2-Benzylthio-3-allyl-4-pyrimidone, m.p. 42–43°, is very soluble in benzene, relatively insoluble in petroleum ether, and can be crystallized conveniently from the mixed solvents.

2-Benzylthio-1-allyl-4-pyrimidone, m.p. 64–66°, can be crystallized from benzene in which it is moderately soluble.

2,4-Diallyloxypyrimidine (1).—2,4-Dichloropyrimidine (100 g., 0.672 mole) was dissolved in 500 ml. of allyl alcohol. To this was added a solution of 30.9 g. (1.34 g.-atoms) of sodium dissolved in 600 ml. of allyl alcohol. After standing 1 hr., the mixture was spin evaporated *in vacuo*. The oily residue was mixed with ether and the ether solution was washed several times with water. After drying over magnesium sulfate, the ether was removed by flash distillation and the product was distilled *in vacuo*, b.p. 85° (0.5 mm.). The distillate weighed 116.6 g. (90% yield).

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.81; H, 6.34; N, 14.66.

1-Methyl-4-allyloxy-2-pyrimidone (2).—2,4-Diallyloxypyrimidine (20 g.) was mixed with 60 ml. of freshly distilled methyl iodide and the reaction mixture was placed in the dark at room temperature. After 24 hr. most of the methyl iodide was evaporated, during which time several crops of crystals were collected and washed with small quantities of ether. The dried crude product weighed 14.9 g. (90%), m.p. 109–113°. After recrystallization from a small amount of benzene, 12.4 g. (74%) of white crystals was obtained: m.p. 110–112°, λ_{max}^{EtOH} 276 mμ (ε 6100).

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.86. Found: C, 58.12; H, 5.97; N, 16.54.

1-Methyl-3-allyl-2,4-pyrimidinedione (1-Methyl-3-allyluracil) (3).—1-Methyl-4-allyloxy-2-pyrimidone (1.00 g., 0.00602 mole) was heated 1.75 hr. at 240°. After cooling to room temperature, methylene chloride was added to the dark viscous residue. Insoluble material (0.06 g.) was removed by filtration and the filtrate was chromatographed on 75 g. of neutral alumina.[29] 1-Methyl-3-allyl-2,4-pyrimidinedione (0.70 g., 70%) was eluted from the column with ethyl acetate. An analytical sample was obtained by chromatographing the product a second time using the above procedure: λ_{max}^{EtOH} 266 mμ (ε 8700).

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.86. Found: C, 57.64; H, 6.27; N, 16.87.

1-Allyl-4-allyloxy-2-pyrimidone (4).—2,4-Diallyloxypyrimidine (5.0 g., 0.0260 mole) and allyl iodide (5.0 g., 0.0297 mole) were mixed and placed in the dark for 72 hr. Excess allyl iodide was removed under reduced pressure at room temperature. The red residue was mixed with a small volume of benzene and chromatographed on 125 g. of neutral alumina.[29] 1-Allyl-4-allyloxy-2-pyrimidone (4.8 g., 96%) was eluted with chloroform. The analytical sample was obtained by chromatographing the product a second time using the above procedure: λ_{max}^{EtOH} 274 mμ (ε 6000).

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.17; H, 6.52; N, 14.24.

1,3-Diallyl-2,4-pyrimidinedione (1,3-Diallyluracil) (5)—1-Allyl-4-allyloxy-2-pyrimidone (1.00 g.) was heated 1.75 hr. at 240°. After cooling to room temperature, methylene chloride–chloroform (1:1) was added to the dark viscous residue. The sample was chromatographed on 75 g. of neutral alumina.[29] 1,3-Diallyl-2,4-pyrimidinedione (0.62 g., 62%) was eluted from the column with chloroform. The analytical sample was obtained by chromatographing the product a second time using the above procedure: λ_{max}^{EtOH} 266 mμ (ε 9300).

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.39; H, 6.45; N, 14.35.

