The Thio-Claisen Rearrangement. Further Studies of the Thermal Rearrangement of β-Methylallyl Phenyl Sulfide

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The neat pyrolysis of β-methylallyl phenyl sulfide has now been shown to produce none of the thio-Claisen rearrangement products, whereas the reaction even at much lower (than usual) temperatures in quinoline solution occurs with formation of both thiachroman and thiacoumaran products. The composition of the neat pyrolysis product has been shown to be a function of time and temperature. The principal components have been identified as phenyl isobutyl sulfide, phenyl isobutenyl sulfide, diphenyl sulfide, thiophenol, and hydrocarbon tars, as well as a minor amount of diphenyl disulfide. These data have been reconciled with a plausible mechanism (Scheme I) initiated by isomerization of β-methylallyl to isobutenyl sulfide. The surprising formation of diphenyl sulfide from pyrolysis of both thiophenol and diphenyl sidulfide has received attention in view of previous reports of the formation of thianthrene under thermolytic conditions. Evidence has also been presented which suggests that the two cyclic products of a thio-Claisen rearrangement, the thiacoumaran and the thiachroman, both arise from two different reaction intermediates, a thiirane and an *o*-allylthiophenol. These intermediates appear to be formed in analogous fashion but possess very different activation parameters for their product-forming steps. Some consideration has been given to the roles of the indispensible amine solvent both in preventing irreversible isomerization of the allyl thio ether substrate and in promoting the transformation to the reaction intermediates. The factors contributing to the determination of the product composition have also been treated in this discussion.

In a recent article[1] discussing evidence bearing on the mechanism of the thio-Claisen reaction, it was reported that β-methylallyl phenyl sulfide (**1**) rearranged with extraordinary facility with formation of 2,2-dimethyl-1-thiacoumaran (**2**) even in the absence of the familiar[1,2] high-boiling amine solvent. At that time we had projected a fuller discussion for the opportunity of a future publication. We now wish to report the results of a detailed analysis of the product compositions derived under various conditions of the thio-Claisen reaction which have led to somewhat different data. These findings do not in any essential way alter the conclusions expressed earlier[1] concerning the existence of a powerful β-methyl substituent effect enhancing the rate of rearrangement, compared with the unsubstituted (in the allyl side chain) case. However, the data to be presented have greatly expanded our understanding of the mechanism and have emphasized the essential role of the solvent in the thio-Claisen reaction.

Results

The Neat Thermolysis of β-Methylallyl Phenyl Sulfide.—It had been previously[1] reported that this reaction condition afforded **2** as the sole product, aside from tars. This is the result which has been found to be incorrect. When the thermolysis is carried out at 300° for 2.5 hr, the principal products have now been completely separated and identified as thiophenol, phenyl isobutyl sulfide (**3**), and diphenyl sulfide (**4**). The same result was observed even for shorter periods of exposure (1.5 hr). It is to be noted in Table I, which summarizes these data, that a small amount of phenyl isobutenyl sulfide (**5**), the propenyl isomer of **1**, has also been formed. No cyclization products which are characteristic of the thio-Claisen[1] were detected in the distillate, although very careful retention time and peak enhancement experiments were performed with all the known cyclic products available as authentic samples. The small, tarry residue was shown by means of high-vacuum, short-path distillation to contain 5–10% of diphenyl disulfide (**6**) (amounting to less than 1% of the total yield of product).

TABLE I
RESULTS OF THE NEAT THERMOLYSIS OF METHYLALLYL PHENYL SULFIDE AT 300° FOR 2.75 HR

Glpc peak[a]	Identity	Retention time, min	Distillable product, %	Total product, %
1 (multiplet	Volatile components, exact identity unknown	0.6–3.46	22	10.5
2	Phenyl isobutyl sulfide (**3**)	4.66	30.5	15
3	Phenyl isobutenyl sulfide (**5**)	7.40	2.5	1
4	Diphenyl sulfide (**4**)	30.06	45	21
	Thiophenol (**13**)	...	*b*	32
	Tar[c]	...	...	20

[a] Peaks numbered in the order of their emergence on chromatogram; see Experimental Section. [b] Extracted with base; see Experimental Section. [c] From 5 to 10% of this consists of diphenyl disulfide. The remainder is apparently elemental sulfur and polymeric material of substantially hydrocarbon nature, as viewed by infrared spectra.

