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(22) Where it is generally agreed[3a] that neophyl tosylate ionizes with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity.
(23) This speculation is based on the following assumption: $\delta_m(k_\Delta/k_C)^R/\delta_m(k_\Delta/k_C)^N \sim$ constant where $\delta_m(k_\Delta/k_C)^R$ is defined in the text and $\delta_m(k_\Delta/k_C)^N$ is the participation response to medium effect by the phenyl group in neophyl tosylate.
(24) (a) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, **87**, 1280 (1965); (b) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968).
(25) The calculated strain release[26a] in going from starting material to the ring-expanded product is 19.5 kcal/mol which is equivalent to a log ($k_{4\text{-OBs}}/k_{5\text{-OBs}}$) value of 13; the measured value[26b] is −1.
(26) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 193; (b) H. Duivila and W. Masterson, *J. Amer. Chem. Soc.*, **74**, 4953 (1952).
(27) (a) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); (b) W. Pritzkow and K. H. Schoppler, *Chem. Ber.*, **95**, 834 (1962).
(28) D. D. Roberts, *J. Org. Chem.*, in press.
(29) The nearly identical ΔS^* value observed for acetolysis and trifluoroethanolysis of **5**-OBs is an interesting exception to this general phenomenon. This anomolous behavior of ΔS^* is suggestive that more than a change in solvotion effects is involved in the acetolysis and trifluoroethanolysis of **5**-OBs.
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(31) H. Felkin and G. LeNy, *Bull. Soc. Chim. Fr.*, 1169 (1957).
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(33) Near the end of this series of experiments it was found that dilution of the 2-ml aliquots with 5 ml of acetic acid solvent followed by titration as with acetolysis samples gives much sharper end points.

Mechanism of the Catalyzed Thio-Claisen Reaction. Triggering of Concerted Rearrangement Processes

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Received February 14, 1974

Evidence is presented substantiating a thiophenolic intermediate in the thio-Claisen rearrangement of allylic phenyl sulfides under conditions (amine or carboxylic acid solvents at temperatures in the range 220–300°) only recently found to propitiate this reaction. This includes synthesis of the allyl thiophenol intermediate in relatively pure form, and converting it under normal reaction conditions to the same product distribution observed to form directly from the allyl phenyl sulfide substrate. The intermediate thiophenol is found to resist cyclization when present in its anionic form, and this is a basis for trapping it and preventing formation of the normal cyclization products. The intermediate anion is also shown to generate *o*-allyl side products as a result of nucleophilic displacement on the allylic carbon of the substrate. A number of anionic bases, but not their conjugate acids, are also found to catalyze the thio-Claisen, including phenoxide, acetate, and thiophenolate. Unlike the oxy-Claisen, where electrophilic agents are known to be exclusively catalytic, the thio-Claisen appears to be susceptible only to nucleophilic catalysis. This is confirmed by kinetic studies of the concentration rate dependencies (first order in substrate and catalyst) and reactivity as a function of structure among a series of amine catalysts. The relative catalytic efficiencies of the members of this series show no correlation with their base strengths, but do give evidence of a rough parallel with nucleophilicity. However, the scale of nucleophilic activities is very compressed compared to the range of rate variation in normal SN2 displacements, where a considerable degree of nucleophilic bonding is being created in the activation process. These and a number of other observations can be accounted by the proposal of a pericyclic transition state of thio-Claisen rearrangement which has been triggered by a nucleophilic attack at the allylic carbon of the substrate. The effect of the nucleophile is to bring about a small amount of displacement in the electron density of the C–S bond, and formation of a p orbital on the allylic carbon to accommodate the orbital requirements and the geometry of the [3,3] sigmatropic transition state.

The thermolysis of allylic phenyl sulfides[1] stands in contrast to that of their oxygen analogs in experiencing Claisen rearrangements. They exhibit extraordinary thermal stability and undergo propenylization and subsequent cleavage reactions[2,3] only at temperatures approaching 300°. In fact, the possibility of a thio-Claisen rearrangement to compete with degradative side reactions was established only recently (1962).[1,4-6] It was found that in solutions of carboxylic acid[5] or amine[1,4,6,7] solvents a facile rearrangement of Claisen character can be observed. This reaction has now been widely applied and is recognized to be of general preparative interest.[8-11]

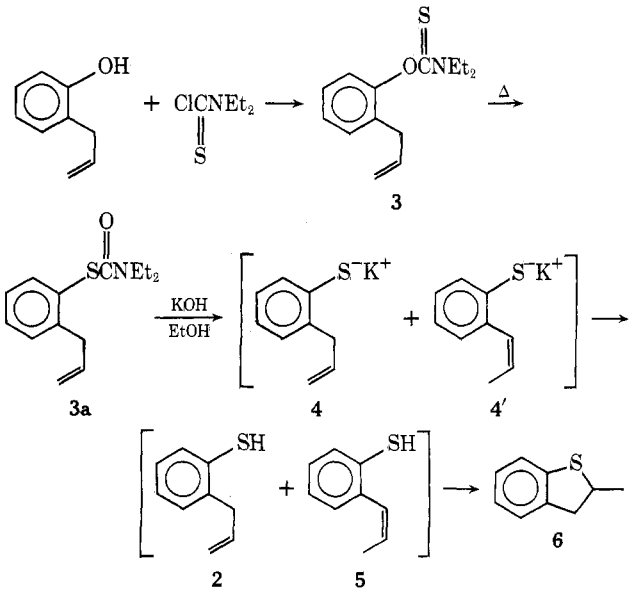
The activation energy[12] for this "catalyzed" thio-Claisen is somewhat greater than for the oxy-Claisen and the products realized are thiocoumarans and thiochromanes which could have arisen from presumed *o*-allylthiophenyl intermediates. In an earlier communication[13] preliminary evidence for this presumption has been described. This is based on trapping some of the intermediate as the *o*-allylmethylthiophenyl ether and preventing cyclic product formation when the reacting mixture is quenched with KOH and CH_3I.

This report is intended to provide full documentation of the evidence bearing on the occurrence of an *o*-allylthiophenol intermediate corroborating the thio-Claisen nature of the catalyzed, thermal rearrangement of allylic phenyl sulfides. Additional lines of experimentation will also be discussed which were directed toward elucidating the role of catalytic agents which are often indispensable to obtaining a thio-Claisen reaction.

Results and Discussion

I. Evidence Substantiating a Thiophenolic Intermediate in the Thio-Claisen Rearrangement of Allyl Phenyl Sulfide (1). A. Cyclization of *o*-Allylthiophenol (2) under Typical Thio-Claisen Reaction Conditions. Independent synthesis of the intermediate **2** was achieved earlier[3] through a two-step reaction involving gas-phase pyrolysis of the *o*-allylthiocarbonate or *o*-allylthiocarbamate, **3**. Hydrolysis of the product, **3a**, in alkaline medium followed by acidification gave rise to **2**. The *o*-allylthiophenol had to be separated from propenylization (**5**) and cyclization (**6**) products, which could not be completely avoided even

Scheme I



under the mildest conditions. This work has now been reviewed; see Scheme I. It is found that the cyclization process, from both thiols **2** and **5**, occurs with great readiness, and is exothermic at room temperature. Acid catalysis of the cyclization reaction is also evident from the fact that neutralization of the potassium thiolates, **4** and **4'**, had to be carried out with the weakest acids to get any significant yield of **2**. However, the thiophenolate anion as its sodio or potassium salt is extremely stable by comparison, and its formation could be quantitatively estimated by admixing with CH_3I and conversion to the unreactive thiomethyl ether. Using $NaOCH_3$ in CH_3OH as the hydrolysis medium and refluxing for 36 hr gives the stable sodio salt **4** in about 90% yield, with the remainder consisting of **4'** and **6**. After the latter are separated by extraction, working in the cold, neutralization is accomplished with dilute acetic acid and the free thiol **2** is obtained for storage at −30° until required.

