stereochemistry of acyclic allene oxymercuration by some reverse reaction leading to starting allene, namely deoxymercuration, failed.¹⁶³ Demercuration of the acetoxymercury adduct **314** by BF_4H in methanol affords a mixture of allylic ethers $\text{MeCH}=\text{CHCH}(\text{OMe})\text{Me}$, whereas treatment of optically active chloromercury adduct **314** gives racemic 2,3-pentadiene **12a** by reaction with an excess of HCl.

The mercurinium ion, postulated to explain the anti mechanism occurring in oxymercuration of acyclic allenes, has been observed in the gas phase by reaction of allene itself and dimethylmercury (entry 3). It was shown that up to 97% is a symmetrical bridged mono-adduct **1d** whereas dissymmetric forms, corresponding to the vinyl ion **1a** and α,β -ethylenic carbonium ion **1b**, are less stable by 19 and 13 kcal/mol, respectively (see Chart I for E = HgMe).

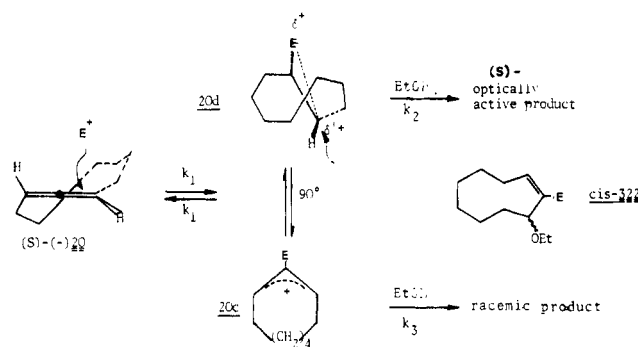


Figure 24. Reference 165.

2. Oxymercuration of Cyclic Allenes

(a) **Regioselectivity and cis Stereoselectivity.** Whatever the size of the ring, oxymercuration of cyclic allenes is completely regioselective with Markovnikov orientation; the mercury was linked to the central carbon atom of the allenic cumulated double bond, leading to allylic alcohols, ethers, and acetates, **321–323** and **335** (entries 33–58). Oxymercuration of the 1,2-cyclononadiene **20**, followed by protodemercuration is 100% *cis* stereoselective. This usual stereochemistry found for electrophilic addition to the strained cyclic allenes, is consistent with the electrophile entering on the less crowded face of the reacting double bond (eq 9 leading to product **19** with $E = \text{HgX}$). Attack from the inside of the ring is only possible with the large cyclic system of the 1,2-cyclotridecadiene **17**, in which the *trans* stereoselectivity obtained is very similar to that formed with open chain allenes (entries 56–58).

Hydration of a macrocyclic allene, namely the 1,2-cyclopentadecadiene, has been used recently for an industrial synthesis of a precursor of muscone; different mercuric salts, such as $\text{Hg}(\text{OAc})_2$, $\text{Hg}(\text{OCOCF}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, and HgSO_4 ¹⁹⁵ were used.

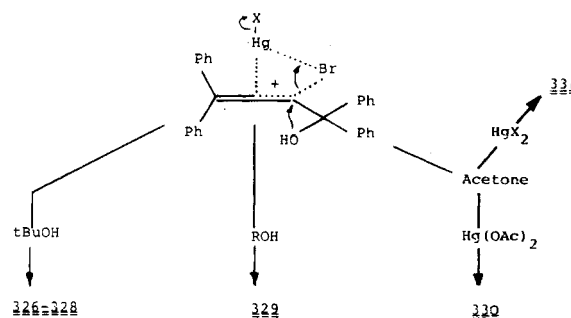
(b) **Anti Stereospecificity.** The syn-anti stereospecificity, of oxymercuration of cyclic allenes has been studied by Bach^{164–166} and Pirkle.¹⁶⁹ At first, it was found that ethoxymercuration of optically active 1,2-cyclononadiene **20** followed by protodemercuration was stereospecific. This transfer of chirality was directly dependent on the nature of mercuric salts and the nature of solvent (entries 42–54).