The thermolysis of **1** was also carried out for 1.5 hr at several temperatures in the range 250–315°. Table II summarizes the identities and proportions of the dis-

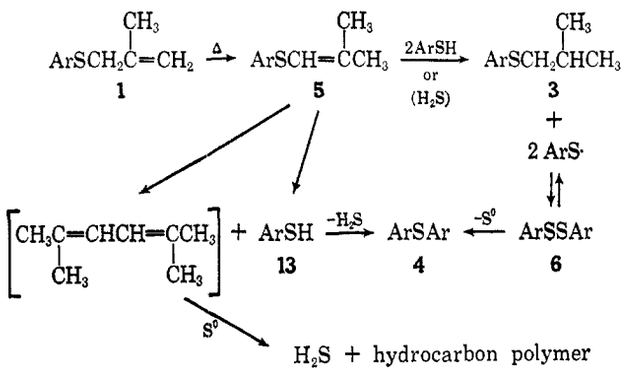
TABLE II
RESULTS OF THE NEAT THERMOLYSIS OF METHYLALLYL SULFIDE AT A VARIETY OF TEMPERATURES FOR 1.5 HR

Glpc peak[a-c]	Identity	Product, % 250°	270°	280°	290°	300°	315°
1	Volatile components, exact identity unknown	0	7	10.5	19	31	36
2	β-Methylallyl phenyl sulfide (**1**)	24	0	0	0	0	0
3	Phenyl isobutyl sulfide (**3**)	0	0.5	4	8.5	22.5	15.5
4	Phenyl isobutenyl sulfide (**5**)	76	90	78	54.5	7	4.5
5	Diphenyl sulfide (**4**)	0	2.5	7.5	18.5	40	43.5

[a] Peaks numbered in the order of their emergence on chromatogram; see Experimental Section. [b] This analysis does not include the thiophenol or tar formed; it includes only the products which can be analyzed on the diethylene glycol adipate chromatographic column. In each of these experiments, the glpc nonvolatile components comprise less than the amounts indicated for the much longer time interval experiments listed in Table I. [c] Since the purpose of this table is to realize how the volatile reaction products varied with respect to each other as a function of temperature, the absolute amount of residue containing hydrocarbon polymer, and elemental sulfur is not taken into consideration, even though it increases with temperature at the expense of distillable product.

(1) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 (1966).
(2) H. Kwart and M. C. Hackett, *J. Am. Chem. Soc.*, **84**, 1754 (1962).

SCHEME I
STOICHIOMETRY OF TRANSFORMATIONS INDUCED BY NEAT PYROLYSIS OF METHYLALLYL PHENYL SULFIDE



tillate products of these reactions. The preponderant isomerization to the isobutenyl sulfide (**5**) apparently begins at temperatures as low as 250°. At the higher temperatures, the ratio of **5** to the other products begins to decline, while isobutyl phenyl sulfide (**3**) and diphenyl sulfide (**4**) are steeply increasing with temperature, though to differing degrees.

When **5** was subjected to thermolysis (neat) for 1.5 hr at 290°, diphenyl sulfide (**4**), but no phenyl isobutyl sulfide (**3**), was formed. When **5** was pyrolyzed at 300° for 1.5 hr, **3** was detected (5.6%) along with **4** (23%), unreacted **5** (47%), and the low-boiling hydrocarbon (multiplet, 24%). When **5** was thermolyzed with (added) thiophenol present at the same temperature and time of exposure, the amount of **3** increased (to 20%) and the amount of **4** formed was considerably increased (to 50%). This suggested that the course of reaction, as summarized in Scheme I, could be represented as involving prior cleavage of **5** to low-boiling olefins and a thiophenol moiety. Apparently the latter subsequently attacks the excess of isobutenyl precursor (**5**) functioning as a reducing agent and ultimately converting itself to diphenyl sulfide. The phenyl isobutyl sulfide may also be formed by hydrogen sulfide reduction (as shown in Scheme I) or perhaps by a disproportionation between thiophenol and either phenyl isobutenyl sulfide or β-methylallyl phenyl sulfide. The results suggested also that, in either case, **6** could be one of the primary products which in turn could give rise to **4** by loss of sulfur.

Several additional experiments were performed in the effort to understand the course of formation of **4**. When **1** was thermolyzed in the presence of added thiophenol at the relatively low temperature of 200° for 4 hr, *no* formation of **3** or **4** was noted. Thus, if the reduction of **5** by thiophenol does occur (as indicated by the higher temperature reaction), it is not very rapid and requires (at least) a much higher temperature than the isomerization of **1** to **5** (see Table II). On the other hand, thermolysis of thiophenol itself at 300° for 1.5 hr gave a 13% yield of diphenyl sulfide while the thermolysis of diphenyl disulfide (**6**) under exactly the same conditions gave a 48% yield of **4**. This may be taken to indicate that diphenyl disulfide could be an intermediate in the formation of **4**, but, under the stressed conditions that lead to its formation from thiophenol (or some precursor thereof), it cannot be accumulated and is very extensively converted to **4**. It is evident, too, (from a close study of Table II) that isobutyl phenyl sulfide also gives rise to **4** at the higher reaction temperatures, presumably through the intervening breakdown to thiophenol.