In earlier experiments when the thiol **2** was heated in quinoline solution from room temperature to reflux, the ratio of thiochroman (**7**) to thiocoumaran (**6**) product was observed to be 4:1. The high tendency of **2** to cyclize (even at ambient) would suggest that this procedure would lead to product compositions which were not strictly comparable to what would form from **2** at the normal temperatures of the thio-Claisen reaction in quinoline (*ca.* 230°). Injecting the thiol **2** into refluxing quinoline, however, would be a more likely way of determining how the putative intermediate behaves on cyclization under the actual thio-Claisen conditions. Table I presents a summary of the results obtained when operating in this fashion. The ratio of **7** to **6** observed (*ca.* 1.44) is very close to the experimental ratio of 1.47 realized from thio-Claisen rearrangement of **1** in refluxing quinoline.

B. Trapping *o*-Allylthiophenol (2).[14-17] To intercept formation of **2** in the course of rearrangement of **1**, two approaches were successfully employed. Both made use of the fact that an aqueous solution of potassium *o*-allylthiophenolate strongly resists the cyclization reaction which takes place so readily in the case of the free thiol.

In the first instance, the reaction in refluxing quinoline was carried out for 1 hr, a time considerably shorter than that required for completion; the mixture was then quenched by addition to 3 *N* aqueous KOH. Neutral and water-insoluble compounds were removed and methyl iodide was added to the basic solution. An immediate reaction occurred to give a small amount of *o*-allylphenyl methyl sulfide as a pale yellow liquid; this accounted for about 5% of the product. In the second approach, **2** was captured as formed *in situ* by adding a strong inorganic base as a trapping agent directly to the quinoline reaction medium; this must inhibit cyclization. Lithium methoxide was chosen, since earlier work with this base had shown that it also produced the least amount of undesirable isomerization of the allyl double bond. The substrate **1** was heated under reflux in the presence of an equivalent amount of lithium methoxide in quinoline. The mixture was quenched and treated as above with methyl iodide. The thiomethyl ether obtained in this reaction accounted for *ca.* 50% of the total thio-Claisen product. These results coupled with the earlier characterization of the cyclization pattern under normal reaction conditions of thiol **2** would seem to substantiate the previous conclusion that *o*-allylthiophenol is formed in the course of rearrangement of allyl phenyl sulfide.

Table I
Cyclization Products Derived from Reaction of Mixtures of 2 and 5 in Refluxing Quinoline[a]

Reactant compositions[b]		Product compositions[b]			
				Ratio 7/6	
2	5	6	7	Uncorrected	Corrected[c]
94.9	5.1	44.4	55.6	1.25	1.41
90.0	10.0	46.7	53.3	1.14	1.45
85.5	14.5	49.4	50.6	1.02	1.45
22.6	77.4	86.7	13.3	0.15	1.43

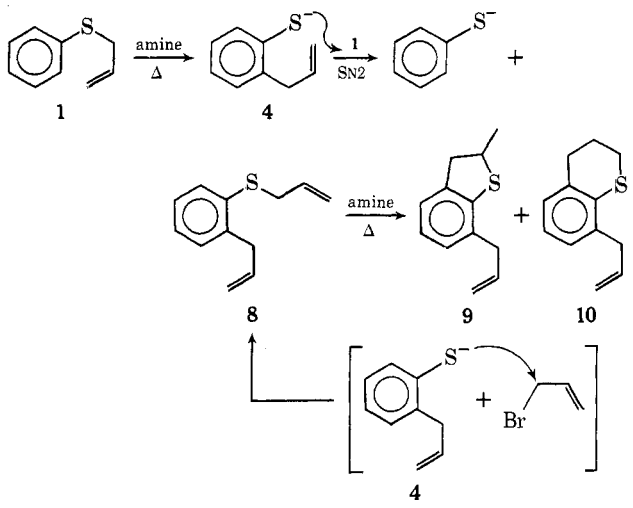
[a] Concentration of reactants 0.8 *M*. [b] Relative concentrations determined by glc analysis of the corresponding thiomethyl ethers. [c] Assumes that **5** cyclizes exclusively to **6**.

II. Isolation and Identification of Side-Reaction Products and Their Significance. Several experiments in which reaction was deliberately terminated prematurely gave indication of an additional product boiling in the range of the normal products **6** and **7**. It became evident that the unknown material, which was formed during the progress of rearrangement of **1**, was accumulated up to a point, but then slowly disappeared as heating continued. It was also evident that the reaction products of this unknown (intermediate) material **8** comprised the series of peaks of higher boiling substances following it in the glc spectrum and accounting for up to 10% of the total product composition. A sufficient quantity of **8** was then isolated for spectroscopic examination and identified as *o*-allylphenyl allyl sulfide. Confirmatory evidence was obtained by its independent synthesis through addition of allyl bromide to aqueous *o*-allylthiophenolate **4**.

A sufficient quantity of the first product peak following **8** was isolated for analytical purposes. The nmr spectrum (see Experimental Section) of this material corresponds to that which would be predicted for 7-allyl-2-methyl-1-thiocoumaran (**9**). It is reasonable to assume that 8-allyl-1-thiochroman (**10**) is one of the constituents of the cluster of four peaks following **8**. Others highly likely to be present are the ortho propenyl isomers of **9** and **10**. The reaction pathways delineated by all these observations are outlined in Scheme II.

It also seems logical to attribute the formation of **8** to a simple S_N2 displacement by intermediate thiolate on the starting sulfide (**1**). This bimolecular reaction accounts for the observed, early accumulation of **8** and its subsequent demise through ultimate thio-Claisen rearrangement to cyclic products. Support for this proposal was found by examining the *neutral* products of thio-Claisen rearrange-

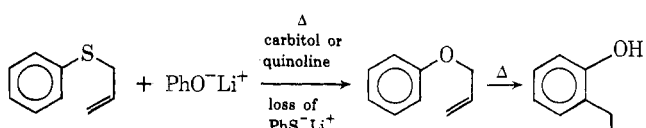
Scheme II



confirming synthesis

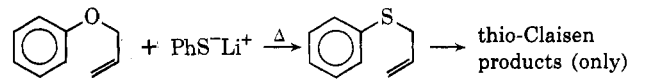
ment under conditions whereby the thiol intermediate 2 was long lived. In the second trapping experiment previously cited, where lithium methoxide was added to the quinoline solution of sulfide, greater than 30% of the extracted neutral products could be accounted for by formation of diallyl derivative 8. The cyclic products 9 and 10, identified by glc retention times, were further observed independently when an authentic sample of 8 was thermolyzed under the usual thio-Claisen conditions (refluxing quinoline).

To further test this interesting SN2 behavior the effect of heating 1 in the presence of lithium phenoxide was examined. Two solvents were chosen: the first, quinoline, to simulate the reaction medium in which displacement was first discovered; the second, diethyl carbitol, a neutral inert solvent in which Claisen rearrangement of allyl phenyl(oxy) ether (as and if it formed) is known to occur readily. The results of these studies are compiled in Table II.