The Vapor Phase Rearrangement of Thioncarbonates and Thioncarbamates

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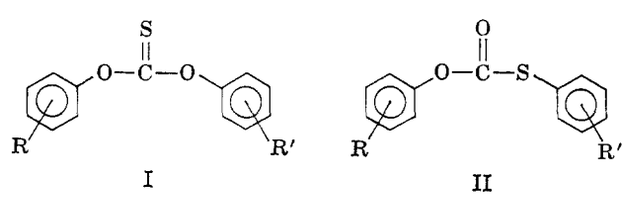
Received August 19, 1965

The Schönberg rearrangement of aryl thioncarbonates has been carried out in a vapor phase pyrolysis with considerable improvement in yield. These results have been reconciled with the cyclic four-membered transition state proposed by Powers and Tarbell and extended to the vapor phase rearrangement of thioncarbamates as an efficient and simple method of preparing certain difficultly available substituted aryl thiols. A procedure involving the steps of these vapor phase rearrangements is conceived as the most generally effective route for deoxygenation of certain substituted phenols which are otherwise not readily subject to reduction or hydrogenolysis (with Raney nickel).

The rearrangement of diaryl thioncarbonates, first described by Schönberg and Vargha[2] has later been shown, largely through the efforts of Tarbell and coworkers,[3,4] to be of synthetic importance in the preparation of substituted thiophenols. The rearrangement is apparently applicable to both symmetrical and unsymmetrical diaryl thioncarbonates. The original reaction conditions call for heating the substrate (neat) at temperatures of 275–300°, and yields are reported to be 50–80%. However, as emphasized by Powers and Tarbell,[4] considerable formation of decomposition products can occur at levels of even 50% conversion of I to II in cases where protracted periods of heating are required.



I II

R or R′ = NO_2, Cl, OMe, or Me

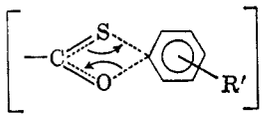
Kinetic data taken by Powers and Tarbell[4] support a first-order rate law governing the rearrangement. Furthermore, where R or R′ are electron-withdrawing substituents, rate accelerations are experienced, and, in unsymmetrically substituted thioncarbonates, the rearrangement was shown[4] to occur primarily in the direction of the ring bearing the most electron-withdrawing substituent. On this basis, the driving force of the rearrangement originates from the nucleophilic character of the sulfur in displacements on carbon and the leaving-group tendency of the oxygen that correlates with its high electronegativity. These facts are quite in keeping with a four-membered cyclic transition state.[4]

(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) A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930).

(3) H. P. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955).

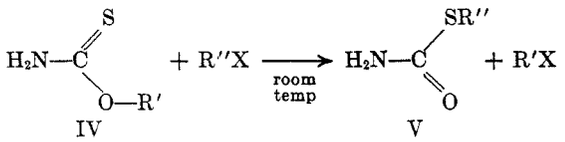
(4) D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).



III

If, indeed, the structure of the critical complex in the Schönberg rearrangement is properly depicted by III, several consequences could be anticipated. For one, reaction should go equally well in the vapor phase, since there is no evident need for solvation of III. For another, since protracted heating at high temperatures in the neat, relatively polar medium tends to promote destructive side reactions involving both reactants and products, short exposures at high temperatures in the gas phase should improve yields. Our results, obtained by proceeding on these premises, thus constitute a test of the proposed[4] mechanism of the Schönberg rearrangement.

Thioncarbamate esters (IV) have been shown[5] to be converted readily to the corresponding thiol esters (V) in direct substitution reactions. Wheeler and



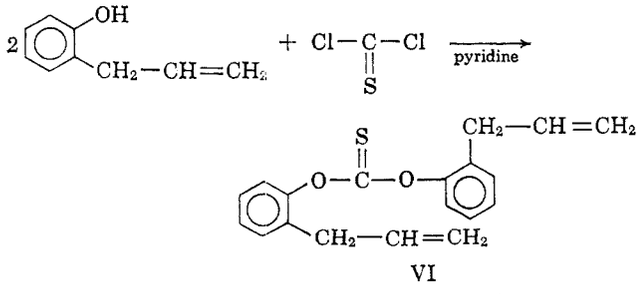
IV V

R′ and R″ = CH_3, C_2H_5; X = Br, Cl, I

Barnes[5] have demonstrated the formation of methyl thiolcarbamate (V, R″ = CH_3) from ethyl thioncarbamate (IV, R′ = C_2H_5) through room-temperature treatment with an equimolar amount of methyl iodide. The ability to form crossover products even with equimolar reactant concentrations must be accepted as strong evidence of the intermolecular nature of this diplacement reaction, rather than cyclic rearrangement. It was conceivable, however, that by conducting the reaction in the vapor phase, a cyclic mechanism (*via* a transition state like III) would be fostered and a rearrangement analogous to the Schönberg reaction of thioncarbonates could be made to occur with thioncarbamates. This proved to be the case.

