correlation in the observed negative $\Delta S°$ direction.

In contrast we note that in the case of Cy·ACA$^-$, $\Delta S° = -1.3 \pm 1.9$ cal mol^{-1} K^{-1} which is about 4 cal mol^{-1} K^{-1} more positive than the value of −5.5 cal mol^{-1} K^{-1} corresponding to the observed $\Delta H° = -3.4$ kcal mol^{-1} on the correlation line. Again we speculate with reservation that this deviation is due to a mechanistic peculiarity involving a partial contribution of hydrophobic bonding to the formation of this complex. The positive entropic deviation may be due to release of solvent water molecules ordered around the exceptionally large hydrocarbon upon complexation with Cy. If this is true, it is important to note that this hydrophobic contribution ($-T\Delta S° \approx -1.2$ kcal mol^{-1}) represents only about one-third of the favorable free energy change ($\Delta G° \approx -3.0$ kcal mol^{-1}) for complexation. The complexation is dominated by the enthalpic contribution of −3.4 kcal mol^{-1}.[16] This behavior turns our attention to the ^{13}C NMR behavior of the 1-adamantanecarboxylate anion system. We note that C1 displacement of Cy in the Cy·ACA$^-$ complex conforms to the $\Delta\delta_1^{Cyl}$ vs. $\Delta H°$ correlation so that the unusual behavior of Cy·ACA$^-$ cannot be ascribed to some difference in macrocycle conformation resulting from interaction with the large hydrocarbon substrate. It is interesting that the binary complex of Cy with the parent acid ACA does seem to conform to the $\Delta H°$ vs. $\Delta S°$ correlation. This is readily explained by a structure involving inclusion of the carboxylic acid terminal of ACA in the Cy cavity. In that case no appreciable change in the substrate solvation would occur, and a "normal" $\Delta H°$ and $\Delta S°$ relationship would be observed. While the postulated Cy·ACA structure seems likely by analogy to other carboxylic acids, we attempted to confirm this hypothesis by NMR spectral measurements but were unable to do so because of the very low solubility of ACA.

We wish to emphasize that our speculations on internal constraint in Cy·CHCA and on hydrophobic effects in Cy·ACA$^-$ are made with reservation. The bonding in these complexes and in the others studied here is predominantly dipolar. This conclusion is based on a variety of thermodynamic and structural evidences, as discussed in earlier sections. Furthermore, the correlations found here strongly support a binding picture in which dipolar interactions between the macrocycle and substrate result in conformational changes in Cy. These directly determine the entropy change on complexation.

Experimental Section

Cyclohexaamylose (α-cyclodextrin) obtained from the Aldrich Chemical Co. was exposed to the atmosphere for several days to ensure complete conversion to the hexahydrate as determined by vacuum drying at 100 °C. ^{13}C NMR spectra obtained under high S/N (>200) conditions indicated negligible impurity concentrations. Finally, pH measurements with 0.1 M Cy solution gave no indication of acidic or basic impurities. All other materials were reagent grade, and most solids were recrystallized from water before use.

Spectrophotometric measurements employed a Beckman Acta III spectrophotometer equipped with a thermostated sample compartment and 1.00-cm quartz cells. pH potentiometric experiments were made with the aid of an Orion 801 pH meter equipped with conventional glass and reference electrodes. The electrodes were recalibrated frequently, and no appreciable meter drift was detected.

Single-temperature (30 ± 2 °C) ^{13}C NMR data were obtained with a Varian CFT-20 nuclear magnetic resonance spectrometer operating in the Fourier transform mode (30° tip angle, 2-s acquisition time, spectral width 4 KHz, 1–2-s pulse delay, and 1–10 K acquisitions). Variable-temperature measurements of Cy ^{13}C resonances were carried out on a Bruker HX-270 spectrometer with instrument settings of 90° tip angle, 7-kHz spectral width, 0.6-s acquisition time, and 200 acquisitions. In all of these experiments proton-decoupled spectra were recorded from a single 10-mm sample tube for each series of measurements.