TABLE III
RESULTS OF THE THERMOLYSIS OF β-METHYLALLYL PHENYL SULFIDE IN QUINOLINE SOLUTION COMPARED

Vpc peak[a]	Identity	Retention time, min	Distillable product,[b] % 170 hr at 150°	0.75 hr at 237°	1.5 hr at 300°
1	2,2-Dimethylthiacoumaran (**2**)	6.06	5.5	19	30.7
2	β-Methylallyl phenyl sulfide (**1**)	6.46	27	10.5	0.00
3	Phenyl isobutenyl sulfide (**5**)	7.40	2	2.5	5.4
4	[c]	8.73	...	...	...
5	3-Methyl-1-thiachroman (**7**)	14.60	56	61	56.5

[a] Peaks are numbered in the order of their emergence on the chromatogram (see Experimental Section). [b] This analysis does not include the thiophenol or tar formed or other components occurring in amounts of 1.5% or less. However, within the limits of error resulting from neglect of this side product, the distillable product, as analyzed by the glpc method, affords a measure of the fraction of the total product which each of the separable components comprises. [c] The identity and significance of this peak comprising *ca.* 5% of the product will be reserved for the subject of a future paper having little bearing on essential nature of the thio-Claisen reaction.

Thermolysis of β-Methylallyl Phenyl Sulfide in Quinoline Solution.—As indicated in the earlier report,[1] on heating in quinoline solution **1** is very rapidly converted to the cyclic thio-Claisen products and at even lower temperatures than are required for the unsubstituted allyl thiophenyl ether (which usually requires refluxing quinoline at *ca.* 200–240°).[2] An experiment was carried out to determine how product composition could be influenced by temperature.

Table III represents a comparison of product composition data obtained from a run at 150° for 7 days *vs.* one at 237° in quinoline for 0.75 hr (when the product has apparently reached something like a steady state with respect to the ratio of the cyclic components). The results would seem to demonstrate that the 3-methylthiachroman (**7**) is formed somewhat faster than the thiacoumaran (**2**) at the lower temperature and that the ratio of **7** to **2** after 170 hr is *ca.* 10 compared to the high-temperature result of *ca.* 3 after 0.75 hr. This trend is further illustrated by the result at 300° in Table III; the ratio is here reduced to *ca.* 2.

Some idea of the relative rates of formation of each of the cyclic products at 237° and the gross rate relative to the same reaction at 150° can be obtained by inspection of Figure 1 plotted from the appropriate data in Table IV. A rough estimate can be arrived at in this fashion suggesting that the reaction at 237° is 100–200 times faster than at 150° and that a half-life of formation for both cyclic products at the higher temperature is about 25 ± 5 min.

In order to determine whether phenyl isobutenyl sulfide is a significant precursor of cyclic product, this compound was heated at 150° in quinoline for 1 week. The result was that the original sulfide (**3**) was recovered essentially unchanged. No cyclic product could be identified under conditions (see Table III) which give rise to more than 60% total yield of thiachroman **7** and thiacourmaran **2**, while nearly 75% of starting sulfide **1** is converted to product.

Since a very small amount of thiophenol always is

TABLE IV
RESULTS OF THE THERMOLYSIS OF β-METHYLALLYL PHENYL SULFIDE IN QUINOLINE AT 237° FOR VARYING LENGTHS OF TIME

Vpc peak[a]	Identity	Distillable product,[b] % — Time of reaction, min: 15	25	35	45	55	65	75	85	95
1	2,2-Dimethyl-1-thiacoumaran (2)	3.5	10	12.5	19	16.5	17	20	17	19
2	β-Methylallyl phenyl sulfide (1)	65	40	23.5	10.5	9	6.5	2.5	3	3
3	Isobutenyl phenyl sulfide (5)	1.5	2	3	2.5	3	2.5	2.5	3	2.5
4	[c]									
5	3-Methyl-1-thiachroman (7)	26.5	42	54	61	63	65	66	65	68

[a] Peak numbers are in the order of emergence from the gas chromatograph. [b] See footnote *b*, Table III. [c] See footnote *c*, Table III.

formed alongside the principal reaction products and this is an acidic material in the basic medium of the thio-Claisen reaction, an attempt was made to ascertain the influence of thiophenol on product proportions. The data (shown in Table V) demonstrate that

TABLE V
THE INFLUENCE OF THIOPHENOL ON PRODUCT PROPORTIONS IN A 15% β-METHYLALLYL PHENYL SULFIDE SOLUTION HEATED AT 225° FOR 1.5 HR

Product	Total distillables,[a] % — 100% quinoline	88% quinoline and 12% thiophenol
2,2-Dimethyl-1-thiacoumaran (2)	19	9
Phenyl isobutenyl sulfide (5)	6.5	15
3-Methylthiachroman (7)	71.5	74

[a] See footnote *b*, Table III.

a profound influence is exerted by the presence of a nearly equimolar amount of thiophenol: the thiacoumaran (2) yield has been depressed by more than a factor of 2, the isomerization to the unreactive isobutenyl compound (5) has been increased by approximately the same amount, while the formation of thiochroman (7) has been little affected.

