An analogous procedure has been carried out with similar results in hydrolyzing VIIa to *o*-allylthiophenol and is discussed in a forthcoming article describing the special properties of this product.

Acknowledgment.—We are obliged to the National Science Foundation for Support of the work reported in this article under NSF-GP1177.

The Thio-Claisen Rearrangement. The Mechanism of Thermal Rearrangement of Allyl Aryl Sulfides

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o-Allylthiophenol has been synthesized and shown to cyclize in a typical thio-Claisen reaction medium to give a mixture of products consisting of nearly four parts of thiachroman (**5**) to one part of thiacoumaran (**4**). The thio-Claisen rearrangement of allyl phenyl sulfide affords nearly equal amounts of the same products. The thiachroman and thiacoumaran are not interconvertible under the familiar reactions conditions. These observations rule out the mechanism previously proposed by Meyers, *et al.* Crotyl phenyl sulfide cannot undergo the thio-Claisen reaction under any conditions tried, but crotyl *m*-tolyl sulfide apparently benefits greatly from the nuclear methyl substitution and is readily transformed to the thio-Claisen product. Appropriate methyl substitution in the side chain has a similarly beneficial effect; β-methylallyl phenyl sulfide undergoes the thio-Claisen without use of the high-boiling amine solvent shown to be indispensible in all previous cases we have studied. Control of the product composition resulting from cyclization of *o*-allylthiophenols is attributed to competition of acid-catalyzed and a bridged free-radical chain mechanism. The driving forces, the energy requirements, and the product composition associated with the thio-Claisen rearrangement are discussed in terms of the formation of a proposed thiirane reaction intermediate (**13**).

The current consensus of authors[2,3] discussing the Claisen rearrangement of allyl aryl ethers holds this to be a highly concerted mechanism involving a cyclic transition state. There are several indications, however, that this familiar reaction is tinged with some polar character, including small polar solvent and substituent rate effects.

Various proposals have been advanced in explanation of these polar features of the Claisen activated complex. Cram[4] has suggested that a highly oriented ion-pair relationship is developed in this complex composed of an allylic fragment of carbanion nature and a dienone moiety possessing carbonium ion features. Side-chain substitution effects on the reaction rate have been cited[5] against Cram's proposals and have suggested the appearance of a charge-transfer complex[6] in the transition state. Here the corresponding allylic and dienone fragments are held together by electronic interactions similar to those which have been earlier invoked for the Diels–Alder reaction.[7]

A continuing element of uncertainty in the Claisen mechanism to which considerable discussion has been addressed is the direction of electron flow in the concerted transition state.[8] A concomitant question is the source of driving force that triggers the cyclic electron displacements. One approach to this problem lies in study of the effects produced through change of the heteroatom in the substrate structure. One very interesting study[9] in which oxygen has been replaced by amino nitrogen (the reaction of allylarylamines) has established that the Claisen rearrangement may often be made to take place in the amine substrates, but it possesses a much higher activation energy demand for reasons that have been correlated with bond-order factors in the aromatic ring.

Several previous attempts to bring about the Claisen rearrangement of allyl thiophenyl ethers[10] (which we have designated the thio-Claisen as compared with the oxy-Claisen and amino-Claisen) were proven to have failed.[10b,11] Recently, we have demonstrated[11] that under rearrangement reaction conditions (that are regarded as more or less traditional for the oxy-Claisen[3]) good yields of a reaction product were obtainable with allyl phenyl sulfide. A major product of this reaction, 2-methyl-1-thiacoumaran, was shown to be analogous to the minor product reported originally by Claisen,[12] *viz.*, 2-methyl-1-coumaran, for the reaction of allyl phenyl ether. In view of many demonstrations[13] that both acidic and basic catalysts promote cyclization of *o*-allylphenols to 1-coumarans, it would appear that *o*-allylthiophenol (**2**) had been initially formed through a Claisen rearrangement of the allyl phenyl sulfide. Conceivably, a special facility for cyclization to the thiacoumaran prevented the isolation of the initial thio-Claisen product.

Somewhat after our preliminary communication, a report by Meyers and co-workers[14] substantiated

(1) Part of the work discussed in this article has been abstracted from the Ph.D. Thesis submitted by E. R. Evans in partial fulfillment of the requirements of the University of Delaware, June 1965.

(2) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 655 ff.

(3) D. S. Tarbell, *Org. Reactions*, **2**, 1 (1944).

(4) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2129 (1952); see also D. J. Cram in "Steric Effects in Organic Chemistry." M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 295–303.

(5) (a) W. N. White, D. Gwynn, R. Schlett, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958); (b) W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961).

(6) R. S. Mulliken, *ibid.*, **74** 811 (1952).,

(7) R. B. Woodward, *ibid.*, **62**, 3058 (1942); R. B. Woodward and H. Baer, *ibid.*, **66**, 645 (1944).

(8) For a more extensive discussion, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 644 ff and ref 5.

(9) S. Marcinkiewicz, J. Green, and P. Mamales, *Tetrahedron*, **14**, 208 (1961); *Chem. Ind.* (London), 438 (1961).

(10) (a) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930); (b) E. N. Karaulova, D. Sh, Meilanova, and G. D. Galpern, *Zh. Obshch. Khim.*, **29**, 662 (1959).

(11) H. Kwart and M. C. Hackett, *J. Am. Chem. Soc.*, **84**, 1754 (1962).

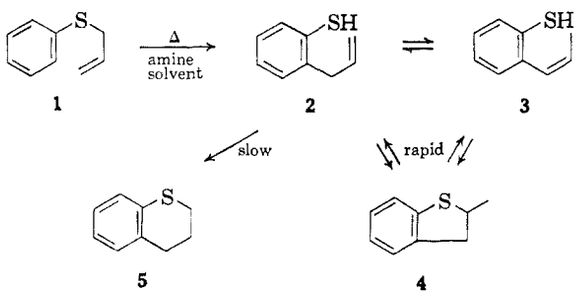
(12) L. Claisen, *Ann.*, **418**, 97 (1919).

