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

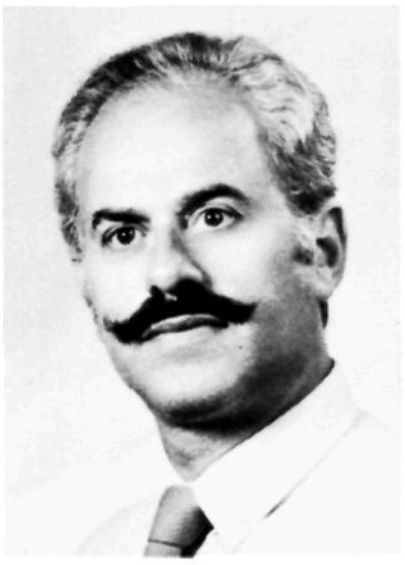
WILLIAM SMADJA

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

Received July 2, 1981 (Revised Manuscript Received February 23, 1982)

Contents

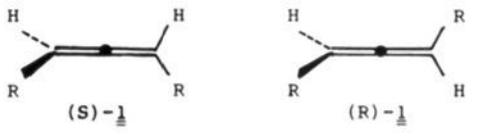
† Dedicated to the memory of Professor Charles Prévost, deceased July 11, 1983.



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 attentiion 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 disymmetry 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

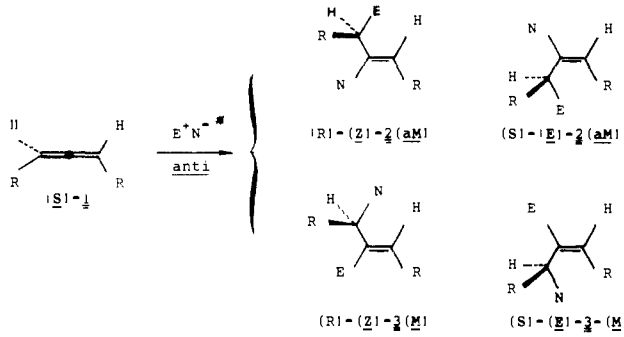


superimposable on the other.

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.

0009-2665/83/0783-0263$06.50/0 © 1983 American Chemical Society

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 derivatives[1-8] 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.

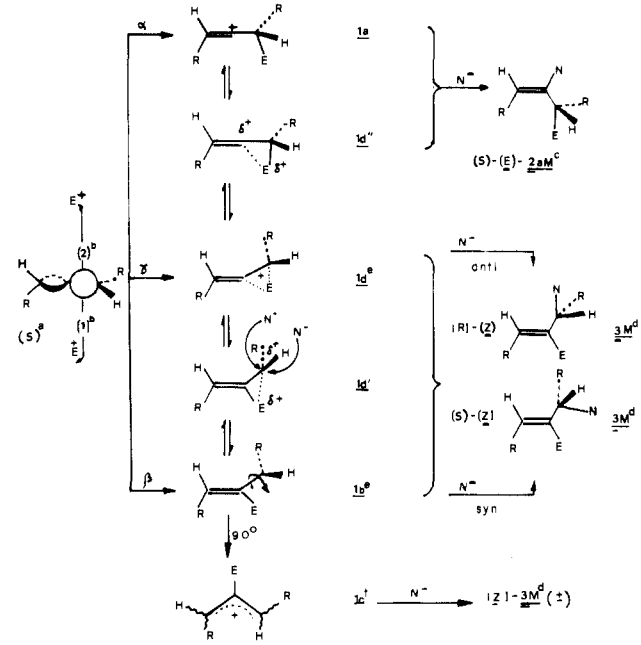
Although the allylic cation **1c** is the most stable intermediate (vide infra), these three pathways can occur according to the nature of reagent, solvent, and unsaturated substrate. (There is probably a spectrum of mechanism between complete onium ion **1d** (no rotation) formation and complete open 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 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.

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.

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-dinitrobenzenesulfenyl chloride; BSC, benzenesulfenyl chloride; PCBSC, *p*-chlorobenzenesulfenyl chloride; BSeB, benzeneselenyl bromide; TMBSeB, 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

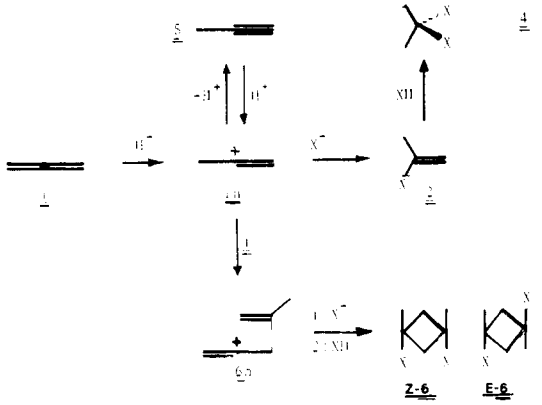


Figure 1. References 2 and 21.

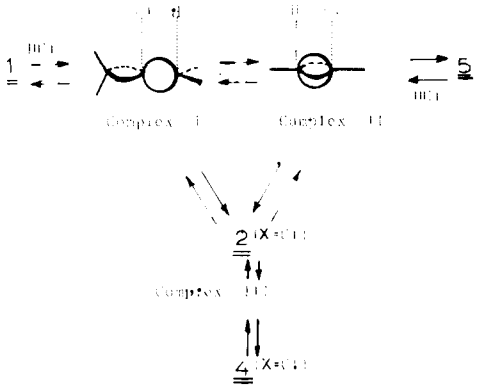


Figure 2. Reference 22. For arabic numerals representing substrates and products see Figure 1. The HCl bond is in the plane. The ^1H NMR showed that the hydrogens of allene 1 are shifted upfield by 2 ± 1 Hz in the presence of HCl whereas the proton of HCl was deshielded by 8 Hz in the presence of 1.

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 E = 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 suggested[22] that in solution the overall hydrochlorination of allene has also to take into account the formation of these complexes. Again, protonation of

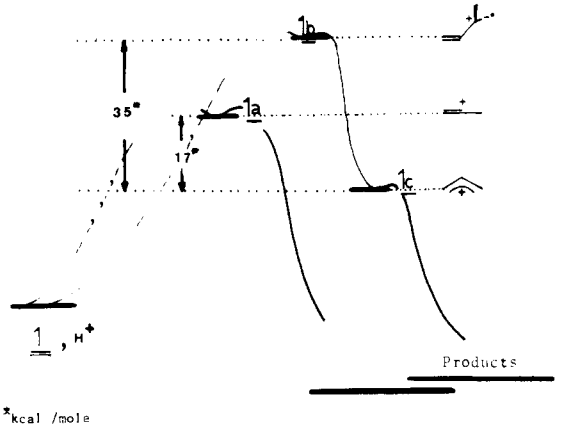


Figure 3. Reference 24.

allene in the gas phase[23] 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

$$\underset{\mathbf{1}}{CH_2{=}C{=}CH_2} \xrightarrow[SH_2]{SH_3^+} \underset{\mathbf{1a}}{CH_3C^+{=}CH_2} \xrightarrow[MeO^+H_2]{MeOH} \mathbf{1} + \underset{\mathbf{5}}{CH_3C{\equiv}CH} \quad (1)^{23}$$

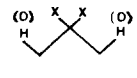
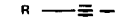
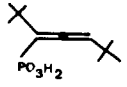
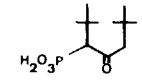
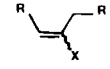
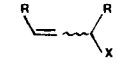
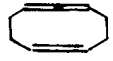
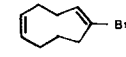
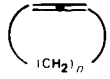
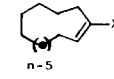
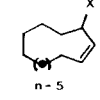
Theoretical calculations[24] are highly revealing, the linear vinyl cation **1a** was shown to be more stable than the twisted olefinic cation **1b** by 18 kcal/mol, thus the protonation of allene will proceed preferentially through the vinyl cation **1a** (Figure 3). Recently,[31b] the kinetics of the 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 hyperconjugaison 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 CF_3CO_2H 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 $k_{CF_3COOH}/k_{CH_3COOD} = 7.4$ (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, %	product composition, %						ref
												
	1					2	4	5	*E*	6	*Z*	
1		HF[b]		−76			100					18
2		HCl/$BiCl_3$[c]		−78	22	60	37	3				19
3		HCl/$TiCl_4$/O_2			80	24	74			2		20
4		HCl/$FeBr_3$/O_2			58[d]	31	67			2		20
5		DCl/$BiCl_3$/O_2		78	0.83[e]	63	35			2		20
6		HCl		−70	12	35	54		8		3	21
7		HCl[f]		−70	71	34[g]	28	38				22
8		HCl[f]		100		58	4	38				22
9		HBr[c]		−70	42	13	35		44		8	21
10		HI		−70	71	6	94					21
												
						Z	8 *E*	9				
11	7a, R = Me	HCl/$BiCl_3$		−78	20	53.5	8.0	38.5[h]				19
12	7a, R = Me	HOCOCF_3	HOCOCF_3	75		28.4[j]	8.4[k]	63.2				25
13	7b, R = *n*-Pr	HOCOCF_3	HOCOCF_3	75		24.6	17.7	62.0				25
14	7c, R = *n*-Bu	HBr	HOAc	0	81	17	83					37a
			HOAc, ether	RT	66	25	75					37a
15		HOCOCF_3	HOCOCF_3	75	85[n]							36
	10						11[m]					
		HX										
	12					13[l]	14[l]					
16	12a, R = Me	HBr	HOAc/ether	RT		100% (*E*)						37b
17	12a, R = Me	HBr[b]		RT	90	20	80					44, 46
18	12a, R = Me	HCl/$BiCl_3$		−78	50	25	75					44, 46
19	12b, R = Et	HBr		RT	90	20	80					44, 46
20		HBr	HOAc/ether		86							37a,c
		HX										
						E-18[w]	*cis*-19					
21	17, (n = 10)	HBr[c]	HOAc	RT	70	45	55					37f
22	20 (n = 6)	HBr[c]	HOAc	RT			100					37a,e,f
23	20 (*n* = 6)	DBr[c]	HOAc	RT	74		100 (2-d)					37f
24	20 (*n* = 6)	HCl/$BiCl_3$		−70	47		100[t]					45
25	22 (*n* = 7)	HBr[c]	HOAc	RT	75		100					37f

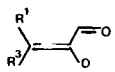
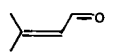
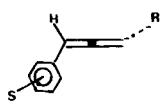
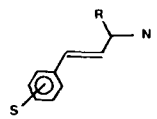
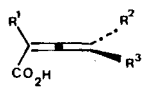
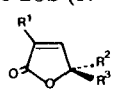
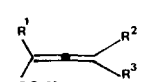
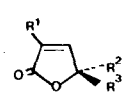
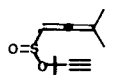
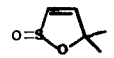
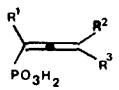
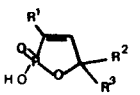
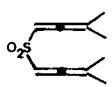
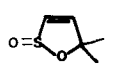
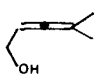
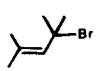
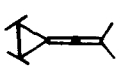
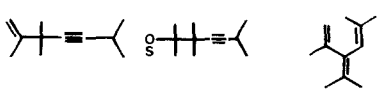
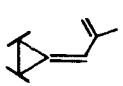
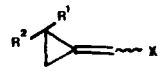
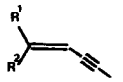
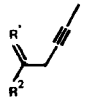
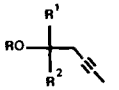
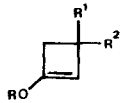
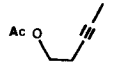
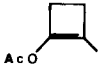
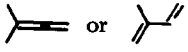
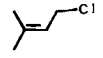
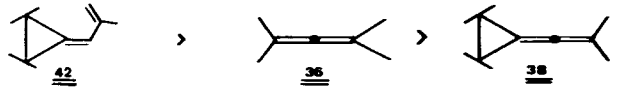
26	20 ($n = 6$)	HBr	HOAc/ether	RT	high	100	37a,d
27	 21	DCl	D_2O		high		39c
28	 23	H_2SO_4	H_2O		high		39e
							
29	24a (S = R = H)	HCl (0.995 M)[o]	HOAc	30.4	98	*trans*-25a (N = Cl)	40, 41
30	24b (S = H, R = Me)	HCl (0.198 M)[p]	HOAc	14.7	100	*trans*-25b (N = OAc)	42
							
	R¹ R² R³						
31	26a Me Et Ph	H_2SO_4	$EtOH/H_2O$	RT	60	27a–d	49
32	26b Me Me Ph				62		
33	26c Et Et Ph				32		
34	26d Ph Ph Ph				93		
35	26e H Ph Me	$HOCOCF_3$	$HOCOCF_3$	RT		27e–l	51
36	(−)-26f H Ph Et				80	−	
37	(+)-26g Et Ph H				71	$+^q$	
38	(−)-26h Et Ph Me				76	$-^q$	
39	(+)-26i Et Ph Et				62	$+^q$	
40	(−)-26j Me Ph Et				84	−	
41	(+)-26k Me Ph Me				66	+	
42	26l Ph Ph naphthyl				68	27m–p	52
43	26e H Ph Me	17% HCl or	H_2O or	reflux	65		
44	26f H Ph Et	H_2SO_4	DME/CCl_4	or RT	53		
45	26m H o-$C_6H_4(CH_2)_3$						
46	26n H *i*-Pr Me						
47	(*S*)-26e H Ph Me					(*R*)-27e (O. Y. = 100%)[u]	
48	(*R*)-26o H Me Ph					(*S*)-27o (O. Y. = 100%)	
49	(*R*)-26p H Et Ph					(*S*)-27p (O. Y. = 100%)	
	 28					 27	
	R¹ R² R³						
50	(*R*)-28e H Ph Me	H_2SO_4	$EtOH/H_2O$	RT		(*R*)-27e (O. Y. ?)	50

TABLE I (*Continued*)

entry	allenic derivatives	reagent	solvent	T, °C	yields, %	product composition, %	ref
51	(*S*)-28p H Et Ph	H_2SO_4	$EtOH/H_2O$	RT		(*S*)-27p (O. Y. ?)	50
52	(*R*)-28e H Et Ph	H_2SO_4	DME/CCl_4	RT		(*R*)-27e (O. Y. = 83%)	52
53	(*S*)-28p H Et Ph	17% HCl	H_2O	reflux		(*S*)-27p (O. Y. = 83%)	52
54	 29	$HOCOCF_3$	$HOCOCF_3$	RT	100	 30	53
55	 31a-d	HCl	H_2O	67	85	 32a-d	54
	R¹ R² R³						
56	31a *t*-Bu Me Me						
57	31b H Me Me						
58	31e H $(CH_2)_5$						
59	31d H $(CH_2)_6$						
60	31a	$HOCOCF_3$		60	100	32a	36
61	 33	$HOCOCF_3$			100	 30	53
62	 34	H_3PO_4			45	 35	198
63	 36^h	HBr^b		−20		 37	44
	 38	HN	SOH			 39 40 41	
		HN				39 40 41	
64		HOTs	C_6H_6	RT	64	87 37	56, 57
65		BF_3, OEt_2	C_6H_6	RT	70	94 6	56, 57
66		TFA	C_6H_6	RT	79	37 54 9	56, 57
67		H_2SO_4	HOAc	reflux		37 63[r]	55, 57
68		H_2SO_4	MeOH	reflux		11 89	57
69		H_2SO_4	H_2O/THF	reflux		22 43 11	57
70		HOTs	HOAc	RT	100	40 60	201
71	 42^s	HOTs	C_6H_6	RT	85	100	57

	 43			ROH	100	 44	 45	 46	 47		
		R¹	R²	X							
72	43a	Me	Me	Cl			10	9	70		60
73	43b	H	H	Br						100	61
74	43c	H	Me	Br					56	16	62
75				HOAc					 46'	 47'	58
	 49	or	50	HCl					 198	 199	
76	49[a,b]			HCl	−78			32.5	64	36	19
77			50[a]	HCl	−78			41	83	17	19

[a] Excess of substrate. [b] Excess of reagent. [c] Substrate and reagent in stoichiometric quantities. [d] Br of $FeBr_3$ is not incorporated in the product. [e] There is no incorporation of deuterium in the recovered allene. [f] In the absence of Lewis acid catalyst. [g] With HCl the chlorinated product 2 gives quantitatively the bisadduct 4. [h] 2-Butyne (9) is inert toward HCl at −78 °C. [i] Although the *Z/E* ratio of trifluoroacetates formed from 3-hexyne is roughly 1, the corresponding ratio at 75 °C from 2-butyne (9) reaches 3.3. [j] Same ratio *Z/E* = 3.3. [k] At the equilibrium this ratio is *Z/E* = 2.3. [l] The phosphonic acid 10 remains intact with 2N HCl in water–dioxane mixture even at 90 °C for 11 days. [m] The perdeuterated ketone 11 is formed by reaction with CF_3COOD and a primary isotope effect (k_H/k_D = 7.4 ± 0.7) has been observed. [n] Yield determined by ^1H NMR, the isolated yield being 42%. [o] The addition is second order in HCl when [HCl] = 0.955 M. [p] The addition is first order in HCl when [HCl] = 0.198 M. [q] Lactones 27g (R = H) and 27h (R = Me) are racemized by CF_3COOH to the extent of 95% and 32%, respectively, after 66 h of contact. The lactone 27i (R = Et) was optically stable under these conditions. [r] The product 40 is a mixture of alcohol (15% (S = H)) and acetate (48% (S = Ac)). [s] The relative rate of diene protonation is as the sequence


42 › 36 › 38

[t] The configuration of the double bond is not given. [u] O. Y. = optical yield.

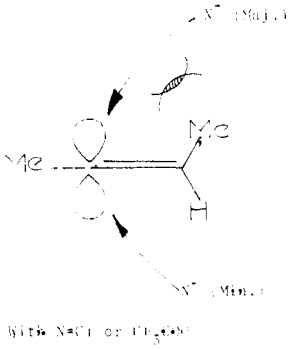
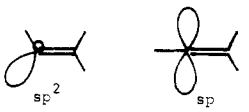
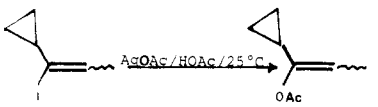


Figure 4. Reference 25. The linearity of vinyl cations[9-16] has been established by three different ways: Theoretical calculations have shown that the linear cation was energetically more favorable than the bent structure by 45–65 kcal/mol.[25] Acetolysis of both

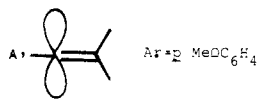


vinylic iodides **44d** gives rise to similar mixtures of enol acetate



(*Z*)-44d $Z/E = 0.87$
(*E*)-44d $Z/E = 0.96$

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).

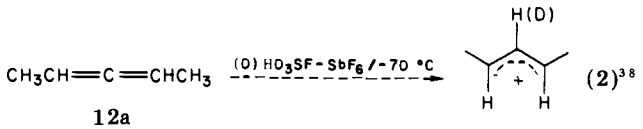
Ketones are generally obtained by acid-catalyzed hydration of allene,[31] alkylallene,[29,30,32,33] and 1,3-dialkylallene[34,35] very probably with a vinylic cation as an intermediate.

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

When highly electron-donating substituents such as RO,[39] F,[64] and Ph[40-42] 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.

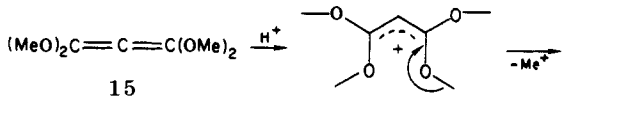
1. Releasing Mesomeric Effect (+M)

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



12a **12ac**

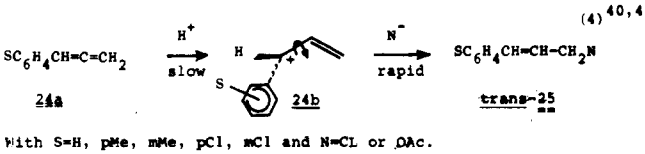
malonic ester is observed after loss of the methyl cation.



15 **16**

Deuterolysis of allenyl ethers with DCl affords α-deuterated α,β-unsaturated aldehydes (entry 27). It has been shown that in acid catalyzed hydrolysis of ethoxypropadiene the proton is transfered 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_E2 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 carbon[40-42] (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.)



With S=H, pMe, mMe, pCl, mCl and N=CL or OAc.

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-

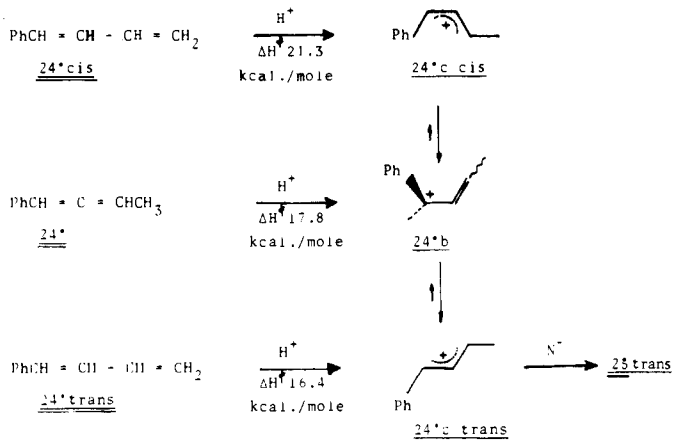


Figure 5. Reference 42.

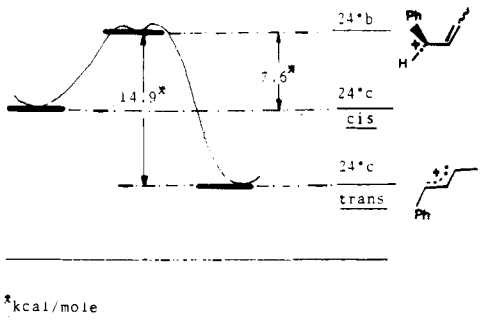


Figure 6. Reference 42.

