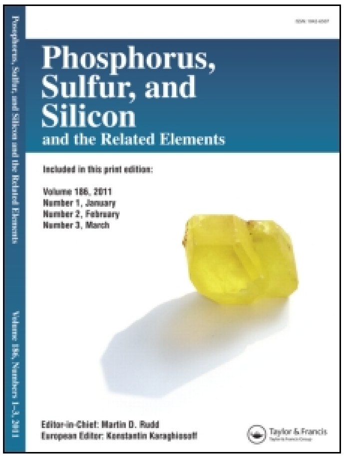


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PATTERNS OF THERMAL REARRANGEMENTS INVOLVING 3RD ROW ELEMENTS

Harold Kwart[a]
[a] Department of Chemistry, The University of Delaware, Newark, DE, U.S.A.

To cite this Article Kwart, Harold(1983) 'PATTERNS OF THERMAL REARRANGEMENTS INVOLVING 3RD ROW ELEMENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 15: 3, 293 — 310

To link to this Article: DOI: 10.1080/03086648308073308

URL: http://dx.doi.org/10.1080/03086648308073308

Phosphorus and Sulfur, 1983, Vol. 15, pp. 293–310
0308-664X/83/1503-0293/$18.50/0

PATTERNS OF THERMAL REARRANGEMENTS INVOLVING 3RD ROW ELEMENTS

HAROLD KWART[†]

The University of Delaware, Department of Chemistry, Newark, DE 19711, U.S.A.

(*Received October 29, 1982; in final form January 12, 1983*)

The thio-Claisen rearrangement of allyl aryl sulfides was found to be catalyzed by nucleophiles exerting only a small fraction of their nucleophilic abilities. A mechanism of nucleophilic triggering of concerted sigmatropic rearrangement was proposed and successfully tested against the rival proposal of cyclization-induced rearrangement on the basis of substituent-rate and secondary D-isotope effects. On the basis of the evidence presented the thioallylic rearrangement of allyl aryl sulfides under light-free, anaerobic conditions was shown to be a 2-step cyclic process in which a zwitterionic thiacyclobutane intermediate intervenes, involving octet expansion of the central sulfur. This is transformed to its rearranged isomer via permutational isomerism. By contrast, the corresponding silaallylic rearrangement, however, follows a concerted pericyclic pathway in which a $3p$ orbital of silicon bridges the allylic framework with complete inversion of configuration and unattended by any racemization. The rearrangement of β-silylketones to siloxyalkenes, however, shows an entirely different pattern—one quite similar to the thioallylic arrangement—in which silicon experiences octet expansion through formation of an intramolecular, apical Si—O bond in the structure of a trigonal bipyramid intermediate. The occurrence of permutational isomerism in this TBP intermediate is confirmed by the observation of retention and racemization of the configuration of an initially chiral silicon reactant.

INTRODUCTION

The subject of discussion here could be titled "changes in reaction pathway produced when sulfur replaces another element in typical thermal rearrangement reaction substrates." Three such rearrangement processes will be treated; in each instance comparisons with respect to mechanistic features will be undertaken in cases where the sulfur replaces oxygen, silicon or carbon in model substrates.

THE THIO-CLAISEN REARRANGEMENT

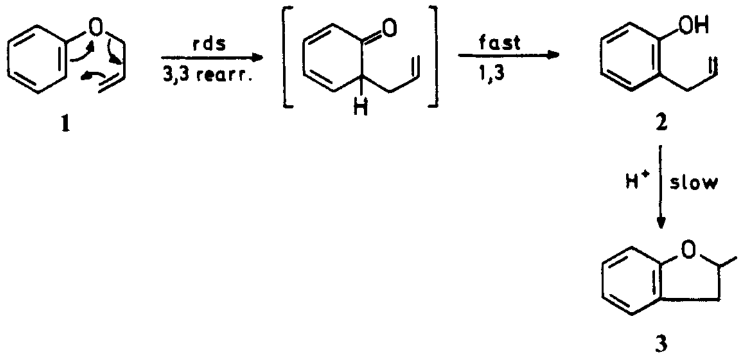
The formally analogous oxy-Claisen rearrangement of allyl arylethers (**1**) is recognized to be a 3,3 sigmatropic process[1-5] which takes place on heating (preferably in a non-hydroxylic solvent) with immediate formation of allylphenols (**2**) as represented in Eq. (1), and formation of benzhydrofuranes (**3**) on further heating.

When allyl aryl thioethers (**4**) are heated under the usual conditions of the oxy-Claisen only dark, intractable substances result from initial propenylization and subsequent polymerization of this vinyl thioether product (**5**) as shown in Eq. (2).

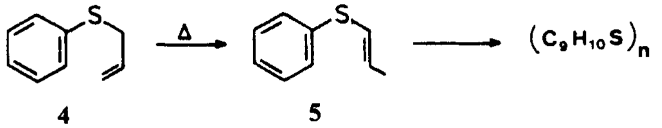
In 1962 it was discovered[6] that if the inert solvent medium contained an equivalent amount of a high boiling amine (for example, quinoline) a cyclic product was formed in excellent yield. This could have originated via the initial formation of

---

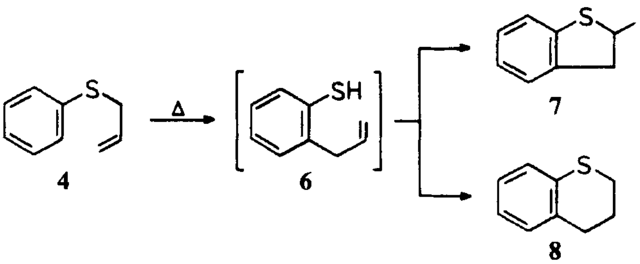
[†] Deceased.



(1)



(2)



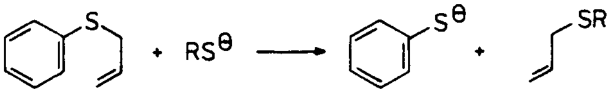
(3)

the anticipated *o*-allylthiophenol, **6**, followed by rapid ring closure as represented in Eq. (3). The product consisted mostly of two components, a thiochromane (**8**) and a 2,3-dihydrobenzothiophene (**7**) in a ratio that varied somewhat with the nature of substitution on the substrate thioether.