It was established that methoxymercuration of the allene **20** was 1.4 times more stereospecific than the corresponding hydroxymercuration (entries 43, 44). The *cis*-allylic alcohol **322** with optical rotation with $\alpha_D +8.3^\circ$ was converted by Williamson synthesis to the corresponding methyl ether with $\alpha_D +5.3^\circ$ whereas the direct methoxymercuration of the same allene affords 3-methoxy-*cis*-cyclononene with $\alpha_D +7.3^\circ$.

It was also reported that stereospecificity of ethoxymercuration of the 1,2-cyclononadiene **20** is maximum with EtHgOAc , and will decrease with the electron-releasing effect of the mercury substituents (entries 45–53). These results have been interpreted by stabilization of mercurinium ion **20d** by electron-donating substituents on mercury, leading to optically active products, whereas electron-withdrawing substituents will favor planar allylic carbonium ion **20b** affording racemic allylic ether (Figure 24 with $E = \text{HgX}$).

Oxymercuration of the 1,2-cyclononadiene **20** was shown to proceed stereospecifically by an anti mecha-

SCHEME XXVII



nism, the *R* and *S* enantiomers of the starting allene was converted to the corresponding optically active *cis*-allylic products **322** with *R* and *S* configurations, respectively (entries 34,54 and Figure 24 with $E = \text{HgX}$); whereas, methoxymercuration of the (*R*)-1,2-cyclotridecadiene **17** was also anti stereospecific leading to the monoadduct **323** with (*S*)-*Z* configuration (entry 58).

B. Mercuration with Intramolecular Participation

Some neighboring group participations have been reported during mercuration of α - and β -functionalized allenes (entries 59–86), whereas, the corresponding homoallylic allene **334** affords normal chloromercury adduct **335** (entry 55).

1. α -Functional Derivatives

Acetoxymercuration of the optically active allenylphosphonic acid (*R*)-**101** occurs stereospecifically leading to the 4-(chloromercurio)oxaphospholene (*R*)-**334** with 86% of optical yield; this mercuration-induced cyclization proceeds by an anti mechanism (entry 64).

Acetoxymercuration of the variously substituted vinylallenes **332**, followed by protodemercuration using hot perchloric acid, affords the cyclopentenones **333** (entries 65–70). The ring-opening process of the mercurinium ion, followed by intramolecular participation of olefinic double bond, is very similar to evolution of α,β -ethylenic allene oxide obtained by epoxidation of the same vinylallene **332** (vide supra).

Mercuration of the halogeno α -allenic alcohol **325Y** ($Y = \text{Cl}, \text{Br}$) (Scheme XXVII) has been extensively studied and shown to occur through a $n-\pi$ mercurinium intermediate by neighboring group participation of both allenyl bromide and α -allenic hydroxy group. The products **326–331** obtained are directly dependent on the nature and the size of the nucleophile and also on the anion of the mercuric salt.

In protic solvents that are weak nucleophiles or bulky such as, AcOH , *t*- BuOH , or *t*- AmOH , intramolecular attack of this intermediate by the hydroxy group is predominant leading to the epoxide **326** and to the thermally more stable dihydrofurans **327** and **328**. This product formation is followed by some exchange between the halogen of the allene **325Y** and anions of mercuric salts (entries 71–77).

In the other protic solvents such as H_2O , MeOH , and EtOH , some mercury-assisted nucleophilic substitution followed by allenyl-propargyl rearrangement seems to occur leading to the 1,4-acetylenic glycol **329** or to its monoether. The yield of this product is very sensitive to the solvent bulkiness, which is in agreement with an