(13) (a) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **58**, 2190 (1936); (b) Q. R. Burtz, R. F. Miller, and R. Adams, *ibid.*, **57**, 531 (1953); (c) L. Claisen and E. Tietze, *Ber.*, **59**, 2344 (1926); (d) L. I. Smith, *Chem. Rev.*, **27**, 287 (1940).

the occurrence of thio-Claisen rearrangement. However, a second product was isolated in major amounts from the reaction mixture and identified by these workers as the 1-thiachroman (**5**). They also described the conversion of thiacoumaran (**4**) to thiachroman (**5**) under the reaction conditions and made these observations the basis of a reaction course depicted in Scheme I.

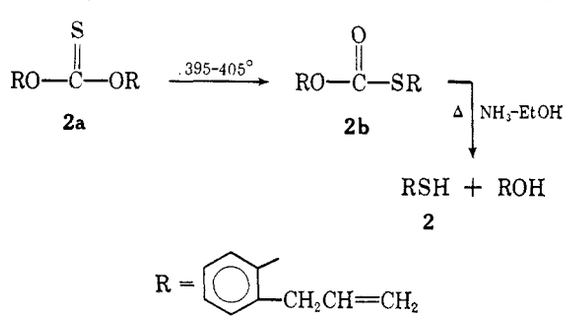
SCHEME I

THIO-CLAISEN MECHANISM OF MEYERS AND CO-WORKERS[14]



At the time that the Note by Meyers and co-workers[14] appeared, we were engaged in synthesizing the *o*-allylthiophenol (**2**). Our objective was to establish its intermediacy in the course of the thio-Claisen reaction through characterization of its properties and reactivity under the conditions that produced the rearrangement of the allyl phenyl sulfide. This undertaking has now been completed and constitutes the basis of this report, together with several other observations we have made of factors governing reactivity and product composition obtainable through thio-Claisen rearrangement of a variety of substrates.

The Synthesis of *o*-Allylthiophenol (2).—The Schönberg rearrangement[15] of O,O-bis(*o*-allylphenyl)thioncarbonate (**2a**) to its corresponding thiolcarbonate (**2b**) proved to be the most productive route to the preparation of *o*-allylthiophenol. The mercaptan **2** was always isolated from a mixture containing the



ROH and the cyclized products [the thiachroman (**5**), and the thiacoumaran (**4**)]. All components of the mixture were effectively separated by means of chromatography on silicic acid. The *o*-allylthiophenol was completely identified by infrared, nmr, and analytical data taken on the pure compound and on the 3,5-dinitrobenzoyl ester made therefrom.

Results

The results have been summarized below in categories that can be more readily recalled in the subsequent discussion section.

A.—Heating of the *o*-allylthiophenol (neat) under distillation conditions (bp 76–80° at 3 mm) resulted only in formation of the thiacoumaran (**4**) and a polymeric pot residue. The effort to distil the thiophenol (**2**) without effecting the ring closure was never successful and **4** was always the *sole* component of the distillate. On dissolving **2** in approximately three times its weight of pure, dry quinoline and heating at 217–241° for 6 hr under a nitrogen blanket (our usual thio-Claisen reaction circumstances), an almost quantitative cyclization resulted. The reaction mixture, consisting of nearly *four* parts of thiachroman (**5**) to *one* part of thiacoumaran (**4**), was separated into its components by chromatographic analysis procedures using a silicic acid column. Under exactly the same reaction conditions, allyl phenyl sulfide (**1**) was converted to a mixture consisting of nearly equal amounts of **5** and **4** (the latter, in fact, slightly predominating). No trace of *o*-allyl- or propenylthiophenol (**2** or **3**) could be detected by careful chromatographic examination of the thio-Claisen reaction mixture.

The compositions of the product mixtures resulting from rearrangement of **1** under some typical reaction conditions are shown in Table I.

TABLE I

Identity of fraction isolated	Compn, %: 6 hr, 217–241°, in quinoline	Compn, %: 6 hr, 219–220°, in 2,6-dimethylaniline
Allylthiophenyl ether (**1**)	None	12
Propenyl thiophenyl ether	None	None
2-Methyl-1-thiacoumaran (**4**)	40	47
1-Thiachroman (**5**)	37	33
Polymeric material	19	6
Thiophenol	4	4

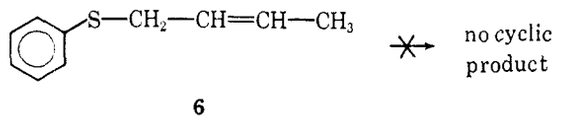
B.—Heating of 2-methyl-1-thiacoumaran (**4**) or of 1-thiachroman (**5**) in high-boiling amine solvent, conditions which led to their simultaneous formation *via* rearrangement of the sulfide **1**, gave no evidence of their interconvertibility. In view of the fact that the thio-Claisen conditions might involve a thiophenol intermediate, whose presence could influence interconvertibility of **4** and **5**, these substances were heated for 6 hr in boiling amine solution to which had been added *o*-thiocresol in equivalent amounts. Again no reaction could be detected representing conversion of **4** to **5** or *vice versa*. These results are at odds with those reported by Meyers and co-workers[14] as well as their basic assumption that **4** gives rise to **5** under the thio-Claisen reaction circumstances.

C.—Crotyl phenyl sulfide (**6**) was heated in a nitrogen atmosphere at constant temperatures ranging between 201 and 294°, neat as well as in a 12% solution of high-boiling amine, for periods of time varying from 2 to 6 hr. In each case, a very small amount of the starting material was cleaved to thiophenol and the remainder was recovered unchanged. Essentially the same result was experienced on gas phase pyrolysis of a toluene solution at *ca.* 420° in a slowly moving nitrogen stream. However, the introduction of a *m*-methyl substituent had a very profound effect. A quinoline solution of crotyl *m*-tolyl sulfide gave more than 80% of pure

(14) C. Y. Meyers, C. Rinaldi, and L. Banoli, *J. Org. Chem.*, **28**, 2440 (1963).