Discussion

Mechanism of the Thio-Claisen Rearrangement.—Apparently the presence of high-boiling amine solvent is indispensable to the occurrence of this reaction of allyl phenyl sulfides. The results presented above have not only established this for a case where reaction is accelerated by a methyl substituent effect, but have also pointed to the existence of several other factors of which some account must be taken in the proposed mechanism,[1] namely, (1) the effect of reaction temperature on the ratio of thiachroman and thiacoumaran formed, (2) the effect of side chain substitution on this ratio, and (3) the factors controlling the relative rates of competing processes in quinoline solution.

The data in Table IV can be construed as a crude demonstration that the two cyclic products are formed from a common intermediate. Thus, the half-time for formation (that is, the time required for half the ultimate amount to be formed at "infinite" time, *ca.* 100 min) of both products is for all purposes identical. If any extensive degree of interconversion were occurring at some rate different from the separate rates of

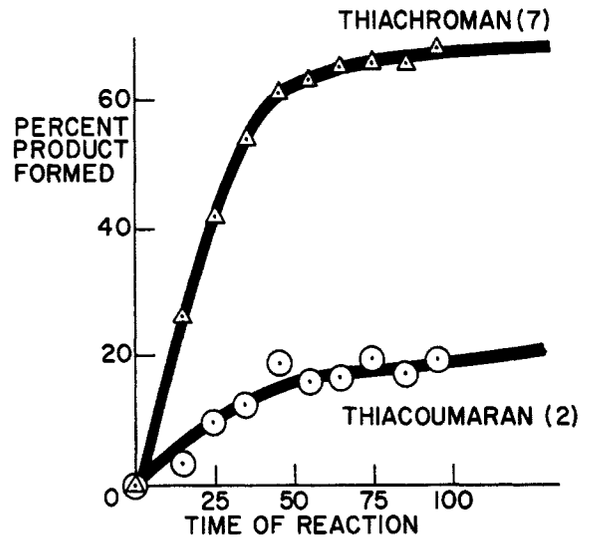


Figure 1.—The relative rates of formation of cyclic products arising from thermolysis of β-methylallyl phenyl sulfide at 237° in quinoline solution.

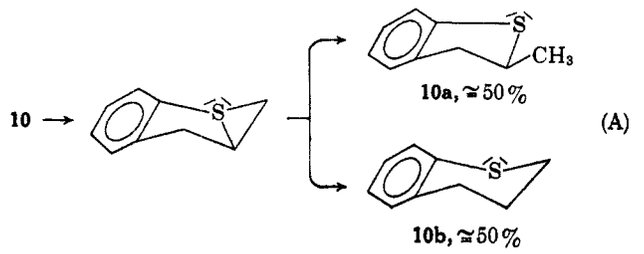
formation of each of the cyclic isomers, we could have anticipated a very different result. Further proof that interconversion of the isomers does not occur under the reaction conditions was obtained by direct measurement. In refluxing quinoline, neither of the pure isomers is altered nor destroyed to an important extent. On the other hand, the Figure 1 plots are also in agreement with product formation from two distinctly different intermediates each capable of affording the same products but at different rates and (therefore) in different proportions.

In fact the great sensitivity of product composition to temperature (see Table III) seems much more consonant with the existence of *two* product forming paths, each possessing different activation parameters. That is to say, each path produces at a given temperature a fraction of the total product as determined by (their) relative activation free energies. The proportion of the two isomers characteristic of each reaction path, however, is relatively independent of the temperature. Our previous work[1] has already served to identify the two possible precursors formed from substrate (1) and capable of yielding both thiachroman **7** and thiacoumaran **2**, namely, the thiirane **8** and the *o*-methylallylthiophenol **9** (see Scheme II, p 3138).

Nonetheless it is also clear that several circumstances may alter the ratio of the two cyclic products arising from each intermediate. Thus, substitution either on the ring or in the side chain of the thio-Claisen substrate has a profound effect on product composition. As discussed in a previous article,[1] the composition of product derived from intermediate **9** is not likely to be influenced by conformational factors related to the stability of the product. However, we may with some confidence apply the assumption that the transition state for product formation from the intermediate **8** looks like the product.