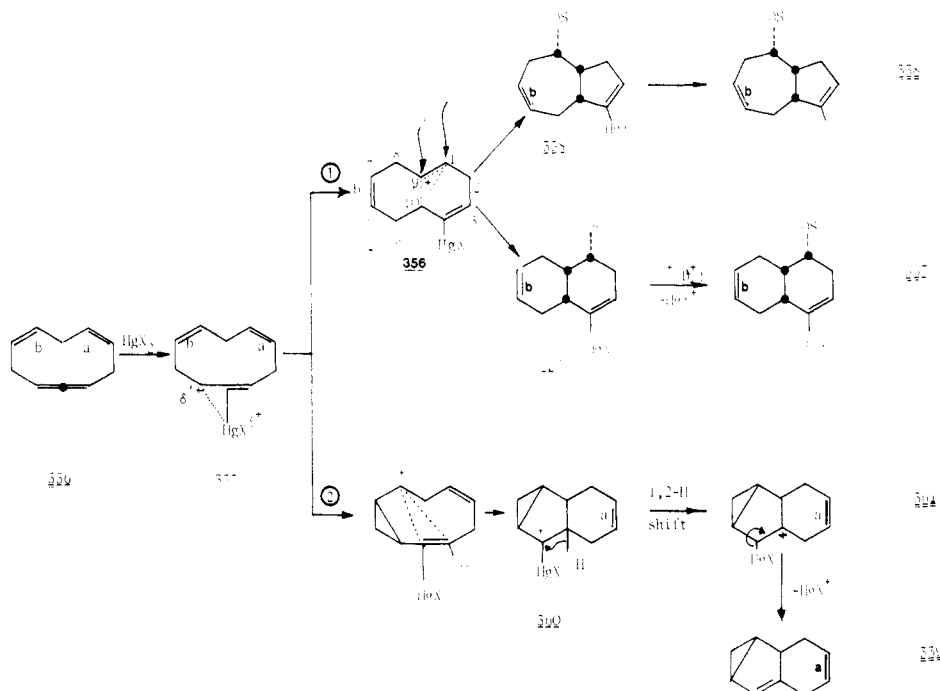


Figure 25. Reference 173.

S_N2' process (entries 78–80).

Finally, the reaction of mercuric halides with the allene **325Y** in aprotic solvents or in acetone gives mainly, if not exclusively, the halobenzofulvenes **331Y** in which transhalogenation occurs again. In mercuric acetate, only the naphthalenone **330** is obtained. These aromatic products have been formed by electrophilic substitution via the long-lived tertiary benzhydrylic carbonium ion (entries 81–86).

2. β -Functional Derivatives

Reaction of mercuric salts with the symmetrical 1,2,5,8-cyclodecatetraene **336** affords cyclic products **337–339** all of which are formed with neighboring group participation of one of the two isolated double bonds, namely a and b (Figure 25 and entries 59–62). The structure of products is related to the nucleophilicity of the solvent. The bicyclic compounds **337** and **338** are formed by participation of the double bond a through path 1 of Figure 25, and the hexahydronaphthalenol **337** becomes the main product in water. The tricyclic hydrocarbon **339** is the major compound when the reaction is performed in trifluoroethanol, a solvent of very weak nucleophilicity; the reaction occurs through path 2 of Figure 25, by participation of allylic double bond b. When AcOD is used, deuterium has been incorporated in the bicyclic product **337**, whereas no incorporation is found in the tricyclic diene **339**. This is in agreement with a protodemercuration of the mercury adduct **357** and with a 1,2-hydride shift followed by demercuration of the carbonium ion **361** (Figure 25).

With the dissymmetrical ten-membered ring allylic allene **340**, the mercuriation is chemoselective, and occurs on the double bond of the cumulated diene which is the nearest to the isolated one. An evolution similar to path 2 of Figure 25 will take place and afford the tricyclic olefin **341** with up to 72% yield (entry 63).

C. Solvothermalation ($E = TlX_2$)

1. Oxythallation of Acyclic and Cyclic Allenes

Acetoxy- and methoxythallation of cyclic and acyclic allenenes is regioselective leading to the stable monoadducts with Markovnikov orientation (entries 87–94). The cyclic monoaddition products have been fully characterized by hydrido-, proto-, and bromodemercuration reactions using, respectively, $NaBH_4$, $BF_3 \cdot OEt_2$, and Br_2 .¹⁷⁷ However, the monoadduct formed by ethoxythallation of the 1,2-cyclononadiene **20** is found to be unstable (entry 89).

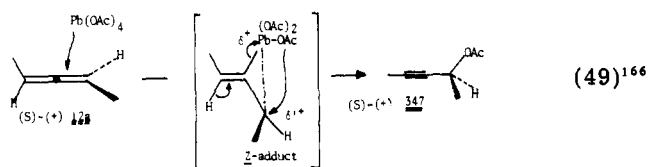
2. Anti Stereospecificity

Oxythallation of the optically active (*S*)-(-)-1,2-cyclononadiene **20** is stereospecific, affording the (*S*)-*cis*-allylic ether **322** after reductive demercuration. It has also been shown that oxymercuration of the allene **20** occurs with a higher degree of stereoselectivity with mercuric acetate than with mercuric nitrate. It has been demonstrated that this partial racemization that occurs when $Hg(NO_3)_2$ is used is not due to nitric acid racemization of the allene. However, the nitratohallic adduct was shown to partially racemize the optically active substrate. Finally, this higher racemization with nitratohallic adduct than with acetatohallic adduct could be due to a destabilization of the bridged species of thallium by their substituents; NO_3 is a more electron-withdrawing group than AcO (cf. entries 89 with 91, see also Figure 24 with $E = TlX_2$).

