recrystallized from methanol this neutral compound was obtained in short stout prisms melting sharply at 120°. The mean of good quadruplicate analyses was C, 61.81; H, 6.15; N, 3.62; OCH_3, 25.86.

Cularimine.—A solution of cularimine (0.4 g.) in ether was treated with an excess of methyl iodide and after twenty-four hours the solvents boiled out. The residue which was sparingly soluble in cold water was digested on the steam-bath with an aqueous suspension of freshly precipitated silver chloride. The cooled filtrate from the insoluble silver salts on rendering alkaline with potassium hydroxide yielded some oily precipitate indicating the presence of non-quaternary salts in solution. The mixture was extracted with ether, the aqueous solution treated with a large excess of potassium hydroxide, and heated on a steam-bath. The liberated base yielded a picrate melting at 167° and a methiodide melting at 213°. These derivatives were proved identical with cularinemethine picrate and cularinemethine methiodide, respectively, by mixed melting point determinations. Nevertheless, the methiodide was decomposed with alkali and the resultant hydrocarbon oxidized as above described for (II). The acids (III) and (VI) were obtained and proved to be identical with those obtained from cularine.

Cularine from Cularimine.—A mixture of 40 mg. of cularimine, 0.1 cc. of formic acid and 0.1 cc. of 35% formaldehyde was heated on a steam-bath for four hours. The resultant resin was dissolved in 20 cc. of boiling dilute aqeuous oxalic acid and the filtered solution cooled. The sparingly-soluble oxalate was separated and decomposed in aqueous suspension with ammonia in the presence of ether. The washed ether solution was evaporated to dryness and the residue crystallized from boiling pentane containing a trace of ether. The colorless stout prisms then obtained melted at 115° either alone or in admixture with cularine. The yield was 27 mg.

N-Benzoylcularimine.—A solution of 50 mg. of cularimine in 50 cc. of ether was treated with an excess of benzoyl chloride and then shaken with successive portions of strong aqueous potassium hydroxide. A little pyridine was added and the ethereal solution washed with several successive portions of water. Evaporation of the ether left a pale-colored oil which was dissolved in a little methanol, treated with a few drops of aqueous potassium hydroxide and after a short time diluted with much water. The precipitate which crystallized readily was washed, dried, and recrystallized from its concentrated solution in methanol by the addition of ether. The colorless rhombic plates of N-benzoylcularimine thus obtained melted sharply at 174°. *Anal.* Calcd. for $C_{26}H_{25}O_5N$: C, 72.39; H, 5.80. Found: C, 72.66; H, 6.20.

Treatment of Cularine with Acetic Anhydride.—When 50 mg. of cularine was treated with 0.2 cc. of acetic anhydride it dissolved at once, but in the course of several minutes the solution crystallized for the greater part. The mixture was washed several times by decantation with ether and then with cold methanol. The crystalline residue was then recrystallized twice from hot methanol in which it is only moderately soluble. Colorless elongated plates melting sharply at 217° were thus obtained. Found: C, 70.44, 70.22; H, 6.73, 6.66; N, 4.23. These analyses do not agree with acetylcularine but fit $C_{20}H_{23}O_4N$ which requires C, 70.38; H, 6.75; N, 4.11. When heated on the steam-bath for two hours with 5 parts of hydrochloric acid to 25 parts of methanol it was unchanged.

Summary

1. Hofmann degradation of cularine has yielded an unsaturated compound which still contains the three methoxyl groups and the indifferent oxygen of the alkaloid. Oxidation of this compound yielded a tribasic acid which is regarded as a derivative of diphenyl ether and a monobasic acid which is probably a derivative of xanthone.

2. Cleavage of cularine with metallic sodium dissolved in liquid ammonia yielded a phenolic base which is a benzylisoquinoline derivative. The latter on oxidation yielded 4-methoxyphthalic acid and on exhaustive methylation followed by oxidation yielded the above acid and asaronic acid.