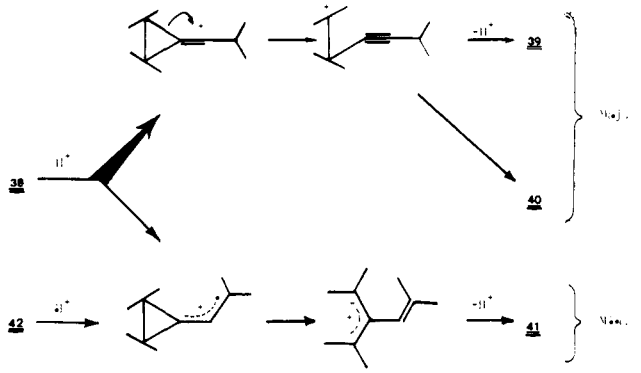
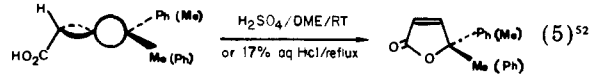


Figure 7. References 55–57.

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

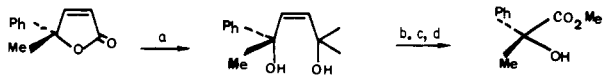


(5)[52]

(*S*)-(+)-26e	O.Y. 100%	(*R*)-(+)-27e
(*R*)-(−)-26o	O.Y. 100%	(*S*)-(−)-27o

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

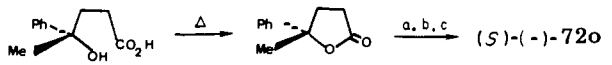
The reaction is 100% stereospecific with the ethyl-substituted acid (*R*)-**26p** (entry 49). Configuration and specific rotation of γ lactones have been determined by the following correlations



γ-lactone (*S*)-(−)-27o — methyl (*R*)-(−)-atrolactate

(6)[52]

(a) 2 MeMgBr/aq NH_4Cl. (b) O_3/Me_2S. (c) AgO/NaOH. (d) CH_2N_2.

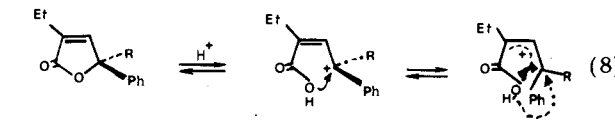


(*S*)-(+)

(7)[52]

(a) Base. (b) PhSeBr. (c) O_2/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).



(8)[52]

optically active γ lactones 27 — twisted cation 27b — planar allylic cation 27c

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).

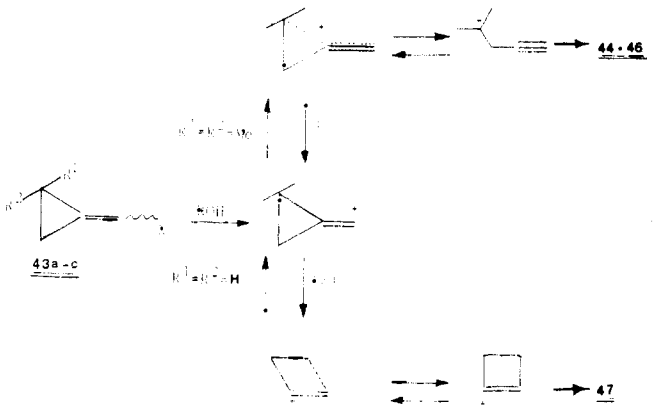
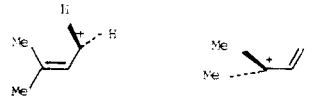


Figure 8. References 60–62.

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).



49b 49b'

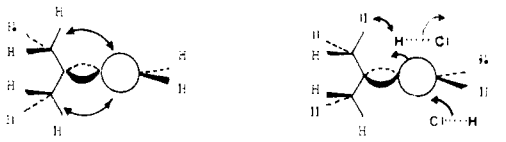
C. Discussion

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

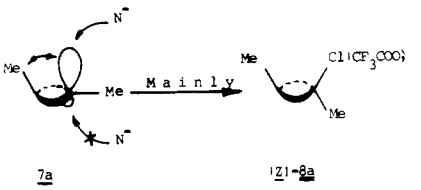
Pathway α in Chart I via vinyl cation is followed when the protonation of allenes occurs on the unsubstituted double bond because of higher stability of vinyl cation vs. twisted olefinic cation (entries 1–14).

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

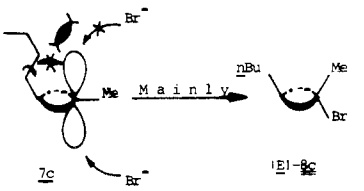
SCHEME II[19,218]



SCHEME III



SCHEME IV



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

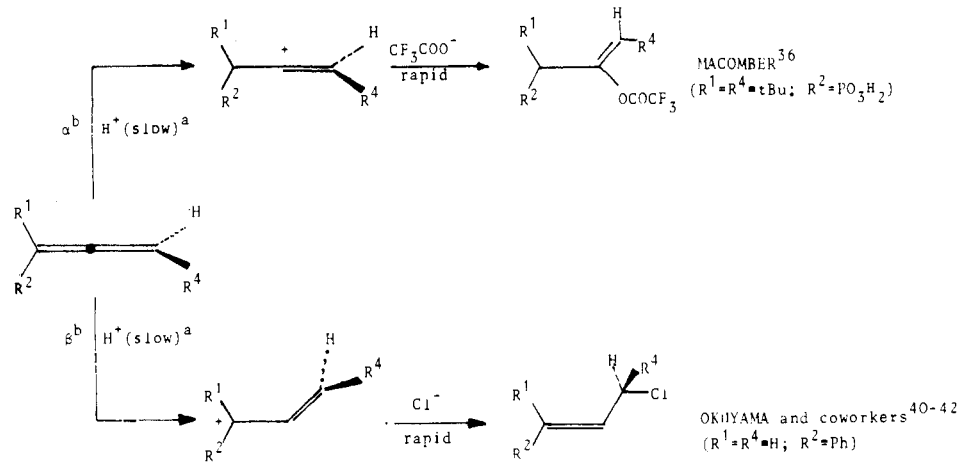
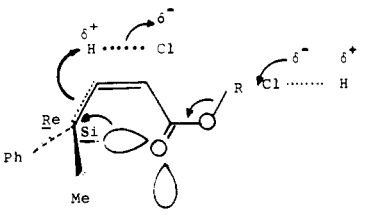


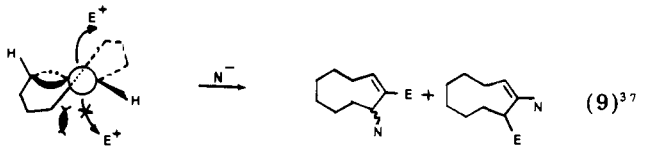
Figure 9. (a) The reaction is second order. (b) Pathways of Chart I.

SCHEME V[a]



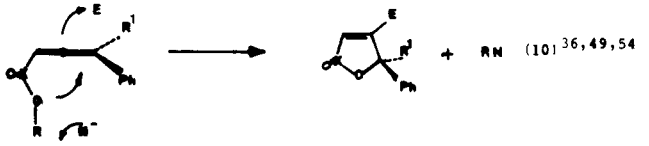
[a] Acid (*R*)-26e with R = H; ester (*R*)-28e with R = Me.

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



20 (*E*)-19 (*E*)-18 (9)[37]

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).



(10)[36,49,54]

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 E_2 (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:

$$^{+}CH_2CH{=}CH_2 < CH_3C^{+}{=}CH_2 < CH_2{\cdots}CH^{+}{\cdots}CH_2 \quad (11)^{12}$$

$$Ph^{+}CHCH{=}CHMe < \textit{cis}\text{-}PhCH{\cdots}CH^{+}{\cdots}CHMe < \textit{trans}\text{-}PhCH{\cdots}CH^{+}{\cdots}CHMe \quad (12)^{42}$$

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

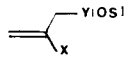
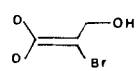
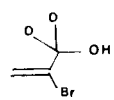
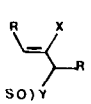
$$RCH_2^{+} < RC^{+}{=}CH_2 < R^{+}CHCH_3 \quad (13)^{111b}$$

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 known[6] 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
	1	X^+Y^-				 51	 52		
1		Cl_2	HOAc			100 (SO = AcO)			65
2		Cl_2	CH_2Cl_2[a]			40	60		66
3		Cl_2	*b*	420		90	10		66, 67
4		Cl_2/O_2	*c*	−30		23	20		68
5		$PhICl_2$	$CHCl_3$[d]	−30		46	20		69
6		BrCl	HOAc			100			65
7		Br_2	HOAc[e]			100			65
8		BrCl	CCl_4			100			65
9		BrOH[f]							
	55			RT	20	56 45.4[g] 43.5[h]	57 54.6[g] 56.5[h]		70
	 59	XY				 60	 (*E*)	61	 (*Z*)	
10	59a (R = CO_2Et)[i,j]	Cl_2	CCl_4	0			50 (45)[m]		16 (45)[m]	73
11		BrCl	CCl_4	RT	*k*, *l*		24		70	73
12		ICl	CCl_4	RT	*k*, *l*		11		89	73
13		IBr	CCl_4	RT	*k*, *l*		13		67	73
14	59b (R = CN)	Br_2	CCl_4					100		75, 74
15	59c (R = R)	Br_2	CCl_4			$RCHBrCBr_2CH_2Br$ major				29
16		Br_2	CCl_4			major		minor		63, 75
17	59d (R = Me)	$PhICl_2$	$CHCl_3$[n]	−20		26	1		73	69
18	59e (R = Et)	ClOH			70	90		10		81
19	59f (R = *n*-Pr)	ClOH			70	92		8		81
20	59g (R = *n*-Bu)	IOCOPh	C_6H_6	RT		100 {X = I, Y = OCOPh}				76b
	 12	XY					 (*Z*)	63	 (*E*)	
21	12a (R = Me)	BrCl	CCl_4				72[r]		28[r]	78
22	(*R*)-12a α_D −15.9°	Br_2	CCl_4[p,q]				(*S*) 83	α_D −7.35°	17	77
23	12a α_D −15.9°	Br_2 or BrCl	MeOH				(*S*) 83	α_D −5.7°	17	77
	12a	IY					(*Z*)	64[u,t]	(*E*)	
24	(*R*)-12a α_D −15.9°	I_2	MeOH	RT			(*S*) 90	α_D −4.1°	10	77
25	(*R*)-12a α_D −19.8°	ICl[w]	MeOH	RT			(*S*) 94	α_D −13.4°	6	78
26	(*R*)-12a α_D −19.8°	IBr	MeOH	RT			(*S*) 94	α_D −7.8°	6	78
27	(*R*)-12a α_D −19.8°	I_2[v,x]	MeOH	RT			(*S*) 94	α_D −5.5°	6	78
28	12a	I_2-MgI_2[a,l]	ether	RT	51		82 (SO = HO)[y]		79	

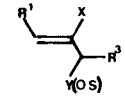
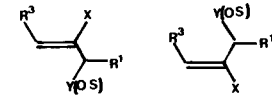
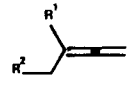
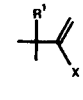
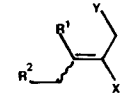
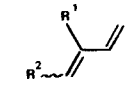
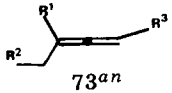
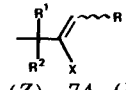
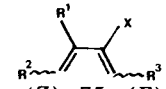
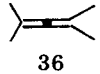
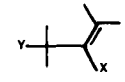
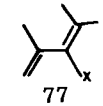
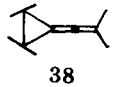
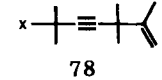
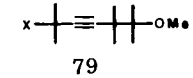
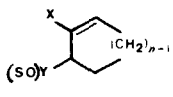
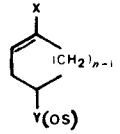
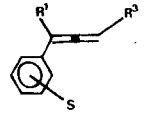
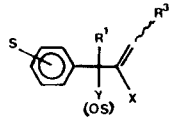
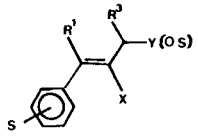
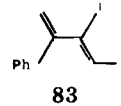
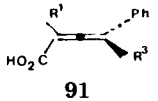
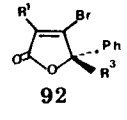
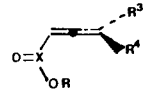
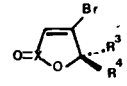
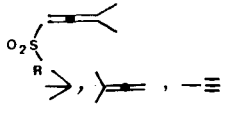
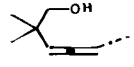
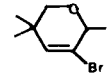
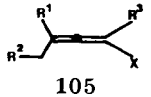
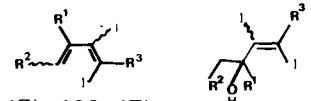
		ClY					(*Z*)	65	(*E*)			
29	12a	ClOH						100				81
30	(*R*)-12a α_D −11.3°	Cl_2/O_2	$CHCl_3$	−20			85 α_D −1.3°		15 α_D −5.2°			69
31	12b (R = Et)	IOCOPh	C_6H_6	RT			(*Z*) (80)	66	(*E*) (20)			76b
	 12	XY					 (*Z*) 67 (*E*)		 (*Z*) 68 (*E*)			
32	12c (R^1 = Me, R^3 = Et)	ClOH			60			50		50		81
33	12d (R^1 = Me, R^3 = *n*-Pr)	IOCOPh	C_6H_6	RT			45	5	45	5		76b
	 69	XY					 70	 71	 72			
34	69a (R^1 = Me, R^2 = H)	Cl_2/O_2	$C_2F_3Cl_3$				2	13	85			67
35		$PhICl_2$	$CHCl_3$[ag]	0			28	56[ah]				69
36		ClOH			85		100					81
37		I_2–MgI_2[al]	ether	RT	76			100[am]				79
38		I_2	$CHCl_3$	RT	95			100				181a
39	69b (R^1 = R^2 = Me)	ClOH			85		100					81
40	69c (R^1 = Et, R^2 = Me)	I_2	$CHCl_3$	RT	95			100				181a
	 73[an]	XY					 (*Z*) 74 (*E*)		 (*Z*) 75 (*E*)			
	R^1 R^2 R^3											
41	73a Me H Me	I_2–MgI_2[al]	ether	RT	42				100			79
42	73b Me H *i*-Pr	I_2–MgI_2[al]	ether	RT	58		15		85			79
43	73c Me H *t*-Bu	I_2–MgI_2[al]	ether	RT	75		56		*ar* 34.5			79
44	73d $(CH_2)_4$ Me	I_2–MgI_2[al]	ether	RT	58				100			79
45	73a Me H Me	ClOH	ether	RT	72		100					81
	 36	XY					 76		 77			
46		I_2–MgI_2[al]	ether	RT					100			79
47		Cl_2/O_2	$C_2F_3Cl_3$						100			67
48		$PhICl_2$		0	45				100			69
49		ClOH			63		100					81
	 38	XY					 78		 79			
50		Cl_2/O_2	CCl_4	−78	80–85		100					57
51		Br_2	MeOH	25			minor		major			57

TABLE II (*Continued*)

entry	allenic derivatives	reagents	solvent	T, °C	yield, %	product composition, %		ref
		XY				 (*E*)-80	 (*E*)-81	
52	20 (n = 6)	$PhICl_2$	THF	−5		90[af]		69
53	20	I_2-MgI_2[al]	ether	RT	84	100		79
54	20	Br_2				60	40	82, 88
55	(*R*)-(+)-20	Br_2	CCl_4	z	78	61 (*R*)-(+)[t,aa,ab]	39 (+)[aa,ab]	80
56	(*R*)-(+)-20 α_D 23.4°	Br_2[ae]	MeOH	0	85	32 (*R*)-(+)[t,ad]	68 (+)[ac]	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
	 84	XY				 85	 86	
	R[1] R[2] S							
62	84a H H H	Br_2	MeOH	0		84 (SO = MeO)	16	87
63	84b H H *m*-Cl	Br_2	MeOH	0		89 (SO = MeO)	11	87
64	84c H H *p*-Cl	Br_2	MeOH	0		78 (SO = MeO)	22	87
65	84d Me H H	Br_2	MeOH	0		54 (SO = MeO)	46	87
66	84a H H H	Br_2	CS_2	0		2	98	87
67	84a H H H	IBr	CS_2	0		20	80	87
68	84a H H H	Br_2	CS_2	−70		25	75	87
69	84a H H H	Cl_2	MeOH	0		70 (SO = MeO)	30	87
70	84a H H H	Br_2	MeOH	0		84 (SO = MeO)	16	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	 83	80 (*E*) (SO = OH)	79
	 91					 92		

		R¹	R³						
75	(*S*)-(+)-91a-d			Br_2	CCl_4		70–90	(*S*)-(+)-92a-d (O.Y. = 100%)	85
	91a	H	H	Br_2	CCl_4			(*S*)-(+)-92a-d (O.Y. = 100%)	
	91b	H	Me	Br_2	CCl_4			(*S*)-(+)-92a-d (O.Y. = 100%)	
	91c	H	*i*-Pr	Br_2	CCl_4			(*S*)-(+)-92a-d (O.Y. = 100%)	
	91d	H	*t*-Bu	Br_2	CCl_4			(*S*)-(+)-92a-d (O.Y. = 100%)	
76	(*S*)-(−)-91e	H	Et	Br_2	CCl_4			(*S*)-(−)-92e (O.Y. = 100%)	85
77	91f	Et	H	Br_2	CCl_4			92f	51
78	(+)-91g	Et	Me	Br_2	CCl_4			(+)-92g	51
79	(−)-91h	Et	Et	Br_2	CCl_4			(−)-92h	51
80	(+)-91i	Me	Et	Br_2	CCl_4			(+)-92i	51
81	(−)-91j	H	H	Br_2	CCl_4			(−)-92j	51
82	91k	H	Et	Br_2	CCl_4			92k	51
83	91l	Ph	naphthyl	Br_2	CCl_4			92l	51
				Br_2	CCl_4	RT			
84	93 (X = C) allenecarboxylate[i]			Br_2	CCl_4	RT		94 γ-lactone	83
85	95 (X = S) allenesulfinate[i]			Br_2	CCl_4	RT		96 γ-sultine	53, 83
86	97 (X = PPh) allenephosphinate[i]			Br_2	CCl_4	RT		98 phospholene oxide	53, 83
87	99 (X = POR') allenephosphonate			Br_2	CCl_4	RT		100 phospholene oxide	83
88	101 (X = POH) (*R*)-(−)-allenephosphonic acid (R = R³ = H, R⁴ = *t*-Bu)			Br_2	CCl_4	RT		100 (*R*)-(+) (O.Y. = 42%)	86
89				Br_2	CCl_4	RT		96 γ-sultine	53, 83
90				Br_2	CCl_4	0	48		84
	103 (α_D 9.3°)							104 (α_D 0°)	
	 105			I_2–MgI_2 ether				 (*Z*) 106 (*E*) (*Z*) 107 (*E*)	79

		R¹	R²	R³	X					
91	105a	H	H	H	I	ambient	70		100	
92	105b	Me	H	H	Cl	reflux	60	27	54[ao] 18	
93	105c	Me	H	H	Br	reflux	54	24	48[ao] 9	18
94	105d	Me	H	H	I	reflux	83	31	62	6
95	105e	$(CH_2)_4$		H	I	reflux	80		100	
96	105f	Me	H	Me	I	reflux			100	
97	105g	H	CH_2Ph	H	I	reflux	61	37	55	8
98	105h	Ph	H	H	I	reflux	90		14.6	

TABLE II (*Continued*)

[a] The presence of BF_3–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 $k_H:k_D = 0.83$ (for two deuterium) or $k_H:k_D = 0.91$ (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 $k_H':k_D' = 0.77$ (for two deuterium) or $k_H':k_D' = 0.88$ (for one deuterium) has been determined from the 56:57 ratio after acid equilibration. [i] The halogens used are XY = Cl_2, BrCl, ICl, 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 $(PhCOO)_2Ag^+I^-$ is used. [p] The E2 elimination reacti on by I^- and the S_N2 substitution reaction using MeO^- in DMSO are not able to point out the stereoselective formation of dibromide 63 by some known reverse process. 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**. [q] By means of silver-assisted methanolysis the mixture of chiral dibromides **63Z**:**63E** = 83:17 with α_D −7.35° is transformed into a chiral mixture of bromo ethers **63Z**:**63E** = 95:5 with α_D +0.6°. [r] 16% of dibromide is also present. [s] 5% of dibromide is also formed. [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 $O(CHMeCl{=}CHMe)_2$ 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 α_D +2.38° affords a bromomethoxy mixture with α_D +1.00 and roughly the same geometrical isomerism for the product. [ac] The reduction of the bromomethoxy 81 with α_D +6.26° by Na in liq. NH_3 affords the *cis*-4-methoxycyclononene. [ad] The same reaction of bromomethoxy (*E*)-80 gives rise to the (*R*)-*cis*-3-methoxycyclononene. [ae] The optical rotation (α_D +12.92°) 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] R = R^2 = R^3 = 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. [an] 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 $Me_2C{=}ClCHOHBu\text{-}t$ (**89**) is also formed.

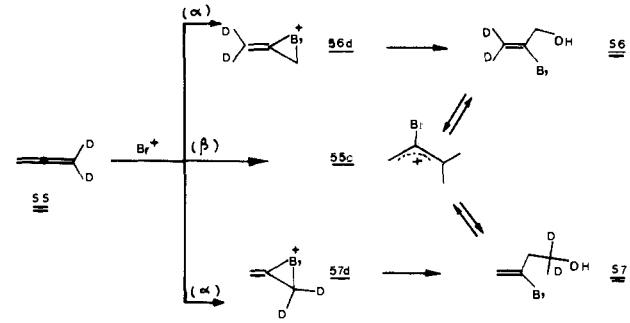


Figure 10. Reference 70. Secondary isotopic effect of deuterium $k_H/k_D = 0.71$ is generally attributed to the change of the out-of-plane C–H vibration (800 cm^{-1} to 1350 cm^{-1}) which derives from the change of carbon hybridization (sp^2 to sp^3) as it occurs during addition to a double bond.[71]

when halogenation takes place in CCl_4 and $C_2F_3Cl_3$.

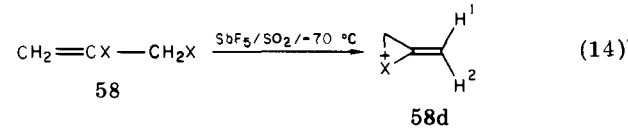
A. Acyclic Derivatives

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-dideuteriopropadiene **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 $k_H/k_D = 0.83$. 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** $k'_H/k'_D = 0.77$ 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.