D. Solvoplumbation ($E = PbX_3$)¹⁷⁴

1. Acetoxyplumbation of Acyclic and Cyclic Allenes

Acetoxyplumbation of acyclic allenenes affords propargylic acetates very probably through a nonisolable vinylic lead adduct with *Z* configuration, the lead tetraacetate adding on the more crowded face of the



remaining double bond. This configuration is in good agreement with an anti-elimination process leading to the formation of the triple bond (entries 95, 96). Very interestingly, the optically active (*S*)-2,3-pentadiene **12** affords the 2-acetoxy-3-pentyne (*S*)-**347** by acetoxylumbation. The metalation reaction is 57% stereoselective and proceeds by a syn mechanism which implies front-side attack of the *Z* adduct by the acetoxy group (entry 95). The structure and the optical purity of the propargylic acetate **347** have been correlated to the 2-pentanol (see footnote w of the Table XII).

Acetoxylumbation of the (*S*)-1,2-cyclononadiene **20** gives the dextrorotatory 2-cyclononyl-1-ol acetate **349** that has been shown to have the *R* configuration. The reaction is then stereospecific and proceeds by a syn addition mechanism. The structure and the optical purity of the acetylenic acetate **349** have been correlated to the known *cis*-2-cyclononyl-1-ol acetate **322** that is (*R*)-(-) (entry 97).

E. Discussion

Metalation of allenes is regioselective with formation of the Markovnikov orientation product by reaction of metallic salt with the central carbon atom of cumulated double bond. Metalation of acyclic and large ring cyclic allenes is *Z* stereoselective, whereas the strained cyclic allenes afford a monoadduct with complete *E* stereoselectivity.

Oxymercuration and oxythallation of allenes afford stable monoadducts, whereas corresponding electrophilic addition of lead tetraacetate does not.

Oxymercuration of acyclic allenes is the most stereospecific addition reaction among the three metalation methods, whereas oxyplumbation of the 1,2-cyclononadiene is by far the most stereospecific process (cf entries 54 with 97).

Importantly, acetoxymercuration and acetoxylumbation of cyclic and acyclic allenes proceed by an anti addition mechanism, whereas the mechanism of the acetoxylumbation is syn.

IX. Conclusion

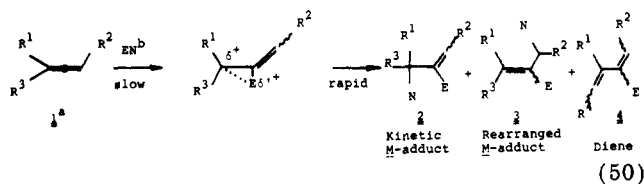
To conclude this review dealing with electrophilic addition to allenes, it could be worthwhile to show how information taken from the study of the chemo-, regio-, *E* vs. *Z* stereoselectivities, and especially the syn vs. anti stereospecificity will be very helpful for distinguishing between mechanisms of this ionic reaction. Stereospecific addition to allenes also affords synthesis of valuable new cyclic and acyclic compounds. It was established that these selectivities were related to structural factors of substrates and nature of reagents. Moreover, it should be kept in mind that solvent polarity plays an important role for the stereochemical course of the reaction studied.

A. Chemo- and Regioselectivities

1. Electrophiles with Poor Bridging Ability (H^+ , R_3C^+ , Cl^+ , Br^+ , $ArSe^+$)

Electrophilic reaction to well-differentiated dissymmetrical aliphatic and aromatic allenes occurs exclusively on the central carbon atom of the cumulated diene and on the double bond that gives a transition state resembling the most stabilized α,β -ethylenic carbenium ion with an open or a partially bridged structure.