On this basis it is possible to correlate product composition with the nonbonded interactions that distinguish the respective products. These Pitzer strains must surely be reflected in the corresponding transition states forming **7** and **2** from **8**. In the case of the unsubstituted substrate **10**, a measure of the repulsive

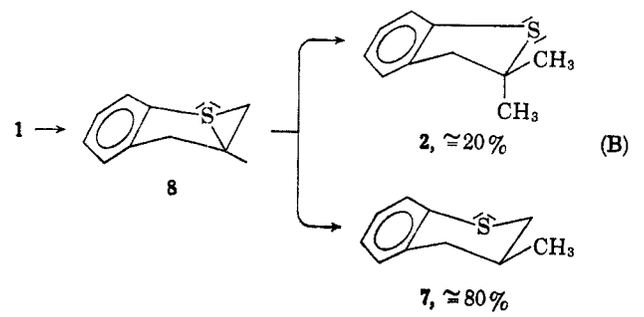
interaction between the methyl and the unshared orbitals on the adjacent sulfur atom the thiacoumaran **10b** may create favor for producing the thiachroman **10a**, where this repulsion is absent (see eq A). The



(A)

1:1 product proportions may be regarded as an indication of the competing mechanism forming **10a** from the corresponding *o*-allylthiophenol.

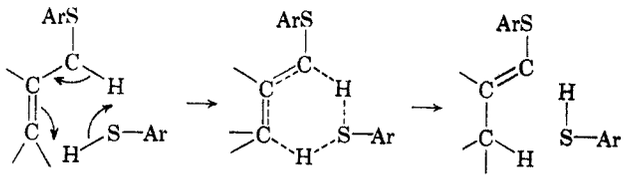
In the case of substrate **1**, the predominance of product **7** may be correlated with the considerable Pitzer strain in the alternative product **2** originating with the α-geminal methyls. The fact that about one-fifth of the yield is comprised of **1a** may be regarded as an indication of the considerable favor for the competing *o*-methylallylthiophenol intermediate induced by the side chain methyl substituent (also observed in the oxy-Claisen rearrangement which proceeds entirely through this pathway); see eq B.



(B)

The Role of the Amine Solvent in the Thio-Claisen Rearrangement.—A fundamental point is encompassed by the observation that even at temperatures as low as 150° less than 3% of the product is the isobutenyl sulfide **5**. As stated earlier, this substance was shown here to be formed irreversibly in the medium and resisted thermal conversion to any cyclic product. On the basis of previously reported studies,[3-5] base would be expected to catalyze the isomerization of **1** to **5**. It is all the more remarkable, therefore, that the thio-Claisen reaction takes place so extensively in the basic medium while so little of **5** is produced in this irreversible manner. However, the data in Table V bear evidence that the isomerization reaction is (also) strongly accelerated relative to the thio-Claisen by the presence of an equimolar amount of added thiophenol. Apparently the isomerization of double bonds into the position of conjugation with the sulfur atom is even more subject to general acid or general acid–base catalysis or to specific acid catalysis of the type illustrated by the six-center cyclic transition. Further study of this question is currently in progress in these laboratories.

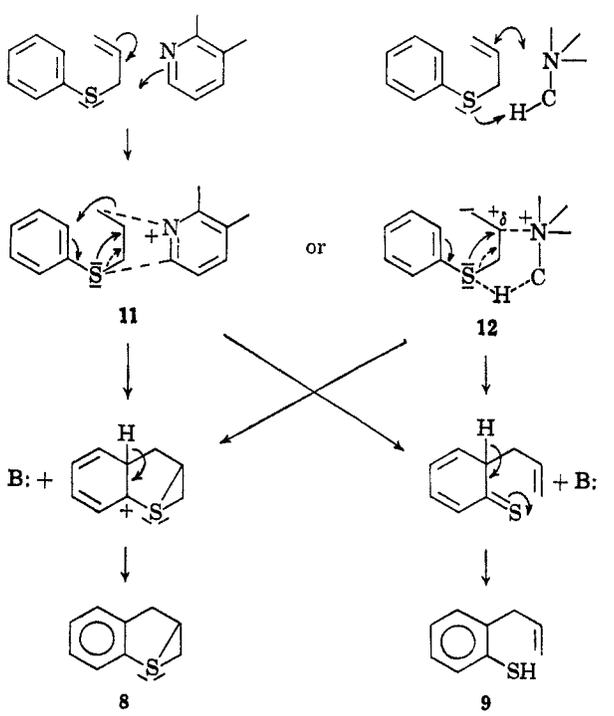
(3) R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.*, **68**, 2229 (1946).
(4) D. S. Tarbell and M. A. McCall, *ibid.*, **74**, 48 (1952).
(5) D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).