(15) A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930); A. Schönberg, L. Vargha, and W. Paul, *Ann.*, **483**, 107 (1930).

4,7-dimethyl-1-thiachroman (**7**), apparently uncontaminated by any significant amounts of the other possible thiachroman or thiacoumaran isomers. The same rearrangement could not be brought about by thermal means alone (*i.e.*, the absence of high-boiling amine solvent or gas phase pyrolysis).



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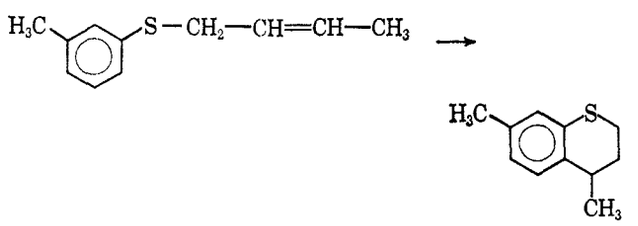

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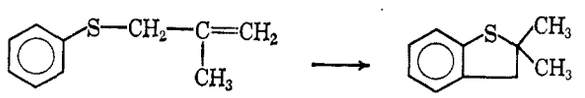
D.—The rearrangement of β-methylallyl phenyl sulfide (**8**) was found to take place at 300° in the absence of high-boiling amine solvent to yield as the exclusive product, 2,2-dimethyl-1-thiacoumaran (**9**). This represents the first instance of a simple allyl phenyl sulfide with which the thio-Claisen rearrangement could be accomplished without the benefit of a high-boiling amine solvent. However, the temperature required was some 60° more than in the reaction of the simplest substrate (**1**) in the presence of amine solvent.

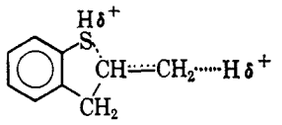


8 **9**

Discussion

The Cyclization Reaction of *o*-Allylthiophenol (2).—The extreme readiness (temperatures below 100°) with which **2** is cyclized to the thiacoumaran (**4**) recalls the earlier studies[12,13] of the formation of coumarans from *o*-allylphenols. It has long been recognized that even weak acids at high temperatures catalyze this reaction very effectively.[13] Recently, Shulgin and Baker[16] have described catalysis of the cyclization process by a high-boiling phenolic medium (*e.g.*, 2,6-xylenol, 73% conversion). High-boiling amine media tended to reduce the conversion to coumaran (*e.g.*, 2,6-xylidene, 32% conversion), whereas the neat material heated at some 10° lower temperature still afforded a 26% conversion, possibly *via* self-catalysis by the initial *o*-allylphenol. Examples of acid-catalyzed additions of thiols to olefins are familiar.[17]

In view of the greatly increased acidity of *o*-allylthiophenol, compared with the (oxy) phenol, a reasonable explanation of the path to thiacoumaran (**4**) formation is at hand. Attack of a proton at the allyl double bond, furthermore, should experience great assistance through participation of the neighboring mercapto group and development of a sulfonium ion transition state (**10**).



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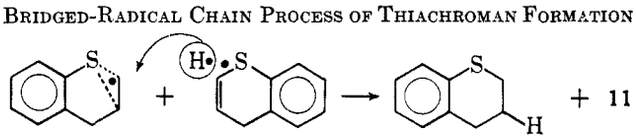
It is at once apparent that the presence of the high-boiling amine (base) would tend to suppress this cyclization mechanism *via* the reduction of acidity originating in the mercaptan function. Under such circumstances we could anticipate the enhancement of a competing radical-addition reaction which is characteristic of mercaptans.[18] This (and related) addition mechanisms, which have been recently formulated by Skell and co-workers[19] with a bridged free-radical intermediate, could be expected to compete because of a structural feature favorable to anchimeric assistance of the proposed process. We may cite as precedence in support of this proposal the observation of Martin and Bentrude[20] of anchimeric acceleration of aroyl per ester homolysis *via* radical bridging by an *o*-thioether function. Analogously we may describe thiachroman formation as a chain process carried by a bridge-stabilized radical (**11**) (Scheme II).

SCHEME II

BRIDGED-RADICAL CHAIN PROCESS OF THIACHROMAN FORMATION



11 **2** **5**

It might be anticipated, also, that the presence of radical-chain catalysts would foster the formation of thiachroman. Evidence for this occurrence is to be found in the composition of the products formed alongside of *o*-allylthiophenol *via* cyclization of **1** at the elevated temperatures required for its formation by Schönberg rearrangement of **2a** (neat). In almost all cases the thiacoumaran (**4**) is the exclusive cyclic side product, but in one instance an almost equal quantity of thiachroman (**5**) was unaccountably obtained. We attribute this unusual result to the presence of adventitious promoters of the radical-chain process.

In the extremely low-acid medium, buffered by the high-boiling amine solvent, the radical-chain mechanism apparently occurs *ca.* four times as rapidly as the acid-catalyzed, ionic process leading to thiacoumaran (**4**). Failure to obtain chromans[16] from *o*-allyl-(oxy-) phenols in the presence of an amine solvent at high temperatures is a reflection of the inability of the oxygen atom to bridge through expansion of its octet (as in the case of the sulfur analog).

Finally, we must consider the possibility that rapid isomerization of the *o*-allyl- to *o*-propenylthiophenol (**3**) could be responsible for formation of all or part of the thiacoumaran product *via* the analogous sulfur

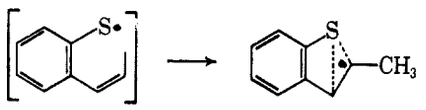
(16) A. T. Shulgin and A. W. Baker, *J. Org. Chem.*, **28**, 2468 (1963).