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The Mechanism of Catalysis of the Thio-Claisen Rearrangement

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Abstract: The cyclization-induced rearrangement mechanism proposed by Overman[10] to account for nucleophilic catalysis of the thio-Claisen rearrangement has been tested by application of two criteria, viz., the secondary kinetic deuterium isotope effect at the β (side chain) carbon in phenyl allyl sulfide and the substituent rate effect. The results ($k_H/k_D = 1.05$ and log $k_{X_p}/k_H = 0.25\sigma^+$) do not support the mechanism. Instead, they can be construed to support the previously validated mechanism of nucleophilic triggering of sigmatropic rearrangement.[9]

The thio-Claisen rearrangement has been recognized to be of general preparative interest and widely applied for such purposes.[1-3] Since the first recorded example[4] of this reaction in 1962, the mechanistic relationship to the oxy-Claisen has been elucidated in a series of articles[5-8] culminating in the formulation of a mechanism of nucleophilic triggering of concerted (3,3) sigmatropic rearrangement of phenyl allyl sulfides (**1**) to account for the role of a wide variety of both neutral and anionic nucleophiles.[9] The proposed reaction course and details of the TS‡

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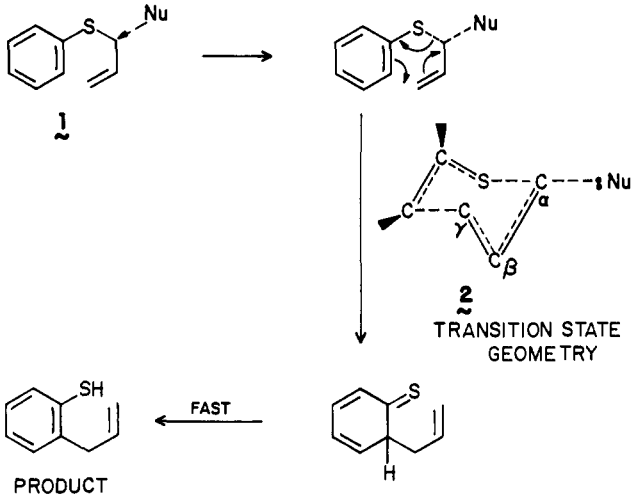
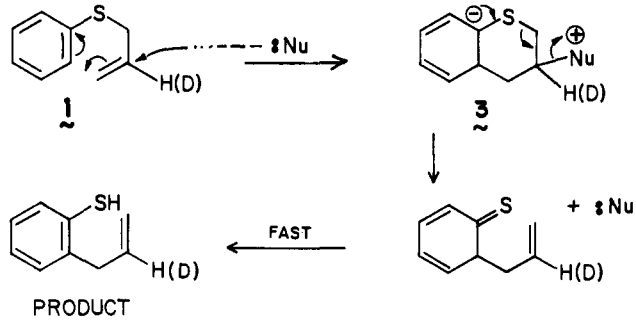
Scheme I. The Mechanism of Nucleophilic Triggering of the Pericyclic Thio-Claisen Rearrangement



Scheme II. Proposed Mechanism of Nucleophilic Cyclization-Induced Thio-Claisen Rearrangement



(TS‡ = transition state) geometry (**2**) are illustrated in Scheme I.

Recently Overman and co-workers,[10] in an attempt to generalize cyclization-induced catalysis of 3,3 sigmatropic rearrangement, advanced a mechanistic proposal engendering the following pathway (Scheme II) for the thio-Claisen. σ bonding of the catalyst at the β (side chain) carbon is completed in a reaction intermediate (**3**) closely resembling the TS‡. The evidence which permits a clear distinction between these alternative proposals is presented for consideration in the ensuing report.