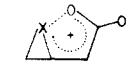
(14)[72]

58 58d

X = Cl, Br, and I

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-

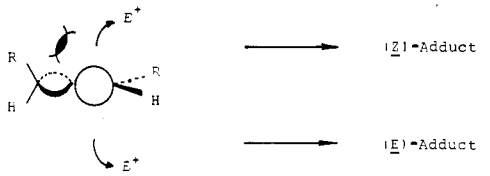


59ad

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



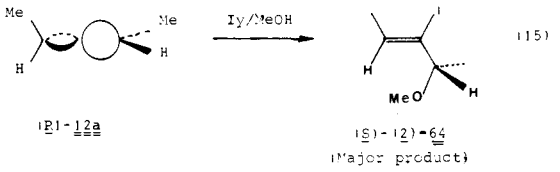
highly electron-withdrawing effect of the cyano group (entry 14).

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).

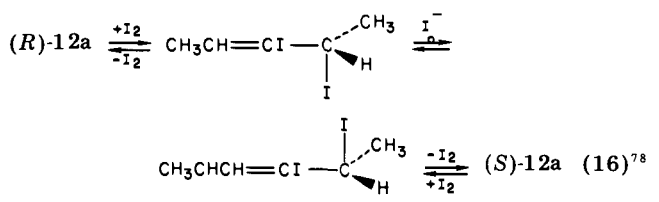
3. 1,3-Disubstituted Allenes

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



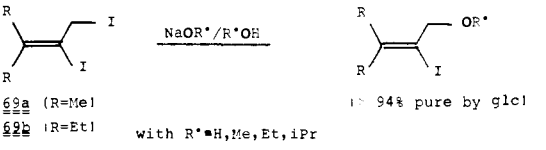
The degree of this anti stereospecificity, measured by the rotation of optically active ether **64Z**, will decrease with increasing nucleophilicity of the counter ion Y: $Cl^- < Br^- < I^-$ (entries 25–27). The product **64Z** is found to be inactive when methoxyiodination of chiral allene **12a** is 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*-diodides by the excess of iodide, which occurs with inversion (S_N2). 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).

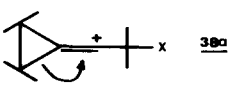
5. Trisubstituted Allenes

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 substitutent 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

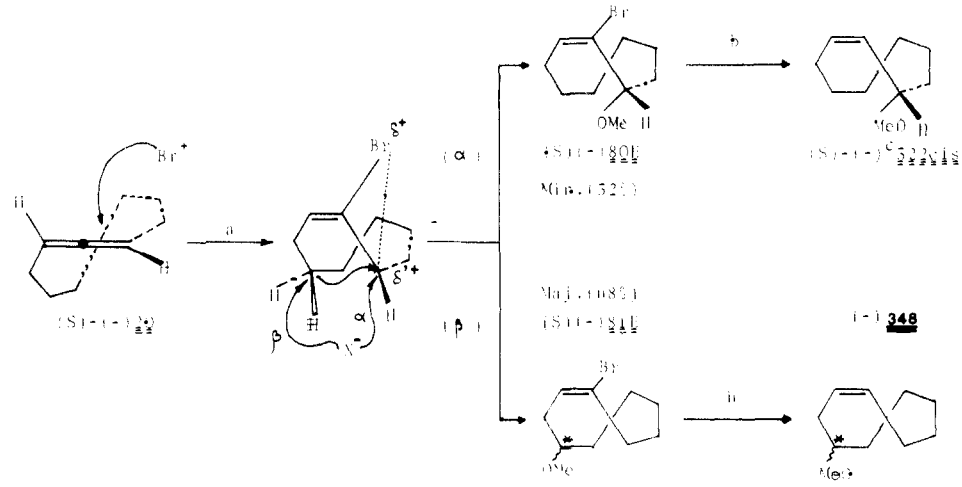


Figure 11. References 80 and 90. (a) Br_2, MeOH. (α) Pathway to the normal adduct 80. (β) Pathway to the transannular product 81. (b) Na–liquid NH_3. (c) See footnotes *ac* and *ad* of Table II.

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 = $PhSO_2$, Y = I, n = 6) is responsible for the formation of 18% of the transannular 4-methoxy-1-(phenylsulfonyl)cyclononene (*E*)-**81** (X = $PhSO_2$, SO = MeO, n = 6)[80].

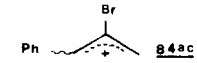
(b) **Anti Stereospecificity.** The syn–anti stereochemistry of the bromination of 1,2-cyclononadiene **20** has been simultaneously studied by Caserio[80] and Bach[90] using (*R*)-(+) and (*S*)-(−) enantiomers of the chiral substrate, respectively. In polar solvent (MeOH), the bromomethoxy **80** formed 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 CCl_4 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 halobenzylic ether **85** with Markovnikov orientation was formed by attack of the internal double bond. A solvent change from protic (MeOH) to aprotic (CS_2) 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-



84ac

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

When R^1 = 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

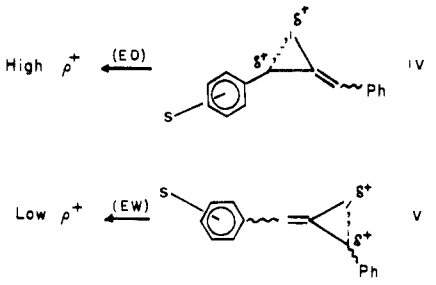
84ad

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).

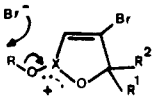
2. Kinetics

Kinetic study of the iodination of 12 1,3-diarylallenes 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.

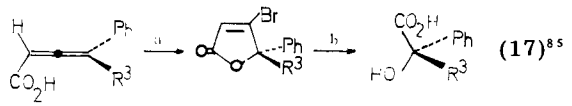
D. Functional Derivatives

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, bromooxaphospholenes **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 settled[85] (entries 75, 76), the (*S*)-(+) enantiomer of chiral acid **91a–d** leading to the 4-bromo-γ-lactone



(17)[85]

(*S*)-(+)-**91a–d** (*S*)-(+)-**92a–d** (*S*)-(+)-**90**

R = H, Me, *i*-Pr, *t*-Bu

(a) Br_2/CCl_4. (b) $KMnO_4$, OH^-.

92a–d with the same configuration and 100% optical yield. The structure and the optical purity have been correlated to the known α-hydroxy acid.

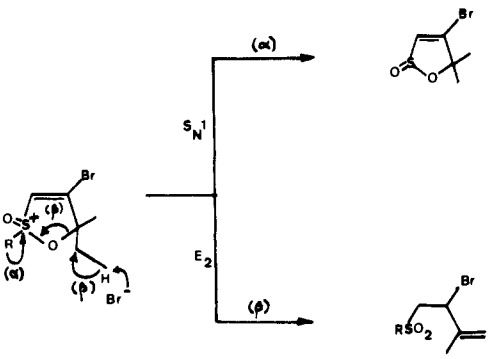


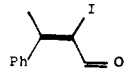
Figure 12. References 83 and 91.

Bromolactonization of tetrasubstituted allenic carboxylic acids is stereospecific[51] (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 preceeded 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



82

double bond bearing the iodine (entry 98).

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

73i **105i**

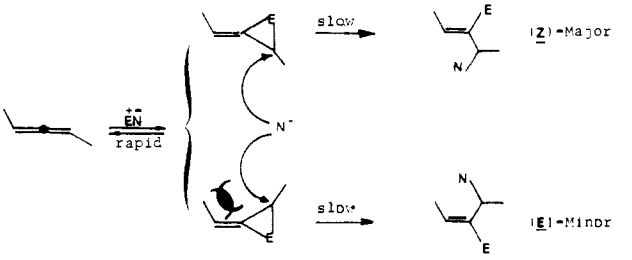
in the presence of excess of I_2–MgI_2 in ether solution.

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



volved 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).

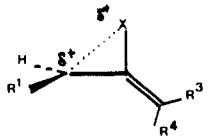
Solvents play a very important role in the steric course of the reaction. The replacement of a nonpolar solvent by a protic one increases the amount of transannular product **81** during the bromination of 1,2-cyclononadiene and in this latter solvent the optical purity of the bromides **80** and **81** 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.

$$\underset{\text{rates } 15}{(Me_2C{=})_2C} > \underset{6.5}{(EtCH{=})_2C} > \underset{1}{n\text{-BuCH}{=}C{=}CH_2} \qquad (18)^{76b}$$

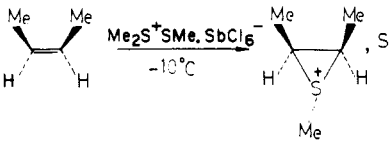
The variation in the character of the transition state, in going from the stereospecific anti addition to 1,3-dialkylallenes[77,78] to the nonstereospecific iodination of 1,3-diarylallenes[92] via symmetrical intermediates, is quite similar to that found for addition to olefins,[93-95] the former proceeding 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)

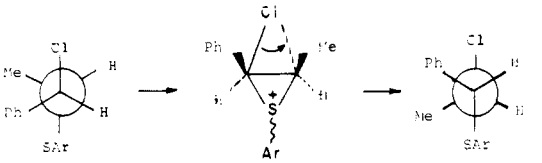
Electrophilic addition of reagent ArSX on olefins[110] and unsaturated substrates has been reviewed recently.[96] It has been shown that from *cis*-2-butene an



(19)[97]

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 arenesulfenyl chloride addition on *cis*-methylstyrene has been shown to be anti.



(20)[98]

threo threo

The kinetically controlled threo adduct PhCHClCH(ArS)Me with Markovinkov 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. Allene[203]

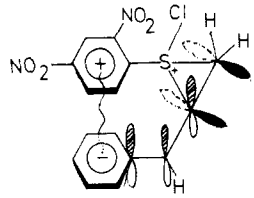
Sulfenyl chlorides (RSCl) add to allene itself leading mainly (entries 1–4), if not exclusively (entry 5), to a monoadduct **108** with Markovnikov orientation in which the sulfur is bound to the central carbon. The kinetically controlled product **108** is stable only when the substituent on the reagent 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 sufenylation 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 ≃ Ph ≃ AcS ≃ 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-dinitrobenzenesulfenyl 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 stereosomers **115** (*Z*/*E* = 1.66) when the reagent is benzenesulfenyl 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 XI[104]



E)-EtOOCCCl=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=CD_2 using DNBSC as reagent; under the same conditions no isotopic effect is found with PhCD=C=CH_2 (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 DNBSC (Scheme XI). A very similar trend was obtained during the sulfenylation of 1-phenylpropyne.[105]

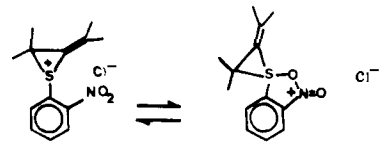
C. Disubstituted Derivatives

1. 1,3-Disubstituted Acyclic Allenes

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

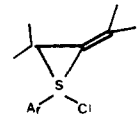
The reaction was also shown to be *E* stereoselective, the kinetically controlled ratio of stereoisomers *E*/*Z* was shown to increase with the bulkiness of alkyl substitutent cis to the arylthio group (entries 14–16). This steric course was confirmed with variously substituted arenesulfenyl chlorides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

SCHEME XII



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 recently[101] 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 benzeneselenyl bromide (BSeB) and 2,4,6-trimethylbenzeneselenyl bromide (TMBSeB) with 1,3-disubstituted allenes have been fully investigated.[185]

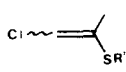
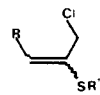
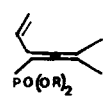
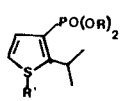
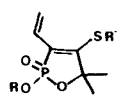
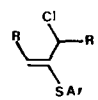
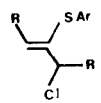
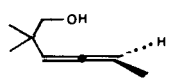
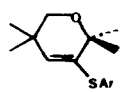
In all cases the phenylseleno moiety of benzeneselenyl chloride (BSeC) attacks regioselectively the central carbon atom with *Z* preference under kinetic control. This stereochemistry is reversed with the crowded selenyl reagent TMBSeB independent of which allene is used; perhaps "steric approach control"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

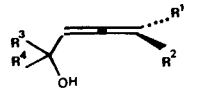
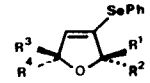
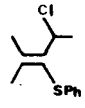
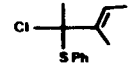
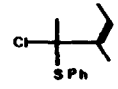
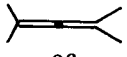
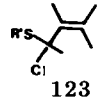
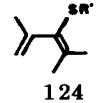
Whereas benzenesulfenyl chloride shows only minor variation in the second-order kinetics when 1,3-alkyl substituents of allenes are changed, the corresponding selenyl reagent exhibits very large fluctuations (Table VII). In contrast to the corresponding sulfur reagent,[101] the rates of BSeC addition 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 DNBSC with 1,2-cyclononadiene **20** can be rationalized in terms of steric hindrance. The *Z* isomer

TABLE III. Sulfenylation and Selenylation of Allenic Derivatives

entry	allenic derivatives	reagents	solvent	T, °C	yields, %	product composition, %[a]				ref
		R'SCl								
	1					108	109	110(E+Z)	111	
1		DNBSC[b]	$CHCl_3$			87[c,d]				100
2		MeSCl	CH_2Cl_2	-30		67[6]	10[0]	8[70]	9[20]	99
3		PhSCl	CH_2Cl_2	-30		75[9]	17]2]	0[64]	3[15]	99
4		AcSSCl	CH_2Cl_2	-30		85[78]	10[10]	0[3]	0[5]	99
5		PhSCl	CH_2Cl_2	RT		100[e]				101
		R'SCl								
	59					114	(E)	115	(Z)	116	
6	59d (R = Me)	DNBSC	CH_2Cl_2	0		100[f]				103
7	59e (R = Et)	DNBSC	CH_2Cl_2			100[f]				103
8	59f (R = *n*-Pr)	DNBSC	CH_2Cl_2	RT		100[f]				103
9	59h (R = Ph)	DNBSC	AcOH	RT	64	*g*		95[h]		104
10	59a (R = CO_2Et)	EtSCl	AcOH	RT		50[i]		50	trace	106
11	59a (R = CO_2Et)	PhSCl	CH_2Cl_2	RT		33[i]		66	trace	106
12	59d (R = Me)	PhSCl	CH_2Cl_2	RT		68	12	20		101
13	59i (R = $P(O)OMe_2$)	PhSCl	CH_2Cl_2	15-16		100				102a
14		R'SCl	$CHCl_3$	-10						102b
	59j					87		88		
	R = R' = Me, Et, *i*-Pr									
		ArSCl								
	12					(E)	117	(Z)		
15	12a (R = Me)	DNBSC	CH_2Cl_2	RT	(82)	64(60)		36(40)[j]		183, 103
16	12b (R = Et)	DNBSC	CH_2Cl_2	RT	(79)	80		20		183, 103
17	12e (R = *i*-Pr)	DNBSC	CH_2Cl_2	RT		92		8		183
18	12a (R = Me)	PhSCl	CH_2Cl_2	RT		45		55		101
19	20 (2R = $(CH_2)_6$)	DNBSC	CH_2Cl_2	RT		100				183, 103
20	17 (2R = $(CH_2)_{10}$)	DNBSC	CH_2Cl_2	RT		86		13		183, 103
21		DNBSC	EtOH	RT	80					84
		DNBSC	CH_2Cl_2	RT	(50)					84
	103 (α_D 9.3°)					104 (α_D 36.0°)				

22		PhSeCl			70-98					
	112 a-q (17 examples)					113 a-q				182
		R'SN								
	49					119		120		
23		DNBSC				Major				100
24		DNBSC				40		*k*		109
25		Me_2S^+SMe	BF_4^-			100 (N = SMe_2)[n]				109
26		PhSCl	CH_2Cl_2			20		74[l]		101
										
27	73a	PhSCl[o]	CH_2Cl_2			121(15)	*Z* (40)	122	*E* (32)	101
		R'SCl								
	36					123		124		
28		AcSSCl			80			100		99
29		DNBSC[b]			55			55[m]		103
30		PhSCl	CH_2Cl_2	RT	75	25		75		101

[a] Values in brackets are ratios after isomerization. [b] 2,4-Dinitrobenzenesulfenyl 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)=CH_2 and (*Z* + *E*)-PhCCl=C(SR)CH_3 125 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*-$C_2H_5OCOCCl$=C(SR)CH_3 130. [j] The monoadduct (*Z*)-117 with Markovnikov orientation was previously attributed to the anti-Markovnikov orientation product 118. [k] Conjugated diene CH_2=C(CH_3)—C(SAr)=CH_2 (60%) is also formed with Ar = 2,4-$(NO_2)_2C_6H_3$. [l] Conjugated diene 138 CH_2=C(CH_3)—C(SPh)=CH_2 (6%) is also formed. [m] Unidentified oil (30%) is also obtained. [n] MeS^+ is the electrophile and Me_2S the nucleophile. [o] Conjugated dienes (13%) are also formed.

TABLE IV. Kinetically Controlled Product Distributions for the Reaction of Arenesulfenyl Chlorides with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR[187]

	E/*Z* composition, %			
	C_6H_5S	2,4,6-$Me_3C_6H_2S$	2,4,6-*i*-$Pr_3C_6H_2S$	2-NO_2-4-XC_6H_3S[a]
Me	55/45	60/40	76/24	60/40
Et	72/28	83/17	98/2	78/28
i-Pr	80/20	100/0	100/0	90/10
t-Bu	97/3	100/0	100/0	100/0

[a] The ratio is independent of X; X = NO_2, Cl, MeO.

TABLE V. Relative Rate of the Addition of Various Arenesulfenyl Chlorides to 1,3-Dimethylallene[187]

arenesulfenyl chloride substituents	k_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-$Me_3C_6H_2Br$·(TMBSeB) with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR[185]

R	E/Z composition, % BSeB[a]	TMBSeB
Me	28:72	55:45
i-Pr	30:70	80:20
t-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 PhSCl(BSC) and PhSeCl(BSeC) with Symmetrically 1,3-Disubstituted Allenes RCH=C=CHR[185]

R	k rel. BSC	BSeC
Me	1.00	1.00
Et	0.83	0.34
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 $Me_2S^+SMe\ BF_4^-$ 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.

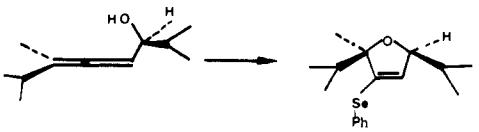
3. Anti Stereospecificity

(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 Jacobs[84] (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]

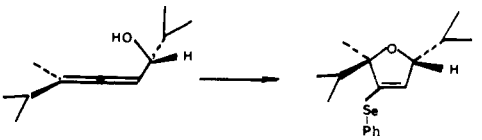
(b) Selenylation. The same group, in the synthesis of various configurationally well-defined 2,5-dihydrofurans by selenylation-induced cyclization of α-allenic alcohols, has established the anti stereospecificity of the addition. One diastereoisomer (3S,5R) of the allenic alcohol **112** affords the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



(21)[182]

(3S,5R)-112 (Z)-113



(22)[182]

(3R,5R)-112 (E)-113

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 $Me_2S^+SMe\ BF_4^-$ 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).

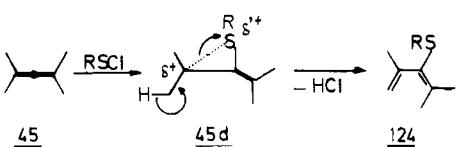
The unexpected chemoselectivity has been attributed to the existence of the homohyperconjugation of the methyl substituents that may increase the nucleophilicity of the external double bond. The ^1H NMR of the 1,1-dimethylallene **49** shows an upfield shift of 0.2 ppm for the methylenic hydrogens compares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

D. Trimethylallene

The addition of benzenesulfenyl 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 PhSCl, 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 (δ' >> δ when R' is an electron-donating substituent, δ' << δ when R' is an electron-withdrawing substituent such as R = AcS and 2,4-$(NO_2)_2C_6H_3$). 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).

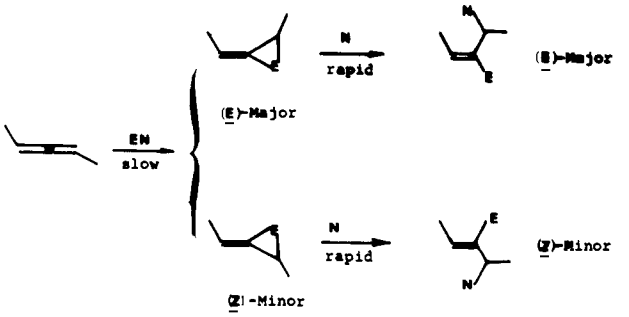


45 45d 124 (23)

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 benzenesulfenyl 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]

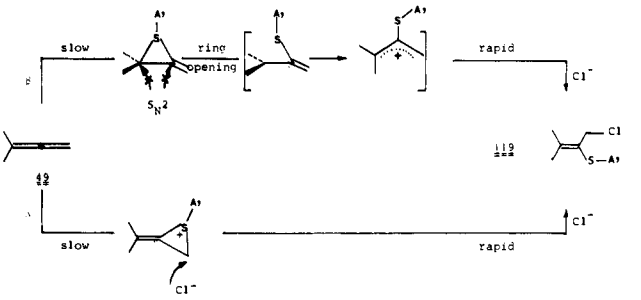
The kinetically controlled selenylation follows an Ad_E2 mechanism and may go via a seleniranium intermediate, which, in the product-determining step, undergoes an anti stereospecific attack by Cl^- to give predominantly the *Z* isomers[186] (Scheme X with E = SeAr and N = Cl). These data indicate that the structure of the rate-determining and the product-determining transition states are different for benzenesulfenyl chloride (BSC) and benzeneselenyl chloride (BSeC).[188] These differences are very similar to those observed in the electrophilic addition of arenesulfenyl and areneselenyl chlorides to alkenes in which, unlike the addition of 4-chlorobenzenesulfenyl chloride (CBSC), 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 thiiranium 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.

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 discuss this reaction with allenic compounds[114] and their α- and β-functional derivatives.