(17) V. N. Ipatief, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).

(18) R. Back, G. Trick, C. McDonald, and C. Sivertz, *Can. J. Chem.*, **30**, 1078 (1954); M. Onyszchuk and C. Sivertz, *ibid.*, **33**, 1034 (1955).

(19) P. S. Skell, private communication, Feb 1965, and related bridged-radical cases published: P. S. Skell, D. L. Tuleen, and P. D. Reades, *J. Am. Chem. Soc.*, **85**, 2849, 2850 (1963); P. S. Skell and P. D. Reades, *ibid.*, **86**, 3334 (1964); P. S. Skell and R. R. Pavlis, *ibid.*, **86**, 2956 (1964). See also P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

(20) J. C. Martin and W. G. Bentrude, *Chem. Ind.* (London), 192 (1959.)



12

radical bridging (**12**). However, this seems very unlikely since the conditions which are apt to produce the most rapid and extensive isomerization of *o*-allyl to *o*-propenyl, namely, high temperature in basic solvents,[21] *appear to decrease vastly the proportion of thiacoumaran* from what we observe for the low-temperature, neat reaction.

The Paths of Thiachroman and Thiacoumaran Formation in the Thio-Claisen Reaction.—While *o*-allylthiophenol appears to be capable of forming both products, this fact tends to obfuscate the essential features of the rearrangement of allyl aryl sulfides. Clearly, the great disparity in the proportions of these products formed under identical conditions by the allylthiophenol cyclization, on the one hand, and the thio-Claisen rearrangement, on the other, is of key significance. We have concluded that stoichiometric differences of this nature point to a special mechanism for the thio-Claisen rearrangement. Its driving force (in some respects) is unlike that of the oxy- and amino-Claisen rearrangements and, apparently, it possesses a unique transition state.

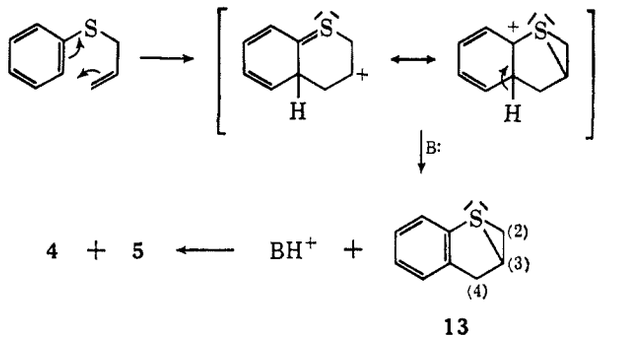
Many of the characteristics of the oxy-Claisen reaction transition state and particularly the polar-substitution effect[5,22] ($\rho^+ = -0.61$) and polar-solvent rate response, suggest a driving force for bond making and bond breaking in the cyclic complex which is triggered by the electronegative properties of the heteroatom. The greater electronegativity of oxygen may account for the lower activation energy of the oxy-Claisen *vs.* the amino-Claisen reaction. Since the electronegativity of sulfur is only comparable with that of carbon, it is difficult to conceive that the thio-Claisen reaction is driven by the same forces. Yet, as we have noted previously, the same kind of substituent effects[5,22] (*m*-methyl increasing the ease of reaction) and polar solvent effects[22] (amino solvents are most often essential to the occurrence of reaction) appear to prevail. We look, therefore, to another source of electron withdrawal and 1,2-bond delocalization from the ring (through the agency of the sulfur) to parallel this activity in the oxy- and amino-Claisen cases. The recognized ability of sulfur to expand its octet affords a good basis for anticipating all the subsequent bond-making and bond-breaking events depicted in Scheme III.

The site to which BH^+ transfers its proton is dependent on the factors determining carbon–sulfur bond breaking in the thiirane intermediate **13**. The nearly equal proportions in which the two products are formed would seem to imply that no factor is dominant in the unsubstituted case. However, we may expect that substitution at C-2, C-3, or C-4 could shift these considerations decisively and create favor for one product or the other. Experiments presently in progress in these laboratories have been undertaken to elucidate the details that control the course of the product-forming step.

(21) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952); D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

SCHEME III

PROPOSED MECHANISM OF THE THIO-CLAISEN REARRANGEMENT



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The inability of either **4** or **5** to isomerize at high temperatures in the presence of amine or amine–mercaptan solvent mixtures can be regarded as evidence against the occurrence of an *o*-propenylthiophenol (**3**) as per Meyer's scheme.[14]

The possibility of such an intermediate in the thio-Claisen has not been ruled out directly. However, the inference drawn (above) regarding the improbability of the *o*-allylthiophenol (**2**) intermediate must also be taken to apply to the propenyl isomer, recognizing that the high temperature and basic solvents induce rapid isomerizations that make the two (**2** and **3**) equivalent as reaction intermediates.[21]

The Magnitudes and Origins of Polar Substituent and Polar Solvent Effects in the Thio-Claisen Reaction.—It seems appropriate to compare the effect of substituting alkyl groups at various positions of the Claisen substrates as we change the heteroatom from oxygen to sulfur. Thus, we perceive that a nuclear methyl in the *meta* position affords only a small rate enhancement for the oxy-Claisen rearrangement.[22] For the corresponding substitution in crotyl aryl sulfide, our data indicate a relatively enormous effect; the thio-Claisen reaction which was immeasureably slow for the unsubstituted crotyl case is notably accelerated by the *m*-methyl substitution (as in crotyl *m*-tolyl sulfide). Seemingly, the nuclear alkyl group is able to provide great facilitation for the 1,2-bond delocalization[9] that ultimately gives rise to a thiirane intermediate like **13** through expansion of the sulfur octet. Apparently, the substituent response is much greater in the thio-Claisen rearrangement because of the greater electron demand identified with this difference in driving force.