The product compositions from these reactions (shown in Table II) demonstrate that SN2 displacement by phenoxide forming allyl phenyl ether is never realized. A bimolecular side reaction (SN2) involving displacement of thiophenolate anion from the allyl carbon by *thiophenolate anions* in solution has been implicated as the source of diallyl side-reaction products. Yet phenoxide ion is incapable of effecting displacement of the allyl chain. If it had, the products of oxy-Claisen rearrangement would have been readily visible in the glc, since this reaction has a much lower activation energy than the thio-Claisen. Clearly, the bimolecular displacement side reaction occurs only in the presence of very powerful nucleophiles in the medium.

A final experiment illustrates the competition of bimolecular displacement and Claisen rearrangement steps occurring at normal reaction temperatures. Here the effect of heating allyl phenyl *ether* in the presence of lithium thiophenolate in diethyl carbitol at 230° was examined. In sharp contrast to the case cited earlier for phen-



oxide, thiophenoxide readily displaced the allyl side chain to such an extent that only thio-Claisen products were observed; little or no oxy-Claisen products could be detected. These results and their mechanistic implications will receive further consideration in a subsequent section of this report.

III. Role of the Medium. Several alternatives can be considered. (1) A special solvent effect could be operating to complex the double bond in such a way as to inhibit or prevent irreversible isomerization to propenyl and simultaneously to maintain the structural, intramolecular relationships necessary for rearrangement to occur. (2) Basicity of the amine may produce the proper circumstances for rearrangement *via* a proton-transfer mechanism involving the substrate or a reactive equivalent thereof. (3) The nucleophilic character of the amine could be brought to bear to accelerate rearrangement at the expense of isomerization in some as yet undetermined manner.

In the final analysis it was concluded that nucleophilicity was the key parameter. This conclusion was generalized by verifying that rearrangement could be carried out in a neutral, inert solvent so long as the required presence of a nucleophilic agent was satisfied. In the following sections the basis for reaching this conclusion is discussed.

A. Complexation Effect of the Medium. Two alternative ways in which amine could complex with the substrate 1 have been considered previously.[2,3] Both of these visualize an interaction that serves to retain the allylic sulfide configuration and thus promotes rearrangement at the expense of propenylization; *i.e.*, the nature of the substrate–amine complex inhibits propenylization.[18] Evidence is at hand to indicate that very specific effects are involved in promoting and/or preventing propenylization of allylic sulfides.[19,20] Thus, it has been demonstrated that the proper choice of conditions for the hydrolysis of **3a** results in the prevention of extensive propenylization of the carbamate prior to cleavage of the ester link. For example, a reaction medium consisting of ethanolic potassium hydroxide at reflux reduces the purity of the desired *o*-allylthiophenolate anion 4 to only 20%, whereas treatment with sodium methoxide in anhydrous methanol affords 90% of pure 4 after hydrolysis is complete in the same period of time. The limited ability of sodium methoxide in methanol to promote isomerization was corroborated by the observation that heating *o*-allylphenyl methyl sulfide or *o*-allylphenyl methyl ether with

Table II
Reaction of Allyl Phenyl Sulfide and Lithium Phenoxide in Equimolar Amounts (0.8 *M*) at 240° for 3 Hr

Solvent	Product distribution, %				
	Allylic substrate 1	Propenylized substrate 1′	Thiocoumaran 6	Thiochroman 7	Higher boiling products 9 + 10
Quinoline	Trace	4	48	33	10
Diethyl carbitol	5.4	4.6	50.6	24.7	9.9
Quinoline[a]	2	2	33	49	8
Diethyl carbitol[a]	67.2	29.7	Trace	Trace	Trace

[a] Control reaction—no phenoxide added.

Table III
Influence of Equimolar Concentrations of Various Acids on the Isomerization of a 0.1 *M* Solution of Allyl Phenyl Sulfide in Diethyl Carbitol at 240° for 3 Hr

Proton source	Substrate, % Unreacted	Substrate, % Propenylized	Cyclic products[a]
Phenol	70.7	29.3	Trace
Octanoic acid	73.5	26.5	Trace
Thiophenol	50.4	49.6	Trace
Methanesulfonic acid	71.2	28.8	Trace
None	68.9	31.1	Trace

[a] These cyclic materials are the normal thio-Claisen products—thiochromans, thiocoumarans, etc.

quinoline had no effect on these materials. After 6 hr at 240°, circumstances sufficient to complete the rearrangement of allyl phenyl sulfide, analysis of the isolated reaction products by gas chromatography failed to detect the presence of propenyl isomer in each case.

The diminished ability of the amine (as opposed to other bases) to promote the competing propenylization only explains part of its role. It is possible that in the absence of amine solvent propenylization is much faster than rearrangement, so that inhibiting propenylization may make rearrangement a more visible reaction. However, this does not account for the fact that other bases, such as $LiOCH_3$ in quinoline and $LiOC_6H_5$ in carbitol, which promote propenylization, can catalyze rearrangement to the extent that it is the predominant product-forming reaction. In all likelihood, therefore, amine solvents also exert an accelerating effect on the rearrangement reaction while affording no catalysis of propenylization; thus, nearly total conversion to thio-Claisen product is found.

B. Effect of Acids and Their Conjugate Bases in the Medium. It is well known that proton sources influence the kinetic pattern and increase the rate of the oxy-Claisen rearrangement. Kincaid and Tarbell[21] have observed that the rate of rearrangement of allyl *p*-tolyl ether in the absence of solvent gradually increased to about four times the initial rate as the medium changed from ether to phenol. Goering and Jacobson[22] have studied the relative rates of rearrangement of allyl *p*-cresyl ether in various solvents and report a 22-fold difference in the rate in phenol compared with diphenyl ether. Whether the greater rate in phenolic solvent might in some way be connected with hydrogen bonding between the solvent and substrate[22] or be a consequence of acid catalysis[21] is a matter of controversy, but, regardless of the reason, the fact that proton sources influence the oxy-Claisen rearrangement has been established. On the other hand, base catalysis of the oxy-Claisen rearrangement cannot be confirmed.

The possibility of general acid–base catalysis of the thio-Claisen must be considered in view of the fact that the reaction is known to take place readily in both (weakly acid) carboxylic and in (weakly basic) amine media, but is too slow to compete with propenylization in the absence of either of these medium components. Moreover, it has also been shown (above) that bases such as phenoxide anion increase the rate of the thio-Claisen *vs.* propenylization even in neutral media such as diethyl carbitol. However, the data in Table III show that when equimolar amounts of acids of widely varying strength are heated with substrate 1 in a 0.1 *M* solution of diethyl carbitol only propenylization takes place to all intents and purposes. In contrast to these results the conjugate bases of the same acids formed in quinoline, when the quinoline solution was heated under the same reaction conditions (time and temperature), allow nearly total thio-Claisen reaction accompanied by only minor amounts of propenylization.

Table IV
Influence of Various Lithium Salts on Thio-Claisen Rearrangement of Allyl Phenyl Sulfide (1) in Diethyl Carbitol Solution

Products	Lithium salt: Acetate[a]	Lithium salt: Phenoxide[b]	Lithium salt: Thiophenoxide[c]
Recovered substrate, %	55	5.4	15
Propenylized substrate, %	25	4.6	12
Thio-Claisen product, %	20	90	73

[a] 230°, 6 days. [b] 240°, 3 hr. [c] 230°, 6 hr.

The catalytic influence of the anions of these weak acids on the thio-Claisen, independent of the quinoline solvent, was confirmed by allowing 1 to react in the presence of their lithium salts in diethyl carbitol solution, as summarized by Table IV.