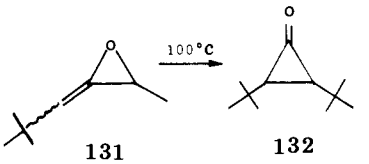
SCHEME XIV



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

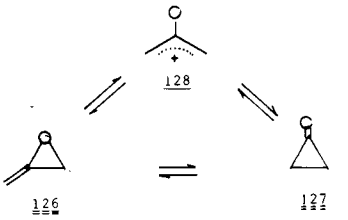


(24)

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 **134**[136] (entries 2,7).

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



(25)[137,161]

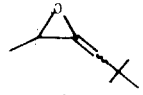
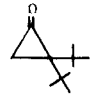
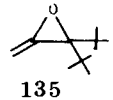
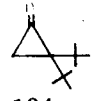
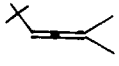
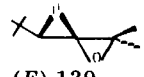
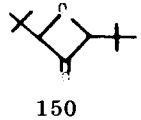
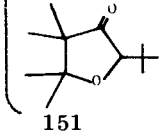
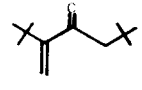
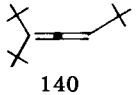
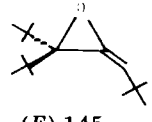
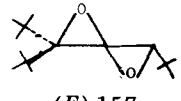
Some interconversion can occur either directly **126** ⇌ **127** or through the zwitterionic species **128**.[161]

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 spirodioxacyclopentane **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	 130	MCPBA[a]	Hexane			 131	115
2	 133	PAA[c]	CH_2Cl_2	RT	90	 134	116, 117
3		PNPBA[b]		-30	80	 135	117
4		O_3				 134  160	123
5	 137	2 PAA[c]	CH_2Cl_2	RT	100	 (*E*)-139	117, 118
6	 148	PNPBA[b]	CH_2Cl_2	RT		 149 46  150 36  151 12  152 6	117
7	 140	MCPBA[a,e]	CH_2Cl_2	reflux	91	 (*E*)-145 major	117, 119
8		O_3				 (*E*)-157 (*E*+*Z*)-145	123

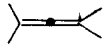
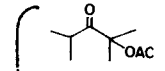
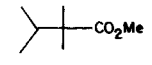
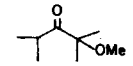
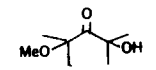
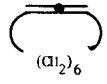
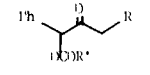
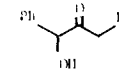
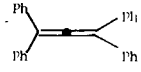
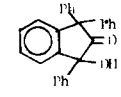
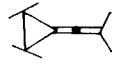
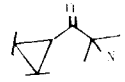
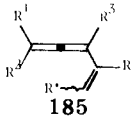
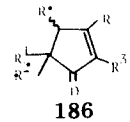
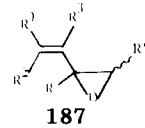
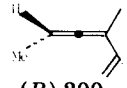
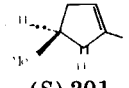
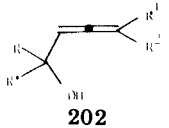
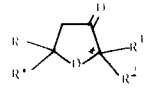
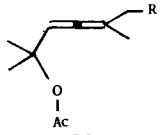
9	 36	PAA[q]	MeOH	0	High	 153 72	 154 9		120–122
						 155 9	 156 9		
10	 49	3 PAA[c]	CH_2Cl_2	0		 157 25	 158 50		120, 125
						 159 8	 160 17		
	 20(recovered)					 162	 163	 164	120, 124
11	(16%)	PAA[c]	CH_2Cl_2	0	High	11	29	44	
12		3 PAA[c]	CH_2Cl_2	0	High		31	69	
13	(12%)	MCPBA[a]	CH_2Cl_2	0	High		4	84	
14		3 PNPBA[b]	CH_2Cl_2	0	High		18	72	
	 174					PhCHO 169	 170	 171	
15	a (R = H)	PFA[d]	CH_2Cl_2				30	30	126
16	a (R = H)	2 MCPBA[a]	CH_2Cl_2			50	9		
17	b (R = Ph)	PFA[d]	CH_2Cl_2				68		
18	b (R = Ph)	2 MCPBA[a]				20	40		
19	 175	3 MCPBA[a]	CH_2Cl_2				 176		126

TABLE VIII (*Continued*)

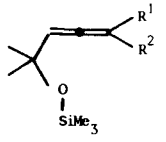
entry		allenic derivatives					reagents	solvent	*T*, °C	yield, %	product composition, %		ref
													
		38									179	180	
20							PAA[c]	CH_2Cl_2	0	91	64	27	55
21							MCPBA[a]	CH_2Cl_2	0	84	100		57
													
		185									186	187	
		R^1	R^2	R^3	R	R'							
22	a	H	H	Me	H	H	PNPBA[b]	CH_2Cl_2		80	100		129-131
23		H	H	i-Pr	H	H	PNPBA[b]	CH_2Cl_2		60	100		129-131
24	c	*n*-Pr	H	H	H	H	PNPBA[b]	CH_2Cl_2		55	95	5	129-131
25	d	H	H	Me	H	Me	PNPBA[b]	CH_2Cl_2		60	65	35	129-131
26	e	H	H	Am	H	H	PNPBA[b]	CH_2Cl_2		65	100		132
27	f	H	H	Am	Me	H	PNPBA[b]	CH_2Cl_2		80	100		132
28	g	H	H	C_6H_9[s]	H	H	PNPBA[b]	CH_2Cl_2		45	100		133
29	h	H	H	C_6H_9[s]	Me	H	PNPBA[b]	CH_2Cl_2		70	100		133
30	i	H	Me	H	Me	C≡CH	PNPBA[b]	CH_2Cl_2	0	45	100		140
31	j	H	C_8H_{17}	H	Me	C≡CH	PNPBA[b]	CH_2Cl_2	0	49	100		140
32	k	Me	Et	H	Me	C≡CH	PNPBA[b]	CH_2Cl_2	0	58	100		140
33	l	H	H	Me	H	H	$O_2/h\nu$	CH_2Cl_2		57	100		138
34	m	H	H	Me	$(CH_2)_4$		$O_2/h\nu$	CH_2Cl_2			60	40	139
													
		(*R*)-200									(*S*)-201		134a
35		α_D −5.74°					MCPBA[a]				α_D −1.24° (0.Y − 100%)		
36		α_D −5.74°					Payne (H_2O_2, PhCN)				α_D −1.15° (0.Y − 95%)		
													134a
		202									203		
		R^1	R^2	R	R'								
37	a	Me	He	H	H		Payne			10			
38	b	Me	Me	Me	H		Payne			60			
39	c	Me	Et	Me	Me		Payne			100			
40		(−)-202c α_D 0.550°					Payne				(−)-203c α_D 5.370°		
41		(−)-202c α_D 0.550°					MCPBA[a]				(−)-203c α_D 5.466°		



190

43 190a (R = H)

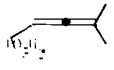
44 190b (R = Me)



193

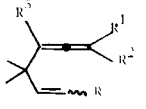
		R^1	R^2
45	a	Me	Me
46	b	Me	Et

47 (*R*)-193b α_D −2.59°



48 31b

49 31b



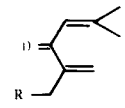
207

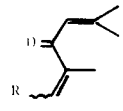
		R^1	R^2	R^3	R
50	a	Me	H	H	H
51	b	*n*-Pr	H	H	H
52	c	Me	Me	H	H
53	c	Me	Me	H	H
54	d	Me	Et	H	H
55	d	Me	Et	H	H
56	e	$(CH_2)_5$		H	H
57	f	Me	H	Et	H

58 (−)-207d α_D 0.72°

59 α_D 0.72°

Payne CH_2Cl_2/MeOH

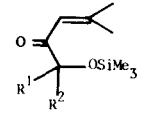




191 192 134b

72 100

63 24 76



Payne CH_2Cl_2/MeOH

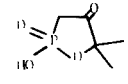
194

62 194a

75 194b

(*S*)-194b α_D^{20} −0.20° (0.Y. 100%)

$CHCl_3$



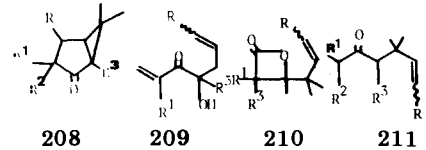
141

206 160

PAA[c] 50 75 25

MCPBA[a] 100 75 25

PNPBA[e] 0 50



144-146

208 209 210 211

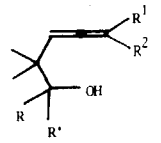
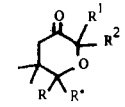
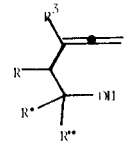
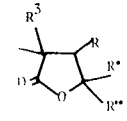
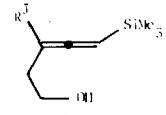
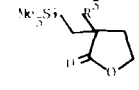
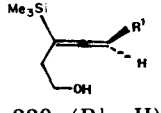
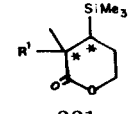
bicyclic ketone | α-ketone | β-lactone | γ-enone

CH_2Cl_2			35	60
CH_2Cl_2			80	20
CH_2Cl_2		20	80	
MeOH	100			
CH_2Cl_2	50		50	
MeOH	90		10	
CH_2Cl_2	25	30	40[o,p]	
			50	50

MCPBA[a] (−)-208d α_D 0.818° (0.Y. ?) 134a

Payne α_D 0.666° (0.Y. ?) 134a

TABLE VIII (*Continued*)

entry		allenic derivatives	reagents	yield, %	product composition, %	ref
		 212			 213	
		R¹ R² R R'				
60	a	Me Me H H	Payne	10		142, 143
61	b	Me Me H Me	Payne	60		142, 143
62	c	Me Et Me Me	Payne	100		142, 143
63		(+)-212c α_D = 2.76°	Payne		(−)-213 α_D 1.76° (O.Y. ?)	134
64		(+)-212c α_D = 2.76°	MCPBA[a]		(−)-213 α_D 1.25° (O.Y. ?)	134
		 216	Payne		 217	
		R" R' R R³				
65	a	H H H Me			217a	142, 143
66	b	H Me H Me			217b	142, 143
67	c	H Me Me Me			217c	142, 143
68	d	Me Me H Me			217d	142, 143
69	e	H $(CH_2)_4$	Me(*cis*-216e)		*cis*-217e	135
70	e	H $(CH_2)_4$	Me(*trans*-216e)		*trans*-217e	135
71	f	Me H	$(CH_2)_4$(*threo*-216f)		*cis*-217f (70) *trans*-217f (30)	135
72	g	H Me	$(CH_2)_4$(*erythro*-216g)		*cis*-217f (100)	135
		 218	Payne		 219	
			Payne			192
74		220a (R¹ = H)		quantitative	221a	
75		(*S*)-(+)-220b (R¹ = Et)		quantitative	(+)-221b	

[a] *m*-Chloroperbenzoic. [b] *p*-Nitroperbenzoic acid. [c] Peracetic acid. [d] Performic acid. [e] Excess of reagents. [f] Excess of allene. [g] *n* equiv of reagents for 1 equiv of allenic substrate. [h] Stereochemistry of the allene oxide 131 is not given. [i] 20% of starting allene 133 was recovered. [j] 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*-ClC_6H_4. [m] The Payne reagent[127] (=50% H_2O_2, PhCN, MeOH) does not afford the Baeyer-Villiger reaction with cyclopropanone intermediate whereas the peroxy acids do. [n] When $NaHCO_3$ (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] C_6H_9 = $CH_3(CH_2)_2C{\equiv}C{-}CH_2$.

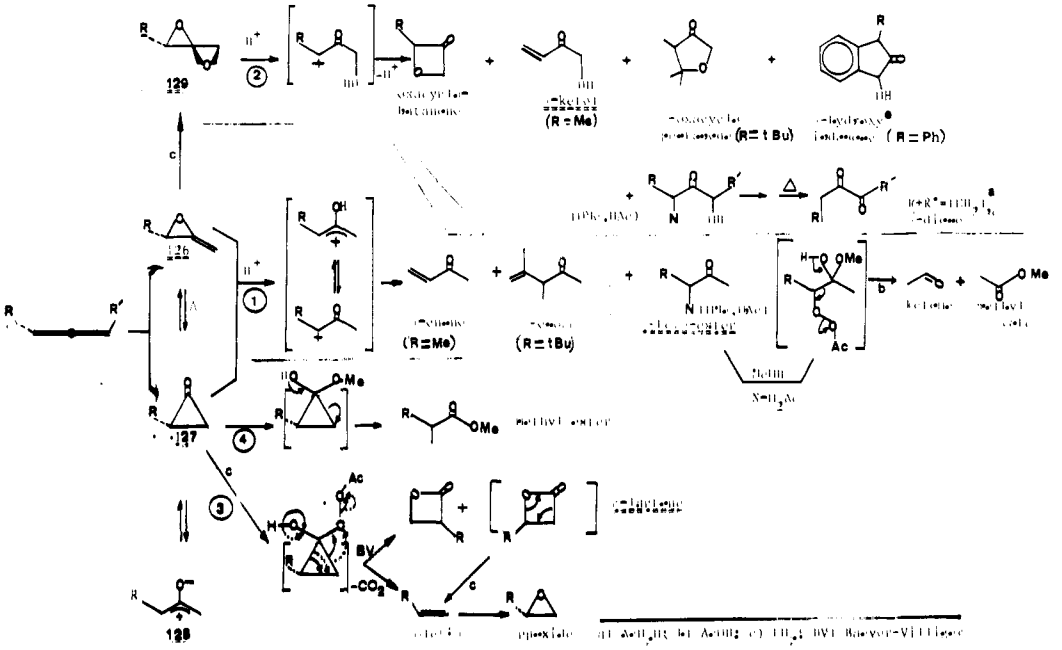
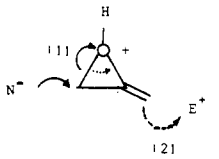


Figure 13. (a) For clarity the alkyl substituent R′ of the starting allene has been drawn in the product only when it is necessary for the comprehension of the process. (b) Main products are doubly underlined. (c) Peracetic acid. BV = Baeyer–Villiger.

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 reagent[127] (H_2O_2, PhCN, MeOH) is used.

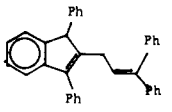
Predominant α-keto esters and α-keto ethers are formed more likely by a concerted nucleophilic attack of the protonated monoadducts than on the unstable α-acyl carbonium ion (path 1 of Figure 13).



(26)

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).

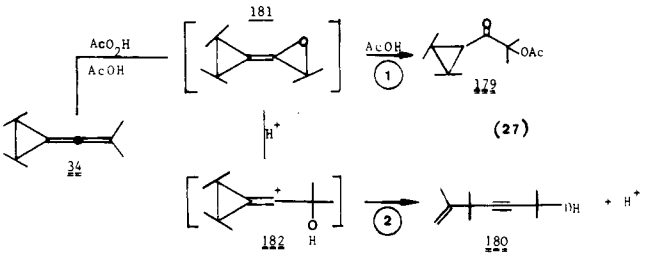
The acid-sensitive triphenylallene **177** affords the indene **178**[126]



178

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**,



(27)

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

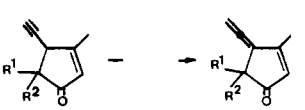
Nucleophilic groups on allenes can participate during epoxidation; cyclic products will then be obtained.

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 dihydrojasmone **186e** and dehydrojasmone **186g** (entries 26,28).

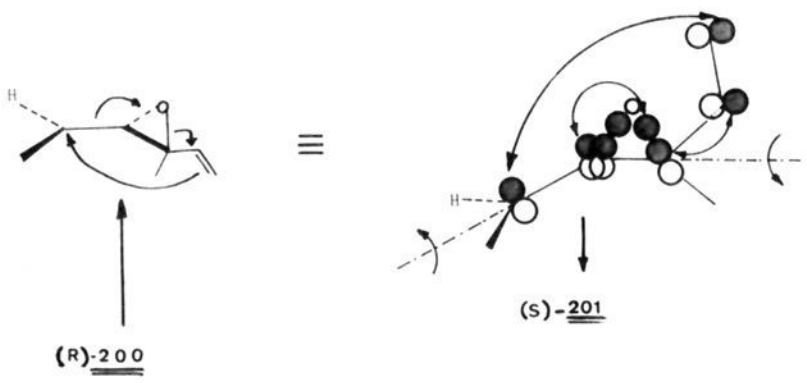
When a triple bond is conjugated with the 1,2,4-triene, as in the compound **185i**, the epoxidation reaction affords the expected 4-ethynylcyclopent-2-ene-1-one **186i**, which gives the corresponding allenylidene de-



(28)

186i **188**

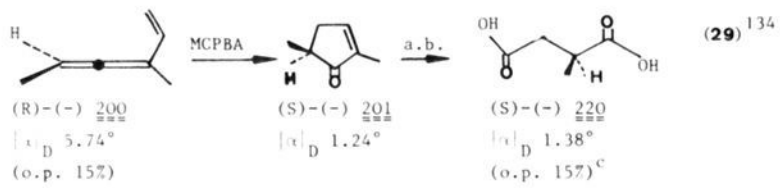
SCHEME XV



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

Some cyclopentenone (**186l** 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-



(a) O_3/CH_2Cl_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*.

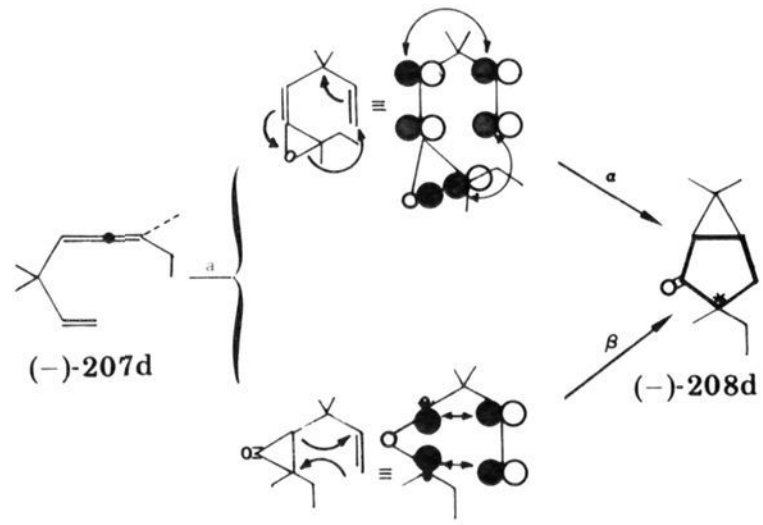
This transfer of chirality prevents the exclusive formation of the planar zwitteronic oxallyl species **129** as the valence isomerism of the intermediate allene oxide *200d* in which the attack by oxygen occurs through the less hindered face of the external double bond. A thermally allowed pericyclic 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 reagent[127] (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

SCHEME XVI[a]



[a] (a) RCO_3H/MeOH; (α) $_\pi 2 + _\pi 2 + _\sigma 2$; (β) $_\pi 2_s + _\sigma 2_a$.

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-oxooxaphospholane **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

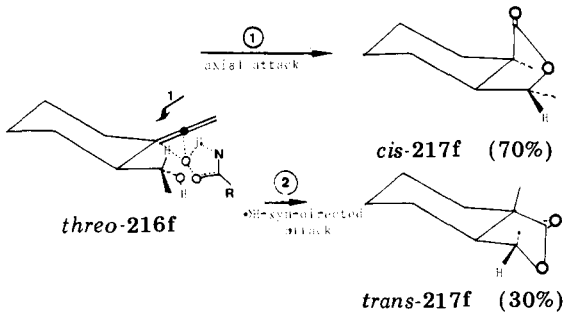
1,2,5-Triene **207** epoxidation is very complex. The bicyclic ketone **208**, a product of neighboring group participation, is obtained when the allene **207** is *gem* disubstituted (entries 53–56). This product is formed exclusively in methanol (entry 53). α-Ketols **209**, β-lactone **210**, and 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 stereospecific and may occur by concerted processes, through allene oxide or cyclopropanone, both being thermally allowed (entries 58, 59).

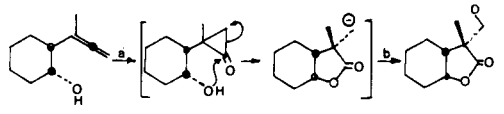
2. β-Allenic Alcohols

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



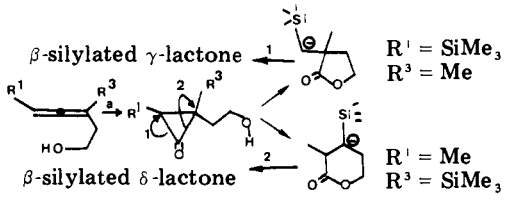
SCHEME XVIII[a]



trans-216e[c,d] α-D-trans-217e

[a] (a) H_2O_2, 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)[135] 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 R^1 and R^3 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, allylallene, and β-allenic alcohol proceed stereospecifically.

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

In a functional allenic derivative >C(X)—$(CH_2)_n$—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 Modena[10] 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 (R^3 = 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).

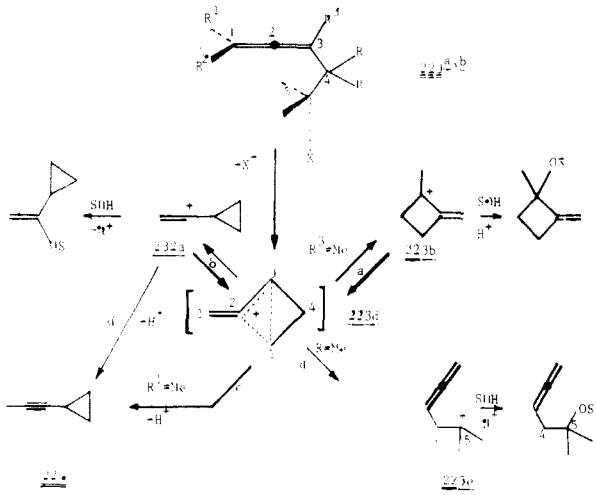
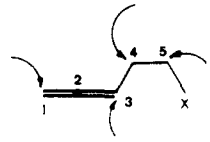


Figure 14. Rationalization of product formation during solvolysis of acyclic β-allenic esters.[10] (a) X = Br, ONs, OTs, OBs, and DNB. (b) The alkyl substituents R^1, R^2, R^3, and R will be mentioned in the species **223a–e** only when they are different from hydrogen.