Proof that the overall course of thermal rearrangement of **4** corresponded to that depicted in Eq. (3) was obtained both by trapping (as a derivative) the intermediate thiophenol, **6**, and by synthesizing it[7] and showing that it formed the same reaction products (**7** + **8**) in the same ratio as found under thio-Claisen reaction conditions. Trapping the intermediate was effected[8] by adding CH_3I to the reaction mixture catalyzed by a strong base-nucleophile ($^{\ominus}OCH_3$), which inhibited the cyclization reaction through conversion to the thiolate anion of **6**. The latter was shown to have no tendency to cyclize to **7** + **8** and at the same time reacted readily with CH_3I to form in almost quantitative yields the methyl ether of **6**, which was, of course, completely stable in the reaction medium.

The effect of the catalyst apparently was to promote the attainment of a 3,3 sigmatropic TS of the thio-Claisen in competition with the irreversible propenylization at the higher temperatures required for reaction. It was estimated[8] from the small amount of propenylization side-product that the typical catalyst increased the rate of the 3,3 sigmatropic rearrangement by a factor of no more than 20 over the competing rate of propenylization. Without the catalyst, propenylization is at least 20 times faster than 3,3 sigmatropic rearrangement in an inert medium.

The kinetics of thio-Claisen reaction were found to be very cleanly first order in catalyst and first order in allyl phenyl sulfide substrate, indicating that only one mole of catalyst was required to initiate the concert of bond making and breaking that is characteristic of a 3,3 sigmatropic TS. The nature of the catalyst and the locus and manner of its action was elucidated through studies of the rate effects of a large number of catalysts; (see Table I). It was found[8] that catalytic activity followed a nucleophilic order, but thiolate super-nucleophiles engaged nearly exclusively in a displacement side reaction illustrated by Eq. (3a), which gave rise to products **9** + **10** in proportion to $RS^{\ominus}$ present. This suggested that the locus of catalysis by the ordinary nucleophiles was at the allylic carbon of the substrate and the mode of catalysis was through (S_N2-like) rearward nucleophilic approach causing some displacement of the phenylthiolate moiety, **9**, as the leaving group.



4 **9** **10**

(3a)

However, from the Table I data it is evident that the catalytic effect of ordinary nucleophiles correlated only with a small fraction of the usual rate effect exerted by these reagents in the usual S_N2 process.[9a] That is to say, the relative rates of a given

TABLE I

Part A

Rates of thio-Claisen rearrangement of allyl phenyl sulfide in the presence of various amine catalysts

pK_a[a]	Amine	$10^5 k_{obs.}$ sec.$^{-1}$
4.6	Aniline	2.52
5.15	*N,N*-Dimethalaniline	3.42
4.90	Quinoline	7.26
11.0	Triethylamine	9.41
5.25	Pyridine	9.85
0.75	α-Pyridone	14.2
6.95	Imidazole	18.4
8.86	Dabco[b]	19.5

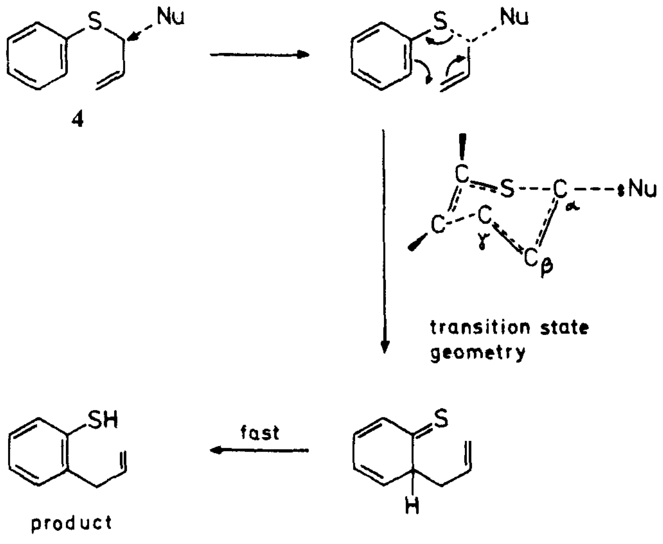
[a] In H_2O solvent.
[b] 1,4-Diazabicyclooctane.

Part B

Relative reactivity of thio-Claisen rearrangement in the presence of various catalyst-nucleophiles

Nucleophile	Relative rate in the thio-Claisen	Relative nucleophilicity[a]
$C_6H_5S^-$	1.43	16000
$C_6H_5O^-$	1.33	13.3
CH_3COO^-	1.02	0.67
$(CH_3)_3N$	1.00	1.00

[a] Streitweiser's average relative rate of displacement in a typical nucleophilic displacement process.[9b]

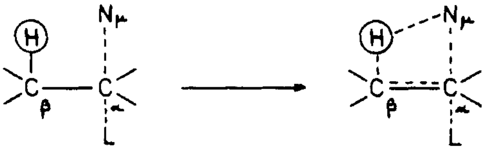


6

SCHEME 1 The mechanism of nucleophilic triggering of the pericyclic thio-Claisen rearrangement.

pair of nucleophilic reagents in the S_N2 could be > 100 but the relative rates of the pair in catalysis of the thio-Claisen would be < 10. From these observations it was inferred that a nucleophilic catalyst achieved very little covalent bonding to the allylic carbon in the TS; i.e. only a small amount of leaving group ($\geq$C—S) bond displacement was effected by the rearward approach of the catalyst before the pericyclic bond making and breaking in the TS was set into action.

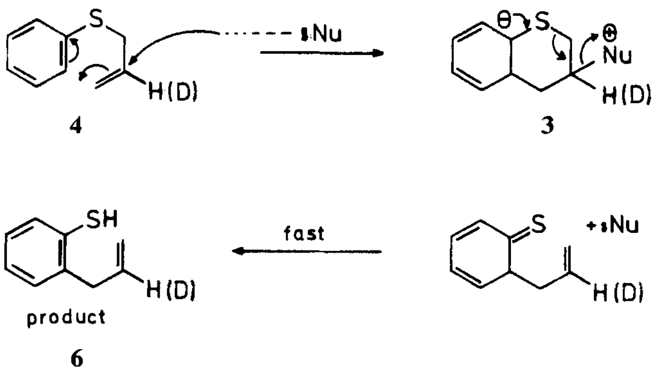
This scenario (Scheme 1) has been called[9] a nucleophilic trigger of concerted rearrangement. It is not an unprecedented mechanism, but its potential for providing catalytic assistance in reaction mechanism has not been widely probed as yet. A good example of a nucleophilic trigger mechanism has recently[9b] been elaborated in the case of the weak base promoted, β-elimination of HX called the E2C process (Eq. (4)) by Winstein[10] and Parker.[11] Here, a base possessing only minimum nucleophilic properties brings about elimination in a bent TS (**12**), preliminary to which only a small fraction of a covalent bond to the nucleophile-base and some leaving group departure must be achieved in an orienting TBP intermediate (**11**) focused at C_α.