The Secondary Deuterium Isotope Effect Criterion. The contending mechanisms could be sorted on the basis of the rate effects stemming from deuterium substitution at the β (side chain) carbon. The Overman[10] Scheme II, requiring as it does a full σ bond between the catalytic nucleophile and the β-carbon in intermediate **3**, must anticipate a large, inverse isotope effect. The CNS^- ion-catalyzed maleic–fumaric isomerization[11] in which the carbon attacked is slightly more than half-way to tetrahedral in the TS‡ shows a $k_H/k_D \simeq 0.90$ (calculated for comparison to the Scheme II mechanism).

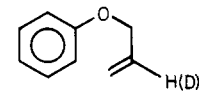
The finding of a normal rather than an inverse isotope effect (Table I) is thus in complete disagreement with any picture involving increased bonding at the β-carbon in the TS‡ for 3. To calibrate this conclusion the secondary deuterium isotope criterion was applied in the oxy-Claisen rearrangement,[12] probing for any change in coordination number at the β-carbon in its TS‡. This test was run under exactly the same conditions as the thio-Claisen, namely, in diethyl carbitol with pyridine, and the isotope effect

Table I. Kinetic Deuterium Isotope Effect[a] in the Rearrangement of 1 at 204.4 °C, 0.8 M in Diethyl Carbitol in the Presence of 0.80 M Pyridine

initial isotope ratio R_{a_0}	fraction of *Rn* completed f	measd isotope ratio R_{a_f}	k_H/k_D[b]
	0.0	1.158 ± 0.001	1.0569 ± 0.0004
1.1663	0.30	1.1896 ± 0.0004	1.056 ± 0.002
1.1663	0.40	1.199 ± 0.003	1.056 ± 0.003
1.1663	0.50	1.211 ± 0.004	1.056 ± 0.003
1.1663	0.60	1.2264 ± 0.005	1.0562 ± 0.0003
1.1663	0.73	1.2225 ± 0.0009	1.0365 ± 0.0008
0.9001	0.40	0.922 ± 0.002	1.048 ± 0.002
0.9001	0.60	0.9506 ± 0.0009	1.061 ± 0.001
0.9001	0.70	0.955 ± 0.003	1.050 ± 0.003

[a] Samples were prepared with the usual quantitative kinetic technique.[9] The products and reactants were fully separated by base-line GLC procedures.[9] Only the unreacted starting material purified in this fashion was analyzed as described previously.[19a] [b] Calculated by application of the equation[19a] $1/(k_H/k_D) = \ln (R_{a_f}/R_{a_0})/\ln [(1-f)(1+R_{a_0})/(1+R_{a_f})] + 1$, where R_{a_0} is the ratio of heavy to light isotope at $t = 0$ and R_{a_f} is the heavy to light ratio after f fraction of reaction is completed. The molecular ions of allyl phenyl sulfide and 2-deuterioallyl phenyl sulfide were measured at 150 and 151 amu, respectively. An ionizing voltage of 70 eV was employed. No correction of the observed ratio M_H/M_D was necessary[19b] since the equality $(M_H + 1)/M_H = (M_D + 1)/M_D$ existed. The quantity voltage at parent ion/voltage at base line = 1×10^3 to 5×10^2 is large so that error due to background noise is virtually nonexistent. Average $k_H/k_D = 1.053 \pm 0.007$ (0.7% error).

Table II. Kinetic Deuterium Isotope Effect[a] in the Rearrangement of

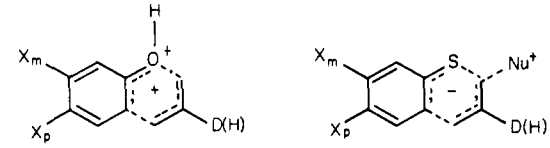


at 204.4 °C, 0.8 M in Diethyl Carbitol in the Presence of 0.80 M Pyridine

initial isotope ratio R_{a_0}	fraction of *Rn* completed f	measd isotope ratio R_{a_f}	k_H/k_D[b]
	0.0	0.5865 ± 0.0007	
0.5883	0.30	0.586 ± 0.001	0.989 ± 0.002
0.5883	0.40	0.5855 ± 0.0001	0.9907 ± 0.0001
0.5883	0.50	0.5848 ± 0.0003	0.9914 ± 0.0003
0.5883	0.60	0.5831 ± 0.0003	0.9904 ± 0.0006
0.5883	0.70	0.5814 ± 0.0007	0.990 ± 0.001