In polar solvent, these solvated species will react rapidly with nucleophiles present in the medium leading to products with Markovnikov orientation. In nonpolar solvent, however, the entity that is probably an ion pair will isomerize to allylic cation that subsequently produces rearranged products with Markovnikov orientation. This happens when rotation and bending of α,β -ethylenic cation is more rapid than nucleophilic attack that could be slowed by steric hindrance. A loss of proton may also occur from an adjacent methyl group of this entity giving a conjugated diene (eq 50).



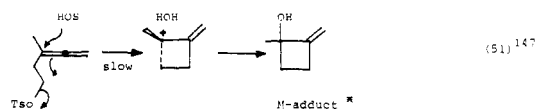
In polar solvent (H_2O , $MeOH_2$)	Major	Minor	No
In non-polar solvent (CCl_4 , CS_2)	Minor	Major	

^a R^1, R^3 strongly electron-donating substituents such as Pb , OEt , Me and R^3 electron-withdrawing substituent CH_2OR or alkyl group; ^belectrophiles with poor bridging ability HX , R_3CX , Cl_2^+ , Br_2^+ .

Then it was shown that hydrochlorination of phenylallene (eq 4) and ethoxyallene (entry 27 of Table I) follows a stepwise process in which rate-determining proton transfer on the β -carbon leads to a transition state resembling the perpendicular α -vinylbenzyl and α -vinylethoxy cation. This is supported by the high value of the ρ^+ constant (-4.2) and a solvent isotope effect $k_{H_2O}/k_{D_2O} = 3.05$,^{39d} respectively. [The ρ^+ values for a transition state resembling allyl cation was found to be -3.2 in the iodination of 1,3-diaryllallenes (see Scheme VIII).]

Substituent effects of α -methyl- and *p*-(chlorophenyl)allene during methoxybromination also agree with the existence of a partially bridged bromonium ion with strong benzylic carbocationic character (entries 62, 64, 65 of Table II). This carbenium species is also responsible for a transannular product obtained in methoxybromination of the 1,2-cyclononadiene (Figure 11 and entries 55, 56 of Table II).

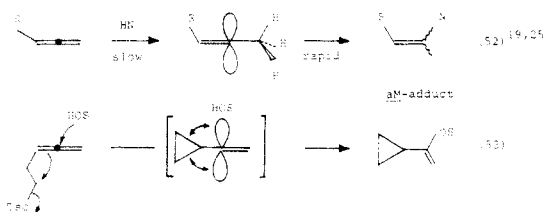
Although it follows a concerted process that is the reverse of anti-elimination mechanism, the hydrolysis (eq 51, see also entry 6 of Table IX and path a of Figure



14) of the 3-methylated β -allenic tosylate follows the same chemo- and regioselectivities.

Protonation (eq 52, entries 11-13 of Table I, when $R = Me$, configuration of the αM -adduct is mainly *Z*),

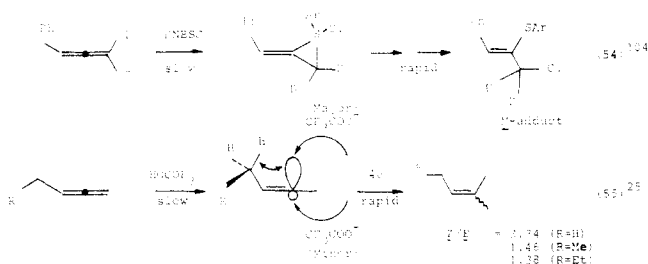
amino- and oxymercuration of 1,2-dienes (entries 4,6 of Table XI), and finally hydrolysis of the non-methyl-substituted β -allenic tosylate (eq 53 and entries 1,2 of Table IX, path of Figure 14) afford products with



anti-Markovnikov orientation through a transition state resembling the vinyl cation that is more stable than the corresponding secondary α,β -ethylenic cation. This vinylic carbenium ion could be stabilized by some through-space interaction such as hyperconjugation.

2. Electrophiles with Good Bridging Ability (I^+ , ArS^+)²⁰²

Electrophilic addition of these reagents to well-differentiated dissymmetrical allenes affords products with exclusive Markovnikov orientation by reaction of the most substituted or the least deactivated double bond through an ionium ion intermediate of iodine and sulfur. Sulfenylation of phenylallene (eq 54) was shown



to occur predominantly on the unsubstituted and the less conjugated double bond, the sulfurane-like transition state being formed in the rate-determining step. In eq 54 the α -secondary isotope effect $k_H/k_D = 0.92$ (for one D) and the configuration of the M adduct is Z when $Ar = 2,4-(NO_2)_2C_6H_3$ (entry 9 of Table III).