It must be emphasized that these lithium salts were only partially soluble in the diethyl carbitol. Since the amount of undissolved salt in each case could not be determined, the data in Table IV cannot be applied for comparison of the catalytic efficiencies of the respective anions. They can be cited, however, to support the conclusion that only the conjugate bases and not the weak acid themselves possess the ability to accelerate thio-Claisen rearrangement *vs.* the competing propenylization.

As noted previously,[2] thiophenol exerts a specific effect in promoting propenylization in both the carbitol and quinoline solutions. Nonetheless, the rearrangement with thiophenol is still considerably faster than propenylization in quinoline, while occurring only to a trace extent in the carbitol. As mentioned above, the phenoxide promotes the rearrangement even in the carbitol. Since the acid phenol does *not* have a catalytic effect in this solvent (Table III), the role of catalyst must be distinctively different from in the oxy-Claisen, where phenolic acids afford significant acceleration in direct proportion to their concentration.[21]

In connection with catalysis by octanoic acid and other carboxylic acids it should be recognized that somewhat forcing conditions (300°) were required to bring about the thio-Claisen. Moreover, a large amount (54%) of propenylization was observed under these conditions. Most probably this reflects the exceedingly low concentration of octanoate anion, which is the actual catalytic species in the presence of an enormous dilution of octanoic acid. The latter is capable of promoting only the degradative propenylization side reaction.

C. Kinetic Factors. In the course of studies establishing the intermediacy of *o*-allylthiophenol in the thio-Claisen rearrangement of allyl phenyl sulfide, it was demonstrated that rearrangement could be effected in a solvent of choice so long as an amine or the conjugate base of an acid was included. This constituted an approach in studying the kinetic influence of a wide variety of organic bases and inorganic bases. The kinetic technique consisted, in general, of subjecting diethyl carbitol solutions, 0.8 *M* in sulfide and 0.8 *M* in amine, to heating at some specified temperature. The reaction mixtures, sealed into small glass tubes, were placed in a suitably controlled constant-temperature bath for a prescribed period of time. At appropriate intervals the tubes were pulled, cooled to room temperature, and analyzed directly using gas chromatographic peak area ratios of sulfide and products compared to an internal standard, 1,3,5- or 1,2,4-trichlorobenzene. Chromatographic columns which afforded complete resolution of solvent, amine, standard, sulfide, and products were selected.

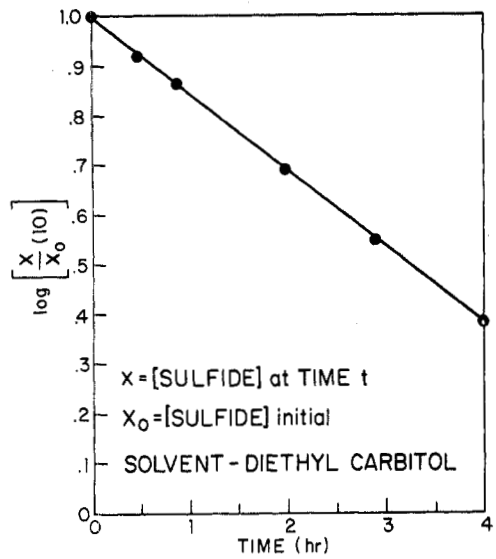


Figure 1. First-order kinetic behavior of allyl phenyl sulfide at 228.7° in the presence of an equimolar amount of pyridine (0.8 mol/l.).

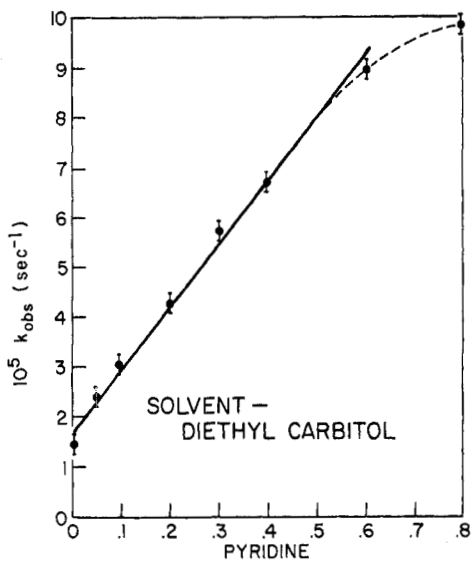


Figure 2. First-order kinetic behavior of allyl phenyl sulfide at 228.7° in the presence of various amounts of pyridine.

In view of earlier studies by Tarbell and Kincaid[21] of the oxy-Claisen rearrangement, first-order kinetics were anticipated. The approach, therefore, was to make this assumption and examine a first-order plot of the disappearance of sulfide. The data for reaction between pyridine and allyl phenyl sulfide are tabulated in Table V and plotted according to a first-order relationship (see Figure 1) in which x_0 is the initial concentration of allyl phenyl sulfide and x is the concentration of sulfide remaining at time t (in seconds). The results show that the reaction is strictly first order over the range studied. It is recognized, however, that the linear (first order) rate of disappearance of 1 represented by the plot in Figure 1 is the sum of two first-order rates, the propenylization rate being only a minor component of the total.

The dependence of rearrangement rate on the concentration of pyridine can be perceived from data summarized in Table VI and plotted in Figure 2. Within a concentration span in which the activity (basicity or nucleophilicity) of the pyridine may be assumed to be relatively constant, the rate depends on the first power of the amine. Furthermore, it remains at constant concentration effectiveness throughout the course of reaction. Only at

Table V
Kinetics of Allyl Phenyl Sulfide Reaction at 228.7°, 0.8 mol/l. in Diethyl Carbitol, in the Presence of 0.8 mol/l. of Pyridine (Calculated as a First-Order Rate)

Time, sec	% reaction	$k_{obsd} \times 10^5$, sec^{-1}
1,800	17.6	10.8
3,000	27.8	10.9
7,200	50.8	9.9
10,200	65.4	10.4
14,400	75.8	9.9
		10.4 av

Table VI
First-Order Rates Determined at Various Pyridine Concentrations in Thio-Claisen Reaction of 1 in Diethyl Carbitol Solvent at 228.7°

[Pyridine], mol/l.	$10^5 k_{obsd}$, sec^{-1}
0.050	2.42
0.100	3.06
0.200	4.33
0.301	5.75
0.401	6.71
0.602	8.90
0.802	9.85
0.000	1.45

the higher amine concentrations, which begin to alter the nature of the medium, and perhaps to produce a somewhat greater degree of propenylization, or both of these influences, can the relative catalyst efficiency be seen (Figure 2) to depart from the linear relationship. Moreover, since a function of the rate of disappearance of substrate is being considered in the plot, there is some significance to be associated with the fact that the intercept ([pyridine] = 0) nearly coincides with the experimental rate of thermal propenylization determined in the absence of catalyst. This result confirms the deduction (made in an earlier section) that within a limited range of concentrations the amine only influences the rearrangement to occur faster than the competing propenylization. Thus, in the absence of amine, propenylization occurs some 10–20 times faster than rearrangement at *ca.* 230° and only a trace of thio-Claisen can be noted. In the presence of moderate amine concentrations rearrangement is accelerated to the point where it is more than ten times faster than propenylization. For practical purposes it can be said that the ability to isolate a better than 90% yield of thio-Claisen products depends on catalysis which accelerates rearrangement by factors of about 20. The difference between being able to realize a practical preparation and failure to achieve the desired reaction is due only to comparatively small catalytic effects.