Results and Discussion

Bis(*o*-allylphenyl)thioncarbonate (VI) was prepared by analogy to the procedure of Rivier.[6] The pyrolysis of VI as a neat material in a sealed tube at



VI

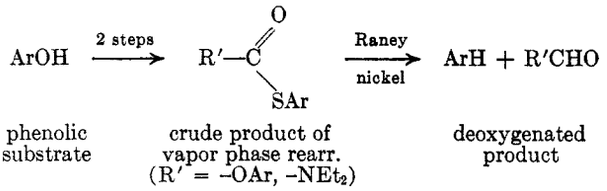
290° gave a 40% yield of the rearranged material, O,S-bis(*o*-allylphenyl)thiolcarbonate (VIa), when the dark, crude product was chromatographed over silicic acid. No unreacted starting material, VI, could be recovered. The yield, however, was increased to 84% and some unreacted material could still be recovered when the rearrangement was carried out under the vapor phase conditions described in the Experimental Section of this report. The degree of rearrangement as a function of vapor flow rate through the heated zone could be readily monitored by the formation of the infrared thiocarbonyl band at 1520 cm^{-1} and the disappearance of carbonyl band at 1740 cm^{-1}. A small amount of polymeric material could be observed to form in the condensate at very high residence times in the thermal zone.

The rearrangements of O-*o*-allylphenyl N,N-diethylthioncarbamate (VII) and O-*m*-tolyl N,N-diethylthioncarbamate (VIII) were carried out at 395–405° under the same vapor phase conditions developed for the Schönberg rearrangement. Chromatography of the pyrolysates over silicic acid afforded high yields of the corresponding thiol esters, VIIa and VIIIa (*ca.* 85 and 81%, respectively). The extent of reaction for a given residence time appears to be quite temperature dependent since pyrolysis of VIII at 383–387° only gave a 70% yield of the *m*-tolyl thiolcarbamate (VIIIa).

The rearrangement of aryl thioncarbamates and the Schönberg rearrangement of the corresponding thioncarbonates must have similar activation energies (*ca.* 38 kcal/mole[4]), since the temperatures and residence times required to effect good yields are nearly identical. The rearrangement of arylimino ethers (carried out in diphenyl ether solution at high temperatures) has been characterized by Wiberg[7] as possessing a cyclic transition state originating from a driving force of nucleophilic displacement.[8] The activation energy requirement of this thermal rearrangement is roughly similar (ΔH = 37–39 kcal/mole depending on aryl substitution[7]) to that of the Schönberg, suggesting that the convenience and yield benefits to be obtained carrying out the reaction in the vapor phase might also be realized in this case, too.

The hydrolysis of the thiolcarbonate and thiolcarbamate products of vapor phase rearrangement readily afforded nearly quantitative yields of the aryl mercaptans. Thus, the over-all conversion of phenol to phenylthiol has been effected in good yield. In cases of certain substituted aryl mercaptans such as *o*-allylthiophenol, this has until now proven to be the only method of attainment (though we have tried nearly all the common ones). However, if one were merely interested in deoxygenation of a phenol, a more advantageous procedure than the conventional (and frequently difficult or impossible) zinc dust distillation method is now available. The crude product from the vapor phase pyrolysis of thioncarbamate or thioncarbonate can now be readily desulfurized by means of the common Raney nickel procedure before applying the chromatographic method for isolating the desired, pure, deoxygenated product. Of course, this procedure could succeed only in cases where the other functional substituents were not subject to reduction or hydrogenolysis in the Raney nickel step. The most obvious advantages of this

(5) H. L. Wheeler and B. Barnes, *J. Am. Chem. Soc.*, **22**, 141 (1899).
(6) H. Rivier, *Bull. Soc. Chim. France*, [3] **35**, 837 (1906).
(7) K. B. Wiberg and R. J. Rowland, *ibid.*, **77**, 2205 (1955).
(8) For the kinetic characteristics and activation parameters of the analogous bimolecular nucleophilic displacement, see E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).



procedure for deoxygenating phenols over the zinc dust method arise in cases of phenols possessing non-reducible electron-withdrawing substituents (for example, hydroxypyridines), where the latter method almost invariably fails. As stated earlier, electron-attracting groups on the aromatic ring afford both enhancement of the ease of thermal rearrangement and an orienting influence in the case of the Schönberg thioncarbonate rearrangement.[4]

Experimental Section

All melting points and boiling points reported are uncorrected.