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 $LiAlH_4$. Alcohols that are formed can then be compared with those obtained by hydrolysis of the same allenic tosylate.) (SOH = AcOH) and hydrolysis (SOH = H_2O) 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

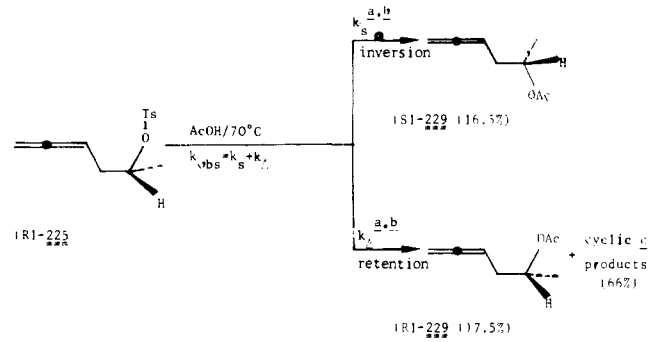


Figure 15. Kinetics and stereochemistry of acetolysis of the tosylate (*R*)-**225**. (a) $k_s = 0.46 \times 10^{-5}$ and $k_\Delta = 2.32 \times 10^{-5}$ are respectively, the rate constant without and with participation of the allenic system. (b) $k_\Delta/k_s = 5.04$. (c) For the structure and the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

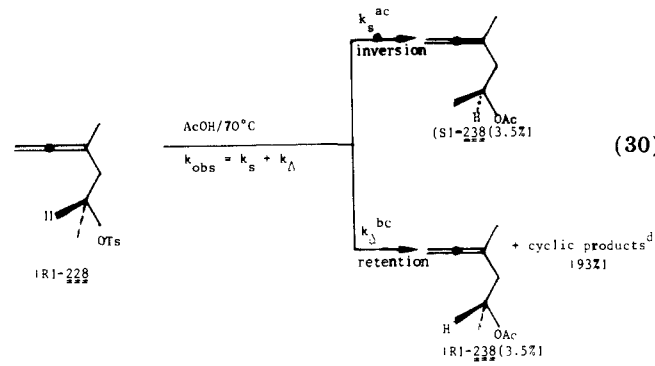


Figure 16. Kinetics and stereochemistry of the acetolysis of the tosylate (*R*)-**228**. (a) $k_s = 0.50 \times 10^{-5}$. (b) $k_\Delta = 13.8 \times 10^{-5}$. (c) $k_\Delta/k_s = 27.6$. (d) See entry 12 in Table IX.

(k_{obsd}) 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 ($k'_s = 4.17\ 10^{-5}$), 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 cyclopropylvinylic cation **227a** or **228a** in which the more nucleophilic σ bond of the cyclopropane ring affords 5 times more β-dimethylated

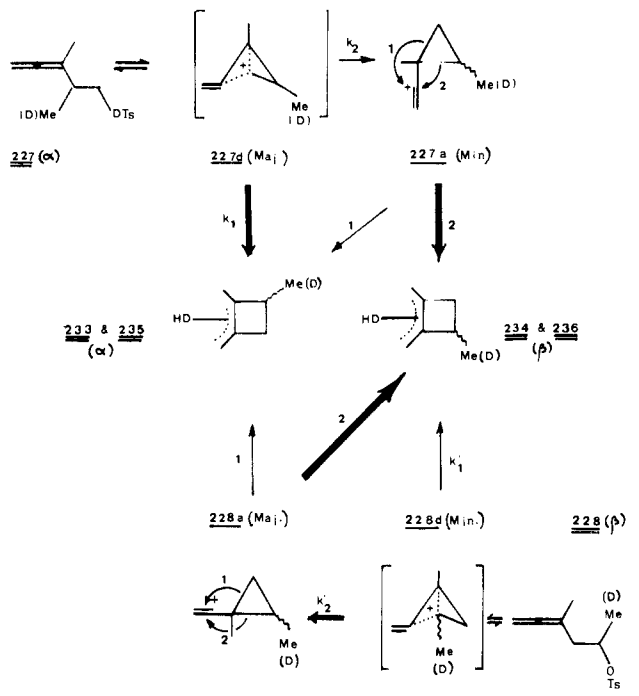
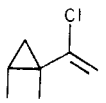


Figure 17.

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 ($k_1 >> k_2$) 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** ($k_2' >> k_1'$) 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 vinylcyclopropylcarbinyl 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

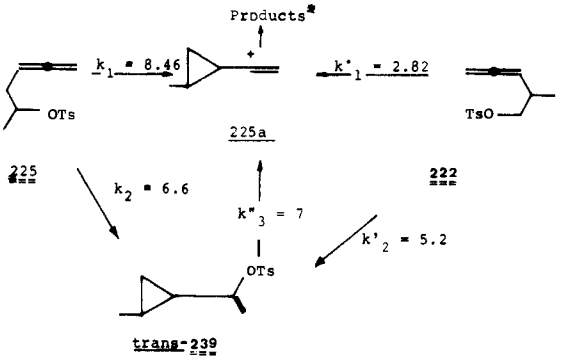
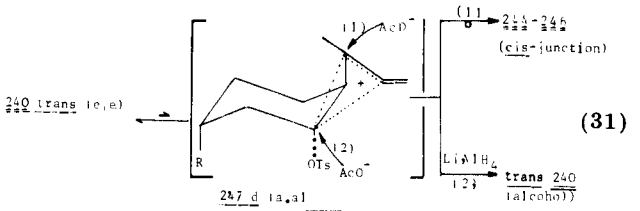
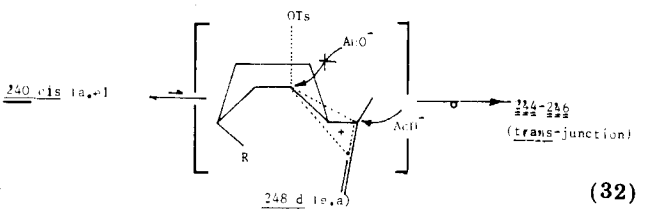


Figure 18. Reference 128. * $k \times 10^5$ s at 85 °C; $k_3 = 6.6$ and $k'_3 = 8.2$ with $k_1 > k_3$ and $k'_1 < k'_3$.

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



(31)



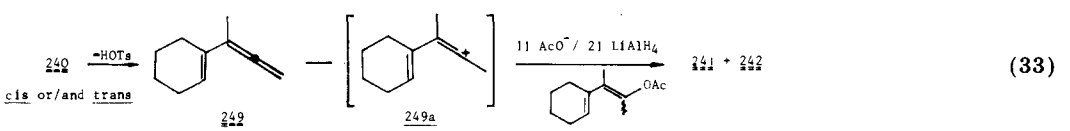
(32)

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 nonclassical 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**



(33)

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

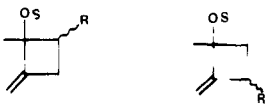
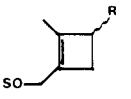
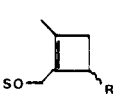
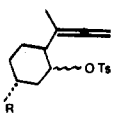
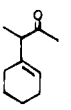
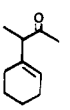
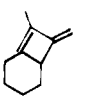
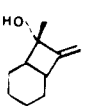
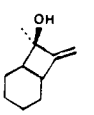
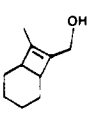
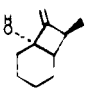
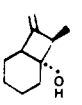
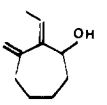
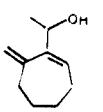
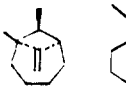
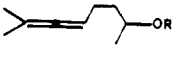
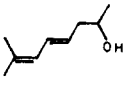
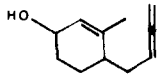
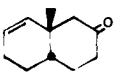
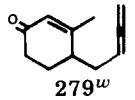
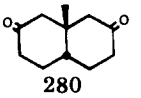
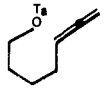
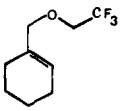
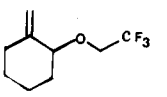
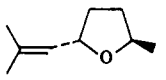
entry	allenic derivatives	reagent and solvent	T, °C	yield	products composition, %						ref
					β-Allenic Esters						
											
	225				(E)	230 (Z)	(E)	231 (Z)			
1		hydrolysis[a,b,p]	100		44.5	22.5					147
2		hydrolysis[a,c,r]	55		48	33					147
3		acetolysis[n,d]	80		25	18.4	8.5		6.5		147
4	(S)-(−)	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)	(Z)	234 (E)	235	236	147
6		hydrolysis[a,e,o,p]			75						
7		acetolysis[a,e,o,q]			37				38		
8		hydrolysis[a,f]	10	1	36.5	19	4.5	10	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 (3S)-(+)		39 (4S)-(+)		14 (3S)	19 (?)	
											
13	*cis*-240 (R = H)	reductive acetolysis[s]			241	242	243	244[t]	245[t]	246[t]	150
					3	4	10	16 (trans)	33 (trans)	34 (trans)	
14	*trans*-240 (R = H)				3.5	5		20 (cis)	50 (cis)	17 (cis)	
											
15	*threo*-250	hydrolysis[p] [H_2O:dioxane (3:1)]	100		251 (4)	252 (34)	253 (22)	254 (12)	255 (28)		151
											
16	*erythro* 250	hydrolysis[p] [H_2O:dioxane (3:1)]	100		251 (4)	256 (41)	257 (11)	*erythro*-258 (44)			151
					γ-Allenic Esters						
											
	270 (X = OTs)				271	272	273 (OH)	274 (OAc)	275		152
17		hydrolysis	80		24	12	44.5[u]		0.5		
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		
		HCO_2H		70							153
21	277[w]						278				
		$CF_3COOH/(CF_3)_2O$		74							153
22	279[w]						280				

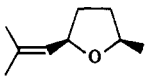
TABLE IX (*Continued*)

entry	allenic derivatives	reagent and solvent	T, °C	yield	products composition, %	ref
			δ-Allenic Esters			
23		CF_3CH_2OH[v]	60	65	 	
	284				285 (45) 286 (45)	154

[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 H_2O and $CaCO_3$. [q] NaOAc in acetic acid is used for the acetolysis. [r] H_2O in acetone is also used for hydrolysis. [s] In the reductive acetolysis, the products of the acetolysis reaction are subsequently treated by $LiAlH_4$. [t] The cis and trans configuration of the products **224–246** concern the junction of the bicyclic products. [u] 15% of a 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.



281 (8%)

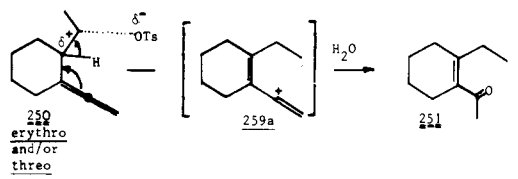


282 (7%)

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



(34)

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

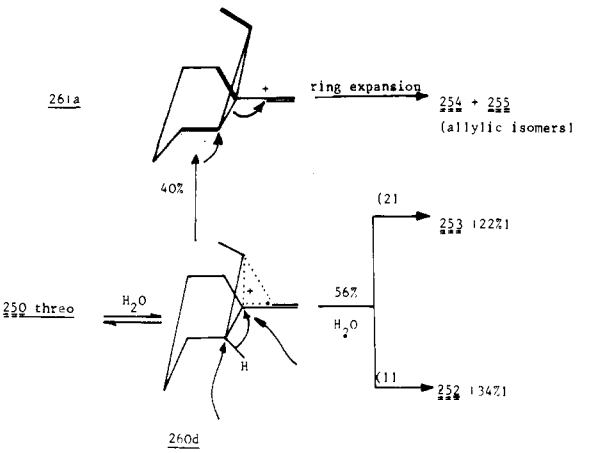


Figure 19. Hydrolysis of the secondary *threo*-tosylate **250**.

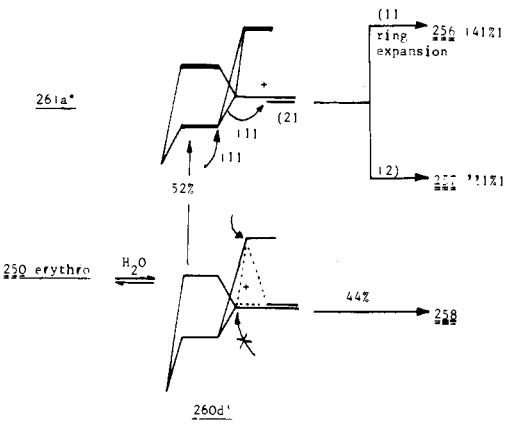


Figure 20. Hydrolysis of the secondary *erythro*-tosylate **250**.

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

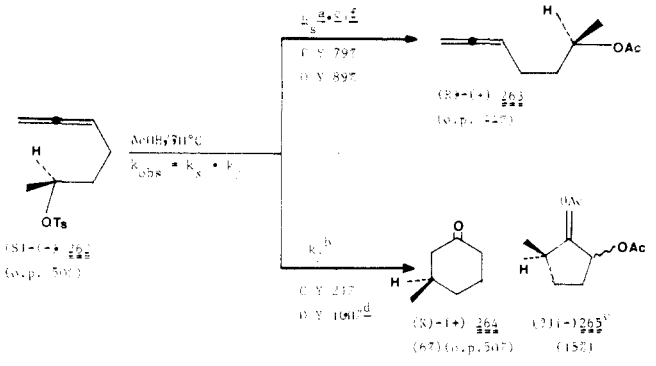


Figure 21. Kinetics and stereochemistry of acetolysis of the nonmethylated γ-allenic tosylate **262**. (a) $k_s = 1.52 \times 10^{-5}$. (b) $k_\Delta = 0.40 \times 10^{-5}$. (c) $k_\Delta/k_s = 0.26$. (d) Optical yield (OY) for **264**. (e) The configuration and the optical purity of the levorotatory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

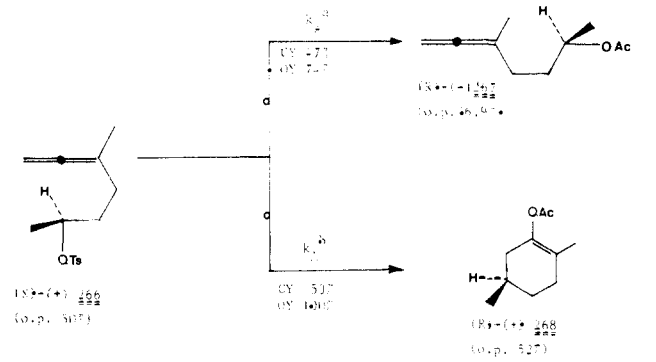


Figure 22. Kinetics and stereochemistry of acetolysis of the monomethylated secondary γ-allenic tosylate **266**. (a) $k_s = 1.31 \times 10^{-5}$. (b) $k_\Delta = 1.47 \times 10^{-5}$. (c) $k_\Delta/k_s = 1.12$. (d) The configuration and the optical purity of the enol acetate **268** have been correlated 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).

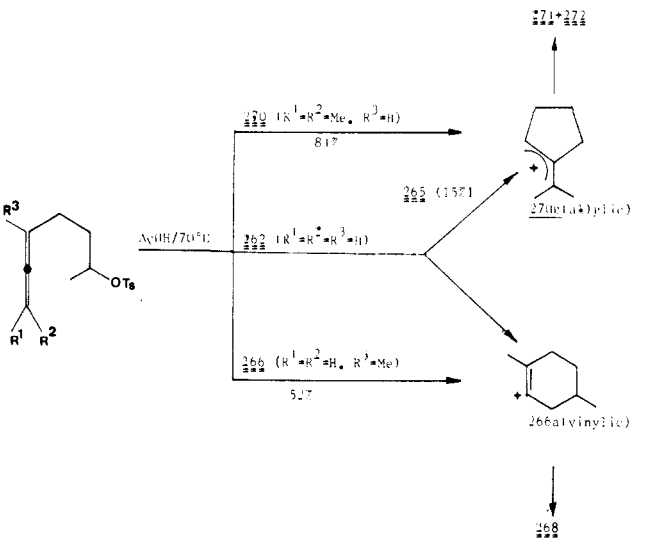
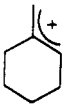


Figure 23. Acetolysis of secondary β-allenic tosylates. Regioselective cyclization.

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



284c

to the β- and γ-tosylates acetolyses the rate constant of this trifluoroethanolysis ($k_{obsd} = 8.15 \times 10^{-7}$ 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_Δ) 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	$k_{obsd} \times 10^5$, s	$k_s \times 10^5$, s	$k_\Delta \times 10^5$, 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).

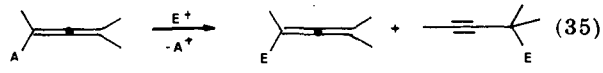
Finally, the reaction of β-allenic tosylates affording cyclic products is stereospecific, the reaction proceeding through an S_N2 pathway taking place on the carbon bearing the leaving group (entries 4,5).

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)



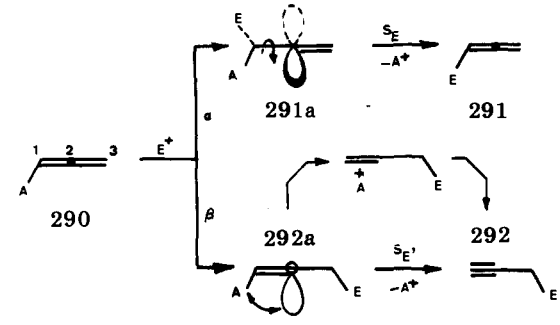
(35)

290 291 (S_E) 292 (S_E')

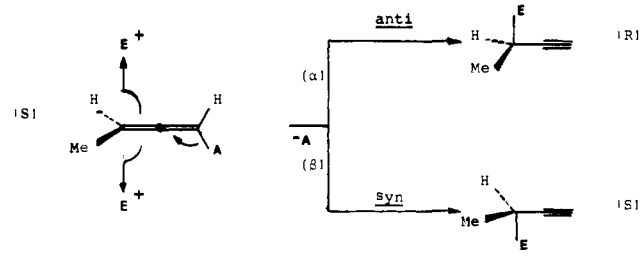
or with allenyl–propargyl isomerization (S_E'). Usually, a mixture of acetylenic and allenic derivatives is formed. Acetylenic and allenic products could arise from two different carbonium ions, which are obtained by attack on terminal carbon atoms of the two double bonds that have different reactivities. 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 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.

SCHEME XX

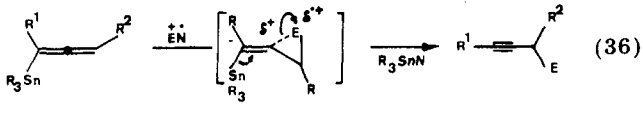


SCHEME XXI



A. Organotin Derivatives

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



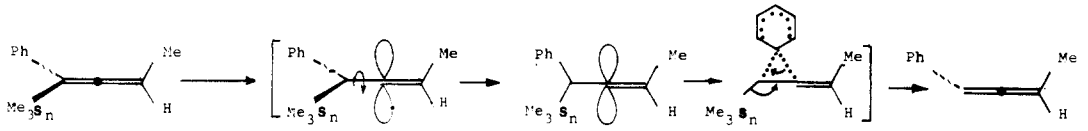
(36)

293 295d 295

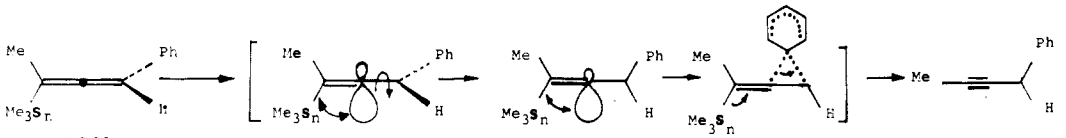
EN = Cl_2, Br_2, DNBSC, SO_2

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

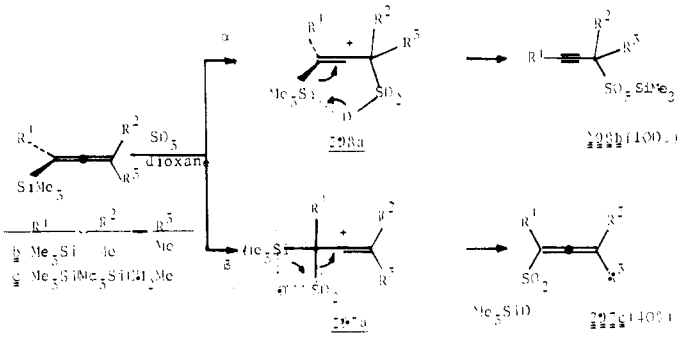


293c 294c (37)



293b 295b (38)

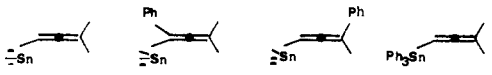
SCHEME XXII



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 = 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 = 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.

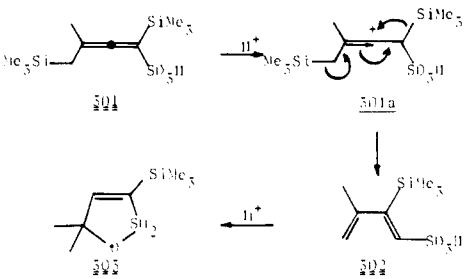


293a	293c	293b	293e	(39)
70	17	15	$1 \simeq k_2$	

B. Organosilicon Derivatives

Proto- and halodesilylation of alkenylsilanes have been extensively studied and shown to occur often with retention of the double bond configuration.[190]

SCHEME XXIII

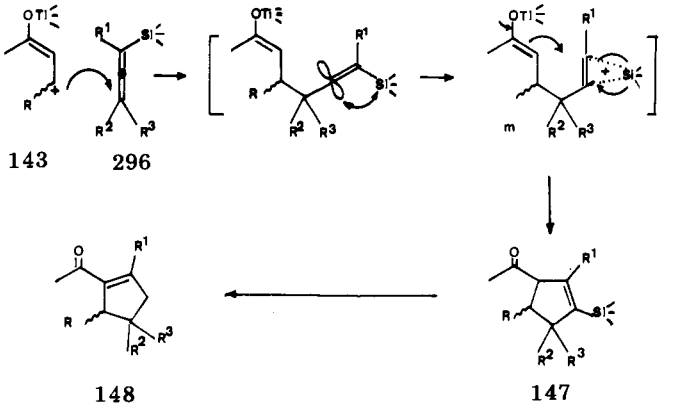


Sulfonation of the silylated allenes **296** using SO_3 or $ClSO_3SiMe_3$ as electrophilic reagent, affords variously unsaturated silyl esters of sulfonic acid **297–299** with E = $O_2SOSiMe_3$ (entries 11–14 and 17,18).