Clearly, the amine solvent in the thio-Claisen reaction is not functioning as a mere proton-transfer agent[3] (which might also cause destructive isomerization to the isobutenyl derivative).[4,5] Rather, it seems to serve for complexing the substrate in the allylic thiophenyl ether configuration in which (alone) the formation of the thiirane anion intermediate **8** can take place. Two attractive alternatives (see Scheme II), depending on whether the amine is heterocyclic or otherwise, may be considered for visualizing the preliminary complex prior to attaining the thio-Claisen transition state.

This picture also accounts for the occurrence of two reaction intermediates analogous to **8**, the thiirane, and **9**, the *o*-allylthiophenol. Each of these originates *via* somewhat different electron displacements occurring within the structure of an initially formed (common) sulfide–amine complex, like **11** or **12**. This conclusion is in keeping with the variation of product composition as a function of temperature, suggesting that the activation parameters for formation of each of the products are different. It seems unlikely that a single, common intermediate giving rise to two products could have such very different temperature coefficients for formation of the respective products, particularly under the existing circumstances where the rate-determining step occurs previous to the product-forming steps in the reaction sequences indicated in Scheme II.

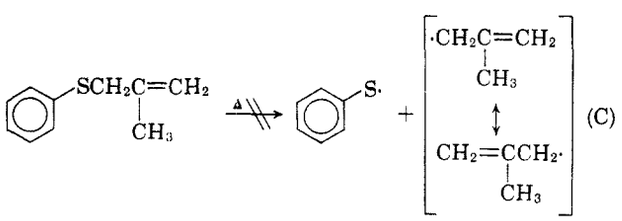
SCHEME II



The least that can be concluded at this point in our continuing studies is that the indispensable solvent medium conducive to reaction apparently must be

capable of some specific complexing interaction with substrate **1**. Only the resulting complex structure accommodates the demands of bond making in the thio-Claisen transition state.

Pertaining to the Thermolytic Decomposition Process.—One of the more significant results to be noted in Table II is that the isomerization of the substrate **1** to the isobutenyl sulfide **5** represents the most rapid process occurring in the absence of the high-boiling amine solvent. This, of course, confirms the considerations discussed above regarding the role of the amine solvent in preserving the allylic structure. It also suggests that all the other products observed in the (neat) thermolysis stem from the decomposition of **5** rather than from **1**. (This possibility was also demonstrated in an independent experiment; see results.) At first glance this would seem to be anomalous, since, if any homolytic scission were the fundamental process accounting for decomposition of the sulfide, it should be expected to occur most readily according to eq C (*which clearly does not take place*).



(C)

The special facility possessed by the isobutenyl sulfide for undergoing these thermal transformations must be attributed, then, to the ability of the double bond to stabilize electronic charge developed on the sulfur to which it is bonded in **5**. Studies directed toward elucidating the nature of charge distributions intervening in the course of this and similar thermolytic reactions of aromatic divalent sulfur substrates[6] are presently in progress in these laboratories.[7]

At this point, however, it will be recalled that the conversion of **6** to **4** in near quantitative yields has been noted again recently,[8a] having been previously identified in 1874. The corresponding reaction we have here described for thiophenol ($\rightarrow$ **4** + H_2S) has not been reported previously. It must be regarded as formally analogous to the pyrolytic transformations of many divalent sulfur derivatives noted by Mayer and Frey[8a] (RSX $\rightarrow$ RX + S), where R = a variety of aryl and alkyl groups and X = –Cl, –SCN, and $-SC_6H_5$. However, previous workers[9,10] in studies of the pyrolysis of diphenyl disulfide under slightly different conditions from those used in this work appear to have obtained somewhat different products. Thus, Schönberg and Mustafa[10] have observed that, under conditions of neat pyrolysis of diphenyl disulfide in which thiophenol formed is permitted to distil out unimpeded, the residual product in nearly 60% conversion is thianthrene. We are presently engaged in the laboratory in seeking an explanation for the palpably disparate courses of the two sets of reactions.

(6) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).

(7) Detailed kinetic studies of this and related reactions will be reported in a forthcoming article.

(8) (a) R. Mayer and H. J. Frey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 705 (1964); (b) C. Graebe, *Ann.*, **174**, 189 (1874).

(9) A. Schönberg, A. Mustafa, and W. Askar, *Science*, **109**, 522 (1949).

(10) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 889 (1949).

Experimental Section

Neat Pyrolysis of β-Methylallyl Phenyl Sulfide.—About 25 g of pure β-methylallyl phenyl sulfide was heated in a sealed tube immersed in an oil bath at 300° for 2.75 hr. After cooling, the tube was opened and the dark liquid diluted with benzene and washed with two 75-ml portions of 10% NaOH in order to remove thiophenol. The benzene solution was then dried with anhydrous $MgSO_4$, the drying agent filtered off, and the benzene removed on the flash evaporator. The resultant liquid was distilled under vacuum, bp 60–105° (1 mm) (yellow liquid). The NaOH solution was acidified with 200 ml of 3 *M* HCl and the resultant aqueous liquid extracted continuously with ethyl ether for 16 hr in order to remove the thiophenol. The ether was then removed on the flash evaporator to yield 7.2 g of thiophenol, 10.8 g of distillate, and 4.5 g of pot residue (tar). Gas chromatographic analysis was carried out in this and all subsequent experiments (unless otherwise noted) with a column of 20% cross-linked diethylene glycol adipate on Chromosorb W heated to 190°.