3. The structure of cularine is therefore that of a diphenyl ether with a seven-membered ring and an isoquinoline nucleus. The positions of the methoxyl groups are fixed by the degradation products.

4. Cularimine, an alkaloid not hitherto named, is N-desmethylcularine.

5. Cularine is the first representative of a new class of isoquinoline alkaloids with a diphenyl ether bridge related biogenetically to the benzylisoquinolines.

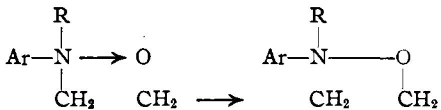
GUELPH, ONTARIO RECEIVED JULY 9, 1949

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF COLUMBIA UNIVERSITY AND THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermal Rearrangement of Allyl-type Sulfoxides, Sulfones and Sulfinates[1]

BY ARTHUR C. COPE,* DWIGHT E. MORRISON[1a] AND LAMAR FIELD[1b]

The rearrangement of allyl groups from nitrogen to oxygen in amine oxides has been reinvestigated recently[2] and explained on the basis of an intramolecular, cyclic mechanism. The reaction resembles the Claisen rearrangement,[3] except for differences which distinguish dyad from triad systems.



This paper reports the preparation of a group of allyl-substituted sulfur compounds, and an investigation of their susceptibility to rearrangement.

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* Harvard University, National Research Fellow, 1932–1934.

[1] Abstracted from portions of the doctoral theses of Dwight E. Morrison (Columbia University) and Lamar Field (Massachusetts Institute of Technology).

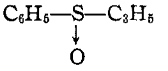
[1a] du Pont Predoctoral Fellow, Columbia University, 1944–1945. Present address: Research Laboratories, Eli Lilly and Co., Indianapolis, Indiana.

[1b] Present address: Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

[2] Kleinschmidt and Cope, THIS JOURNAL, **66**, 1929 (1944); Cope and Towle, *ibid.*, **71**, 3423 (1949).

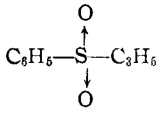
[3] Tarbell, *Chem. Rev.*, **27**, 495 (1940).

As analogs of the amine oxides which undergo rearrangement, allyl phenyl sulfoxide (I) and allyl phenyl sulfone (II) were first investigated. Compound I was prepared by the oxidation of allyl phenyl sulfide with hydrogen peroxide, and II by the reaction of allyl bromide with sodium benzenesulfinate. An isomerization of the sulfoxide analogous to the rearrangement of the amine oxides would produce allyl benzenesulfenate, $C_6H_5\text{–}S\text{–}O\text{–}C_3H_5$; the sulfone would give allyl benzenesulfinate, III. Neither the sulfoxide nor the sulfone were observed to rearrange in this manner on heating. Compound I underwent partial decomposition at 100° during ten hours, giving a mixture from which allyl phenyl sulfide, allyl phenyl sulfoxide and diphenyl disulfide were isolated. It has been observed previously[4] that diphenyl sulfoxide is converted in part to diphenyl sulfide when it is boiled at atmospheric pressure. II proved to be more stable, and was recovered after heating at temperatures which produced partial decomposition (150–250°).



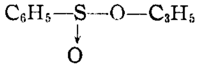
$C_6H_5\text{—}\underset{\substack{\downarrow\\ O}}{S}\text{—}C_3H_5$

I



$C_6H_5\text{—}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{—}C_3H_5$

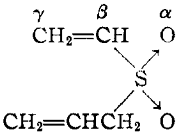
II



$C_6H_5\text{—}\underset{\substack{\downarrow\\ O}}{S}\text{—}O\text{—}C_3H_5$

III

Another compound examined for susceptibility to rearrangement was allyl vinyl sulfone, IV. IV was prepared from allyl β-chloroethyl sulfone, which in turn was obtained by oxidation of allyl β-chloroethyl sulfide. An α,γ-shift of the allyl group from sulfur to carbon in the three-atom system indicated in the formula of IV would give $C_3H_5\text{—}CH_2CH{=}SO_2$. Only decomposition and polymerization were observed when IV was heated at 125, 150 and 175°; at each temperature part of the allyl vinyl sulfone was recovered.