[a] The method and technique of mass ratio measurement was the same as that employed in Table I. [b] The method of calculation is the same as that used in Table I. The molecular ions of allyl phenyl ether and 2-deuterioallyl phenyl ether were measured at 134 and 135 amu, respectively. Average $k_H/k_D = 0.990 \pm 0.002$ (0.2% error).

Chart I. Projection Views of Catalyzed Claisen TS‡



4a electrophilic catalysis of oxy-Claisen

4b nucleophilic catalysis of thio-Claisen (cf. the three-dimensional representation in **2**)

measurements were carried out with somewhat greater precision; $k_H/k_D = 0.990 \pm 0.002$.

A very small inverse isotope effect observed in the oxy-Claisen, where the absence of nucleophilic catalysis has been established,[12,13]

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Table III. Rates of Para-Substituted Allyl Phenyl Sulfides at 204.4 °C, 0.80 M in Diethyl Carbitol in the Presence of 0.80 M Pyridine

substituent X	10^5k, s^{-1}	coeff of correlation	(substituent constant)[17b]	ρ_{calcd}	coeff of correlation
		Para			
OCH_3	1.47 ± 0.06	0.9954	σ_p	+0.33	0.912
CH_3	2.07 ± 0.07	0.9972	σ^-	+0.26	0.859
Cl	2.36 ± 0.06	0.9983	σ^+	+0.25	0.988
Br	2.76 ± 0.15	0.9930			
CN	3.41 ± 0.11	0.9975			
H	2.46 ± 0.04	0.9994			
		Meta	σ^+	−0.4	0.999
CF_3	1.52 ± 0.09	0.9973			
CH_3	3.31 ± 0.11	0.9968			

may have an explanation in the recognized inductive effect of deuterium.[14] The electrophilic catalysis (by the phenolic product)[12] identified previously for this rearrangement calls for some positive charge development on the circle of atoms involved in the pericyclic process. The deuterium at the β (side chain) position, because it is orthogonal to the cyclic TS‡ structure as shown in projection in **4a** (Chart I), is expected to exert an inverse isotope effect (k_H/k_D = 0.985 in analogous cases)[14a,b] through exercise of its inductive effect.

The larger, normal isotope effect (k_H/k_D = 1.05) found for the thio-Claisen can be understood as the result of two factors operating in the same direction. The inductive effect of deuterium[14] operating in the electron-enriched TS‡ of the nucleophilic-catalyzed thio-Claisen, shown in projection in **4b** and in three-dimensional representation in **2**, is responsible for part of the rate advantage observed for the corresponding proteo substrate. The remainder can arise as the consequence of a β-secondary deuterium isotope effect[15] attending the S_N2-like displacement reaction at the allylic carbon triggering the pericyclic rearrangement. In analogous S_N2 displacements the substitution of deuterium at the β-carbon had been characterized by a normal isotope effect. For example, the average value of the β-deuterium isotope effect in the reaction of ethyl sulfonate[15a,b] is $k_H/k_{\beta\text{-}D} \simeq 1.05$ at 25 °C; somewhat higher values have been found for the cyclohexyl ester reaction.[15c] At the higher temperatures of the thio-Claisen this part of the isotope effect should be smaller. Nonetheless, the total effect comprised of the inductive and the S_N2-β-secondary isotope effects appears to be capable of accounting for the observed effect in terms only of the Scheme I, nucleophilic triggering mechanism, and not (by any means) the Scheme II nucleophilic cyclization-induced mechanism.