Identification of the Products of This Reaction.—Diphenyl sulfide was trapped from the vpc and identified by matching its infrared spectrum with the spectrum of authentic diphenyl sulfide. The presence of this compound was also verified by peak enhancement with known diphenyl sulfide and by nmr spectral comparison.

Phenyl isobutyl sulfide was trapped from the vpc and identified by matching its infrared spectrum with the spectrum of authentic phenyl isobutyl sulfide, which was independently synthesized by reaction of isobutyl bromide with thiophenol in sodium methoxide–methanol solution. Again the presence of this compound was verified by peak enhancement with known phenyl isobutyl sulfide. (We are obliged to C. J. Thompson and H. T. Hall for positive mass spectral confirmation of this substance.) Nmr data also provided full confirmation of the structure.

Phenyl isobutenyl sulfide was identified by the infrared and nmr spectra of the compound trapped from the vpc. The nmr showed two methyl peaks (relative intensity 6) at τ 8.18, a methinyl proton at 4.17 (relative intensity 1), and a phenyl group at 2.18 (relative intensity 5). The infrared spectrum showed a monosubstituted ring pattern in the region between 1650 and 1950 cm^{-1}, an unsplit methyl peak at 1361 cm^{-1}, a trisubstituted ($CR_1R_2=CHR_3$) double bond at 809 cm^{-1}, and a monosubstituted benzene-ring pattern at 740 and 690–700 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.10; H, 7.36; S, 19.53. Found: C, 73.24; H, 7.33; S, 19.33.

Pyrolysis of β-Methylallyl Phenyl Sulfide in Quinoline Solution at 150° for 1 Week.—In a 1-l. three-neck flask equipped with nitrogen inlet, water-cooled condenser, and thermometer (to which was attached a temperature controller) was placed a solution of 67.5 g (0.41 mole) of β-methylallyl phenyl sulfide in 450 g (3.49 moles) of quinoline. This was heated with stirring and under nitrogen for 1 week at 150 ± 1.5°. After cooling, the reaction mixture was diluted with benzene and placed in a three-neck 3-l. flask equipped with mechanical stirrer and dropping funnel. A solution of HCl (4 moles of 3 *N*) was added slowly with stirring from the dropping funnel for the purpose of washing out the quinoline. After thoroughly mixing to ensure complete removal of the quinoline, the benzene layer was washed with two 250-ml portions of hot 10% aqueous NaOH to remove thiophenol. (Subsequent acidification and extraction of the NaOH solution yielded little or no thiophenol.) The benzene was then removed on a flash evaporator and the resulting liquid was vacuum distilled (bp 63–110° at 1 mm), yielding 41.8 g of distillate and leaving 25.5 g of pot residue. The distillate was analyzed by gas chromatography.

3-Methyl-1-thiachroman was identified by its infrared and nmr spectra and its elemental analysis. The infrared showed an *ortho*-substituted benzene ring pattern between 1680 and 1880 cm^{-1} and an unsplit methyl band at 740 and 680 cm^{-1}. The nmr showed a doublet methyl peak at τ 9.5, a multiplet methylene group at 7.6, and an aromatic ring multiplet at 3.15. The integration was consistent. Desulfurization and mass and infrared spectral data comparison with an authentic sample was kindly provided by C. J. Thompson and H. J. Hall of the U. S. Bureau of Mines, Bartlesville, Okla.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.10; H, 7.36; S, 19.53. Found: C, 73.18; H, 7.12; S, 19.34.

2,2-Dimethyl-1-thiacoumaran was trapped from the vpc and identified by its infrared, nmr, and mass spectra. The infrared showed an *ortho*-substituted benzene ring pattern between 1660 and 1880 cm^{-1}, a split geminal dimethyl group at 1363–1383 cm^{-1}, and an *ortho*-substituted benzene ring pattern at 740 and 695–702 cm^{-1}. The nmr showed a single methyl peak at τ 8.48, a single methylene peak at 6.99, and an aromatic ring at 3.0. The proton integration was consistent. The mass spectrum showed a base peak at *m/e* 149 and parent peak at *m/e* 164. The mass and infrared spectra were identical with the data obtained by the Bureau of Mines' workers on an authentic sample isolated from "Wasson Crude Oil."