O,O-Bis(*o*-allylphenyl)thioncarbonate (VI).—Pyridine (15.6 g) was slowly added with stirring to a mixture of 40.0 g (0.298 mole of *o*-allylphenol[9] and 17.6 g (0.153 mole) of thiophosgene in 240 ml of dry benzene, and the mixture was stirred and refluxed for 2 hr. While still hot the mixture was filtered and the filtrate was washed with 6 *N* sulfuric acid, 10% aqueous sodium hydroxide, and water, and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* to give 39.5 g (84.3%) of a red oil.

The red oil (27.5 g) was chromatographed over 300 g of 98% activated alumina. A faint yellow oil, 23.9 g, was eluted with pentane–benzene (1:1–4:1). The infrared spectrum of this material has a >C=S at 1520 cm^{-1}. Distillation of 3.0 g of this colorless oil in the short-path bucket distillation apparatus gave 2.3 g (77.5%) of a colorless liquid, distilling between 124 and 126° (0.3 mm), $n^{24.0}D$ 1.5824.

Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.7; H, 5.81; S, 10.33. Found: C, 72.69; H, 5.69; S, 10.68.

O,S-Bis(*o*-allylphenyl)thiolcarbonate (VIa).—O,O-Bis(*o*-allylphenyl)thioncarbonate (5.0 g) in 25 ml of dry toluene was passed through the heated tube (395–405°) under an atmosphere of nitrogen. The rate of addition (0.362 ml/min) was maintained constantly by means of a good metering pump. The solvent was removed from the pyrolysate *in vacuo* to give 4.9 g (98%) of a red oil, later identified to be nearly pure VIa. This oil was chromatographed over 125 g of silicic acid.

Fraction 1, a yellow oil, 4.75 g, was eluted with pentane–benzene (4:1–3:2). The infrared spectrum showed a carbonyl group at 1740 cm^{-1}. Distillation of this oil in a short-path distillation apparatus (silicone oil bath 120–124° at 0.5 mm) gave 4.2 g (84%) of O,S-bis(*o*-allylphenyl)thiolcarbonate, $n^{25.0}D$ 1.5863.

Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.7; H, 5.81; S, 10.33. Found: C, 73.91; H, 5.68; S, 10.70.

The nmr spectrum (no solvent) of VIa shows a peak for $-CH_2-$ at τ 6.7 and a terminal $=CH_2$ at τ 4.95; the lone proton is split between τ 4.0 and 4.4 and the aromatic ring protons are split between τ 2.67 and 2.93.

Fraction 2, a red oil (0.1 g), was eluted with pentane–benzene (2:3). Its infrared spectrum was identical with that of the starting material, VI.

O-*o*-Allylphenyl N,N-Diethylthioncarbamate (VII).—Pyridine (13.2 g) was added slowly to a mixture of 29.2 g (0.217 mole) of *o*-allylphenol[9] and 25.0 g (0.27 mole) of thiophosgene in 400 ml of dry benzene under an atmosphere of nitrogen. After refluxing for 2 hr, a mixture of 15.8 g (0.217 mole) of diethylamine and 17.2 g of pyridine in 50 ml of dry benzene was slowly added over a 30-min period. The refluxing was continued for 2 hr and the mixture was filtered while still hot. The filtrate was washed with 6 *N* sulfuric acid, 10% sodium hydroxide, and water and subsequently dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 49.9 g (92.3% of a dark oil.

A portion of the crude oil (10.0 g) was chromatographed on 250 g of silicic acid.

(1) A yellow oil, 3.7 g, was eluted with benzene and benzene–ether (4:1). The infrared spectrum of this material was identical with that of unreacted O,O-bis(*o*-allylphenyl)thioncarbonate.

(2) A light orange oil, 0.56 g, was eluted with benzene–ether (2:2–2:3). This material was not identified but appears to be a decomposition product.

(3) A yellow oil, 5.33 g, was eluted with benzene–ether (1:4). Distillation of the oil gave 3.76 g of O-*o*-allylphenyl N,N-diethylthioncarbamate, bp 105–108° (0.8 mm), $n^{30.0}D$ 1.5588.

Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.45; H, 7.63; N, 5.62; S, 12.83. Found: C, 67.46; H, 7.52; N, 5.61; S, 12.44.

(4) A black tar, 0.2 g, was eluted with ether–methyl alcohol (5:0–0:5). This material appears to be a polymeric residue.