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 A = $SiMe_3$). 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 intramolecularily 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 desilation reaction via a four-membered cyclic transition state (entry 13 and path β of Scheme XXII).

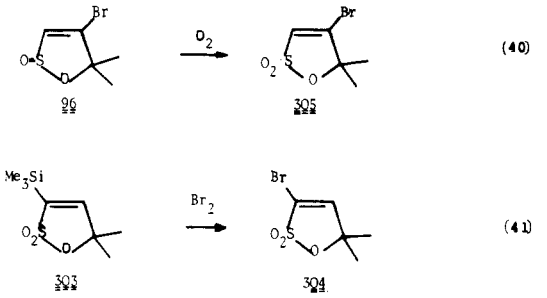
An interesting 1,2-cationic rearrangement of the trimethylsilyl group across the double bond has been observed from a vinylic carbonium intermediate during protonation of the allenesulfonic acid **301** leading to the

SCHEME XXIV



143 296 148 147

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 sulfinic ester followed by oxidation (see entry 85 of Table II and eq 40 and 41).



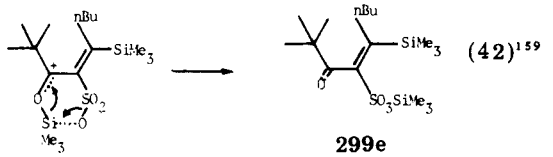
(40)

(41)

It has been shown, very recently,[158b] that (trimethylsilyl)allenes **296** can be used, as three-carbon components, for cyclopentannelation (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.

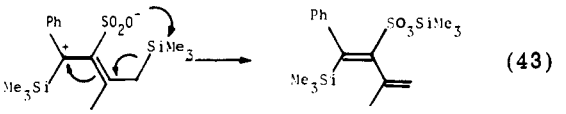
It is noteworthy that the unsubstituted silylallene **296a** ($R^1 = R^2 = R^3 = H$) affords a poor yield of cyclic product because of the relative instability of the primary terminal vinyl cation (entry 19), required in the mechanism proposed[158b] and depicted in Scheme XXIV, whereas a good yield of 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 isomerization will take place during addition reaction, leading to the α-enone **299e** (entry 18 and eq 42). Some conjugated 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).



(42)[159]

299e

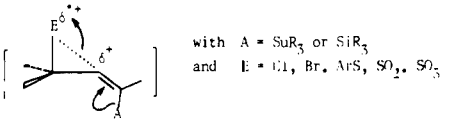


(43)

299d

C. Discussion

Except for protonation, electrophilic addition to allenyltin and -silicon (halogenation, sulfenylation, sulfinylation, sulfonylation) 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.



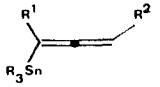
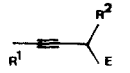
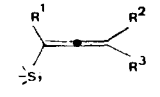
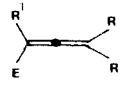
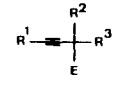
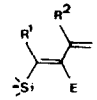
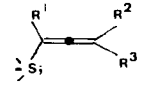
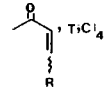
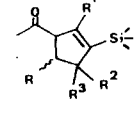
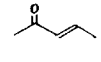
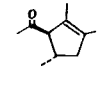
with A = SuR_3 or SiR_3
and E = Cl, Br, ArS, SO_2, SO_3

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 (E = M_nX_{n-1}) (Table XII)

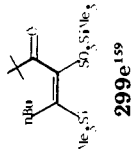
In the last part of this study of electrophilic addition to allenic derivatives, reaction of metallic salts, mercuric (HgX_2), thallic (TlX_3) and plumbic (PbX_4), with various allenes are described. Solvents that are more often

Table XI. Electrophilic Addition to Allenyl Tin and Silicon Derivatives

entry		allenic derivatives	reagents	solvent	T, °C	yields, %	product composition, %		ref
		 293					 294(S_E)	 295(S_E')	
		R R¹ R²							
1	a	Me Me Me	Cl_2			77	100		155
2	a	Me Me Me	Br_2			92	100		155
3	a	Me Me Me	DNBSC			69	100		155
4	f	Me H H	SO_2				100[a]		156, 157
5	g	Ph H H	SO_2				100[a]		156, 157
6	a	Me Me Me	HCl				57	43	155
7	b	Me Me Ph	HCl				40	60	155
8	c	Me Ph Me	HCl				85	15	155
9	d	Et Me Me	HCl				33	66	155
10	e	Ph Me Me	HCl				11	85	155
		 296					 297[b]	 298[b]	 299[b]	
		R¹ R² R³							
11	a	H H H	"SO_3" [c,d]			good	100		158a
12	b	Me_3Si Me Me	"SO_3" [c,d]				100		158a
13	c	Me_3Si Me_3SiCH_2 Me	"SO_3" [c,d]				(25)[c] 40[d]	(75)[c] 60[d]		157, 158a
14	c	Me_3Si Me_3SiCH_2 Me	$MeSO_3H$			70	100		157
15	c	Me_3Si Me_3SiCH_2 Me	Br_2			70	[e]		157
16	c	Me_3Si Me_3SiCH_2 Me	t-BuOCl, $AlCl_3$[i]			70	100[f]		157
17	d	Ph Me CH_2SiMe_3	"SO_3" [c,d]					100	158a
18	e	n-Bu t-Bu $OSiMe_3$	"SO_3" [c,d]					100[g]	158a, 159
		 296	 143	CH_2Cl_2	-78		 147		158b
		R¹ R² R³							
19	a	H H H				17-19			
20	f	Me H H				48-94			
21	g	i-Pr H H				69-85			
22	h	Me Me H				68			
23	i	Me Et H				79			
24	j	Me Me Me				60-80			
25		296f	144  , $TiCl_4$	CH_2Cl_2	-78	69			158b

26	296i	145	 , $TiCl_4$	CH_2Cl_2	-78	79	95	158b
27	296a	146	 , $TiCl_4$	CH_2Cl_2		80–85	94	158c

300



299e[159]

[a] With sulfur dioxide the product **295** is a propargyl sulfinic tin ester with E = $OSOSnR_3$ 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 E = $O_2SOSiMe_3$. [c] "SO_3" = $ClSO_3SiMe_3$. [d] "SO_3" = SO_3/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] E = O-*t*-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 solvometalation. Reactivity of these salts are directly dependent upon the nature of their anions X^- (AcO^-, ClO_4^-, NO_3^-, F^-, Cl^-, CF_3COO^-, and $0.5(SO_4)^{2-}$); it has been shown that mercuration of olefins occurs faster with the increasing ionic character of Hg–X bond as follows: $Hg(ClO_4)_2 > Hg(ClO)_2 >> HgCl_2$.[196]

A. Solvomercuration (E = HgX)

Early in 1967, oxymercuration of allenes has been studied simultaneously by Gardner[45] and Kiefer[160] 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 dissymetric 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).

$$\underset{\mathbf{59}}{RCH{=}C{=}CH_2} \xrightarrow[-HX]{HgX_2/R'OH} \underset{\mathbf{310}\ (M)}{RCN(OR')C(HgX){=}CH_2} \qquad (44)[160]$$

X = AcO, CF_3CO_2, ClO_4, NO_3, F, Cl, $0.5(SO_4)$

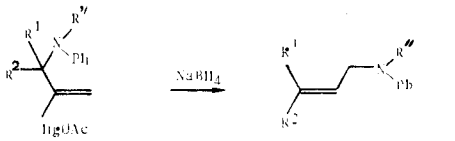
R = H, Me, Et, *i*-Pr, t-Bu, Ac, $PhCH_2$

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



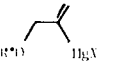
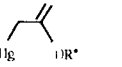
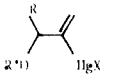
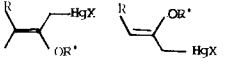
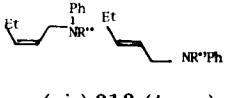
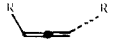
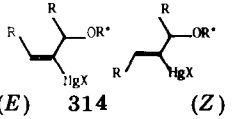
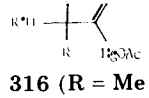
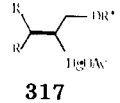
(45)[168]

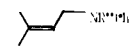
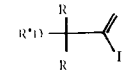
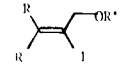
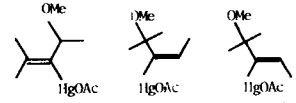
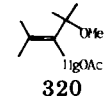
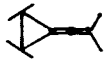
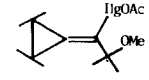
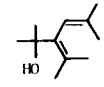
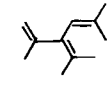
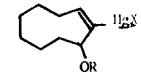
(*cis* + *trans*)-313 and 317

R¹ = Et, R² = H, R'' = H (entry 5)
R¹ = Et, R² = H, R'' = Me (entry 6)
R¹ = R² = Me R'' = H (entry 21)
R¹ = R² = Me R'' = Me (entry 22)

followed by reductive demercuration of the corre-

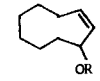
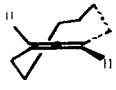
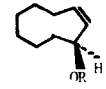
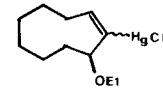
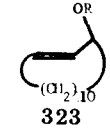
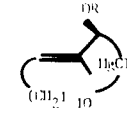
TABLE XII. Metalation of Allenic Derivatives

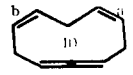
entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %	ref
	1					 308(M)  307 (aM)	
1		$Hg(OAc)_2$	$MeOH/H_2O$	RT	95		$(MeO)_2C(CH_2HgOAc)_2$[a]	160
2		$Hg(OAc)_2$,[b] $NaBH_4$	$PhNH_2$/ THF/H_2O		10	$PhNHCH_2CH{=}CH_2$		168
3		$HgMe_2$[c]			97	309 		170
	 59					 310(M)  (*E*) 311(aM) (*Z*)	
4	59d (R = Me)	$Hg(OAc)_2$	MeOH	RT	95	310, (R = R = Me) 67	$MeCH(HgOAc)C(OMe)_2$ CH_2HgOAc[a] 33	160
	59e (R = Et)	$Hg(OAc)_2$,[b] $NaBH_4$[b]	PhNHR''/ THF/H_2O			 312  (*cis*) 313 (*trans*)	
5			R'' = H		55	20	80	168
6			R'' = Me		30	*d*	15 25	168
	 12					 (*E*) 314 (*Z*)	
7	12a (R = Me)	$HgCl_2$[e]	EtOH	RT		100[f,h]		45
8		$Hg(OAc)_2$	MeOH	RT	93	25	75	160
9		$Hg(OAc)_2$	MeOH	RT	100[h]	17	83	6
10		$Hg(OAc)_2$	*i*-PrOH	RT	95[h,i]	17	83	6
11		$Hg(OAc)_2$	*t*-BuOH	RT	75[h,i]	14	86	6
12	(*R*)-12a α_D −15.9[g,z]	$Hg(OAc)_2$	MeOH	RT	*h*	17	*S* 83 (op 7.0)	77
13	(*R*)-12a α_D −14.5	$Hg(OAc)_2$	MeOH	RT	*h*	*R* 14 (ee 6)	*S* 86 (ee 9.2)	169
14	(*R*)-12a α_D -29.6 12b (R = Et)	$Hg(OAc)_2$	MeOH	−78	*h*	5 (*E*) 315	*S* 95 (ee 19.0) (*Z*)	169 169
15	(*R*)-12b α_D −22.7[z]	$Hg(OAc)_2$	MeOH	−78	*h*	4	*S* 96 (ee 21.6)	169
16	(*S*)-12b α_D +33.8	$Hg(OAc)_2$	MeOH	−78	*h*	6	*R* 94 (ee 31.1)	169
17	(*R*)-12b α_D −26.4	$EtHgOAc$, $BF_3{\cdot}OEt_2$		0	*j*	5	*S* 95 (ee 25)	169
	 49a (R = Me)					 316 (R = Me)  317	

						R'O	HO	AcO
18		$Hg(OAc)_2$	MeOH			100		
19		$Hg(OAc)_2$	*i*-PrOH			50	28	14
20		$Hg(OAc)_2$	*t*-BuOH			10	60	30
		$Hg(OAc)_2$,[b] $NaBH_4$	PhNHR''/ THF/H_2O					
21					50	343 100 (R'' = H)		
22					45	344 50 (R'' = Me)		
		$Hg(OAc)_2$, I_2				 350	 351	
						R'O	HO	R'O HO
23			H_2O		87	90		10
24			MeOH		76	95	1	4
25			EtOH		84	85	5	10
26			*i*-PrOH		72	75	10	15
			H		66	75		25
27	49b (R = Et)		*i*-PrOH		60	40	32	6 8
29	 73a	$Hg(OAc)_2$	MeOH	RT	90	 319 18 (*E*) 318 (*Z*) 72		
30	 36	$Hg(OAc)_2$	MeOH	RT	90	 320		
31	 38	$Hg(OAc)_2$	MeOH	RT	40	 195		
32	 20	$Hg(OAc)_2$, $NaBH_4$	AcOH	0	83	 196 (79[a,b])  197 (21)  321		
33		HgCl	EtOH		55	100		
34	(*R*)-20[z] α_D 18.8°	$Hg(OAc)_2$	MeOH		*h*	(*R*)-(*E*) 100 (ee 8.4)		

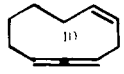
18								160
19								160
20								160
21								168
22								168
								181a
23								
24								
25								
26								
27								
29								160
30								160
31								57
32								201
33								45, 178, 179
34								169

TABLE XII (*Continued*)

entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %	ref
	20	HgO/BF_3[l]					
35		HgO/BF_3[l]	MeOH		69	(*cis*)-322	164
36		HgO/BF_3[l]	*i*-PrOH		81	(*cis*)-322	164
37		HgO/BF_3[l]	EtOH (reflux)		80 (71)	(*cis*)-322	45, 164
38		HgO/BF_3[l]	*t*-BuOH		63	(*cis*)-322	164
39		HgO/BF_3[l]	$PhCH_2OH$		85	(*cis*)-322	164
40		$HgSO_4$–H_2SO_4	MeOH		75 (56)	(*cis*)-322	45, 164
41		$HgSO_4$–H_2SO_4	H_2O:AcMe(H_2O,THF)		78 (30)	(*cis*)-322	
							
	(*S*)-20					(*S*)-*cis*-322	
42	(*S*)-20 α_D −145.3°	HgO/BF_3 HgO/BF_3	EtOH			α_D + 17.7°	164
43		HgO/BF_3	MeOH				164
44			H_2O: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°	$HgCl_2$	EtOH			α^{25}_D + 0°	165
54	(o.p. 6.5%)[169]	$Hg(OAc)_2$	AcOH			α^{25}_D + 1.1°	166
55	 334	$HgCl_2$	EtOH			 335	45
						 323	
56	17	$HgSO_4/H_2SO_4$	MeOH		65	15 (cis) 85 (trans) (R = Me)	164, 179
57	17	HgO/BF_3	EtOH		78	85 (trans) (R = Et)	164
58	(*R*)-17[z] α_D + 15.2°	$Hg(OAc)_2$, NaCl	MeOH		86	 (*S*)-(*Z*)-323	169

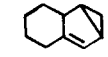


336

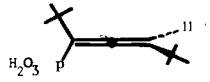
59		$Hg(OAc)_2$[m]	AcOH		47	50	5	45	173
60		$HgSO_4$	H_2O/AcMe		67	80	6	6	
61		$HgSO_4$[m]	AcOH	RT	52	43	3	54	
62		$HgSO_4$	CF_3CH_2CH		74		30	70	
		$HgCl_2$	AcOH		72				
63		$Hg(OAc)_2$	AcOH		55				
		$Hg(OCOCF_3)_2$	AcOH		35				173
		$HgSO_4$	AcOH		53				

340

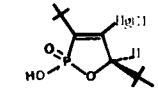
337 338 339[n]



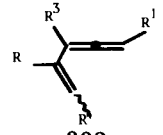
341

64		$Hg(OAc)_2$, NaCl	AcOH				

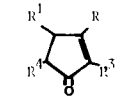
(*R*)-101
α^{26}_D −43.4°



(*R*)-324 (O.Y. = 86%)[o]
α^{26}_D + 14.3° 86

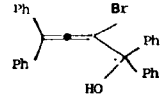
		$Hg(OAc)_2$, $HClO_4$	AcOH	RT, 1 h at 70°		172

332

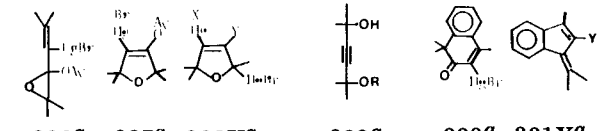


333

		R^1	R^3	R	R'		
65	a	H	Me	H	H	31	
66	b	Me	Me	H	H	20	
67	c	H	Am	H	H	59 (70)[p]	
68	d	Me	Am	H	H	42 (50)[p]	
69	e	H	Am	Me	H	55	
70	f	H	Me	$(CH_2)_6$		75	

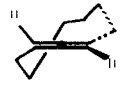
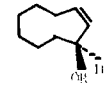
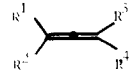
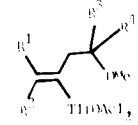
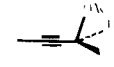
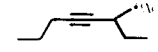
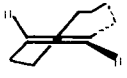
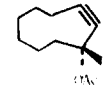
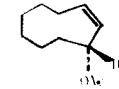


325 (Y = Br)



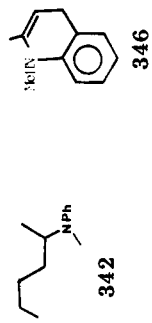
						326[q]	327[q]	328Y[q]	329[q]	330[q]	331Y[q]	
71		$Hg(OAc)_2$	AcOH	RT	92	100						171a
72		$Hg(OAc)_2$	AcOH	*u*	67		100					171a
73		$HgBr_2$	*t*-BuOH	65	19			100				171b
74		$HgCl_2$	*t*-BuOH	65	95			80 (Cl)			15 (Cl)	171b
75		$HgCl_2$	*t*-AmOH	65	84			100 (Cl)				171b
76	325 (Y = Cl)	$HgBr_2$	*t*-BuOH	65	65			100				171b
77		$HgCl_2$	*t*-BuOH	65	85			100				171b
78	325 (Y = Br)	$HgOAc_2$	H_2O	RT	71				100 (R = H)			171a
79		$HgOAc_2$	MeOH	RT	68			21	79 (R = Me)			171a
80		$HgOAc_2$	EtOH	RT	59			31	69 (R = Et)			171a
81		$HgOAc_2$	acetone	RT	35					100[r]		171a

TABLE XII (*Continued*)

entry	allenic derivatives	reagents	solvents	T, °C	yields, %	product composition, %		ref
	325 (Y = Br)					328 Y	331Y	
82		$HgBr_2$	acetone	RT	49		100 (Br)	171b
83		$HgCl_2$	acetone	RT	56		100 (Cl)	171b
84		$HgCl_2$	aprotic solvents[s]	variable	61–97	0–12 (Cl)	56–97 (Cl)	171b
85	325 (Y = Cl)	$HgCl_2$	acetone	RT	56		100	171b
86	325 (Y = Cl)	$HgBr_2$	acetone	RT	55		100 (Cl)	
								
	(*S*)-20					(*S*)-(*cis*)-322		177
87	α_D −15.6° (o.p. 7%)	$Tl(OAc)_3/NaBH_4/BF_3$	AcOH	RT	(84)[t] 61	α_D +0.9°		
88		$Tl(OAc)_3/NaBH_4/BF_3$	MeOH	RT	(76)[t] 73	+2.8°		
89		$Tl(OAc)_3/NaBH_4/BF_3$	EtOH	RT		+4.0°		
90	α_D −22.7° (o.p. 10.2%)	$Tl(NO_3)_3NaBH_4$	MeOH	RT		+2.2°		
91		$Tl(NO_3)_3NaBH_4$	EtOH	RT		+2.7°		
		$Tl(OAc)_3/BF_3$	MeOH					176
	345					346		
	R[1] R[2] R[3] R[4]							
92	a Me Me Me Me				100			
93	b Me H Me H				94			
94	c H H H Et				50			
		$Pb(OAc)_4$[u]	AcOH,THF	RT	41.4[v]			
95	(*S*)-12a					(*S*)-347[w]		
	α_D + 22.4° (o.p. 12.9%)[g,169]					α_D +6.6° (o.p. 7.4%)[w] (O.Y. = 57%)		175
96		$Pb(OAc)_4$	AcOH	RT				175
	12b					348 (>75%)		
		$Pb(OAc)_4$	AcOH					166
97	(*S*)-20					(*R*)-349 (major)	(*R*)-322[x]	
	α^{25}_D − 14.6° (o.p. 6.5%)[169]					α^{25}_D +7.6°	α^{25}_D −9.3° (o.p. ?)	