B. E vs. Z Stereoselectivity

1. Predominant Z Configuration for the Products

Under kinetic control, addition of acids to 1,2-dienes gives anti-Markovnikov oriented products with predominant Z configuration. This has been rationalized²⁵ by a higher electron deficiency on the more crowded face of the linear vinyl cation due to C-H homohyperconjugation of the β -methyl group. The greater change in the Z/E ratio of trifluoroacetate stereoisomers is found in going from methyl to ethyl substituent. (In eq 55 the acetylene $RCH_2C\equiv CMe$ (60%) is also formed and the Z/E equilibrium ratio is always roughly 2.3.)

The two-step process of halogenation, selenylation, and metalation of acyclic allenes leads mainly to a Z configuration for the products formed with Markovnikov orientation. This could be attributed to a *product development control*²⁰⁰ with a late product-like transition state in which the observed ratio reflects the thermodynamic stabilities of the adducts. A reversible formation of an onium ion followed by the rate-deter-

mining attack by nucleophile that should approach the intermediate from the least hindered side (Scheme X with $E = X, SeAr, HgOAc, and Tl(OAc)_2$).

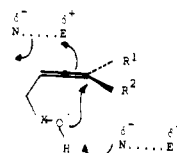
2. Predominant E Configuration for the Products

Sulfenylation and epoxidation of acyclic allenes that go through stepwise and concerted processes, respectively, afford products with predominant E configuration. This is in good agreement with a *steric approach control*²⁰⁰ which implies an early reactant-like transition state in which the entering electrophile approaches the least hindered face of the allene during the rate-determining step (Scheme XIII with $E = SAR$).

C. Syn vs. Anti Stereospecificity

1. Anti Addition Mechanism

(a) **Concerted Process.** Electrophile-induced cyclizations of α -, β -, and γ -functionalized allenic derivatives proceed by a highly if not completely stereospecific pathway. An anti addition mechanism, which is formally the reverse of the anti elimination, is found. This could be reasonably attributed to a concerted process due to neighboring group participation of the functional group. This is the case with protonation and bromination of allenyl carboxylic acids, mercuration of allenylphosphonic acid, sulfenylation, selenylation, and epoxidation of α - and β -allenic alcohols, and finally solvolyses of β - and γ -tosylates (see corresponding tables).



(b) **Stepwise Process.** Bromination in polar and nonpolar solvents, methoxymercuration by the Caserio⁷⁷ and Bach¹⁶⁶ procedures (respectively, $Hg(OAc)_2, MeOH$ and $EtHgOAc, BF_3, MeOH$), and acetoxythallation of cyclic and acyclic allenes take place by a stereochemical course that is highly stereospecific and proceed by an anti mechanism. This result is in agreement with the occurrence of symmetrical bridged onium ion as intermediate and back-side attack by the nucleophile or the solvent (see path γ of Chart I with $E = Br, HgX, Tl(OAc)_2$), this species having no carbocationic character.

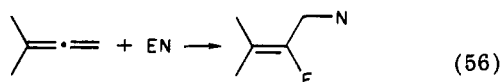
(c) **Nonstereospecific Process.** The nonstereospecific iodination of 1,3-diaryllallenes is nonpolar solvents and the bromination of β -allenic alcohol are interpretable in terms of equal values for racemization and addition rate affording planar allyl cation in a slow step common to both reactions. The attack by DNBSC on the same β -allenic primary alcohol is stereospecific (vide supra). ArS^+ attack usually involves a cyclic intermediate that is less subject to competition from an open cation than Br^+ (see path β of Chart I for $E = Br, ArS, and I$, entry 90 of Table II, and Scheme VIII). The symmetrical structure of the bridged thiiranium intermediate has been established by the cumulated rate acceleration observed during substitution of the hydrogens of allene by methyl groups. Each substitution helps equally to stabilize the species directly or across the unreacted double bond.