11 **12**

(4)

The E2C Process



SCHEME 2 Proposed mechanism of nucleophilic cyclization-induced thio-Claisen rearrangement.

In support of the nucleophilic trigger mechanism[8] of the pericyclic thio-Claisen process is evidence found[12] in the course of consideration given to an alternative mechanistic possibility proposed by Overman.[13] The latter is called the cyclization-induced mechanism of nucleophilic catalysis and is represented in Scheme 2.

The Overman mechanism provides for a non-concerted process involving a definite, stabilized α-thiocarbanion intermediate. It calls for a large degree of negative charge to be developed on the aromatic ring near the TS, which in turn demands a large, positive Hammett ρ[14] and reflects a large degree of rate assistance to be realized from electrophilic substituents on the aromatic ring. In point of fact, however, both the thio-Claisen and oxy-Claisen rearrangements appear to be devoid of any significant charge development, as befits a pericyclic[15] TS, and this point of difference from the Overman mechanism is evidence by the data in Table II.

Further evidence to be gleaned from the Table II data is found in the results of α-secondary deuterium isotope effect studies. The Overman mechanism, which provides for full (nucleophilic) covalent (sp^3) bonding in the TS at a carbon which is sp^2 hybridized in the substrate, calls for an inverse value of $(k_H/k_D)_\alpha$. The actual finding of a normal $(k_H/k_D)_\alpha$ is seen to be in keeping with the nucleophilic trigger mechanism which anticipates an inductive effect to arise from substituting H by D at the internal double bond position.

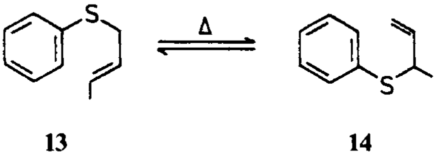
TABLE II

Rates of para-substituted allyl phenyl sulfide rearrangement at 204.4°C in the presence of pyridine catalyst in diethyl-carbitol-solvent

p-substituent	$10^5 k$ sec^{-1}	
—OCH_3	1.47	$\rho = +0.25$;
—CH_3	2.07	δ^+ correlation
—Cl	2.36	*compare*
—Br	2.76	oxy-Claisen rearrangement
—CN	3.41	$\rho = -0.61$;
—H	2.46	δ^+ correlation

THIOALLYLIC REARRANGEMENTS

The complex mixture of cyclized products (substituted thiachromans and thiacoumarins) arising in the course of thio-Claisen rearrangement[16, 17] of both α and γ-methylallyl-phenyl-sulfides (**14** and **13** respectively) first suggested the possibility of a relatively mobile α → γ migration of the phenyl-thio group across the allylic framework, as shown in Eq. (5). The possibility of such a thioallylic rearrangement had earlier been investigated by Cope *et al.*[18] but these authors failed to detect the thermal reaction of Eq. (5) for lack of modern instrumentation, i.e., a gas chromatograph. The viability of such a rearrangement even in the unsubstituted (deuterium tagged) case was readily established[19, 20] in 1970. Reaction was shown to proceed to an equilibrium composition (Eq. (5)) at temperatures far below those required for the thio-Claisen rearrangement, thus accounting[16] for the identical complex mixture of cyclic sulfides when α and γ isomeric substrates were subjected to thio-Claisen reaction conditions.



(5)

Kinetic studies[20-22] soon brought to light the fact that the thioallylic rate was highly sensitive to oxygen catalysis (accelerated), to adventitious impurities (particularly strong acid) and even to visible light. The subsequent studies were therefore conducted with highly purified reagents and complete exclusion of air, and light.

Related information gathered in the course of these kinetic studies led to a number of significant conclusions regarding the mechanistic features of the uncatalyzed reaction (as follows):

(1) The rate of thioallylic rearrangement is not seriously inhibited by all the conventional free radical chain inhibitors tried including quinones, dinitrobenzenes, 9,10-dihydroanthracene. Moreover, free radical chain initiators such as peroxides and azo-bis-isobutyronitrile also had negligible effects on the thioallylic rearrangement rate. These results permitted the conclusion that the uncatalyzed rearrangement did not proceed via a dissociative, free radical chain mechanism such as has been identified by Kochi and Krusic[23] for alkyl allyl sulfides.

(2) An electronegative substituent on sulfur is essential to the occurrence of uncatalyzed thermal rearrangement at a significant rate in the characteristic temperature range (*ca.* 100–150°C). Thus, while phenyl allyl sulfide rearranges rapidly at these temperatures, the rearrangement of benzyl allyl sulfides is almost 100 × slower and that of cyclohexyl allyl sulfide is virtually undetectable in a week of heating. (The rearrangement was followed in these cases through equilibration of the deutero-labelled side chain).

(3) There is no detectable uncatalyzed oxyallylic rearrangement to correspond; (γ-deuteroallyl-phenyl ether showed no signs of rearrangement prior to or concomitant with the occurrence of the oxy-Claisen rearrangement. Evidently the distinctive ability of sulfur to expand its octet was an essential requirement for allylic re-

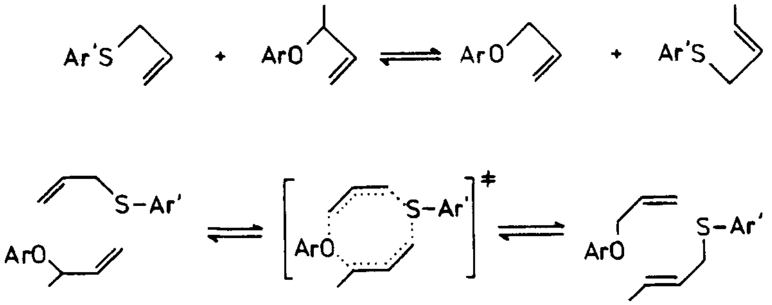
arrangement. Moreover, even chlorine, a neighbor of sulfur in the periodic table capable of octet expansion, seems to require an electronegative substituent (H^+ catalysis) for rapid rearrangement of allylic chlorides.

More detailed kinetic studies using as substrate the unsubstituted, deuterium-labelled allyl phenyl sulfide showed that at the usual dilutions two competing rearrangement processes were occurring; a unimolecular process involving a 4-center TS and a bimolecular one engendering an 8-center TS. As expressed in Eq. 6 the rates of these competing reactions and the factors that control them could be readily sorted.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \quad ; \quad 2\,A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2\,B \qquad (6)$$

$$\text{Thus, } -\ln(A - A_\infty) = 2\,(k_1 + k_3 A_0)\,t$$

It was thus possible to show that while a unimolecular oxyallylic rearrangement does not take place even at higher temperatures, a bimolecular cross-oxyallylic, with a thioallylic substrate acting as host, is experienced as depicted in Eq. (7).