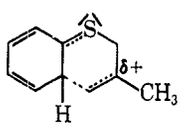
Clearly, methyl substitution at the γ-carbon creates much greater inhibition in the thio-Claisen than the oxy-Claisen; crotyl phenyl sulfide fails to rearrange under all chosen conditions. We may attribute this greater sensitivity to steric influences prevailing in the thio-Claisen to a greater degree of concertedness in bond making and bond breaking. This seems to be particularly the case where the aromatic ring is unaided in its ability to accept 1,2-bond delocalization, but, when the assistance of a ring methyl group is available, the requirement for concertedness of the transition state is greatly diminished. Put another way, the favorable *m*-methyl substitution permits a change in the tempo of bond making and breaking in the transition state and, consequently, an opportunity to cir-

(22) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

cumvent the steric difficulties associated with the necessity for completely concerted charge-transfer events.

A methyl group at the β position has the ability to aid the thio-Claisen transition state in several ways (see below). It is, therefore, not surprising that an extraordinary effect is realized through this substitution. Ordinarily, the thio-Claisen does not occur without the benefit of a high-boiling amine solvent, whereas the oxy-Claisen gains little in the way of rate acceleration from these polar solvents. This can be taken as an indication of the greater need for solvation and assistance for charge transfer in the thio-Claisen activated complex. The influence of the β-methyl substituent is so large that reaction in β-methylallyl phenyl sulfide can take place without the amine solvent. Of course, the thio-Claisen reaction can be realized at even lower temperatures in the presence of amine solvent.[23]

The effect of β-methyl in lowering the activation energy demand is traceable to the existence of two important factors in the cyclic transition state (**14**): (a) the requirement to attain a six-membered arrangement which imposes restraints on the motions of several bonds; and (b) the development of positive charge at the β position in this transition state (**14**).



The two requirements are better satisfied when methyl replaces hydrogen at C-3. Sufficient bulk is provided to inhibit free rotations in both ground and activated states. Thus, the attainment of the structure of the cyclic complex and the development of positive charge is better tolerated at C-3 as a direct result of this substitution.

Experimental Section

General.—Melting points were determined on a Fisher-Johns block and are corrected. Boiling points have not been corrected. Nmr spectra were determined in deuteriochloroform (unless otherwise specified) on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

***o*-Allylthiophenol** (**2**).—O,S-Bis(*o*-allylphenyl)thiolcarbonate[24] (18.4 g) and 7.8 ml of ammonium hydroxide (30% in 100 ml of ethyl alcohol) was heated at 130–150° for 4 hr in a 250-ml Pyrex pressure bottle. The reaction mixture was acidified, the solvent was removed under reduced pressure, and the residue was taken up in ether and dried over anhydrous magnesium sulfate.

After filtering, the ethereal solution was evaporated to give a mixture (17.3 g) of *o*-allylphenol and *o*-allylthiophenol (band at 2600 cm^{-1}). The phenol–mercaptan mixture was chromatographed over silicic acid. Typical data taken for several different runs are given in Table II.

A crystalline material was obtained from *o*-allylthiophenol and 3,5-dinitrobenzoyl chloride.[25] The compound was recrystallized from ethanol to give *o*-allylphenyl 3,5-dinitrothiolbenzoate, mp 148.5–149.0°.

Anal. Calcd for $C_{16}H_{12}N_2O_5S$: C, 55.70; H, 3.49; N, 8.14; S, 9.30. Found: C, 55.66; H, 3.46; N, 8.12; S, 9.34.

The infrared spectrum of the thiolbenzoate has an absorption at 1575 cm^{-1} (C=O).

TABLE II

Mixture	Wt, g: *o*-Allylphenol	*o*-Allylthiophenol	2-Methyl-1-thiacoumaran	1-Thiachroman
4.5	1.9	0.7	1.5	...
5.0	1.7	0.9	0.6	...
10.0	4.3	1.0	3.4	...
10.3	4.2	2.12	0.51	1.79

Pyrolysis of *o*-Allylthiophenol.—A mixture of 1.5 g (0.01 mole) of *o*-allylthiophenol and 5.0 g of freshly distilled quinoline was refluxed for 6 hr under an atmosphere of nitrogen. The pyrolysate was taken up in ether and washed with aqueous hydrochloric acid, and the ethereal layer was dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue (1.4 g) was chromatographed on 30 g of silicic acid to give 0.3 g of 2-methyl-1-thiacoumaran and 1.1 g of 1-thiachroman.

Pyrolysis of 2-Methyl-1-thiacoumaran (**4**). **A.**—A heavy Pyrex tube (18 mm i.d. × 17 cm) fitted with a pressure cap was used for the pyrolysis of 4.3 g of **4** at 294–300° for 3.5 hr. The residue was taken up in ether and extracted with aqueous sodium hydroxide, and the ethereal layer was dried over anhydrous magnesium sulfate. The solvent was evaporated to give 3.8 g of an oil, which on distillation yielded 2.9 g of starting material, bp 112–115° (15 mm), $n^{23.0}D$ 1.5944. No other material was isolated from the base extracts.

B.—A mixture (1.5 g) of **4** and 4.0 g of distilled quinoline was heated in a Pyrex tube at 300–315° for 10 hr. The pyrolysate was taken up in ether, washed with aqueous hydrochloric acid (6 *N*), and extracted with sodium hydroxide (10%), and the ether layer was finally dried over anhydrous magnesium sulfate. Only starting material was recovered from this treatment.

C.—A mixture of 1.4 g of **4**, 0.45 g of *o*-thiocresol, and 4.5 g of quinoline (freshly distilled) was refluxed under nitrogen for 6 hr. The residue was dissolved in ether, washed with aqueous hydrochloric acid (6 *N*), extracted with sodium hydroxide (10%), and finally dried over anhydrous magnesium sulfate. The solvent was evaporated to yield 0.98 g of starting material (**4**).