The Substituent–Rate Effect Criterion. This was applied as a second test of the Overman mechanism[10] of cyclization-induced catalysis. The development in the TS‡ for **3** of a negative charge which is stabilized as an α-thiocarbanion,[16] as required by this mechanism, also demands a large rate enhancement by electro negative substituents para to the locus of negative charge development in the intermediate **3**. The data gathered in Table III show, however, that little more than a factor of 2 distinguishes the rates of the most electronegative and electropositive para substituents. The reaction constant which can be correlated with the effects of all the para substituents, ρ = +0.25, cannot be considered as characteristic of an α-thiocarbanion mechanism involving development of a full negative charge on the ring in the proposed intermediate **3**. Thus, even where the negative charge in the reaction intermediate has developed in an β (side chain) position as in the saponification of substituted benzoate esters,[17a] ρ = +2.47, an order of magnitude larger than is found for the thio-Claisen.

The isokinetic temperature[18] for the thio-Claisen under these reaction conditions was found to be ~450 °C, which is comparable to that determined[12c] for the oxy-Claisen, and far above the temperature (204.4 °C) at which the substituent rate effects were measured. Consequently, this could not be the cause of the very small ρ values exhibited by both the thio- and oxy-Claisen rearrangements.

Substituent–rate data of the nature arrayed in Table III have their analogy in data reported by White and others[12] in studies of the oxy-Claisen rearrangement. The fact that in both oxy- and thio-Claisen cases meta (X_m) and para (X_p) substituted rates are not correlated by the same, simple Hammett relationship, while exerting only very small rate effects and in opposite direction, demonstrates the mechanistic resemblance of the oxy- and thio-Claisen. The small ρ values estimated from the data in Table III can be easily "overinterpreted". We believe they originate in small field and inductive interactions of variably oriented substituent dipoles with those induced by the respective heteroatom centers in both the ground and transition states. It is to be emphasized that these interactions are characteristically quite small, i.e., less than 1 kcal, and cannot be readily sorted out.

But despite this the differeing signs of ρ(meta) and ρ(para) for the oxy- and thio-Claisen may be interpreted as an index of the electronegativity differences of oxygen and sulfur in relation to their carbon seats of attachment to the ring. Since the oxy-Claisen is susceptible only to electrophilic catalysis[12] and the thio-Claisen only to nucleophilic catalysis,[9] the differences in the signs of their ρ values might be correlated with the requirements for triggering their respective pericyclic rearrangement processes. In effect, it can be considered that, in such sigmatropic rearrangements, catalytic and substituent influences are exercised in triggering the concert of bond-making and bond-breaking steps rather than in creating new reaction pathways such as that proposed in Scheme II.

Experimental Section

Kinetic Method. The procedure developed earlier by Kwart and Schwartz[9] was followed in detail. Diethyl carbitol solutions, 0.8 M in the sulfide, the pyridine catalyst, and the internal standard 1,3,5-trichlorobenzene were sealed in 6-in. heavy-walled glass ampules after careful degassing and submerged in a constant temperature bath at 204.4 ± 0.1 °C. The tubes were withdrawn from the heating bath and rapidly cooled at predetermined intervals. The reaction mixtures were analyzed

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Table IV. Materials Used in Rate and Isotope Effect Studies

compd	method of preparation[a]	additional data	% yield
phenyl allyl sulfide	A	49–53 °C (0.33 mm) 84–86 °C (4.9 mm)	79
p-methylphenyl allyl sulfide	A	89–92 °C (1.5 mm)	78
p-chlorophenyl allyl sulfide	A	68–70 °C (0.02 mm)	65
p-bromophenyl allyl sulfide	A	111–114 °C (2 mm)	76
m-methylphenyl allyl sulfide	A	82–87 °C (1.5 mm)	70
allyl-2-*d* alcohol	B	75–98 °C (760 mm)	40
allyl-2-*d* chloride	A	42–44 °C (760 mm)	73
phenyl allyl-2-*d* sulfide	A	61–63 °C (1.1 mm)	55
p-methoxyphenyl allyl sulfide	A	85–100 °C (0.1 mm)	80
p-cyanophenyl allyl sulfide	A	121–125 °C (0.4 mm)	11
m-(trifluoromethyl)-phenyl allyl sulfide	C	ca. 94–100 °C (1.5 mm)	
phenyl allyl ether	D	192 °C (760 mm)	
phenyl allyl-2-*d* ether	E	60–65 °C (6 mm)	42