(7)

The competing rearrangement processes here are invisible because each of the substrates in Eq. (7) only reproduces itself unimolecularly or in bimolecular reaction with a second mole of itself. Only the much slower cross rearrangement process is visible in which the ability of sulfur to expand its octet, most probably via electron donation from the (oxy) allylic double bond to the host (allylic) sulfur, is the essential factor in reaching the bimolecular TS, shown in Eq. (7).

It should also be noted that the bimolecular mode of cyclic rearrangement is more subject to steric hindrance. In cases such as the rearrangement of α,α'dimethylallyl-phenyl-sulfide to the more stable γ,γ' isomer, only the unimolecular mechanism is observed in all the solvents used.

A powerful solvent effect is evident from the fact that in the medium of decalin both unimolecular and bimolecular processes (Eq. (6)) are competing, but in a nitrobenzene medium the bimolecular one is suppressed. The origins of this phenomenon can be perceived from the data in Table III which show that in the unimolecular reaction it is the entropy factor which is responsible for the greater rate in nitrobenzene; [$\Delta(\Delta S^\ddagger) = 8$ e.u.]. This is a reflection of large charge development in the thioallylic TS; the decalin solvent which is unstructured in the ground state of

TABLE III

Solvent effect on the activation parameters of unimolecular rearrangement of deuteroallyl phenyl sulfide

	(Unimolecular) $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Solvent	Kcal/Mole	e.u.
Decalin	31.0	−9.2
Nitrobenzene	32.0	−1.3

the reaction becomes somewhat organized in response to the charge field created in the TS. But the substrate which finds itself surrounded by a highly structured solvation sphere in nitrobenzene creates very little additional organization in the solvent as a result of reaching its highly-charged, unimolecular TS.

The effect of nitrobenzene in suppressing the bimolecular reaction is made evident, however, in the crossed products study whose results are listed in Table IV. The positive $\Delta S^{\ddagger}$ and higher $\Delta H^{\ddagger}$ of the bimolecular reaction in decalin is a reflection of the fact that there is no ground state solvation in this solvent to interfere with the two reactant molecules coming together. A bimolecular, charged complex which forms most readily in this solvent loses its charge in the 8-centered TS; in accompaniment to this the organization imposed on the nonpolar solvent in the charge field of the initial complex is also lost in the TS in which the charge is destroyed, thereby accounting for its positive $\Delta S^{\ddagger}$ in the bimolecular process.

However, in nitrobenzene the solvent structure which encases each reactant must be stripped away to permit two of them to form a complex. It is this factor which accounts for the negative $\Delta S^{\ddagger}$ attending the bimolecular process in nitrobenzene, despite the fact that the $\Delta H^{\ddagger}$ is nearly 6 Kcal lower than in decalin, indicative of the high degree of charge stabilization afforded by the polar nitrobenzene solvation structure. Thus, it is the larger, negative $\Delta S^{\ddagger}$ (3.6 e.u.) of the bimolecular pathway which allows the unimolecular one to predominate, even while having a 1.4 Kcal greater $\Delta H^{\ddagger}$ demand.

Another indication of the large degree of charge development in the typical thioallylic TS has been gleaned from substituent-rate effect studies. In Table V are arrayed the activation parameters determined for a series of para substituted phenyl

TABLE IV

Bimolecular reaction, seemingly suppressed in nitrobenzene, is made visible in the crossed products experiment

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{—S—CH}_2\text{—CH=CH}_2 + \text{C}_6\text{H}_5\text{—S—CH}_2\text{—C(CH}_3\text{)=CH}_2 \rightleftharpoons$$
$$p\text{-CH}_3\text{C}_6\text{H}_4\text{—S—CH}_2\text{—C(CH}_3\text{)=CH}_2 + \text{C}_6\text{H}_5\text{—S—CH}_2\text{—CH=CH}_2$$

	(Bimolecular) $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Solvent	Kcal/Mole	e.u.
Decalin	36.6	+4.6
Nitrobenzene	30.7	−4.9

TABLE V

Substituent effects in unimolecular thioallylic rearrangement in nitrobenzene solution

$p\text{-X—C}_6\text{H}_4\text{—S—CH}_2\text{—CH=CD}_2 \rightleftharpoons p\text{-X—C}_6\text{H}_4\text{—S—CD}_2\text{—CH=CH}_2$

p-X	$\Delta H^‡$ Kcal/Mole	$\Delta S^‡$ e.u.	δ^-
$—NO_2$	27.2 ± 0.2	−15.9 ± 0.4	1.000
—Cl	30.4 ± 0.6	−5.2 ± 1.4	0.286
—H	32.1 ± 0.2	−1.3 ± 0.4	−0.023
$—OCH_3$	32.4 ± 0.8	−0.4 ± 2.0	−0.112
$—CH_3$	33.0 ± 0.2	+1.3 ± 0.2	−0.128
ΔE_H = +1.15 ± 0.10		Corr. coeff. = 0.993	

allyl sulfides in unimolecular rearrangement in nitrobenzene. The reaction rates at a single temperature are well correlated in a linear free energy relationship only by the δ^- values of the substituents[24] which are a measure of the degree of negative charge developing on sulfur in the TS. The value of $\rho = +1.15$, at first glance, would suggest only scant negative charge development; but this is illusory because the activation parameter variations with temperature tell us that we are dealing here with neither an isoentropic or isoenthalpic relationship. In fact, the change in $\Delta H^‡$ in going from p-NO_2 to p-CH_3 is nearly 6 Kcal. This would correspond to an enormous substituent rate effect were it not for the compensating influence of a *ca.* 17 e.u. swing in the opposite (rate) direction. This very large range of $\Delta H^‡$ and compensating $\Delta S^‡$ variation thus reveals the large degree of TS charge development in the thioallylic rearrangement. A negative charge is highly stabilized on sulfur when electron withdrawing substituents lower $\Delta H^‡$, but the dipolar character of the TS exerts an equally powerful influence in solvent striction and elevation of the (negative) $\Delta S^‡$ factor, which largely cancels the rate acceleration at these temperatures fostered by the lowering of $\Delta H^‡$.

From these considerations it may be inferred that the unimolecular process involves a 4-membered dipolar intermediate **15** lying close to the TS. Further evidence supporting this premise has been deduced from the results of substituent effects in the allyl side chain, where the positive center of the dipole resides transannularly to the negative sulfur. As shown in Table VI, a β-methyl substituent attached directly to the cationic center lowers the $\Delta H^‡$ by > 4 Kcal/Mole. Two methyl substituents in the α-position, which is more remote from the designated seat of positive charge development, lower $\Delta H^‡$ by only 1.7 Kcal/Mole, presumably due to the weaker effect of steric strain relief acceleration.