D. Structure–Rate Relationships among Amine Catalysts. Basicity *vs.* Nucleophilicity as the Rate-Controlling Factor. The effect on rate of eight amines differing in their basicity (in water) by 11 orders of magnitude has been examined. The results are tabulated in Table VII. Apparently there is a complete lack of correlation of rate and basicity. In view of all the evidence presented above and in previous sections of this report, it is reasonable to conclude that basicity is not a significant consideration in understanding the catalytic activity of amines.

On the other hand, reactivity appears roughly to parallel the order of nucleophilicity[23] of the amines listed in Table VII. Two distinct classes of amine nucleophiles have been examined: those (the first five entries) which might be called "normal" and those (the last three entries) which could be classified as "facilitated." Among the latter, the most active catalysts are α nucleophiles

Table VII
Rates of Thio-Claisen Rearrangement of Allyl Phenyl Sulfide in the Presence of Various Amines in Equimolar Concentration (0.8 mol/l.) in Diethyl Carbitol at 228.7°

pK_a	Amine	10^5 k_{obsd}, sec^{-1}
4.63	Aniline	2.52
5.15	*N,N*-Dimethylaniline	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[a]	19.5

[a] 1,4-Diazabicyclooctane; Dabco is the commercial product of Houdry Co.

possessing an enhanced degree of effectiveness in displacement reactions which is independent of the basicity of the attacking atom.[24] In terms of their relative catalytic activities in the thio-Claisen reaction the facilitated nucleophiles are two to six times more effective than the normal. The fact that relative rate is directly correlated with the nucleophilicity of the catalyst is also evident for anionic nucleophiles, as summarized in Table VIII.

However, the reactivity order does not reflect the full range of nucleophilic "power" available for use if the transition state of the thio-Claisen involved the bond-making step of a normal SN2 displacement reaction. In the classical SN2 reaction[24b] the bond between the advancing nucleophile and the reaction seat is at least half complete in the transition state and this bond-forming step is completed in the product. However, in the thio-Claisen the nucleophilic catalyst never completes a bond to carbon. The very small range of reactivites displayed by catalysts, which as nucleophiles in ordinary SN2 displacements show enormously greater reactivity differences, suggests that in the activation step of the thio-Claisen only a very small degree of bonding between the nucleophilic catalyst and the seat of displacement is ever achieved. That is to say, only a small degree of the nucleophilic capabilities of the amine reagents is exerted in the activation step of the thio-Claisen. Consequently, only a small fraction of the rate differences that distinguish these nucleophiles in ordinary SN2 reactions is actually realized. This assumption accounts for the severely compressed scale of catalytic activities as well as the rough parallel with nucleophilicity. Further evidence in support of this conclusion is considered in connection with identifying the seat of nucleophilic attack in the thio-Claisen substrate.

E. Relative Reactivities among Nucleophilic Catalysts of Widely Varying Nature. A series of experiments, designed to estimate the full range of nucleophilic activities available to catalyze the thio-Claisen, involved measurement of the relative rates of rearrangement, each in the presence of known quantities of various catalytic anions. A solution was prepared consisting of diethyl carbitol containing 0.4 mol/l. of allyl phenyl sulfide and 0.4 mol/l. of triethylamine. Aliquots of this solution were made up to 0.4 mol/l., respectively, with acetic acid, phenol, or thiophenol and each was allowed to react in sealed tubes at 227°. The equilibrium concentrations of the anionic nucleophiles and free triethylamine in these reaction mixtures were calculated assuming the following relationships to hold in the neutral solvent.

$$R_3N + HA \rightleftharpoons R_3\overset{+}{N}H + A^-$$

$$K_{eq} = \frac{[R_3NH^+][A^-]}{[R_3N][HA]} = K_a^{HA}/K_a^{R_3\overset{+}{N}H}$$

Table VIII
Relative Reactivity of Allyl Phenyl Sulfide in the Presence of Various Catalysts

Nucleophile	Catalytic[a] relative rate	Displacement[b] relative rate
$C_6H_5S^-$	1.43	16,000
$C_6H_5O^-$	1.33	13.3
CH_3COO^-	1.02	0.67
$(C_2H_5)_3N$:	1.00	1.00[c]

[a] Determined for thio-Claisen rearrangement. [b] Streitweiser's average relative rate of displacement for the nucleophile in a typical displacement process. [c] This value is for trimethylamine.

Table IX
Effect of Methyl Substitution on Reactivity in the Thio-Claisen Rearrangement (0.25 mol/l. Substrate, 0.25 mol/l. Pyridine in Diethyl Carbitol Solvent at 227.8°)

Sulfide substrate	10^5 k_{obsd}, sec^{-1}	Rel rate
Allyl phenyl[a]	3.40	2.1
1,3-Dimethylallyl phenyl[b]	1.65	1.0

[a] Registry no., 5296-64-0. [b] Registry no., 17417-79-7.

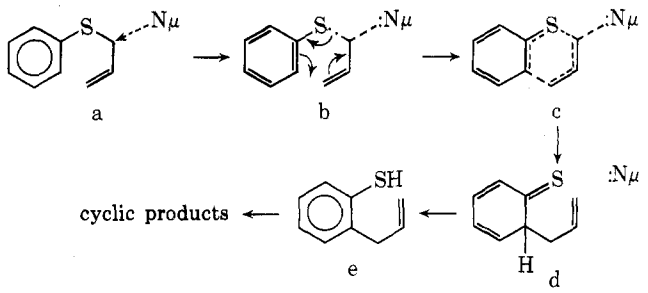
The K_a values used were those reported for pure water.[25] It was considered unlikely that the relative acidities of the three uncharged acids, in relation to the acidity of the triethylammonium ion, would be greatly affected by the carbitol solvent.

The comparative rates were determined by heating the sealed reaction tubes for a specified period of time and determining the relative extent of thio-Claisen rearrangement. Under the chosen reaction conditions it was shown that only an insignificant amount of propenylization was produced. The results are given in Table VIII.

Streitweiser[25] has compiled the list of relative nucleophilic activities by reviewing a multitude of displacement reactions. Included in Table VIII are his values for the "average relative displacements rates" of the nucleophiles examined. Although the catalytic activities of the nucleophiles in the thio-Claisen are in more or less the same order as their nucleophilic activities in the SN2, the range of relative activities is enormously compressed compared to their inherent bond-making capabilities. Thus, the relative activity of thiophenolate and acetate anions in the thio-Claisen is only 1.4, whereas in normal SN2 reactivity this ratio is more than 15,000. This confirms the suggestion that only a small degree of nucleophilic bonding between catalyst and substrate exists in the transition state of the thio-Claisen.

F. The Seat of Nucleophilic Susceptibility. It will be recalled that "diallyl" products such as 8 and 9 can be isolated from thio-Claisen rearrangement. These are most reasonably accounted for on the basis of an act of SN2 displacement on the starting sulfide by the rearrangement intermediate, *o*-allylthiophenol, in the form of its anion. Moreover, when allyl phenyl(oxy) ether was treated with lithium thiophenoxide, a quantitative SN2 displacement, ultimately giving thio-Claisen products, was observed. On the other hand, phenoxide ion was found to be incapable of effecting displacement, but, instead, was shown to be a functioning catalyst for thio-Claisen rearrangement. Both of these observations establish the allyl side chain as the position susceptible to attack. However, this may not be unrelated to the question (previously noted) as to why thiophenolate produces both bimolecular reaction as well as catalysis, whereas somewhat weaker nucleophiles produce only catalysis.