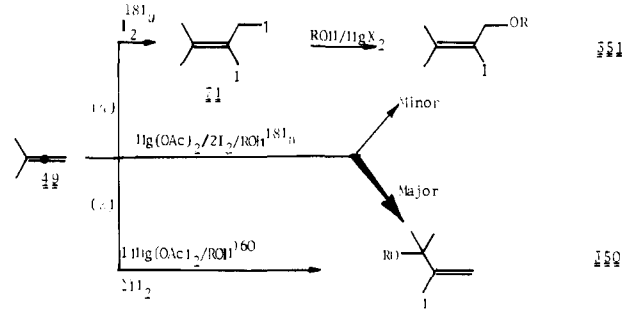
[a] These bisadducts are easily hydrolyzed during aqueous workup affording remarkably stable α,α'-dimercury ketones. [b] Solvomercuration is followed by reductive demercuration reaction using $NaBH_4$ under basic conditions. [c] This mercurinium ion has been observed in gas phase. [d] 60% of the saturated amine 342 is also obtained (see Scheme XXVI. [e] Methoxymercuration of the optically active 2,3-pentadiene (*R*)-(-)-12a by using $HgCl_2$ 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 Brewster[162] and found to be 9.1%. The specific rotation of the 2,3-pentadiene α_D 174° 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 BF_3OEt_2, 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] $BF_3{\cdot}OEt_2$ is present in a catalytic amount (0.1 molar equiv). [m] $HgSO_4$ 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 $HClO_4$. [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 protodemercurated. [s] The solvents used are Me_2CO, t-Bu_2CO, THF, OEt_2, CS_2, 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 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]

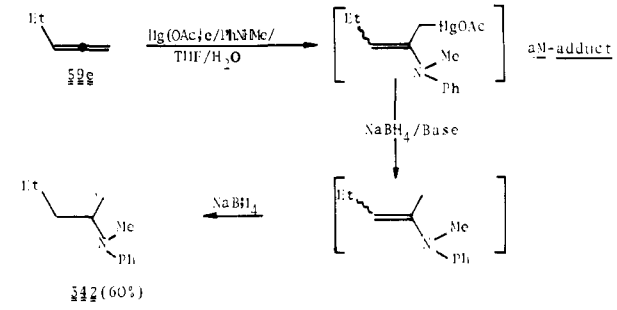


346 342

SCHEME XXV



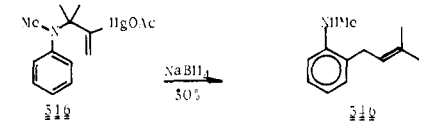
SCHEME XXVI



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).

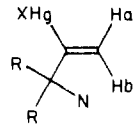


(46)[168]

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 ketones[203] (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, $^3J^1$Hb,^{199}Hg, Hz	cis, $^3J^1$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).

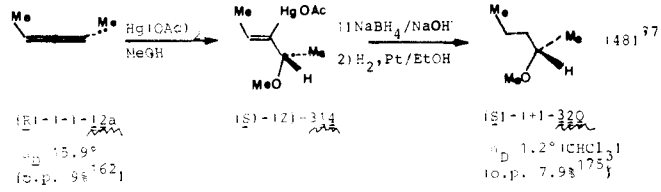
The overcrowded mercury-containing ion, obtained by methoxymercuration of tetramethylallene **36**, undergoes nucleophilic attack leading to the expected Markovnikov monoadduct **320** with excellent yield (entry 30). Methoxymercuration of cyclopropylideneallene **38** occurs on the isopropylidene double 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 a 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 (BF_3·OEt_2, H_2SO_4, HNO_3) or under basic conditions ($NaBH_4$/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.

$$\underset{\substack{\textbf{12a},\ R = Me\\ \textbf{12b},\ R = Et}}{RCH{=}C{=}CHR} \xrightarrow{Hg(OAc)_2/MeOH} RCH(OMe)CHgX{=}CHR \xrightarrow{NaBH_4} \underset{(Z)\text{-}\mathbf{314}\ (major)}{RCH(OMe)CHgX{=}CHR} \rightarrow \underset{\mathbf{345},\ >94\%\ trans}{RCH(OMe)CH{=}CHR} \quad (47)$$

(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]

Pirkle[169] has recently shown that methoxymercuration of the (*R*)- and (*S*)-3,4-pentadiene **12b** using $Hg(OAc)_2$ 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 ± 1° and 104 ± 1°, 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 acetyoxymercury adduct **314** by BF_4H in methanol affords a mixture of allylic ethers MeCH=CHCH(OMe)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).

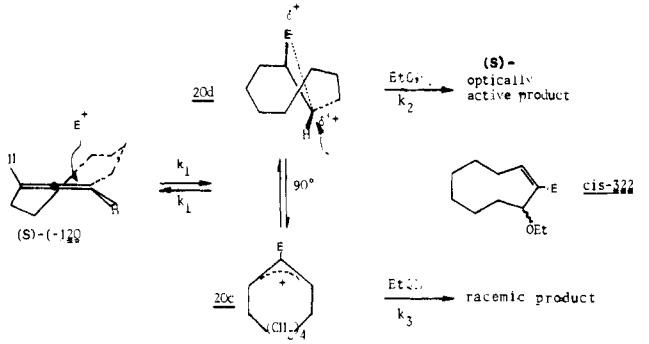


Figure 24. Reference 165.

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 = 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 $Hg(OAc)_2$, $Hg(OCOCF_3)_2$, $Hg(NO_3)_2$, and $HgSO_4$[195] were used.

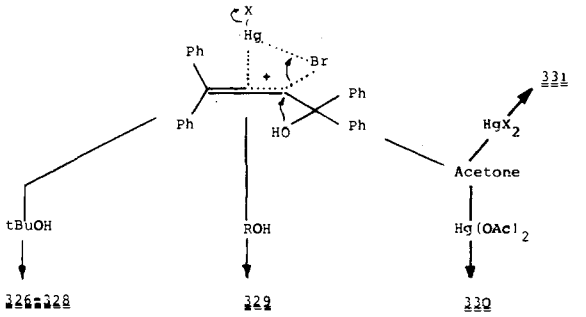
(b) Anti Stereospecificity. The syn–anti stereospecificity, of oxymercuration of cyclic allenes has been studied by Bach[164-166] and Pirkle.[169] At first, it was found that ethoxymercuration of optically active 1,2-cyclononadiene **20** followed by protodemercuration was stereospecific. This transfer 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 α_D +8.3° was converted by Williamson synthesis to the corresponding methyl ether with α_D +5.3° whereas the direct methoxymercuration of the same allene affords 3-methoxy-*cis*-cyclononene with α_D +7.3°.

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 = HgX).

Oxymercuration of the 1,2-cyclononadiene **20** was shown to proceed stereospecifically by an anti mechanism, 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 = 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).

SCHEME XXVII



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 = Cl, Br) (Scheme XXVII) has been extensively studied and shown to occur through a n–π mercurinium intermediate by neighboring group participation of both allenylic 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 predominent 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

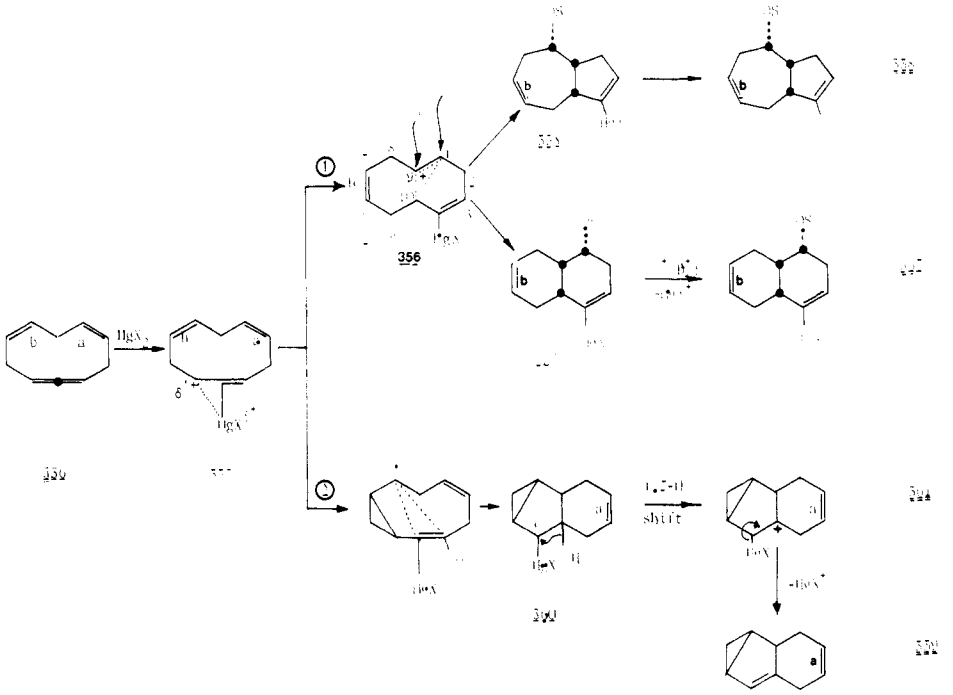


Figure 25. Reference 173.

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 mercuration 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. Solvothallation (E = TlX_2)

1. Oxythallation of Acyclic and Cyclic Allenes

Acetoxy- and methoxythallation of cyclic and acyclic allenes 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).

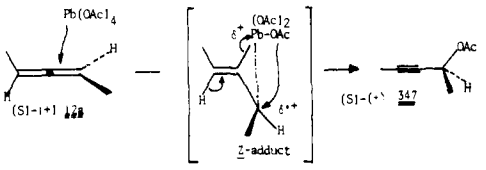
2. Anti Stereospecificity

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 than this partial racemization that occurs when $Hg(NO_3)_2$ is used is not due to nitric acid racemization of the allene. However, the nitratothallic adduct was shown to partially racemize the optically active substrate. Finally, this higher racemization with nitratothallic adduct than with acetatothallic 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 allenes 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



(49)[166]

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 acetoxyplumbation. 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).

Acetoxyplumbation of the (*S*)-1,2-cyclononadiene **20** gives the dextrorotatory 2-cyclononyn-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-cyclononen-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 acetoxythallation of cyclic and acyclic allenes proceed by an anti addition mechanism, whereas the mechanism of the acetoxyplumbation is syn.

IX. Conclusion

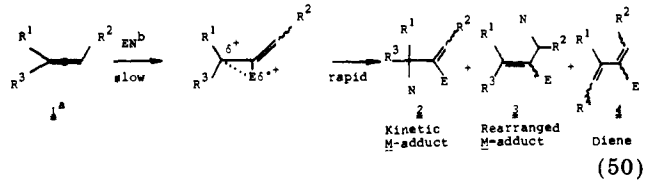
To conclude this review dealing with electrophilic addition to allenes, it could be worthwhile to show how information taken from the study of the chemo-, regio-, *E* vs. *Z* stereoselectivities, and especially the syn vs. anti stereospecificity will be very helpful for distinguishing between mechanisms 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 dissymetrical 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).



(50)

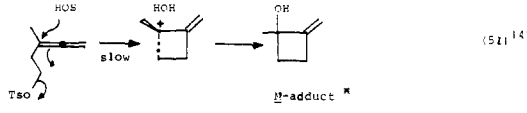
	Kinetic M-adduct	Rearranged M-adduct	Diene
In polar solvent (H_2O, $MeOH_2$)	Major	Minor	No
In non-polar solvent (CCl_4, CS_2)	Minor	Major	

[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 ; [b] electrophiles 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-diarylallenes (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

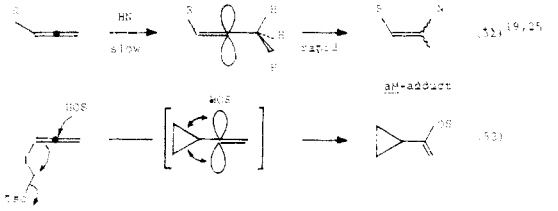


(51)[167]

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 aM-adduct is mainly *Z*),

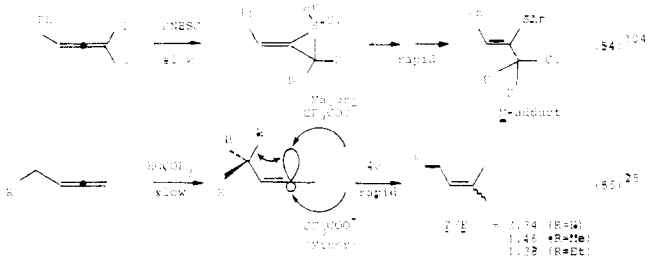
amino- and oxymercuration of 1,2-dienes (entries 4,6 of Table XI), and finally hydrolysis of the non-methyl-substituted β-allenic tosylate (eq 53 and entries 1,2 of Table IX, path of Figure 14) afford products with



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 dissymetrical 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 predominently on the nonsubstituted 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. Predominent Z Configuration for the Products

Under kinetic control, addition of acids to 1,2-dienes gives anti-Markovnikov oriented products with predominent *Z* configuration. This has been rationalized[25] 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 substitutent. (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-determining attack by nucleophile that should approach the intermediate from the least hindered side (Scheme X with E = X, SeAr, HgOAc, and $Tl(OAc)_2$).

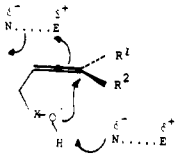
2. Predominent E Configuration for the Products

Sulfenylation and epoxidation of acyclic allenes that go through stepwise and concerted processes, respectively, afford products with predominent *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 Caserio[77] and Bach[166] procedures (respectively, $Hg(AOc)_2$, 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.

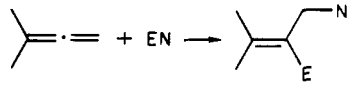
(c) Nonstereospecific Process. The nonstereospecific iodination of 1,3-diarylallenes is nonpolar solvents and the bromination of β-allenic alcohol are interpretable in terms of equal values for racemization and addition rate affording planar allyl cation in a slow step common to both reactions. The attack 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, $Me_2S^+SMe\ BF_4^-$, CCl_4 solvent) of 3-methyl-

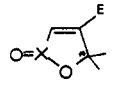


(56)

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.

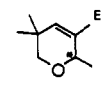


1

E = H, Br, HO, HgX; X = C, S, POH

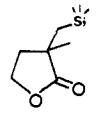
2

E = H, Br, S–, Se–, HgX



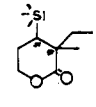
3

E = Br, S–



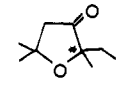
4

Table VIII, entries 65–73



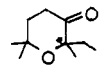
5

Table VIII, entry 75



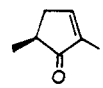
6

Table VIII, entry 40



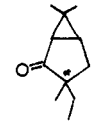
7

Table VIII, entry 63



8

Table VIII, entry 35



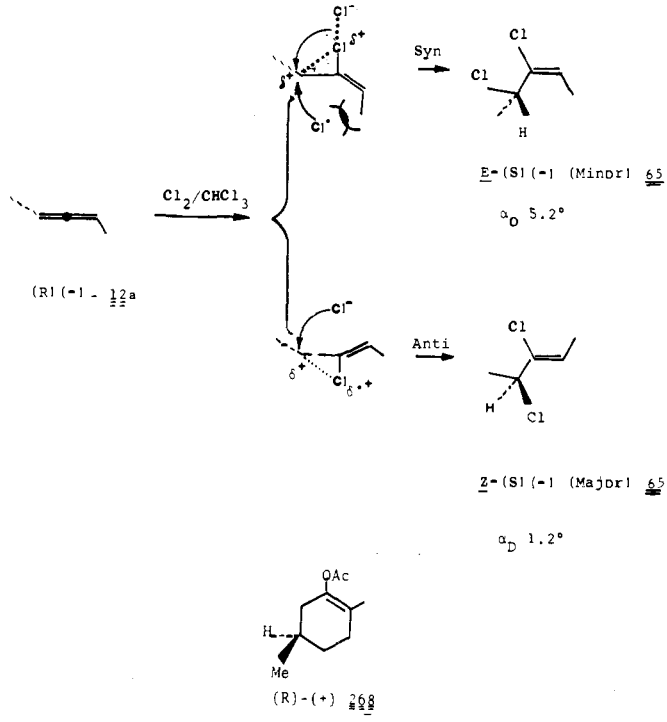
9

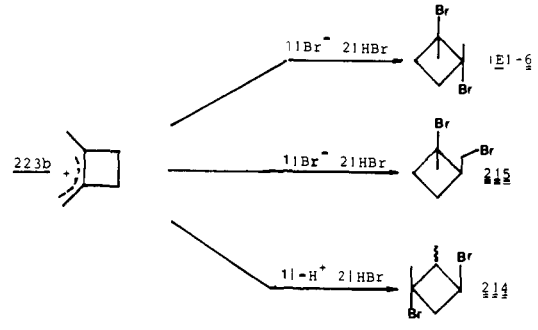
Table VIII, entry 58

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

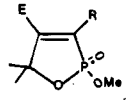
Note Added in Proof. Formation of cycloadducts from reaction of hydrogen bromide and propadiene **1** has been recently investigated.[204] This investigation showed that *trans*-1,2-dibromo- (*E*-**6**), 1,3-dibromo- (**214**), and bromomethylcyclobutanes (**215**) were obtained in low yields through allylic carbocation **223b** formed by addition of vinyl cation **1a** to allene **1** (cf. also entries 1–10 of Table I).

SCHEME XXVIII

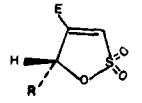




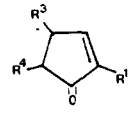
Electrophile-promoted cyclization of α-functional allenic derivatives, such as phosphonates,[205–208] chiral sulfones[209] and sulfinate,[209] silyl-substituted vinylallene,[210] and butadienylallene,[211] which afford 4-heterooxaphospholene **352**, optically active sultones **354**,



352, E = Cl, Br,[205] SR,[206,207] SAr,[209] SePh,[208] R = vinyl,[205] H[206–208]



(*R*)-(+)-**354**[209] E = Br, MeS, R = Me, *t*-Bu



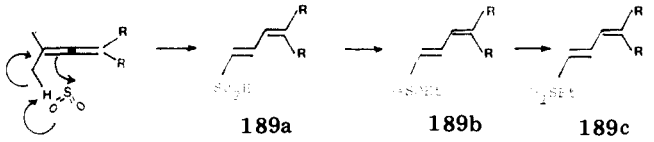
358 R¹ = Me, R³ = H, R⁴ = $SiMe_3$[210] R¹ = Et, R³ = vinyl, R⁴ = H[211]

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 (BF_3–HOAc complex in CH_2Cl_2 at −78 °C) affords conjugated dienes[212]

whereas a similar reaction with allenyltins (4% aqueous MeOH) gives rise to an acetylenic–allenic hydrocarbon mixture.[213] Electrophilic displacements by Cl_2, Br_2, and DNBSC 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 sulfinic acid **189a** from the ene reaction of methyl-substituted allenes and SO_2[215] is also noteworthy. When **189a** is converted to



189a **189b** **189c**

36, R = Me
49, R = H

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

Stereospecific oxymetalation (Hg, Tl, Pb) of 1,2-cyclononadiene **20** has been widely complemented[216] 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 $[\alpha]^{25}_D$ 47.9°, 76.2°, and 30.5°, respectively (see Table XII).

Finally a short review[217] and an extensive review[218] on the subject have appeared very recently.

Acknowledgments. I acknowledge the Centre National de la Recherche Scientifique for supporting this work in its French and English versions. I am deeply indebted to Professor Sir Derek Barton and Dr. P. Potier (CNRS, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France) for their interest and their encouragement. I have the pleasure of expressing my thanks to Dr. C. Georgoulis (ER 84 du CNRS associé à l'Université Pierre et Marie Curie, Paris), Dr. P. Potier, and Dr. D. Grierson (CNRS–ICSN) for going through the entire manuscript of the first English version and for providing helpful comments. I am particularly grateful to the referee for many exceedingly useful suggestions and essential help. It is a pleasure to acknowledge the linguistic assistance of K. Vijayakumaran, S. Weeds, and K. Gray. I wish to thank Y. Quiot, who typed most of the manuscript, and H. Marion for her assistance in various ways. Finally, my wife Danielle requires a special acknowledgment for her patience and for bringing this work to completion. I owe you very much Nathalie, Valérie, and Hélène, my daughters, for your patience and love.