The ideal substituent-rate effect, however, is one for which it can be confidently assumed that the substitution has not altered the TS structure. This, of course, is the case when an isotope is substituted at the seat of reaction. The change (only) in isotopic mass affects the TS structure in a precisely, predictable way and beyond the cavil that otherwise arises in connection with the possibility of electronic-(substituent) effects on the TS structure.

The substitution of ^{32}S by ^{34}S must produce a rate effect which is directly correlatable with TS structure.[25] Table VII lists the three possibilities which are

TABLE VI

Substituent effects in the allylic moiety in $C_6H_5NO_2$ solvent

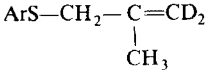
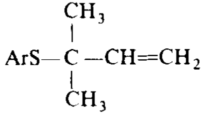
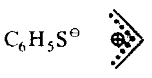
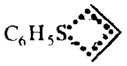
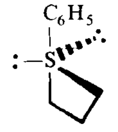
	$\Delta H^{\ddagger}$ Kcal/Mole	$\Delta(\Delta H^{\ddagger})$ Kcal/Mole observed	Anticipated for symm. TS; Kcal Mole
$ArS—CH_2—CH{=}CD_2$	32.1	—	—
 $ArS—CH_2—C(CH_3){=}CD_2$	27.7	−4.4	0
 $ArS—C(CH_3)_2—CH{=}CH_2$	30.3	−1.7	−4 → −8

TABLE VII

Heavy atom isotope effect evaluated for various TS models

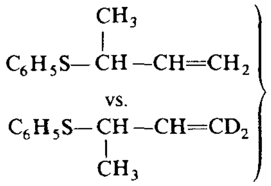
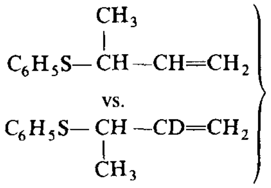
	$k_{^{32}S}/k_{^{34}S}$	
TS Model	Calculated[25]	Experimental
 Dissociative TS; Ion-pair model	1.012	—
 Concerted TS; Sigmatropic model	1.008	—
 Associative TS; TBP model	1.004	1.004 ± 0.0016 based on 60,000 MS determinations

eligible for consideration on the basis of the kinetics and other results discussed above. For each of these TS models a value of $k_{^{32}S}/k_{^{34}S}$ can be computed by means of the Bigeleisen–Mayer equation.[26] Using a high-precision method of estimating isotopic mass ratios gives results which are clearly congruent only with the associative dipolar TS of thioallylic rearrangement, and which have been vouchsafed by the conclusions deduced in the various studies discussed above.

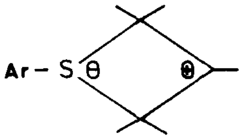
Secondary deuterium isotope effects are frequently applied as a means of elaborating the details of TS structure. The data gathered in studies[27] of the thioallylic rearrangement of appropriately deuterated α-methylallyl phenylsulfides are listed in Table VIII.

TABLE VIII

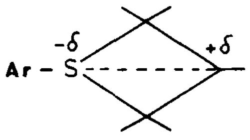
Secondary deuterium isotope effects at 198°C in $C_6H_5NO_2$ solvent

 $\mathrm{C_6H_5S{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH{=}CH_2}$ vs. $\mathrm{C_6H_5S{-}\underset{CH_3}{\underset{\vert}{C}}H{-}CH{=}CD_2}$	k_H/k_D = 0.936 per deuterium
 $\mathrm{C_6H_5S{-}\overset{CH_3}{\overset{\vert}{C}}H{-}CH{=}CH_2}$ vs. $\mathrm{C_6H_5S{-}\underset{CH_3}{\underset{\vert}{C}}H{-}CD{=}CH_2}$	k_H/k_D = 0.918 per deuterium

The large inverse $(K_H/K_D)_\alpha$ per deuterium realized for the isotope effect at the (sp^2 ground state) γ-position is fully in keeping with the assumption of a dipolar intermediate lying close to the TS in which the γ-carbon has become sp^3-bonded to the sulfur. The finding of a similarly large inverse $(k_H/k_D)_\alpha$ per deuterium for the isotope effect at the (sp^2 ground state) β-position is at first glance surprising, since it would appear that the hybridization of the β-carbon is still sp^2 in the dipolar intermediate in which it is represented as a full carbonium ion center. To interpret this result it must be realized that the negatively charged sulfur is capable of covalent interaction over long bond distances. A transannular, partly covalent interaction between the negative sulfur and the positive β-carbon may be held responsible for the increased coordination number at the β-carbon in the TS, as revealed by the inverse $(k_H/k_D)_\alpha$. A thiabicyclobutane-like structure (**16**) is therefore a more refined portrayal of the dipolar intermediate intervening in the course of the thioallylic rearrangement.