Scheme III
A Proposal for the Mechanism of Thio-Claisen Catalysis



Another line of evidence bearing on this point is concerned with the effect of methyl substitution on the allyl side chain, which was initially examined to ascertain the magnitude of steric factors on the bimolecular kinetics. Under identical reaction circumstances the first-order rate of disappearance of 1,3-dimethylallyl phenyl sulfide[26] was compared with the rate of allyl phenyl sulfide in diethyl carbitol containing an equimolar amount of pyridine. The data listed in Table IX indicate that methyl substitution at the allylic carbon retards the rate by a factor of only about 2 for a reaction taking place at 227°. This is to be compared with a typical displacement at 25° (for example, chloride displacement on alkyl iodide),[27] where the rate ratio of ethyl to isopropyl is 32. However, since the steric rate effect is almost entirely in the entropy term, the rate ratio must be very considerably greater at 227°. It may therefore be estimated that the steric rate effect due to methyl substitution at the allylic carbon in thio-Claisen substrates is only 0.05–0.0005 as great as is observable in a reaction possessing a "full" S_N2 transition state.

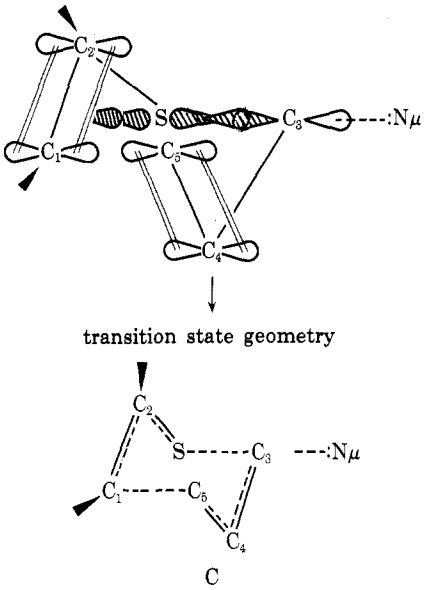
This inference is again to be correlated with the conclusion (reached in a previous section) that the nucleophilic catalyst approaches the rear of the allyl carbon in the act of displacing sulfur from its bond. However, this occurs only to a small fraction of the extent to which bond making and breaking takes place in a typical S_N2 transition state. The smaller extent of Nu–C bond formation in the thio-Claisen thus results in a much smaller steric rate effect than is experienced in the S_N2. Apparently the nucleophile causes only as much displacement of the sulfur from the allylic carbon as is necessary to trigger the concerted events of the sigmatropic rearrangement process.

IV. Proposed Reaction Mechanism. The Nucleophilic Trigger of Sigmatropic Rearrangement. The thio-Claisen is regarded as a typical hetero-Cope[28] reaction, *i.e.*, a concerted, sigmatropic rearrangement following a low-energy pathway as a consequence of orbital symmetry conservation. This thermal reaction can take place at readily accessible temperatures, but all too often it cannot be observed[1,18,29] in competition with the nonallowed[30] propenylization reaction without benefit of a *ca.* 20-fold acceleration by an exclusively nucleophilic, catalytic agent.

The (otherwise) completely analogous oxy-Claisen rearrangement is susceptible only to electrophilic catalysis, in clear distinction to the thio-Claisen, which, as demonstrated here, responds exclusively to nucleophilic agents. In both Claisen cases catalysis has altered the transition state in only a very subtle way. The evidence would seem to suggest that catalysis has not changed the concerted, sigmatropic nature of the reaction, but has merely made it easier to attain its driving force.[28b] Thus, through an understanding of the role of catalyst in a hetero-Cope[28] transition state it may be possible to define the nature of the driving force of this class of reactions.

The mechanistic picture shown appears to fulfill all the specifications and properties of the catalyzed thio-Claisen reaction which are cited above. The mechanism can be most readily considered with the aid of Scheme III, which represents the progress of reaction by a series of glimpses taken along the reaction coordinate. In a the nucleophile (Nu) approaches the rear of the allylic carbon, displacing the bonding electrons of C–S in the direction of the sulfur. This creates a 2p orbital on the allylic carbon which is still mostly coordinated with the sulfur and only slightly with the Nu. This development is diagrammed in b and is shown by Scheme IV in geometric detail as the orbital organization required to produce the arrangement of the critical bonds involved in the concerted transition state C. The transformation of the transition state C to the initial product d destroys all bonding of Nu to the substrate and frees it for further activity. Tautomerism in d produces the final product e and allows subsequent cyclization to the isolated product.

Scheme IV
Nμ: Ordering of Orbital Organization for [3,3]Sigmatropic Rearrangement



The role of the nucleophilic catalyst is, therefore, to aid in developing a 2p center on the allylic carbon which can participate in the pericyclic transition state[31] characteristic of Claisen and other hetero-Cope rearrangements. On this basis it would appear that the driving force of Claisen rearrangement derives from electron displacements in the direction of the heteroatom producing trigonal hybridization of the allylic carbon. In the case of the thio-Claisen there is almost no difference in electronegativity of sulfur and carbon which would create a heterolytic tendency in the C–S bond. Only nucleophilic assistance for this process can be utilized when the C–S bond reaches a critical level of vibrational excitement.

In the oxy-Claisen substrate, where the critical bond is comprised of two atoms (C–O) with a large electronegativity difference, the heterolytic tendency already exists to a significant extent and is enhanced by electrophilic agents which coordinate the oxygen. The rate-enhancing effect of polar solvents reported[22] for the oxy-Claisen also supports this conclusion. Failure to utilize nucleophilic catalysis can therefore be attributed to the fact that oxygen is a poorer leaving group. Thus, the activation energy for S_N2 displacement of C–O to the required degree in the transition state is higher than needed for naturally attaining the critical degree of heterolysis, *i.e.*, development of sufficient p-orbital character at the allylic carbon, in the oxy-Claisen.

In the same vein, failure of the thio-Claisen to utilize electrophilic catalysis may be an indication of unfavorable equilibria, *viz.*, in coordination of acids by sulfur, at the higher temperatures required for the thio-Claisen activated complex. On the other hand, the recently demonstrated[32] susceptibility of the amino-Claisen to electrophilic catalysis, and the increased facility when the nitrogen is in its charged (cationic) form, is to be contrasted with the ordinarily high activation energy[12] and complex character of the uncatalyzed reaction. This is yet another indication of the essentially heterolytic driving force of all Claisen rearrangements localized at the critical bond between the allylic carbon and the hetero atom.

A number of well-precedented mechanistic alternatives have been considered in the course of arriving at the proposal above. Two of the more conventional mechanisms which have been advocated for consideration by referees are treated in some detail in a footnote.[33]

Experimental Section

Analytical samples for spectrophotometric characterization were collected at the thermal conductivity detector exit port of an F and M Model 500 gas chromatograph, using a 10 ft × 0.25 in. stainless steel tube packed with 25% Silicone Oil 200 on 60–80 mesh neutral Chromosorb W or a 6 ft × 0.25 in. copper tube packed with 20% Carbowax 20M on 60–80 mesh Chromosorb W. To ensure purity, all such samples were collected from one column and recollected from the other.

Gas chromatographic quantitative analyses were conducted using an F and M Model 700 Linear-Temperature-Programmed instrument equipped with a flame ionization detector. As the case dictated, a 4 ft × 0.25 in. copper tube packed with either 25% Silicone Oil 200 or 20% Carbowax 20M, on a 60–80 mesh neutral Chromosorb W, was used to effect separation of reactants and products and monitor reaction progress. All chromatograms were obtained in the range of 150–200° using helium as a carrier gas at a flow rate of 60 ml/min (optimum for 0.25 in. column).