Pyrolysis of 1-Thiachroman (**5**).—A mixture of 1.01 g of thiachroman, 0.64 g of *o*-thiocresol, and 5.5 ml of quinoline was refluxed under nitrogen for 6 hr. The residue was dissolved in ether, washed with aqueous hydrochloric acid (6 *N*), and extracted with sodium hydroxide (10%), and the ether layer was dried over anhydrous magnesium sulfate. After filtering, the solvent was evaporated to yield only starting material.

Synthesis of Allyl Phenyl Sulfide.—Thiophenol (48.2 g) was added with stirring to a solution of sodium ethoxide (10.0 g of sodium metal in 200 ml of absolute ethanol). This mixture was cooled to 0° and 67.0 g (0.94 mole) of allyl chloride was slowly added. The reaction mixture was stirred for 1 hr with cooling; the bath was removed and stirring was continued for 24 hr at room temperature. The solvent was evaporated and the residue was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 63.7 g (94.0%) of a yellow oil which on distillation yielded 58.0 g (85.5%) of a colorless liquid, bp 84–86° (4.9 mm), $n^{25.2}D$ 1.5732 (lit.[26] $n^{20.0}D$ 1.5753).

The infrared spectrum of allyl phenyl sulfide has absorptions at 1650 (C=C), 990, and 917 cm^{-1} (CH out of plane) for allyl-type unsaturation.

The nmr spectrum of allyl phenyl sulfide (neat) showed a split peak at τ 6.64 for the $-CH_2-$, a triplet at τ 5.0 ($=CH_2$), a series of peaks split between τ 2.7 and 3.01 for the lone β proton, and the aromatic ring protons split between τ 2.7 and 3.01.

Rearrangement of Allyl Phenyl Sulfide.—Allyl phenyl sulfide (30.0 g) and 26.0 g of freshly distilled quinoline were refluxed under nitrogen at 229–241° for 7 hr. The pyrolysate was taken up in ether, washed with aqueous hydrochloric acid (6 *N*), extracted with sodium hydroxide (10%), and then dried over anhydrous magnesium sulfate.

The base extracts were combined, acidified, and extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. After filtering, the solvent was evaporated to yield 1.1 g of thiophenol.

(23) Unpublished results of M. Cohen in these laboratories.

(24) The preparation of this compound is discussed in the preceding article: H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).

(25) G. F. Grillot, H. R. Felton, B. G. Garrett, H. Greenberg, R. Green, R. Clemente, and M. Moskowitz, *J. Am. Chem. Soc.*, **76**, 3969 (1954).

(26) A. C. Cope, D. E. Morrison, and L. Field, *ibid.*, **72**, 59 (1950).

TABLE III

SOME TYPICAL RESULTS ON PYROLYSIS OF β-METHYLALLYL PHENYL SULFIDE

Thioether, g	Temp, °C	Time, hr.	Thiophenol, g	Product	% conversion
3.0	295–300[a]	4.5	0.31	2,2-Dimethyl-1-thiacoumaran	56.3
5.0	295–300[a]	1.25	0.51	2,2-Dimethyl-1-thiacoumaran	52.0
4.0	265[b]	2	0.40	Starting compound	0
15.0	228–242[c]	5	1.20	Tars, some starting compound, and unidentified residue	0
5.0	400[d]	Short contact time	0.52	Starting compound	0

[a] Reference 1. [b] Sealed tube reaction. [c] Reflux with 2,6-dimethylaniline. [d] Thermal vapor phase in toluene.

The solvent was evaporated from the original ether solution to give 28.7 g of a red oil which was chromatographed in two equal portions on 250 g of silicic acid.

(1) Elution with pentane–benzene (1:1–1:4) gave 11.74 g of 2-methyl-1-thiacoumaran. The 2-methyl-1-thiacoumaran-1,1-dioxide (from ethanol) melted at 115–116.0° (lit.[11] mp 115.0–115.5°).

(2) Elution with benzene–ether (5:0–4:1) gave 10.86 g of crude **5**. Distillation of 4.0 g of **5** in a short-path distillation apparatus (bath temperature 85–89°) at 0.2 mm gave 3.5 g of thiachroman, $n^{27.0}$D 1.6106. The thiachroman 1,1-dioxide (from ethanol) melted at 88–89° (lit.[27] mp 88–89°).

(3) Elution with benzene–ether (3:2–2:3) gave 4.92 g of polymeric material.

(4) A black polymeric residue (0.93 g) was eluted with ether–methanol (5:0–4:1).

A repeat of the above reaction with 2,6-dimethylaniline gave similar results.

The nmr spectrum of 2-methyl-1-thiacoumaran showed a split peak at τ 8.66 for the C-2 methyl group, a group of 17 peaks split between τ 5.96 and 7.59 (thiopyran ring protons), and the aromatic ring protons split between τ 2.76 and 3.05.

The nmr spectrum of 1-thiachroman showed a peak split four times for the α-CH_2 group at τ 8.06, six peaks split between τ 7.03 and 7.5 (β- and γ-CH_2–), and the aromatic ring protons split between τ 2.95 and 3.18.

The nmr spectrum of 1-thiachroman 1,1-dioxide showed four peaks for the α-CH_2– at τ 7.55, six peaks split between τ 6.55 and 7.23 (β- and γ-CH_2–), and the aromatic ring protons split between τ 2.02 and 3.0.

The nmr spectrum of 2-methyl-1-thiacoumaran 1,1-dioxide showed a split peak for the C-2 methyl at τ 8.50, 11 peaks split between τ 6.25 and 7.31 (thiopyran ring), and the aromatic ring protons split between τ 2.15 and 2.75.