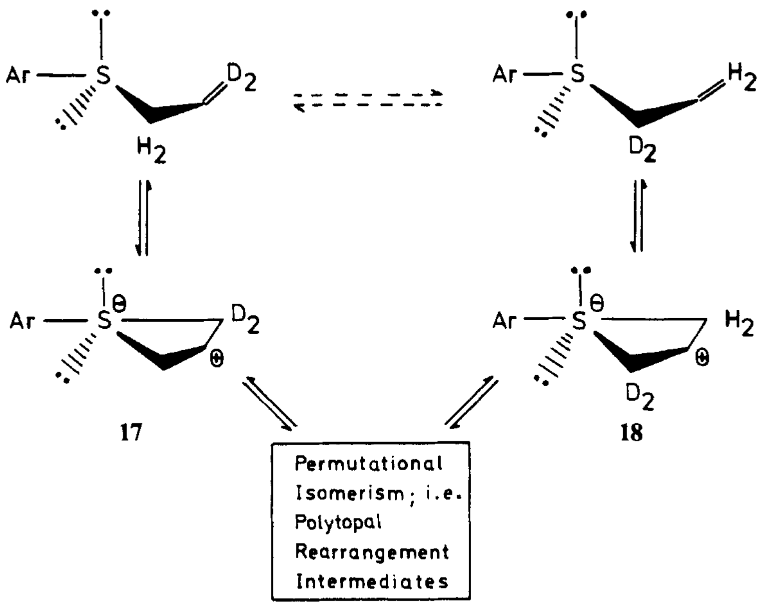


15



16

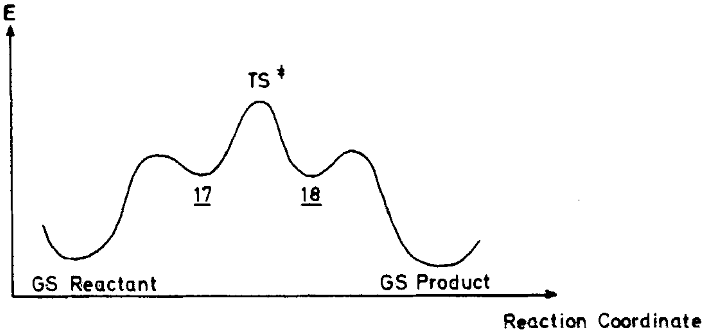
In the light of the catalogue of data assembled for the discussion above, a proposal for the mechanistic course of the thioallylic can now be outlined (Scheme 3). This recognizes that, in this readily reversible process, the substrates for reaction in both directions respectively form different dipolar intermediates of trigonal bipyramid (TBP) structure in which sulfur has expanded its octet. Microscopic reversibility requires that these intermediates (**17** and **18**) cannot be interconverted without an expense of energy since this would involve the interchange of basal and apical bonds of different energy content. Such an interchange necessitates invoking a



SCHEME 3 Pathway of thermal thioallylic rearrangement.

process of permutational isomerism of the hypervalent sulfur (dipolar) intermediates. Although several mechanisms of polytopal rearrangement are possible,[28] they can be said to be equivalent to the assumption represented in Scheme 3, i.e., that the TBP structure is converted to a square pyramid. The energy expense involved may amount to the activation requirement for reaction; i.e., permutational isomerism may be the rate determining step of the thioallylic rearrangement, as represented in Scheme 4.

The high susceptibility to catalysis by oxygen and by strong acids is regarded as an indication that the TBP intermediate, having an unshared pair on sulfur as well as dipolar character, can coordinate electron seeking reagents and thus form a new

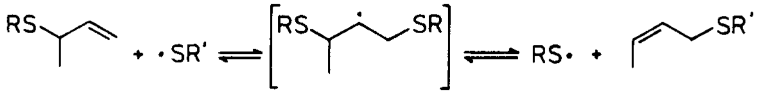


SCHEME 4 Reaction profile of the thioallylic rearrangement. The major TS is that which effects permutational isomerism (see Scheme 3), interconverting intermediates **17** and **18**.

TBP of higher hypervalency[29] of sulfur. The barrier to permutational isomerism and, therefore, the activation barrier is lowered by increasing hypervalency.

A good example in corroboration of this picture is found in the catalytic activity of diaryl disulfides in reaction with allyl aryl sulfides under thioallylic conditions.[21] The coordination of the disulfide sulfur to the allylic sulfur organizes a cyclic mechanism of bond making and breaking within this TBP intermediate structure. The necessity of invoking an octet expanded sulfur in a TBP intermediate is evident from the fact that allyl cyclohexyl sulfide strongly resists reaction with diphenyl disulfide. This result is reminiscent of the failure of allyl cyclohexyl sulfide to undergo thioallylic rearrangement at a measurable rate.[20]

The requirement of an electron withdrawing substituent on sulfur to effect octet expansion originates with the ability of such substituents to shrink the *d*-orbitals on sulfur and thus stabilize the apical bonding in a TBP structure. However, it has long been recognized that this associative pathway is not the only course of bringing about thioallylic rearrangement. Krusic and Kochi[23] were the first to identify (by ESR methods) a radical dissociation mechanism proceeding according to Eq. (8).

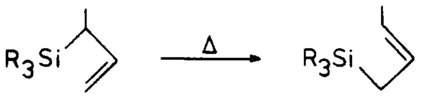


(8)

This chain mechanism, which depends on high temperature or photoinitiation, does not require that the R-substituent be an electron withdrawing group and, unlike the polytopal mechanism of thioallylic rearrangement documented in the discussion above, it is subject to serious inhibition by common free radical-chain inhibitors. Similar dissociative radical chain mechanisms have been observed by Brownbridge and Warren[30] in 1976 and, most recently, by Kozikowski[31] *et al.* in 1982.

SILAALLYLIC REARRANGEMENT

Though it is a third row relative of sulfur in the periodic system, the involvement of octet expansion in the chemistry of silicon has not been unequivocally established previously. The discovery of a silaallylic rearrangement (Eq. (9)) superficially analogous to the thioallylic process (above) called for studies to evaluate the mechanistic relationships.

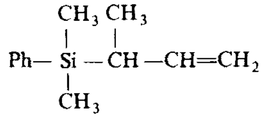
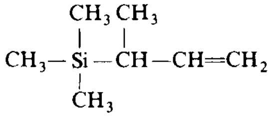
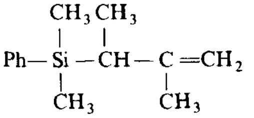
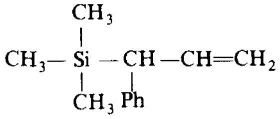


(9)

The kinetics of the very clean rearrangements expressed by eq. (9) were studied[32] in a specially constructed gold coil, flow microreactor designed to afford high precision results in carrying out short period exposure of a dilute (with He) gaseous allylsilane substrate to a carefully controlled temperature in the region of 450°–600°C. A listing of some of the data obtained is presented in Table IX.

TABLE IX

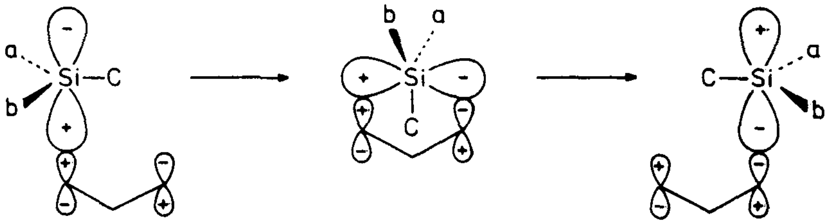
Gas phase thermolysis of allyl silanes in gold coil flow microreactor in a helium atmosphere

Substrate	Temp. range °C	E_a	$\Delta S^\ddagger$
 $\mathrm{Ph{-}Si(CH_3)_2{-}CH(CH_3){-}CH{=}CH_2}$	500°-580°	47.4 ± 0.2	-6.1 ± 0.3
 $\mathrm{CH_3{-}Si(CH_3)_2{-}CH(CH_3){-}CH{=}CH_2}$	506°-577°	47.4 ± 0.3	-6.1 ± 0.4
 $\mathrm{Ph{-}Si(CH_3)_2{-}CH(CH_3){-}C(CH_3){=}CH_2}$	516°-577°	47.7 ± 0.3	-6.5 ± 0.3
 $\mathrm{CH_3{-}Si(CH_3)_2{-}CH(Ph){-}CH{=}CH_2}$	420°-504°	43.2 ± 0.2	-6.6 ± 0.3

The variation (or lack thereof) in the activation parameters determined as a function of substitution on silicon and on the allylic side chain are seen to be dramatically different than what has been reported (above) for the thioallylic process. Thus, when the electronegative phenyl substituent on sulfur was replaced by alkyl in a thioallylic reaction substrate, the activation energy for rearrangement was enormously increased. The first two entries in Table IX show that the corresponding substituent change on silicon has no effect on either the E_a or $\Delta S^\ddagger$ parameters, suggesting that octet expansion is not a factor in the silaallylic mechanism.