Infrared spectra were taken of neat liquid films between salt blocks using a Perkin-Elmer Infracord equipped with sodium chloride optics. Nuclear magnetic resonance spectra were recorded on a Varian A-60, HA-100, or HD-220 nmr spectrometer using tetramethylsilane as an internal standard and carbon tetrachloride as solvent. Mass spectral information was obtained using a C. E. C. 21-110B double focusing high resolution spectrometer. All samples whose elemental analysis is reported below to have been carried out by high-resolution mass spectroscopy (exact mass determination) were analytically pure by accepted gas chromatographic standards.

***N,N*-Diethyl *O*-*o*-Allylphenylthiocarbamate.** A solution of 134.2 g (1.00 mol) of *o*-allylphenol and 166.8 g (1.10 mol) of freshly distilled *N,N*-diethylthiocarbamyl chloride in 1 l. of dry pyridine was prepared. The solution, contained in a 3-l., three-neck, round-bottom flask equipped with a mechanical stirrer, Friedrich condenser, thermometer, and nitrogen inlet, was refluxed for 6 hr. A steady flow of nitrogen was maintained for the entire period.

The mixture was cooled to room temperature and diluted with 1 l. of cold (5°) water. A solution prepared by adding 1 l. of concentrated hydrochloric acid to 1 l. of water was slowly introduced with the aid of a dropping funnel; the flask contents were stirred and cooled during the addition and then transferred to a 5-l. flask. The acidified mixture was continuously extracted with petroleum ether (bp 40–60°) for 24 hr. This extract was washed with five 100-ml portions of water, dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated.

Fractionation of the residue under reduced pressure yielded 201.5 g (80.8%) of a pale yellow liquid boiling at 130° (0.6 mm). The infrared spectrum of a sample of this product was identical with the spectrum determined by Evans[3,34] for this same material prepared by a different route. Particularly significant absorption bands were observed at λ_{max} (film) 1520 cm^{-1} (C–N bending characteristics of a monosubstituted alkene).

***N,N*-Diethyl *S*-*o*-Allylphenylthiocarbamate.** The gas-phase thermal rearrangement of the thiocarbamate was accomplished by introducing a 20% (w/v) toluene solution of the ester dropwise into the uppermost section of a 25-mm Vycor tube held vertically and heated with a temperature-regulated split furnace. The rate of addition was adjusted by a Harvard Compact Infusion Pump-Model 972 and the residence time of the volatilized material was controlled by varying the flow of a stream of dry nitrogen gas sweeping through the heated tube. A water-cooled condenser-receiver assembly attached below the tube served to trap the thermolysis product.

To determine the correct conditions for complete conversion of the carbamate, two methods proved useful. Infrared spectroscopy, the most convenient, was hampered by the presence of residual trace quantities of toluene.

After 36 hr the reaction mixture was cooled to room temperature and poured into 150 ml of water. The resulting cloudy solution was extracted with three 150-ml portions of petroleum ether to remove residual undecomposed starting material and most of the *N,N*-diethyl methyl carbamate formed during hydrolysis. The aqueous layer, which contains dissolved potassium *o*-allylthiophenolate (the desired product) and *o*-propenylthiophenolate, was stored as such under nitrogen.

Identification of Products. *o*-Allylphenyl methyl sulfide had bp 81.5° (2.2 mm); ir 910 (s), 990 (s), 1405 cm^{-1} (s) (monosubstituted alkene); nmr (CCl_4) τ 2.88 (m, 4, ArH), 3.76–4.40 (m, 1, β-CH=), 4.77–5.20 (m, 2, γ-CH=), 6.55 (d, 2, J = 6.5 Hz, ArCH), 7.60 (s, 3, -SCH); mass spectrum (high resolution, 10,000 at 10% valley) molecular ion 164.0671 ± 0.003 (calcd for $C_{10}H_{12}S$, 164.0660). *Anal.*[34] Calcd for $C_{10}H_{12}S$: C, 73.11; H, 7.37; S, 19.52. Found: C, 73.11; H, 7.40; S, 19.36.

***o*-Propenylphenyl methyl sulfide** had ir (film) 960 cm^{-1} (trans double bond); nmr (CCl_4) τ 2.50–3.12 (m, 4, ArH), 3.30 (m, 1, α-CH=), 3.84 (q, 1, J = 7.1 Hz, β-CH=), 7.65 (s, 3, -SCH), 8.10 (d, 3, J = 6.2 Hz, CH_3C=C); mass spectrum (high resolution, 10,000 at 10% valley) molecular ion 164.0662 ± 0.003 (calcd for $C_{10}H_{12}S$, 164.0660).

***o*-Allylthiophenol.** It was not possible to obtain pure analytical data on this substance except by conversion to the methyl sulfide derivative (above). However, by working in solution in the cold it was possible to establish the nmr spectrum, which identifies this product directly (as follows): nmr (CCl_4) τ 2.60–3.30 (m, 4, ArH), 3.80–4.44 (m, 1, β-CH=) 4.84–5.28 (m, 2, $-CH_2$=), 6.62 (d, 2, J = 7 Hz, $ArCH_2$), 6.85 (s, 1, -SH).

Allyl *o*-Allylphenyl Sulfide. This product, bp 88.5–89.5° (0.70 mm), was identified by synthesis as well as by its spectral and analytical data. It was readily prepared in 95% purity by adding allyl bromide to the aqueous basic *S*-carbamate hydrolysate containing (95% pure) potassium *o*-allylthiophenolate. In a manner identical with the reaction with methyl iodide described earlier, the addition of allyl bromide caused an immediate turbidity that coalesced into oily droplets of insoluble product. The allyl sulfide was extracted with petroleum ether and analytical samples were collected from the gas chromatograph: ir 6.09 (m, $C=CH_2$ stretch), 10.05 (s, $C=CH_2$ bending), 10.85 (s, $C=CH_2$ bending), 13.35 μ (s, aromatic); nmr (CCl_4) τ 2.50–3.02 (m, 4, ArH), 3.66–4.44 (m, 2, β-CH=), 4.71–5.20 (m, 4, γ-CH=), 6.43 (d, 2, J = 4.7 Hz, $ArCH_2$); mass spectrum (high resolution, 5000 at base line) molecular ion 190.0819 ± 0.003 (calcd for $C_{12}H_{14}S$, 190.0816).

7-Allyl-2-methyl-1-thiacourmaran. This component was identified, after separation from the total product by glc methods, principally by nmr and mass spectral data: nmr (CCl_4) τ 3.10 (s, 3, ArH), 3.83–4.44 (m, 1, β-CH=), 4.70–5.18 (m, 2, γ-CH=), 6.15 (q, 1, J = 7 Hz, SCH), 6.45–7.39 (m, H-3), 6.75 (d, 7-CH_2), 8.64 (d, 3, 2-CH_3); mass spectrum (high resolution, 5000 at base line) molecular ion 190.0806 ± 0.003 (calcd for $C_{12}H_{14}S$, 190.0816).