2. Syn Addition Mechanism

Interestingly, it has been established that acetoxyplumbation of allenes occurs stereospecifically by a syn addition mechanism (entries 95, 97). Furthermore, for cyclononadiene, this process was found to be more stereospecific than the corresponding anti acetoxymercuration and thallation (entries 54, 87, 97; see also ref 216).

It could be then possible that the *E*-dichloride **65**, obtained with a 4 times higher stereospecificity than the *Z* isomer during chlorination of optically active 2,3-pentadiene **12a**, was formed by a syn process (entry 30 of Table II). An ion pair bridged species obtained in nonpolar solvent by reaction on the least hindered side of the allene **12a** will collapse more rapidly with retention than by backside nucleophilic attack (Scheme XXVIII).

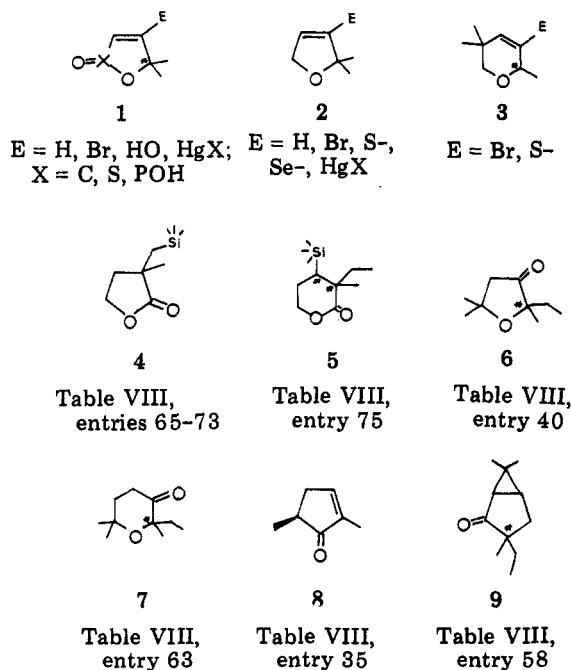
Finally, chemoselectivity found for hydrochlorination (eq 56, EN = HCl, -78 °C, no solvent) and sulfenylation (eq 56, Me₂S⁺SMe BF₄⁻, CCl₄ solvent) of 3-methyl-



1,3-butadiene remains puzzling.

D. Synthesis

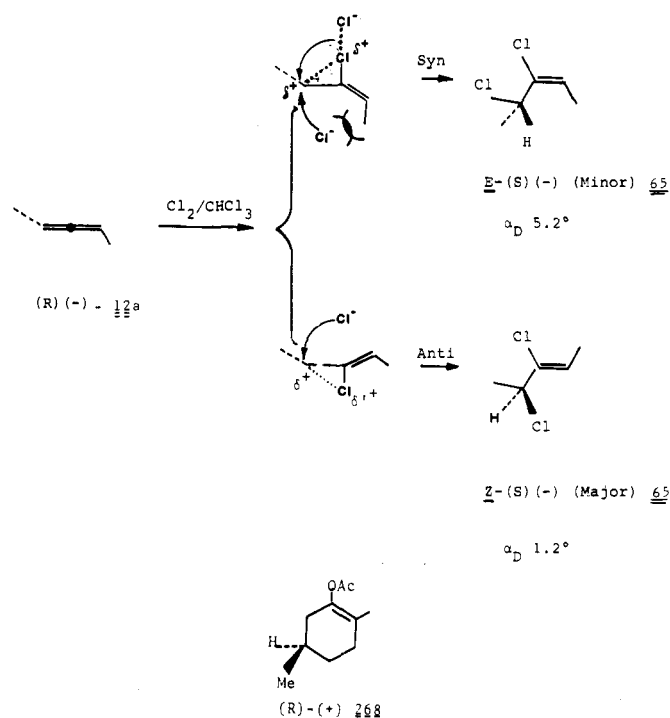
Cyclizations induced by electrophilic addition to α -, β -, and γ -functionalized allenic derivatives afford syntheses of variously substituted five- and six-membered ring products, such as butenolides **1**,¹⁹⁷ 2,5-dihydrofurans **2**, Δ^3 -dihydropyrans **3**, γ -lactones **4**, β -lactone **5**, oxacyclopentanone **6**, β -oxacyclohexanone **7**, conjugated cyclopentenone **8**, and bicyclohexanone **9**; some of them are formed by stereospecific processes.