In the thioallylic, the dipolar, TBP intermediate, mirrored in the E_a parameter, was found to be 4.4 Kcal/Mole more stable as a consequence of a β-methyl substituent in the allylic side chain. Comparing entries 1 and 3 in Table IX demonstrates that β-methyl substitution is completely without effect on both E_a and $\Delta S^\ddagger$ in the silaallylic. The only effect of side chain substitution to be perceived is through comparison of entries 2 and 4 in Table IX. An α-phenyl (cinnamyl) substituent, which in the rearranged product becomes a γ-phenyl (styryl) substituent, lowers the E_a by 4.5 Kcal but is completely without effect on the $\Delta S^\ddagger$ parameter. The concerted, pericyclic nature of the silicon migration is thus revealed in the fact that the only significant substituent influence on the rate and activation parameters of this reversible gas phase process arises exclusively from the difference in resonance energies of products and reactants; i.e., the ΔE_a of the reactions in entries 2 and 4 of Table IX is equal to the resonance energy gained in converting phenyl from an unconjugated cinnamyl to a conjugated styryl substituent.

Final proof that the silaallylic rearrangement occurs as a 1,3 suprafacial sigmatropic migration *via* a $3p$ orbital bridging the allylic framework with inversion of the silicon has been obtained through studies of the course of rearrangement of the

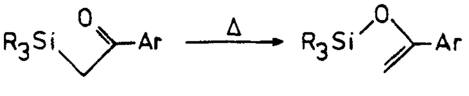


SCHEME 5 1,3 sigmatropic migration of $3p$ silicon orbital across the allylic (framework) HOMO.

appropriate optically active allylsilane. The data[32] show (Scheme 5) that the reaction occurs with complete inversion of the silicon configuration and with no detectable accompaniment of racemization. The lower activation demand compared to the corresponding reaction involving migration of a $2p$ carbon orbital has been attributed to the greater amplitude of a $3p$ silicon orbital and therefore greater accommodation to the geometric requirements for 1,3 bridging in the pericyclic TS.

THE SILOXYALLYLIC REARRANGEMENT

The question arises as to what mechanistic circumstances would permit silicon to utilize its $3d$ orbitals in a rearrangement process analogous to that established for the thioallylic. The answer emerges in connection with studies[33,34] of the rearrangement of β-silylketones to siloxyalkenes expressed by Eq. (10).



(10)

The kinetics of reaction are cleanly unimolecular. When applied in Linear Free Energy (LFE) studies in reaction series where substitution at R_1 and R_2 are varied, it is found that the reaction exhibits an isokinetic temperature $\beta = 380 \pm 27°K$. Thus, while $\rho_{R_1}^{393°K} = -0.78$ and $\rho_{R_2}^{433°K} = +0.54$, the actually large degree of (dipolar) charge development in this TS can be perceived only from the variation of the activation parameters with change in substitution at R_1 and R_2. It will be recalled that entirely similar circumstances were encountered in connection with the substituent-rate effects in the thioallylic. Thus, in the siloxyallylic (as shown in Table X)

TABLE X

Substituent effects observed[33] in the siloxyallylic rearrangement

$$(R_1)_3Si{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}R_2 \xrightarrow{\Delta} (R_1)_3Si{-}O{-}C(R_2){=}CH_2$$

Substituent change	E_a (Kcal)	$\Delta S^{\ddagger}$ e.u.
$R_1 = Ph \rightarrow CH_3$	~ 2	10.5
$R_2 = Ph \rightarrow CH_3$	3.5 → 5.0	3 → 8

TABLE XI

Solvent effect on the activation parameters in the siloxyallylic rearrangement[36]

Solvent composition	Medium dielectric ϵ	E_a (Kcal/Mole)	$\Delta S^{\ddagger}$ e.u.
benzene (pure)	2.3	30.6	+2.7
$\frac{\text{nitrobenzene}}{\text{benzene}} = 4$	28.3	22.9	−14.9

the substituent change $R_1 = Ph \rightarrow CH_3$ results in an E_a increase of 2 Kcal/Mole and a compensating $\Delta S^{\ddagger}$ increase 10.5 e.u. The similar change in R_2 substitution produces a somewhat larger increase in E_a but a smaller increase in $\Delta S^{\ddagger}$, while leaving the rate (near the isokinetic temperature) virtually unchanged.

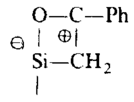
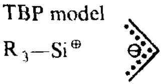
Again, as in the thioallylic, the polar solvent effect on rate is small but the effect on the activation parameters is very large, indicative of the operation of the compensation law[35] in a strongly dipolar TS. For example, as shown by the data presented in Table XI, a *ca.* 10-fold increase in medium dielectric decreases E_a by almost 10 Kcal/Mole, while a compensating decrease in $\Delta S^{\ddagger}$ of almost 18 e.u. is experienced.

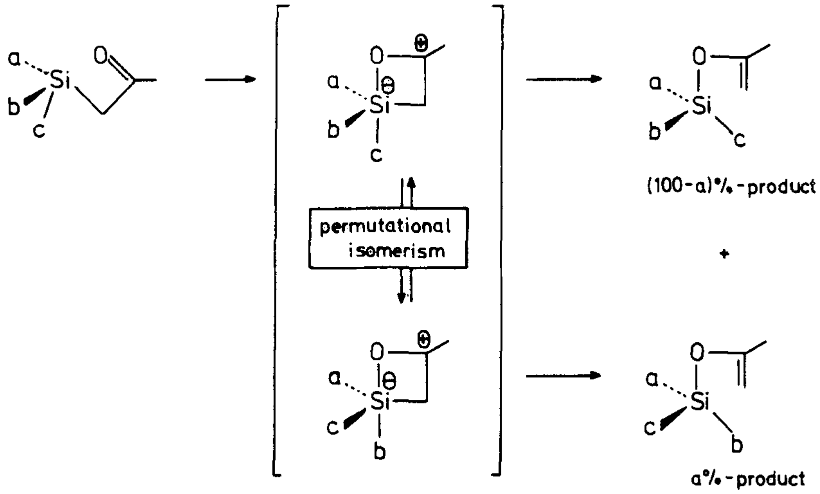
Just as in the case of the thioallylic, the heavy atom isotope effect has been applied[36] as an ideal substituent effect criterion of TS structure. The data presented in Table XII fully verify the occurrence of an associative TS and, therefore, the octet expansion of silicon in the course of the siloxyallylic rearrangement, in agreement with the interpretation conferred on the kinetic data discussed above.