Pyrolysis of β-Methylallyl Phenyl Sulfide in Refluxing Quinoline for Varying Amounts of Time.—In a three-neck 500-ml flask equipped with magnetic stirrer, nitrogen inlet, water-cooled condenser, and dropping funnel was placed 200 g of pure quinoline. The quinoline was brought to reflux with stirring and under nitrogen and then 36 g of pure β-methylallyl phenyl sulfide added in a period of 3 min. The reaction temperature was kept at 237 ± 3°. Samples (10 ml) were withdrawn at 10-min intervals for 1.5 hr. In all, nine samples were taken. Each sample was diluted with ether, washed with 40 ml of 3 *M* HCl to remove the quinoline, and dried with anhydrous $MgSO_4$. The ether was removed under vacuum and the resultant liquid analyzed by gas chromatography. The results of the experiment are summarized in Table III.

Pyrolysis of β-Methylallyl Phenyl Sulfide in Quinoline at 300°.—A 15% solution of β-methylallyl phenyl sulfide in quinoline was sealed in a tube and heated for 1.5 hr at 300°. The reaction mixture was diluted with ether and the quinoline removed by washing with 3 *M* HCl. After the ether solution was dried with anhydrous $MgSO_4$, the ether was removed under vacuum and the resultant liquid was analyzed by gas chromatography. The results of this experiment are summarized in Table III.

Pyrolysis of Diphenyl Disulfide.—About 1 g of diphenyl disulfide was sealed in a small tube and heated in an oil bath for 2 hr at 300°. The tube was then cooled down, opened, and analyzed by vpc. A calibration curve was constructed for this analysis by measuring the intensities of peaks from solutions of known concentrations. From this curve it was determined that the pyrolysate consisted of 48% diphenyl sulfide (and thus 52% unconverted diphenyl disulfide). A silicone oil gas chromatography column was used in this study.

Pyrolysis of Thiophenol.—Thiophenol was also pyrolyzed at 300° for 2 hr in a sealed tube. The pyrolysate was analyzed by vpc in exactly the same way as in the pyrolysis of diphenyl disulfide. This analysis showed that diphenyl sulfide had been formed in the amount representing 13% conversion of the thiophenol.

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Thiapyrone Chemistry. I. The Thermal Rearrangement of 2,6-Dialkylthio-3,5-diphenyl-4-thiothiapyrones[1]

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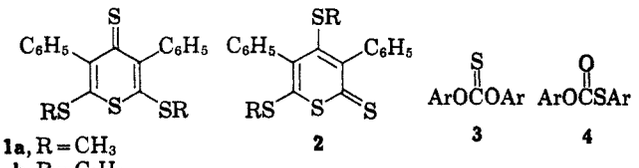
The thermal rearrangement of 2,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**1**), first reported by Schönberg, has been reexamined and clarified. The major product of the rearrangement is the isomeric 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrone (**2**), but, contrary to the earlier reports, this isomerization has been found to be reversible. An equilibrium constant for the reaction has been determined and a structure is suggested for one of the by-products of the thermal process. It has been demonstrated by means of a crossover experiment that the isomerization is intermolecular rather than intramolecular as had been previously proposed by Schönberg. Heating a mixture of two different 4-thiothiapyrones above their melting temperatures produced a complex reaction mixture from which a crossover product was isolated and characterized.

Some 20 years ago, Schönberg and Asker[2] described the chemistry of 2,6-dialkylthio-3,5-diphenyl-4-thiothiapyrones (**1**). Included in these earlier investigations was the thermal isomerization of **1** to 4,6-dialkylthio-3,5-diphenyl-2-thiothiapyrones (**2**). Schönberg[3] had previously reported the thermal isomerization of diaryl thioncarbonates (**3**) to diaryl thiolcarbonates (**4**) and suggested that both rearrangements involved a similar mechanistic pathway.[2b] The mechanism proposed for these rearrangements was intramolecular and was explained by assuming that at high temperatures ionic structures make a contribution to resonance stabilization. The rotation of the anion portion of one of the contributing structures about an axis going through the center of the molecule and perpendicular to the plane of the ring was postulated to account for the observed isomerization. These pathways are shown in Scheme I. The mechanism of the carbonate rearrangement, which now bears Schönberg's name, has been carefully elucidated by Tarbell and co-workers.[4] These investigators found the isomerization to be intramolecular, involving nucleophilic displacement by sulfur rather than aryl migration, and requiring a four-membered cyclic transition state (A). An intramolecular rearrangement of this type in the thiapyrone



1a, R = CH_3
b, R = C_2H_5
c, R = $(CH_3)_2CH$
d, R = $C_6H_5CH_2$
e, R = *p*-$NO_2C_6H_4CH_2$

2 **3** **4**

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