Synthesis of Crotyl Phenyl Sulfide.—Thiophenol (60.8 g) was added with stirring to a solution of sodium methoxide prepared from 12.65 g of sodium and 300 ml of anhydrous methanol. The reaction mixture was cooled to 0° by means of an ice–water bath, and crotyl chloride, 50.0 g (0.55 mole), was slowly added to the mixture while cooling was maintained. The mixture was cooled and stirred for 1 hr, the bath was removed, and the flask was allowed to remain at room temperature for 24 hr. After filtering, the filtrate was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 83.1 g (99.1%) of an oil which was distilled to yield 71.2 g (85%) of a colorless liquid, bp 82–83° (0.9 mm), $n^{22.0}$D 1.5694 (lit.[26] $n^{25.0}$D 1.5680).

Preparations to Confirm the Structure Assigned to 2-Methyl-1-Thiacoumaran. Synthesis of 2-Methyl-1-Thiaindan 1,1-Dioxide.—A solution of 120.1 ml of butyllithium–hexane (15%) and 300 ml of anhydrous diethyl ether was cooled to a −10° in an ice–hydrochloric acid bath. At equilibrium, 19.3 g (0.144 mole) of benzothiophene in 150 ml of diethyl ether was slowly added with stirring during a period of 30 min. The mixture was cooled and stirred for 20 min, and 17.3 g (0.137 mole) of dimethyl sulfate in 100 ml of diethyl ether was slowly added with stirring. The mixture was cooled and stirred for 1 hr, the bath was removed, and the contents of the flask were refluxed for 30 min. The product was treated with sodium ethoxide (1.0 g/100 ml of ethanol) and water and finally dried over anhydrous magnesium sulfate. The solvent was evaporated to yield 20.63 g (97.0%) of an oil, which on distillation gave 16.53 g (77.7%) of 2-methyl-1-thiaindene, bp 84–85° (2.7 mm), mp 51–52° (cor) (lit.[28] mp 51–52°).

Treatment of **4** (14.3 g) with 64.5 ml of hydrogen peroxide in 300 ml of glacial acetic acid gave 6.1 g (35.1%) of 2-methyl-1-thiaindene 1,1-dioxide, mp 108–110°.

Reduction of this sulfone (2.3 g) by 0.7 g of 5% palladium-on-carbon catalyst in 120 ml of anhydrous ethyl alcohol under 750 psi of hydrogen at 22° for 10 hr gave 1.8 g (63.6%) of 2-methyl-1-thiacoumaran 1,1-dioxide, mp 115.0–116.0° (lit.[28] mp 115.0–115.5°).

The nmr of the hydrogenated sulfone showed a peak at τ 8.54 (C-2 methyl),[11] a series of peaks split between τ 6.26 and 7.46 (C-2 and C-3 protons), and finally the aromatic ring protons split between τ 2.20 and 2.78.

Pyrolysis of Crotyl Phenyl Sulfide.—Crotyl phenyl sufide (5.0 g) was pyrolyzed in a sealed Pyrex tube at 232–250° for 2.5 hr. The pyrolysate was taken up in ether, extracted with sodium hydroxide (10%), and dried over anhydrous magnesium sulfate. The base extracts were combined, acidified, and extracted with ether. The etheral extracts were combined and dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to give 0.32 g (6.4%) of thiophenol.

The solvent was evaporated from the original ether layer to give 4.5 g of a red oil, which on distillation yielded 4.1 g (82%) of crotyl phenyl sulfide, bp 70–71° (1.4 mm), $n^{25.0}$D 1.5681.

A repeat of the above reaction with 5.0 g of crotyl phenyl sulfide and 30.0 ml of N,N-dimethylaniline at 250° for 2.5 hr gave 0.3 g (6.0%) of thiophenol and 4.1 g (82%) of starting material.

Refluxing of crotyl phenyl sulfide (10.0 g) with 50 ml of quinoline under nitrogen at 222–245° for 3 hr gave 0.3 g (3.0%) of thiophenol and 7.48 g (74.8%) of starting compound.

Synthesis of Crotyl *m*-Tolyl Sulfide.—The reaction of *m*-tolyl mercaptan with crotyl chloride was carried out according to the procedure of Cope, Morrison, and Field[26]: bp 85–87° (0.6 mm), $n^{23.0}$D 1.5627.

The nmr spectrum of crotyl *m*-tolyl sulfide shows a split peak at τ 8.5 (terminal $-CH_3$), a singlet at τ 7.85 (ring $-CH_3$), a peak at τ 6.63 ($-CH_2$–), and a peak split six times at τ 4.53 for the olefinic protons. The aromatic ring protons are split between τ 2.83 and 3.16.

Pyrolysis of Crotyl *m*-Tolyl Sulfide. A.—Crotyl *m*-tolyl sulfide (5.4 g) was refluxed under nitrogen for 5 hr at 253–263°. The pyrolysate was dissolved in ether, extracted with sodium hydroxide (10%), and dried over anhydrous magnesium sulfate. The base extracts were acidified and extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 0.7 g of *m*-tolyl mercaptan. The original ethereal layer was evaporated to yield 3.3 g of starting compound.

B.—Crotyl *m*-tolyl sulfide (6.0 g) was pyrolyzed in a Pyrex tube at 281–294° for 4 hr to give 0.61 g of *m*-tolyl mercaptan and 5.06 g of crotyl *m*-tolyl sulfide.

(27) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

(28) E. N. Karaulova, D. Sh. Meilanova, and G. D. Galpern, *Zh. Obshch. Khim.*, **27**, 3034 (1937).

C.—Crotyl *m*-tolyl sulfide (3.4 g) and 15.0 g of distilled quinoline was refluxed under nitrogen for 6 hr at 234°. The pyrolysate was taken up in ether, washed with aqueous hydrochloric acid, extracted with sodium hydroxide (10%), and dried over anhydrous magnesium sulfate. The base extracts were acidified and taken up in ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. After filtering, the solvent was evaporated to give 0.24 g (7.1%) of *m*-tolyl mercaptan. Evaporation of the solvent from the original ether solution gave 2.81 g (82.1%) of an oil, which on distillation yielded 1.82 g of 4,7-dimethyl-1-thiachroman, bp 81–83° (0.8 mm), $n^{24.0}$D 1.5716.