S-*o*-Allylphenyl N,N-Diethylthiolcarbamate (VIIa).—A mixture of 2.58 g of VII and 50 ml of dry toluene was passed through the vertical Pyrex tube at 395–405° under an atmosphere of nitrogen. The toluene was stripped from the condensate *in vacuo;* the crude oil was chromatographed on 150 g of silicic acid.

(1) A faint yellow oil, 0.2 g, was eluted with pentane–benzene (1:4). The infrared spectrum of this material was not identified. The spectrum was devoid of olefinic-type unsaturation.

(2) A yellow oil was eluted with benzene–ether (4:1). Distillation of this oil in the short-path distilling apparatus gave 2.2 g (85.3%) of S-*o*-allylphenyl N,N-diethylthiolcarbamate, bp 93–96° (0.1 mm), $n^{30.0}D$ 1.5540.

Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.45; H, 7.63; N, 5.62; S, 12.83. Found: C, 67.64; H, 7.68; N, 5.35; S, 12.63.

O-*m*-Tolyl N,N-Diethylthioncarbamate (VIII).—Starting with 23.5 g (0.217 mole) of *m*-cresol and 25.0 g (0.217 mole) of thiophosgene, a procedure quite analogous to that used for the preparation of VII was followed. When the dried solvent extracts were evaporated under reduced pressure there remained 38.8 g (74.8%) of a crude, crystalline product, mp 75–81°. This material was charcoaled and recrystallized from ethyl alcohol to yield 31.2 g (60.2%) of O-*m*-tolyl N,N-diethylthioncarbamate, mp 85.5–87.0°.

Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.60; H, 7.69; N, 6.29; S, 14.36. Found: C, 64.67; H, 7.73; N, 6.41; S, 14.40.

The nmr spectrum (deuteriochloroform) of O-*m*-tolyl N,N-diethylthioncarbamate displayed a triplet at τ 8.69 for the terminal methyls, a singlet peak at τ 7.63 for the methyl group on the ring, and a series of four peaks split between τ 5.95 and 6.42 for the methylenes. The aromatic ring protons were split between τ 2.64 and 3.17.

S-*m*-Tolyl N,N-Diethylthiolcarbamate (VIIIa).—A mixture of 2.0 g of VIII and 50 ml of dry toluene was passed through the vertical Pyrex tube at 383° and under an atmosphere of nitrogen. A uniform rate of 0.537 ml/min was maintained for 1.75 hr by the metering pump. The solvent was removed under reduced pressure to give 1.9 g of an oil which was chromatographed on 300 g of activated alumina (98%).

(1) A crystalline material, 0.1 g, was eluted in pentane–benzene (2:2). This compound was found to melt over a range of 55–74°. The infrared spectrum of this material (mull) was found to be identical with that of the starting compound (VIII).

(2) A yellow liquid, 1.6 g, was eluted in pentane–benzene (2:3–1:4). Distillation of the oil in a short-path vacuum distilling apparatus gave 1.4 g (70%) of s-*m*-tolyl N,N-diethylthiolcarbamate, bp 128–129° (1.1 mm), $n^{25.0}D$ 1.5564.

The rearrangement of VIII to VIIIa was repeated with 4.0 g of VIII in 70 ml of dry toluene and passed through the vertical tube at 400–405°. Chromatography of the pyrolysate gave 3.23 g (80.7%) of VIIIa.

Hydrolysis of S-*m*-Tolyl N,N-Diethylthiolcarbamate.—A mixture of 2.9 g of VIIIa and 2.0 g of potassium hydroxide in 25 ml of methyl alcohol was refluxed for 20 hr. The solvent was removed *in vacuo* and the residue was taken up in ether, washed with water, and extracted with 10% sodium bicarbonate. The extracts were combined, acidified, and extracted with ether. The ether extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on 25 g of silicic acid.

A yellow oil, 0.96 g, was eluted with pentane–benzene (3:2–2:2). Distillation in the short-path vacuum distilling apparatus gave 0.80 g of *m*-tolyl mercaptan, bp 116–116.5° (81 mm), $n^{29.0}D$ 1.5714 (lit.[10] $n^{29.0}D$ 1.5719).

(9) D. S. Tarbell, *Org. Reactions*, **2**, 26 (1944).

(10) D. S. Tarbell and D. K. Fukushima, *J. Am. Chem. Soc.*, **68**, 1456 (1946).

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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Received August 25, 1965

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).