Silicon (in the siloxyallylic) affords an opportunity for evaluating this mechanistic conclusion that is not available to sulfur (in the thioallylic), namely, through observation of the stereochemical course of reaction. In the silaallylic, the finding of complete inversion of the silicon configuration in going from reactant to product, unattended by any racemization, verified the pericyclic nature of the 1,3 migration.

TABLE XII

Heavy atom isotope effect in the siloxyallylic rearrangement

Model of TS‡	$k_{^{28}Si}/k_{^{29}Si}$	
	Estimated[25]	Experimental[36]
 (Associative)‡ TBP model	1.003 (A maximum value)	1.0010 ± .002 based on 20,000 MS determinations
 (Dissociative)‡ Enolate anion-Silicenium ion pair model	1.009 (A minimum value)	—



SCHEME 6 Configuration retention and racemization in the course of the siloxyallylic rearrangement.

Applying the same stereochemical probe in the siloxyallylic[33] has yielded the result which is fully consistent with the formation of a TBP intermediate (see Scheme 6) through octet expansion of the silicon—namely, reaction occurs with predominant retention of configuration and some racemization. This result, moreover, establishes the occurrence of permutational isomerism in the dipolar TBP intermediate of the siloxyallylic, a conclusion which was inferred (vide supra) on other grounds for the thioallylic intermediate.

Obviously octet expansion by silicon is eschewed in regular silaallylic cases presumably because a dipolar intermediate TBP would still be highly unstable regardless of the (original) substituents on the silicon. But the opportunity to share a comparatively stable, apical bond with oxygen in the course of forming the intermediate of the siloxyallylic greatly stabilizes the TBP structure. Most probably, the apical bond to the highly electrophilic oxygen shrinks the d-orbitals sufficiently to construct a stable TBP around silicon.

REFERENCES

1. W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).
2. H. L. Goering and R. F. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).
3. D. S. Tarbell, *Org. Reactions*, **2**, 1 (1948).
4. S. J. Rhoads and N. R. Raulims, *Org. Reactions*, **22**, 1 (1975).
5. J. B. Bennett, *Synthesis*, **9**, 589 (1977).
6. H. Kwart and C. M. Hackett, *J. Am. Chem. Soc.*, **84**, 1754 (1962); see also, J. Myers, C. Rinaldi and J. Banoli, *J. Org. Chem.*, **28**, 2440 (1963).
7. H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 (1966).
8. H. Kwart and J. L. Schwartz, *J.C.S. Chem. Commun.*, 44 (1969), and *J. Org. Chem.*, **39**, 1575 (1975).
9. (a) H. Kwart and K. A. Wilk submitted for publication; (b) A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, N.Y. (1962).
10. (a) S. Winstein, *Chimica Teorica*, 327 (1965); (b) A. J. Parker, *Chem. Tech.*, **1**, 297 (1971).
11. D. J. McLennan, *Tetrahedron*, **31**, 2999 (1975).
12. H. Kwart, W. H. Miles, A. G. Horgan and L. D. Kwart, *J. Am. Chem. Soc.*, **103**, 1757 (1981).
13. L. E. Overman, C. B. Campbell and F. M. Knoll, *Ibid.*, **100**, 4822 (1978).

14. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, N.Y. (1970).
15. A. P. Marchand and R. E. Lehr, "Pericyclic Reactions," Academic Press, N.Y. (1977).
16. (a) H. Kwart and M. H. Cohen, *J. Org. Chem.*, **32**, 3135 (1967); (b) H. Kwart and M. H. Cohen, *J.C.S. Chem. Comm.*, 319 (1968).
17. H. Kwart and T. J. George, *J.C.S. Chem. Comm.*, 433 (1970).
18. A. C. Cope, D. E. Morrison and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).
19. H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970).
20. H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, **99**, 3441 (1977).
21. H. Kwart and N. A. Johnson, *J. Org. Chem.*, **42**, 2855 (1977).
22. H. Kwart, N. A. Johnson, T. Eggerichs and T. J. George, *Ibid.*, **42**, 172 (1977).
23. (a) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **93**, 846 (1971); (b) E. S. Huyser and R. M. Kellog, *J. Org. Chem.*, **30**, 2867 1965); (c) S. N. Lewis, J. J. Miller and S. Winstein, *Ibid.*, **37**, 1478 (1972).
24. (a) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970); (b) F. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 6019 (1953).
25. H. Kwart and J. J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976).
26. See J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949) for discussion.
27. H. Kwart and T. J. George, *J. Am. Chem. Soc.*, **99**, 5214 (1977).
28. For discussion and further references see H. Kwart and K. G. King, "d-Orbitals in the Chemistry of Silicon, Phosphorous and Sulfur," Springer-Verlag, Berlin, Heidelberg, New York (1977), pp. 98–100.
29. J. L. Musher, *Angew. Chem. Int. Ed. Engl.*, **8**, 54 (1969).
30. P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin I*, 2125 (1976).
31. A. P. Kozikowski, E. Huie and J. P. Springer, *J. Am. Chem. Soc.*, **104**, 2059 (1982).
32. (a) H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, **94**, 2415 (1972); (b) J. Slutsky and H. Kwart, *ibid.*, **95**, 8678 (1973).
33. (a) A. G. Brook, D. M. MacRae and W. M. Limberg, *J. Am. Chem. Soc.*, **89**, 5493 (1967); (b) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974); *J. Organomet. Chem.*, **86**, 185 (1975).
34. G. L. Larson and Y. V. Fernandez, *ibid.*, **86**, 193 (1975).
35. (a) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) J. E. Leffler, E. Grunwald, "Rates and Equilibria in Organic Reactions," Wiley, N.Y. (1963).
36. H. Kwart, W. E. Barnette, *J. Am. Chem. Soc.*, **99**, 614 (1977).