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91; S, 17.99. Found: C, 74.06; H, 7.72; S, 18.06.

The nmr spectrum for 4,7-dimethyl-1-thiachroman showed ten peaks split between τ 8.12 and 9.26 attributed to the C-4 methyl, a singlet at τ 7.86 for the C-7 methyl, 13 peaks split between τ 6.12 and 7.5 for the thiopyran ring, and finally the aromatic ring protons split between τ 3.01 and 3.44.

Synthesis of β-Methylallyl Phenyl Sulfide.—The reaction of thiophenol with β-methylallyl chloride was carried out according to the procedure of Cope, Morrison, and Field[26]: bp 89° (3.4 mm), $n^{23.5}$D 1.5605.

The nmr spectrum (neat) showed one peak for methyl at τ 8.24, a singlet for methylene at τ 6.61, a singlet at τ 5.22 for the terminal $=CH_2$, and the aromatic ring protons split between τ 2.58 and 2.99.

Pyrolysis of β-Methylallyl Phenyl Sulfide.—β-Methylallyl phenyl sulfide (6.0 g) was heated in a Pyrex tube at 310° for 1.75 hr. The pyrolysate taken up in ether, extracted with sodium hydroxide (10%), and dried over anhydrous magnesium sulfate. These extracts were combined, acidified, and extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to yield 0.3 g (5.0%) of thiophenol. Table III shows results from several runs.

The solvent was evaporated from the original ether layer to give 5.5 g (91.4%) of a red oil, which on distillation yielded 3.1 g (51.0%) of 2,2-dimethyl-1-thiacoumaran, bp 102–105° (2.4 mm), $n^{26.0}$D 1.5625.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.10; H, 7.50; S, 19.50. Found: C, 72.93; H, 7.60; S, 19.25.

The nmr spectrum showed a singlet for one methyl group at τ 9.01, a singlet for the other methyl at τ 8.16, a methylene peak at τ 7.25, and the aromatic ring protons split between τ 2.67 and 2.90.

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Observations Regarding the Mechanism of Olefin Epoxidation with Per Acids

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A strong similarity is to be observed between the reactivity parameters and general kinetic characteristics of the two typical olefin reactions, epoxidation with per acids and adduct formation with 1,3-dipolar reagents. This comparison is made the basis for proposing an epoxidation mechanism involving 1,3-dipolar addition of a hydroxycarbonyl oxide reagent (derived from the per acid) to the olefinic dipolarophile. Direct experimental evidence which can be construed to support this proposal has been obtained in studies of cases where a carbonyl oxide, generated from a molozonide, can be displaced from its association with the indigenous carbonyl component by the (added) olefin. In such cases a good yield of epoxide can be realized. The epoxidizing activity of other agents (which do not form per acid under the reaction conditions) can also be reconciled with a carbonyl oxide intermediate. Other details of the proposed epoxidation mechanism are also discussed.

The "molecular" mechanism of epoxidation by per acids, first suggested by Bartlett[1] and developed by others,[2] has been a very useful guide for interpreting the course of many epoxidations reported in the literature of the last decade.[3] However, it must be recognized that very important advances in our understanding of the details of molecular mechanisms (in general) have recently developed from the elegant studies of Huisgen and his co-workers.[4] 1,3-Dipolar addition reactions[5] comprise one of the most typical classes of "molecular" reaction mechanisms. Furthermore, many of the reactivity parameters and general kinetic characteristics which have been identified by various groups of workers[2,3] in studies of the per acid epoxidation mechanism show strong parallelism to the related properties of 1,3-dipolar addition examples studied in the same depth.[4]

The relatively small negative value of the Hammett ρ constant (−0.8) has been interpreted by Lynch and Pausacker[2a] as supporting the Bartlett mechanism.[1] However, Criegee[6] has shown that the reaction of olefins with ozone, a reaction recognized as possessing a typical 1,3-dipolar mechanism, is also characterized by a relatively small (olefin) substituent effect.[6,7] The noted absence of general acid catalysis and neutral salt effects,[2] which was also construed by Lynch and Pausacker[2a] as support for the accepted molecular mechanism,[1] is quite in keeping, as well, with the concerted transition state of a 1,3-dipolar addition course.[4]

At first glance, the relatively low response of rate to solvent polarity, established by Huisgen and coworkers[4] for the general case of 1,3-dipolar addition and by others[8,9] for the case of molozonide formation

(1) P. D. Bartlett, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(2) (a) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); (b) see also N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964); M. Vilkas, *Bull. Soc. Chim. France*, 1401 (1959).

(3) For reviews of the earlier literature and earlier interpretations attributing electrophilic character to the epoxidation mechanism, see D. Swern, *Org. Reactions*, **7**, 378 (1953); *J. Am. Chem. Soc.*, **69**, 1692 (1947); A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).

(4) See, for a complete discussion, reviews by R. Huisgen: (a) *Angew. Chem.*, **72**, 359 (1960); (b) *Proc. Chem. Soc.*, 357 (1962); (c) *Ann.*, **658**, 169 (1962); (c) *Angew. Chem.*, **75**, 604 (1963); (e) *ibid.*, **75**, 742 (1963).

(5) L. I. Smith, *Chem. Rev.*, **23**, 193 (1938).

(6) For a thorough discussion of the mechanism of ozonolysis and references to the experimental basis of these conclusions, see (a) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957); (b) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(7) T. Vrbaski and R. J. Cvetanović, *Can. J. Chem*, **38**, 1053 (1960).

(8) F. L. J. Sixma, H. Boer, and J. P. Wibaut, *Rec. Trav. Chim.*, **70**, 1005 (1951).

(9) T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **82**, 269 (1960).