[a] A = prepared by the method used previously[22] from the thiolate anion in reaction with allyl chloride (Aldrich). B = prepared by the method used previously[23] from propargyl alcohol and lithium aluminum deuteride (99.8%, Aldrich) followed by H_2O. C = the *m*-(trifluoromethyl)phenyl mercaptan was prepared by the method used previously[24] from the Grignard of the corresponding iodide reacted with sulfur. The mercaptan was then converted to the allyl sulfide by the procedure of method A. Since this was the only sulfide previously unknown in the literature, it was characterized also by elemental analysis using exact-mass spectrometry: M_{theo} for $C_{10}H_9F_3S$ = 218.0377; M_{exptl} = 218.0379 ± 0.003; resolution = 5000 at 15%. D = commercially available from Aldrich Co. E = the procedure used was identical with that employed previously[22,23,25] from benzenethiolate anion in reaction with allyl-2-*d* chloride.

by gas chromatographic procedures (see below). Generally between six and eight tubes were sampled before the reaction was less than 70% completed. The thio-Claisen rearrangement was previously established[9] to be purely first order out to almost 90% completion with respect to sulfide disappearance. The same pseudo-first-order relation determined previously to apply for allyl phenyl sulfide was found to prevail also in each of the cases studied (see Table III). The respective rate constants were computed from these data by least-squares analysis of the log of the ratio of the initial concentration of sulfide (C_0) to the concentration of sulfide (C_t) at time t; $\ln C_0/C_t = kt$.

In the cases of phenyl allyl ether kinetics, the workup and analysis of each sample were carried out in the manner described by White.[12] In the cases of the phenyl allyl sulfide kinetics, the workup and analysis of each sample followed the directions given by Kwart and Schwartz.[9] The product composition was shown to consist almost entirely of thiocoumarin and thiochroman with very little phenyl propenyl ether formed, always less than 10% and mostly less than 5% of the total product. Correction of the rate constant (in each case) for the actual amount of propenylization observed was carried out in accordance with the procedure used previously.[9]

Instrumentation and Analytical Procedures. Gas chromatographic quantitative analyses were conducted on a F & M 5750 chromatograph connected to a Hewlett-Packard 3370 A electronic integrator. Standard conditions were as follows: column, 12 ft × $^1/_8$ in., 10% carbowax on chromosorb W; oven temperature, 100 °C (2 min) → (10 °C/min) → 200 °C.

Preparative gas chromatography was performed on a F & M dual column gas chromatograph. Standard conditions were as follows: column, 4 ft × $^1/_4$ in., 10% SE-30 on chromosorb W; oven temperature, 85 °C.

Mass spectral determinations were made by using a Hewlett-Packard 5930 A mass spectrometer equipped with a 5932 data system. The high-precision isotope ratio measurement procedure used was originally described by Kwart and Stanulonis[20] (see also ref 19a) and has been most recently applied by Reimschüssel and Paneth.[21]

Nuclear magnetic resonance spectra confirming the structures of all the substrates used in the kinetic studies were obtained on a Perkin Elmer R-12B spectrometer using Me_4Si as the reference. Infrared spectra were obtained on a Unican SP-100 spectrometer. In all cases the spectral results confirmed those previously obtained by Kwart and Johnson.[22]

Acknowledgment. We are greatly obliged to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

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