Thermolysis of *o*-Allylthiophenol in Refluxing Quinoline. A 50-ml round-bottom flask was charged with 8.5 g of purified quinoline and fitted with a 6-in. straight tube condenser. A micropipet was suspended vertically in the condenser so that its tip was just below the surface of the liquid amine. Dry, oxygen-free nitrogen was introduced through the pipet and the quinoline was heated to reflux after the system had been swept for *ca.* 5 min. *o*-Allylthiophenol (1.5 g) was drawn into a hypodermic syringe and rapidly injected into the refluxing quinoline medium. To isolate products, the cooled reaction mixture was diluted with 150 ml of ether and washed consecutively with three 25-ml portions of 3 *N* HCl, three 25-ml portions of 3 *N* KOH, and three 25-ml portions of water. The ether solution was dried with anhydrous sodium sulfate and concentrated under vacuum. The resultant liquid was analyzed by gas chromatography and its components were trapped from the glc. Product identification was accomplished by a combination of infrared and nmr spectrum matching with authentic samples of 2-methyl-1-thiacoumaran and 1-thiachroman. The presence of these materials was also verified by glc peak enhancement.

Thermolysis of Allyl Phenyl Sulfide in Refluxing Quinoline Containing Lithium Methoxide. A solution of lithium methoxide in quinoline was prepared in the following manner. High-purity lithium metal ribbon (0.09 g, 0.013 mol) was washed free of petrolatum with anhydrous ether, cut into slivers, and dropped directly into a solution of 0.32 g (0.01 mol) of anhydrous methanol in 10 ml of dry ether. A vigorous hydrogen gas evolution was noted. However, the small surface area presented by the slivers of lithium made it unnecessary to cool the reactants. When hydrogen evolution ceased, the mixture was refluxed for an additional 15 min and cooled. Residual unreacted metal particles were removed with forceps. The ether was boiled off with the aid of a nitrogen purge and 8.5 g of purified quinoline was added. Mild heating was continued until all of the ether was displaced and then stronger heating raised the quinoline solution to its boiling point (~241°). As described earlier, 1.5 g of allyl phenyl sulfide was injected into the refluxing quinoline–metholate solution; reflux was continued for 3 hr.

Two sets of products, neutral and base soluble, were isolated. The cooled reaction mixture was transferred to a small separatory funnel containing a solution of 0.6 g (0.01 mol) of KOH in 15 ml of water. The mixture was thoroughly shaken. The aqueous basic layer was separated and washed with two 25-ml portions of ether. These washings were added to the organic layer, which had been set aside. An excess of methyl iodide was added to the aqueous layer, forming a copious white dispersion of methylated thiophenolate product. These methyl sulfides were isolated in the usual manner from ether, giving 0.45 g of a colorless liquid, which was analyzed by gas chromatographic peak enhancement with previously identified samples. The base-soluble products thiophenol (23.3%), *o*-allylthiophenol (54.1%), and *o*-propenylthiophenol (21.6%) were found.

The organic layer was washed free of quinoline in the manner described in earlier experiments and 0.37 g of a pale yellow liquid was obtained as product. Glc analysis in the usual manner afforded the neutral products propenyl phenyl sulfide (27.6%), 2-methyl-1-thiacoumaran (39.9%), 1-thiachroman (2.7%), 7-allyl-2-methyl-1-thiacoumaran (22.8%), and unidentified material (7.0%).

Registry No.—**2**, 6165-54-5; **3**, 6410-53-3; **3a**, 6564-78-9; **5**, 51129-97-6; **6**, 6165-55-5; **7**, 2054-35-5; **8**, 51129-98-7; **9**, 51129-99-8; *o*-allylphenol, 1745-81-9; *N,N*-diethylcarbamyl chloride, 88-10-8; *o*-allylphenyl methyl sulfide, 51130-00-8; *o*-propenylphenyl methyl sulfide, 51130-01-9.

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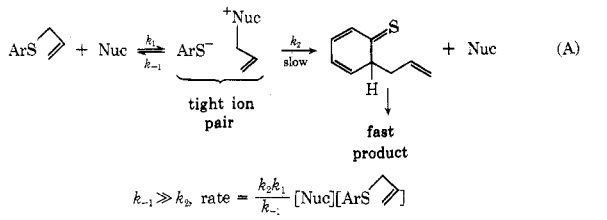
(33) Conventional mechanistic alternatives which do not appear to be in accord with the data are shown below (A and B).



(A)

$$k_{-1} \gg k_2,\ \text{rate} = \frac{k_2 k_1}{k_{-1}}[\text{Nuc}][\text{ArS}\diagup\!\!\!\diagup]$$

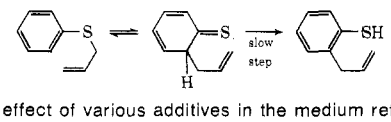
This mechanism fails because it requires a step involving the formation of a full bond between the nucleophile and carbon, which contradicts the evidence presented. The following are three of the points of evidence which exclude this pathway.

(1) If a nucleophilic bond were completed in k_1 we should see a large steric effect arising from substitution of methyls at the seat of displacement (Table IX), and from the size and steric hindrance factor in the structure of the nucleophile. No such correlations can be perceived from the data. Moreover, it would involve a very large coincidence to have k_1 and k_2 remain in essentially constant ratio in order to realize the great attentuation in the range of nucleophilicities, leaving group abilities, and steric effects encompassed by the reagents considered in Tables VII and VIII.

(2) If a bond had been formed resulting in an ion-pair intermediate the relative rates for various nucleophiles still would be enormously different depending on their charge type and leaving-group facilities. Thus, according to mechanism A, when lithium methoxide is the catalyst nucleophile the intermediate is not expected to be an ion pair since the countermolecule is the very volatile allyl methyl(oxy) ether. This boils out of the reaction flask when one tries to heat lithium thiophenoxide with it in carbitol solution; yet when allyl phenyl sulfide is heated in the same flask with lithium methoxide in carbitol, nothing is observed to boil out and normal rearrangement occurs.

When lithium phenoxide is the catalyst, it must be expected in accordance with mechanism A that allyl phenyl ether would be formed as the reaction intermediate. Since the oxy-Claisen has a very much lower activation demand, at the same reaction temperature and medium this ether intermediate should irreversibly undergo much more rapid rearrangement than any thio-Claisen substrate tested in these studies. Since no o-allylphenol or derived coumaran is ever formed in the course of lithium phenoxide catalysis, though the yields of thio-Claisen products are upwards of 90%, it is doubtful that a bimolecular reaction between benzenethiolate anion and allyl phenyl ether, as stipulated in mechanism A, could have been the source of the thio-Claisen rearrangement products observed.

(3) An ion-pair intermediate involving a resonance-stabilized thiophenolate anion cannot account for the absence of even a trace of para thio-Claisen rearrangement product. As shown earlier,[4] when the ortho position is blocked there is no evidence for para rearrangement because the normal dienethione intermediate, which could undergo the para rearrangement, prefers to undergo an alternative sigmatropic rearrangement. This has also been used as evidence for the essentially, concerted nature of the *catalyzed thio-Claisen* rearrangement.



(B)

Here the effect of various additives in the medium reflects the rate of thienolization of the dienethione intermediate relative to its reversal to starting material; *i.e.*, thienolization is either as slow as or slower than rearrangement. However, the most apparent weakness of this mechanism is that it cannot explain the lack of correlation with base strength of the additives. Since general acid–base catalysis cannot be identified as a factor determining the rate of thio-Claisen rearrangement, it is difficult to reconcile this reaction with a mechanism whose slow step involves proton transfer from carbon to sulfur in a triad system.

(34) o-Allylphenyl methyl sulfide has also been prepared in large quantities in analytically pure form: D. Drayer, Ph.D. Thesis, University of Delaware, June 1972.