X. References

(1) Petrov, A. A.; Fedorova, A. V. *Russ. Chem. Rev. (Engl. Transl.)* **1964**, *33*, 1.
(2) Fisher, H. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York 1964; p 1050.
(3) Griesbaum, K. Angew. Chem., Int. Ed. Engl. **1966**, 5,
(4) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.
(5) Maurov, M. Y.; Kucherov, V. F. *Russ. Chem. Rev.* **1967**, *36*,
(6) Caserio, M. C. In "Selective Organic Transformation"; Thyagarayan, Ed.; Wiley: New York, 1970; Vol. 1, p 239.
(7) Murray, M. "Houben Weyl Methoden der Organischen Chemie"; George Thieme Verlag: Stuttgart, 1977; Vol. 5, p 967.
(8) Schmid, G. H.; Garratt, D. G. "Chemistry of Double Bonded Functional Groups"; Patai, S., Ed; Interscience: New York 1977; Part 2 and Suppl. A, p 725.
(9) Richey, H. G.; Richey, J. M. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Interscience: New York, 1970; p 899.
(10) Modena, G.; Tonellato, U. *Adv. Phys. Org. Chem.* **1970**, *9*, 185.
(11) Stang, P. V. *Progr. Phys. Org. Chem.* **1973**, *10*, 205.
(12) Subramanian, L. R.; Hanack, M. *J. Chem. Educ.* **1975**, *32*, 80.
(13) Hanack, M. *Acc. Chem. Res.* **1976**, *9*, 364.
(14) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265.
(15) Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 333.
(16) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.
(17) Krapcho, A. P. *Synthesis* **1978**, 77.
(18) Austin, P. R. U. S. Patent 2585529; *Chem. Abstr.* **1952**, *46*, 3799c.
(19) Jacobs, T. L.; Johnson, R. N. *J. Am. Chem. Soc.* **1960**, *82*, 6397.
(20) Charleston, B. S.; Dalton, C. K., Washburne, S. S.; Dalton, D. R.; Schraeder, S. R. *Tetrahedron Lett.* **1969**, 5147.
(21) Griesbaum, K.; Naegele, W.; Wanless, G. G. *J. Am. Chem. Soc.* **1965**, *87*, 3151.
(22) Amar, F.; Dalton, D. R.; Eisman, G.; Haugh, M. J. *Tetrahedron Lett.* **1974**, 3037.
(23) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700; **1980**, *102*, 4830.
(24) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531.
(25) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *95*, 1110.
(26) (a) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 228. (b) Kelsey, D. R.; Bergman, R. G. *Ibid.* **1971**, *93*, 1941, 1953. (c) Sherrod, S. A.; Bergman, R. G. *Ibid.* **1971**, *93*, 1925.
(27) Siehl, H. U.; Carnahan, J. C., Jr.; Eckes, L.; Hanack, M. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 675.
(28) Masamune, S.; Sakai, M.; Morio, K. *Can. J. Chem.* **1975**, *53*, 784.
(29) Bouis, M.; *Ann. Chem.* **1928**, *9*(10), 402.
(30) Hennion, G. F.; Sheenan, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 1964.
(31) (a) Gustavson, G.; Demjanoff, N. *J. Prakt. Chem.* 1888, *38*(2), 201. (b) Cramer, P.; Tidwell, T. T. *J. Org. Chem.* **1981**, *46*, 2683 and references cited therein.
(32) Carothers, W. H.; Berchet, G. J. *J. Am. Chem. Soc.* **1933**, *55*, 1628.
(33) Bertrand, M.; Legras, J. *C. R. Hebd. Seances Acad. Sci.* **1965**, *261*, 762.
(34) Fedorova, A. V.; Petrov, A. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1962**, *32*, 1740.
(35) Muhlstadt, M.; Graefe, J. *Chem. Ber.* **1967**, *100*, 223.
(36) Macomber, R. S. *J. Org. Chem.* **1977**, *42*, 4297.
(37) (a) Baird, M. S.; Reese, C. B. *Synthesis* **1976**, *6*, 385. (b) Baird, M. S. Ph.D. Thesis, Cambridge University, 1968, p 205. (c) Baird, M. S. Reese, C. B. *J. Chem. Soc. C* **1969**, 1808. (d) Baird, M. S.; Reese, C. B. *J. Chem. Soc. C* **1969**, 1803. (e) Nagendrappa, G.; Mohanakrishnan, P. G.; Devaprabhakara, D. *Chem. Ind. (London)* **1971**, 850. (f) Moorthy, S. N.; Singh, A.; Devaprabhakara, D. *J. Org. Chem.* **1975**, *40*, 3452.
(38) Pittman, C. U., Jr. *J. Chem. Soc., Chem. Commun.* **1969**, 122.
(39) (a) Van Boom, J. H.; Montijin, P. D.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 31. (b) Hoffmann, R. W.; Schafer, W.; Bressel, U. *Chem. Ber.* **1972**, *105*, 2111. (c) Mantione, R.; Alves, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *268*, 365. (d) De Jong, I.; Dreuth, W. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 420. (e) Scheffel, D. J.; Cole, A. R.; Jung, D. M.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 267.
(40) Okuyama, Tr.; Izawa, K.; Fueno, T. *Tetrahedron Lett.* **1970**, 3295.
(41) Okuyama, T.; Izawa, K.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6749.
(42) Izawa, K.; Okuyama, T.; Sakagami, T.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6752.
(43) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
(44) Bianchini, J.-P.; Guillemonat, A. *Bull. Soc. Chim. Fr.* **1968**, 2120.
(45) Sharma, R. K.; Shoulder, B. A.; Gardner, P. D. *J. Org. Chem.* **1967**, *32*, 241.
(46) Fedorova, A. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1963**, *33*, 3508.
(47) Bianchini, J.-P.; Gaydou, E. M. *C. R. Hebd. Seances Acad. Sci.* **1975**, *280*, 205.
(48) Aksnes, G.; Frøyen, P. *Acta Chem. Scand.* **1968**, *22*, 2347.
(49) Kresze, G.; Runge, W.; Ruch, E. *Liebigs Ann. Chem.* **1972**, *756*, 112.
(50) Musierowicz, S.; Wroblewski, A.; Krawczyk, H. *Tetrahedron Lett.* **1975**, 437.

(51) Kresze, G.; Kloimstein, L.; Runge, W. *Liebigs Ann. Chem.* **1976**, 979.
(52) Musierowicz, S.; Wroblewski, A. E. *Tetrahedron* **1978**, *34*, 461.
(53) Baverman, S.; Reisman, D. *J. Am. Chem. Soc.* **1977**, *99*, 605.
(54) Macomber, R. S.; Kennedy, E. R. *J. Org. Chem.* **1976**, *41*, 3191.
(55) Crandall, J. K.; Paulson, D. R.; Bunnell, C. A. *Tetrahedron Lett.* **1968**, 5063.
(56) Leandri, C.; Santelli M.; Rouvier, C. *Bull. Soc. Chim. Fr.* **1970**, 1515.
(57) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 440.
(58) Bergmann, R. G., oral communication to Modena in ref 10.
(59) Kohler, E. P.; Whitcher, W. J. *J. Am. Chem. Soc.* **1940**, *62*, 1489.
(60) Ghenciulescu; Hanack, M. *Tetrahedron Lett.* **1970**, 2827.
(61) Basseler, T.; Hanack, M. *Tetrahedron Lett.* **1971**, 2171.
(62) Hammen, G.; Basseler, T.; Hanack, M. *Chem. Ber.* **1974**, *107*, 1676.
(63) Grimaldi, J.; Cozzone, A.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1967**, 2723.
(64) Banks, R. E.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc.* **1965**, 5602, cited by Taylor, in ref 4.
(65) Peer, H. G. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 113.
(66) Mueller, W. H.; Butler, P. E.; Griesbaum, K. *J. Org. Chem.* **1967**, *32*, 2651.
(67) Van Leeuwen, J. *Chem. Abstr.* **1963**, *58*, 6693.
(68) Poutsma, M. L. *J. Org. Chem.* **1968**, *33*, 4080.
(69) Lasne, M. C.; Thuiller, A. *Bull. Soc. Chim. Fr.* **1974**, 249.
(70) Dolbier, W. R., Jr.; Al-Sader, B. H. *Tetrahedron Lett.* **1975**, 2159.
(71) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper & Row: Scranton, PA, 1976; p 110.
(72) Bollinger, J. M.; Brinich, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4025.
(73) Tendil, J.; Verny, M.; Vessiere, R.; *Bull. Soc. Chim. Fr.* **1972**, 4027.
(74) Kurtz, P.; Gold, H.; Jisselnkotter, H. *Annalen* **1959**, *624*, 1.
(75) Lespiau, M.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1929**, *45*, 632.
(76) (a) Prévost, Ch. *C. R. Hebd. Seances Acad. Sci.* **1933**, *196*, 1129. (b) Smadja, W. *C. R. Hebd. Seances Acad. Sci.* **1969**, *268*, 271.
(77) Waters, W. L.; Linn, W. S.; Caserio, M. C. *J. Am. Chem. Soc.* **1968**, *94*, 6741.
(78) Findlay, M. C.; Waters, W. L.; Caserio, M. C. *J. Org. Chem.* **1971**, *36*, 275.
(79) Coulomb, F.; Roumestant, M. L.; Gore, J. *Bull. Soc. Chim. Fr.* **1973**, 3352.
(80) Byrd, L. R.; Caserio, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 5758.
(81) Bianchini, J.-P.; Cocordano, M. *Tetrahedron* **1970**, *26*, 3401.
(82) Wedegaertner, D. K.; Millan, M. J. *J. Org. Chem.* **1968**, *33*, 3943.
(83) Baverman, S.; Reisman, D. *Tetrahedron Lett.* **1977**, 1753.
(84) Jacobs, T. L.; Macomber, R.; Zunker, D. *J. Am. Chem. Soc.* **1967**, *89*, 7001.
(85) Shingu, K.; Hagishita, S.; Nakagawa, M. *Tetrahedron Lett.* **1967**, 4371.
(86) Macomber, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 3072.
(87) Okuyama, T.; Ohashi, K.; Izawa, K.; Fueno, T. *J. Org. Chem.* **1974**, *39*, 2255.
(88) Baird, M. S.; Reese, C. B.; Shaw, A. *Tetrahedron*, **1971**, *27*, 231.
(89) Reese, C. B.; Shaw, A. *Tetrahedron Lett.* **1971**, 4641.
(90) Bach, R. D.; Mazur, U.; Brummel, R. N.; Lin, L. H. *J. Am. Chem. Soc.* **1971**, *93*, 7180. See also ref 14.
(91) Bordwell, F. G.; Brannen, W. T. *J. Am. Chem. Soc.* **1964**, *86*, 4645.
(92) Rossum, van A. J. G.; Nivard, R. J. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1322.
(93) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469, 1477, 1483.
(94) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.*, **1972**, *37*, 1770.
(95) Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237.
(96) Rasteikiene, L.; Greiciute, D.; Lin'kova, M. G.; Knunyants, I. L. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 548.
(97) Capozzi, G.; Lucchi, de O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.
(98) Schmid, G. H.; Csizmadia, V. M. *Can. J. Chem.* **1972**, *50*, 3565, 2457.
(99) Mueller, W. H.; Butler, P. E. *J. Org. Chem.* **1968**, *33*, 1533.
(100) Jacobs, T. L.; Macomber, R. *J. Org. Chem.* **1968**, *33*, 2988.
(101) Schmid, G. H.; Garratt, D. G.; Yeroushalmi, S. *J. Org. Chem.* **1978**, *43*, 3764.
(102) (a) Khusainova, N. G.; Berdnikov, E. A.; Pudovik, A. N. *Chem. Abstr.* **1978**, *89*, 43608*j*. (b) Angelov, C. M.; Vachkov, K. V. *Tetrahedron Lett.* **1981**, *22*, 2520.
(103) Jacobs, T. L.; Kammerer, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 6213.
(104) Izawa, K.; Okuyama, T.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 4090.
(105) Okuyama, T.; Izawa, K.; Fueno, T. *J. Org. Chem.* **1974**, *39*, 351.
(106) Tendil, J.; Verny, M.; Vessiere, R. *C. R. Hebd. Seances, Ser. C Acad. Sci.* **1972**, *275*, 1301.
(107) Moore, W. R.; Bertelson, R. C. *J. Org. Chem.* **1962**, *27*, 4182.
(108) Ralston, D.; Laserna, E.; Caserio, M. C.; cited by Caserio in ref 6.
(109) Waters, W. L.; Findlay, M.; Caserio, M. C.; cited by Caserio in ref 6.
(110) Schmid, G. H.; Dean, C. L.; Garratt, D. G. *Can. J. Chem.* **1976**, *54*, 1253.
(111) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw Hill Kogakusha Ltd: Tokyo, 1977; (a) p 123, (b) p 157, (c) 750.
(112) Bartlett, P. D. *Rec. Chem. Progr.* **1950**, *11*, 47; **1957**, *18*, 11.
(113) Berti, G. *Top. Stereochem.* **1973**, *7*, 93.
(114) Wasserman, H. H.; Clark, G. M.; Turley, P. C. *Fortschr. Chem. Forsch.* **1974**, *47*, 73.
(115) Camp, R. L.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 7349.
(116) Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7347.
(117) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723.
(118) Crandall, J. K.; Machleder, W. H.; Thomas, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 7346.
(119) Crandall, J. K.; Machleder, W. H. *J. Heterocyc. Chem.* **1969**, *6*, 777.
(120) Crandall, J. K.; Machleder, W. H.; Sojka, S. A. *J. Org. Chem.* **1973**, *38*, 1149.
(121) Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7292.
(122) Crandall, J. K.; Machleder, W. H. *Tetrahedron Lett.* **1966**, 6037.
(123) Crandall, J. K.; Conover, W. W. *J. Chem. Soc., Chem. Commun.* **1973**, 340.
(124) Reeves, W. P.; Stroebel, G. G. *Tetrahedron Lett.* **1971**, 2945.
(125) Boeseken, J. *Recl. Trav. Chim. Pays-Bas*, **1935**, *54*, 657.
(126) Greibrokk, T.; Skattebøl, L. *Acta Chem. Scand.* **1973**, *27*, 1421.
(127) Payne, G. B. *Tetrahedron* **1962**, *18*, 763.
(128) (a) Von Lehman, T.; Macomber, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 1531 and references quoted therein. (b) Jacobs, T. L.; Macomber, R. S. *Ibid.* **1969**, *91*, 4824. (c) Macomber, R. S. *Ibid.* **1970**, *92*, 7101.
(129) Bertrand, M.; Grimaldi, J. *C. R. Hebd. Seances Acad. Sci.* **1967**, *265*, 19.
(130) Grimaldi, J.; Bertrand, M. *Tetrahedron Lett.* **1969**, 3269.
(131) Grimaldi, J.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1971**, 957.
(132) Roumestant, M. L.; Malacria, M.; Gore, J.; Grimaldi, J.; Bertrand, M. *Synthesis* **1976**, 755.
(133) Malacria, M.; Roumestant, M. L. *Tetrahedron* **1977**, *33*, 2813.
(134) (a) Bertrand, M.; Dulcere, J. P.; Gil, G. *Tetrahedron Lett.* **1977**, 4403. (b) Bertrand, M.; Dulcere, J. P.; Gil, G. *Ibid.* **1980**, *21*, 4271.
(135) Bertrand, M.; Dulcere, J. P.; Gil, G. *Tetrahedron Lett.* **1977**, 3807.
(136) Turro, N. J.; Hammond, W. B. *Tetrahedron* **1968**, *24*, 6077.
(137) Turro, N. J.; Edelson, S. S.; Williams, J. R.; Darline, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2283.
(138) Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.
(139) Place, P.; Verniere, C.; Gorê, J. *Tetrahedron* **1981**, 1359.
(140) Doutheau, A.; Gore, J.; Malacria, M. *Tetrahedron* **1977**, *33*, 2393.
(141) Macomber, R. S. *J. Org. Chem.* **1978**, *43*, 1832.
(142) Bertrand, M.; Dulcere, J. P.; Gil, G.; Grimaldi, J.; Sylvestre-Panthet, P. *Tetrahedron Lett.* **1976**, 1507.
(143) Bertrand, M.; Dulcere, J. P.; Gil, G.; Grimaldi, J.; Sylvestre-Panthet, P. *Tetrahedron Lett.* **1976**, 3305.
(144) Grimaldi, J.; Malacria, M.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1975**, 1725.
(145) Grimaldi, J.; Malacria, M.; Bertrand, M. *Bull. Soc. Chim. Fr.*, **1975**, 1731.
(146) Grimaldi, J.; Malacria, M.; Bertrand, M. *Tetrahedron Lett.* **1974**, 275.
(147) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 227.
(148) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 235.
(149) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 243.
(150) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 251.
(151) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 257.
(152) Ragonnet, B.; Santelli, M.; Bertrand, M. *Helv. Chim. Acta* **1974**, *57*, 557.
(153) Harding, K. E.; Cooper, J. L.; Puckett, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 993.
(154) Sekera, M. H.; Weisman, B. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1973**, 679.
(155) Kuivila, H. G.; Cochran, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 7152.
(156) Bourgeois, P. *C. R. Hebd. Seances Acad. Sci.* **1974**, *278*, 969.

(157) Fong, C. W.; Kiching, W. *J. Organomet. Chem.* **1970**, *22*, 107.
(158) (a) Bourgeois, P.; Calas, R.; Merault, G. *J. Organomet. Chem.* **1977**, *141*, 23. (b) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (c) Jellal, A.; Santelli, M.; *Tetrahedron Lett.* **1980**, 4487.
(159) Bourgeois, P.; Herault, G.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1973**, *59*, 145.
(160) Waters, W. L.; Kiefer, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 6261.
(161) For a recent review dealing with the chemistry of allene oxides see Chan, T. H.; Ong, B. S.; *Tetrahedron* **1980**, *36*, 2269.
(162) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 133.
(163) Linn, W. S.; Waters, W. L.; Caserio, M. C. *J. Am. Chem. Soc.* **1970**, *92*, 4018.
(164) Bach, R. D. *Tetrahedron Lett.* **1968**, 5841.
(165) Bach, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 1771, 6741.
(166) Bach, R. D.; Mazur, U.; Brummel, R. N.; Lin, L. H. *J. Am. Chem. Soc.* **1971**, *93*, 7120.
(167) Bach, R. D.; Richter, R. F.; cited by Bach, R. D. et al. in ref 166.
(168) Hodjat-Kachani, H.; Perie, J. J.; Lattes, A. *Chem. Lett.* **1967**, 405. See Hodjat-Kachani, H. Thesis, Toulouse, 1976.
(169) Pirkle, W. H.; Boeder, C. W. *J. Org. Chem.* **1977**, *42*, 3697.
(170) Bach, R. D.; Patane, J.; Kevan, L. *J. Org. Chem.* **1975**, *40*, 257.
(171) (a) Toda, F.; Akagi, K. *Tetrahedron* **1969**, *25*, 3795. (b) Toda, F.; Ooi, N.; Akagi, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1050.
(172) Baudouy, R.; Delbecq, F.; Gore, J. *Tetrahedron*, **1980**, *36*, 189.
(173) Thies, R. W.; Hong, P. K.; Buswell, R.; Boop, J. L. *J. Org. Chem.* **1975**, *40*, 585.
(174) Laforge, F. B.; Acree, F., Jr. *J. Org. Chem.*, **1941**, *6*, 208.
(175) Bach, D.; Brummel, R. N.; Holubka, J. W. *J. Org. Chem.* **1975**, *40*, 2559.
(176) Sharma, R. K.; Martinez, E. D. *J. Chem. Soc., Chem. Commun.* **1972**, 1129.
(177) Bach, R. D.; Holubka, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 7814.
(178) Joshi, G. C.; Devaprabhakara, D. *J. Organomet. Chem.* **1968**, *15*, 497.
(179) Vaidyanathaswamy, R.; Devaprabhakara, D.; Rao, V. V. *Tetrahedron Lett.* **1971**, 915.
(180) De la Mare, P. B. D. "Electrophilic Halogenation"; Cambridge University Press: Cambridge, England, 1976.
(181) (a) Georgoulis, C.; Smadja, W.; Valery, J.-M. *Synthesis* **1981**, 572. (b) Georgoulis, C.; Smadja, W.; Valery, J.-M. unpublished results.
(182) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. *Tetrahedron Lett.* **1980**, *21*, 129.
(183) Garratt, D. G.; Beaulieu, P. L. *Can. J. Chem.* **1979**, *57*, 119.
(184) Garratt, D. G.; Beaulieu, P. L. *Can. J. Chem.* **1980**, *58*, 1275.
(185) Garratt, D. G.; Beaulieu, P. L.; Morisset, V. M.; Ujjainwalla, M. *Can. J. Chem.* **1980**, *58*, 2745.
(186) Garratt, D. G.; Beaulieu, P. L.; Ryan, M. D. *Tetrahedron* **1980**, *36*, 1507.
(187) Garratt, D. G.; Beaulieu, P. L. *Can. J. Chem.* **1980**, *58*, 2737.
(188) Schmid, G. H.; Garratt, D. G.; Beaulieu, P. L. *J. Chem. Soc.* **1980**, *15(3)*, 128; *Chem. Abstr.* **1981**, *94*, 14750*x*.
(189) Schmid, G. H.; Garratt, D. G. *Tetrahedron* **1978**, *34*, 2869.
(190) (a) For a review of the chemistry of vinylsilanes see: Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, England, 1979; Vol. 3, pp 608–662. (b) For a review of electrophilic substitution of organosilicon compounds see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.
(191) Moorthy, S. N.; Devaprabhakara, D. *Chem. Ind. (London)* **1975**, *5*, 217; *Chem. Abstr.* **1975**, *82*, 155486.
(192) Bertrand, M.; Dulcere, J. P.; Gil, G. *Tetrahedron Lett.* **1980**, *21*, 1945.
(193) "Glossary of Terms Used in Physical Organic Chemistry", *Pure Appl. Chem.* **1979**, *51*, 1787, 1792, 1793.
(194) Alwork, W. L. In "Stereochemistry and Its Application in Biochemistry"; Wiley: New York, 1972; pp 5, 178.
(195) Verbrugge, P. A.; Terlouw, W. Ger. Offen 2523764; Chem. Abstr. **1976**, *84*, 89597.
(196) Freeman, F. *Chem. Rev.* **1975**, *75*, 441.
(197) Larock, R. C.; Fellows, C. A. *J. Org. Chem.* **1978**, *43*, 131 and references cited therein.
(198) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chim. Fr.* **1972**, 720.
(199) Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* 1978, *100*, 7645.
(200) Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1977**, *42*, 264.
(201) Pasto, D. J.; Miles, M. F. *J. Org. Chem.* **1976**, *41*, 425.
(202) For recent review concerning electrophilic addition to olefins and acetylenes see: Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.
(203) Rutledge, T. F. "Acetylenes and Allenes. Addition, Cyclization and Polymerization Reactions"; Reinhold: New York, 1969; p 63.
(204) Griesbaum, K.; Mach, H.; Hittich, R., *Chem. Ber.* **1982**, *115*, 1911.
(205) Angelov, Kh.; Stoyanov, N.; Ionin, B. I. *Zh. Obshch. Khim.* **1982**, *52*, 178; *Chem. Abstr.* **1982**, *96*, 162848.
(206) Khusainova, N. G.; Naumova, L. V.; Berdnikov, E. A.; Pudovik, A. N. *Zh. Obshch. Khim.* **1982**, *52*, 1040; *Chem. Abstr.*, **1982**, *97*, 110109c.
(207) Angelov, Kh.; Vachkov, K.; Kirilov, M.; Lebedev, V. B. *Zh. Obshch. Khim.* **1982**, *52*, 538; *Chem. Abstr.* **1982**, *97*, 6420n.
(208) Macomber, R. S., Krudy, G. A.; Seff, K.; Rendon-Diazmiron, L. E. *J. Org. Chem.* **1983**, *48*, 1425.
(209) Baverman, S.; Duar, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1061.
(210) Dulcere, J.-P., Grimaldi, J.; Santelli, M., *Tetrahedron Lett.* **1981**, *22*, 3179.
(211) Balme, G.; Malacria, M.; Goré J. *J. Chem. Res.* **1981**, *8*, 244.
(212) Psaume, B.; Montury, M.; Goré, J. *Synth. Commun.* **1982**, *12*, 409.
(213) Cochran, J. C.; Kuivila, H. G. *Organometallics* **1982**, *1*, 97.
(214) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925.
(215) Capozzi, G.; Lucchini, V.; Marcuzzi, F.; Melloni, G. *Tetrahedron Lett.* **1980**, 3289.
(216) Bach, R. D.; Holubka, J. W.; Willis, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3980.
(217) De la Mare, P. B. D.; Bolton, R. "Electrophilic Additions to Unsaturated Systems"; Elsevier: Amsterdam, 1982; pp 317–325.
(218) Jacobs, T. L. In "The Chemistry of the Allenes", Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, Chapter 4, pp 417–510 with 272 references up to 1980.