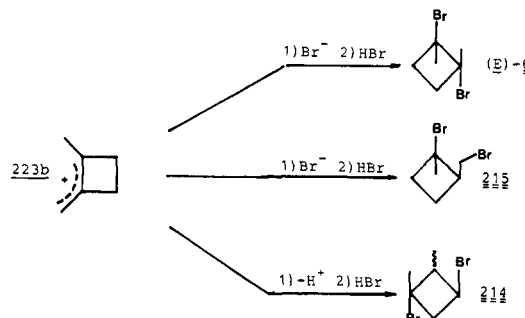
γ -Allenic participation in solvolysis affords stereospecific synthesis of the enol acetate of the β -chiral cyclohexanones **268** (Figure 21).

Note Added in Proof. Formation of cycloadducts from reaction of hydrogen bromide and propadiene **1** has been recently investigated.²⁰⁴ This investigation

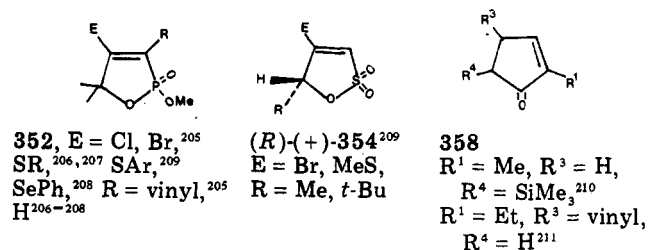
SCHEME XXVIII



showed that *trans*-1,2-dibromo- (*E*-**6**), 1,3-dibromo- (**214**), and bromomethylcyclobutanes (**215**) were obtained in low yields through allylic carbocation **223b** formed by addition of vinyl cation **1a** to allene **1** (cf. also entries 1-10 of Table I).



Electrophile-promoted cyclization of α -functional allenic derivatives, such as phosphonates,²⁰⁵⁻²⁰⁸ chiral sulfones²⁰⁹ and sulfinate,²⁰⁹ silyl-substituted vinylallene,²¹⁰ and butadienylallene,²¹¹ which afford 4-heterooxaphospholene **352**, optically active sultones **354**,

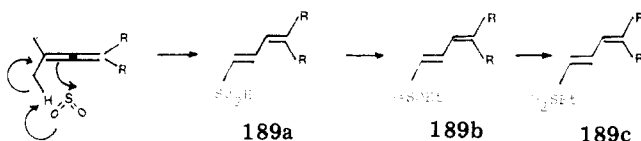


and cyclopentenones **358**, has been extensively studied and the steric course for the formation of oxaphospholenes **352**²⁰⁸ and sultones **354**²⁰⁹ has been well established from the mixture of diastereoisomers of **352** and transfer of chirality leading to **354** (see Tables II, III, and VII).

Protodesilylation of silylallenes (BF₃-HOAc complex in CH₂Cl₂ at -78 °C) affords conjugated dienes²¹²

whereas a similar reaction with allenyltins (4% aqueous MeOH) gives rise to an acetylenic-allenic hydrocarbon mixture.²¹³ Electrophilic displacements by Cl₂, Br₂, and DNBS of allenyltins studied by the same group also involve a competition between S_E2 and S_E2' mechanisms.²¹³

Very interestingly silylallenes have been used as propargylic anions leading to regioselective synthesis of homopropargylic alcohols by reaction with aldehydes and ketones in the presence of titanium tetrachloride.²¹⁴ The formation of conjugated dienyl sulfonic acid **189a** from the ene reaction of methyl-substituted allenes and SO₂²¹⁵ is also noteworthy. When **189a** is converted to



36, R = Me
49, R = H

sulfonic ester **189b**, an easy rearrangement occurs leading to the corresponding sulfone **189c** (see Table XI).

Stereospecific oxymetalation (Hg, Tl, Pb) of 1,2-cyclonadiene **20** has been widely complemented²¹⁶ and allows the determination of calculated absolute rotation of (*R*)-(-)-3-hydroxy-, (*R*)-(-)-3-acetoxy-, and (*R*)-(-)-3-methoxy-*cis*-cyclononenes, which are found to be [α]_D²⁵ 47.9°, 76.2°, and 30.5°, respectively (see Table XII).

Finally a short review²¹⁷ and an extensive review²¹⁸ on the subject have appeared very recently.

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