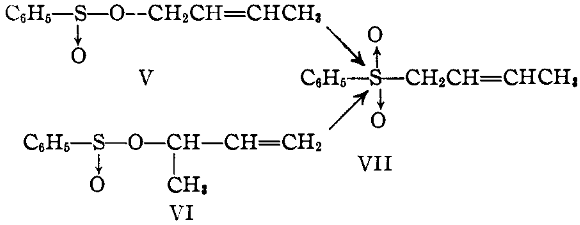
IV

The observation that allyl phenyl sulfone has considerable thermal stability led to an examination of the stability of its isomer, allyl benzenesulfinate (III). α-Phenylethyl p-toluenesulfinate has been reported[5] to isomerize on standing to α-phenylethyl p-tolyl sulfone, by a reaction proceeding in large part through an ionic mechanism. Other observations indicate that this type of rearrangement is not general for sulfinic esters. Ethyl benzenesulfinate gave no evidence of sulfone formation when it was heated in sealed tubes at temperatures of 120 to 150°, and only decomposition was observed to occur.[6] Likewise l-2-octyl p-toluenesulfinate proved to be stable during slow fractional distillation, and although this ester charred slightly when it was heated for two hours at 125–130° and distilled, the pure unchanged ester was recovered in part.[7] In the esterification of p-toluenesulfinic acid with ethyl alcohol, when the reaction mixture was heated above 125° or for longer than five hours, some di-p-tolyl disulfoxide was formed, but no mention was made of the isolation of a sulfone.[8]

In the present investigation the thermal stabilities of allyl benzenesulfinate (III), crotyl benzenesulfinate (V) and α-methylallyl benzenesulfinate (VI) were examined. These esters were prepared by reaction of benzenesulfinyl chloride with the corresponding alcohols in ether solution, in the presence of potassium carbonate. All of them proved to be unstable to heat. V and particularly VI could be purified without danger of extensive loss through decomposition only by distillation in fairly small quantities at low pressures. The structures of V and VI were verified by saponification to crotyl alcohol and α-methylallyl alcohol, respectively, which were identified as the 3,5-dinitrobenzoates.

Allyl benzenesulfinate rearranged incompletely but without much decomposition when the pure ester was heated at 100° for twenty-nine hours, yielding allyl phenyl sulfone, which was identified by hydrogenation to n-propyl phenyl sulfone.

Both crotyl benzenesulfinate (V) and α-methylallyl benzenesulfinate (VI) were rearranged by heating in toluene solution in order to minimize decomposition, which was complete in several instances when the esters were heated without a solvent. After the toluene was removed, any remaining ester was saponified, and the neutral products were distilled. Crotyl phenyl sulfone (VII) was produced in both cases in low yield. The crotyl phenyl sulfone obtained by the rearrangement was identified in each case by hydrogenation to n-butyl phenyl sulfone, which was characterized by nitration, reduction and reaction of the resulting amino compound with m-bromobenzoyl bromide to give the known derivatives, n-butyl m-(3-bromobenzoylamino)-phenyl sulfone and n-butyl m-(di-3-bromobenzoylamino)-phenyl sulfone.[9]



The bearing of this evidence on the mechanism of the rearrangement is inconclusive. An intra-

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[4] Krafft and Lyons, *Ber.*, **29**, 425, 441 (1896).

[5] Kenyon and Phillips, *J. Chem. Soc.*, 1676 (1930); Arcus, Balfe and Kenyon, *ibid.*, 485 (1938).

[6] Otto and Rössing, *J. prakt. Chem.*, [2] **47**, 172 (1893).

[7] Phillips, *J. Chem. Soc.*, 2571 (1925).

[8] Houssa, Kenyon and Phillips, *ibid.*, 1707 (1929).

[9] Ipatieff and Friedman, THIS JOURNAL, **61**, 684 (1939).

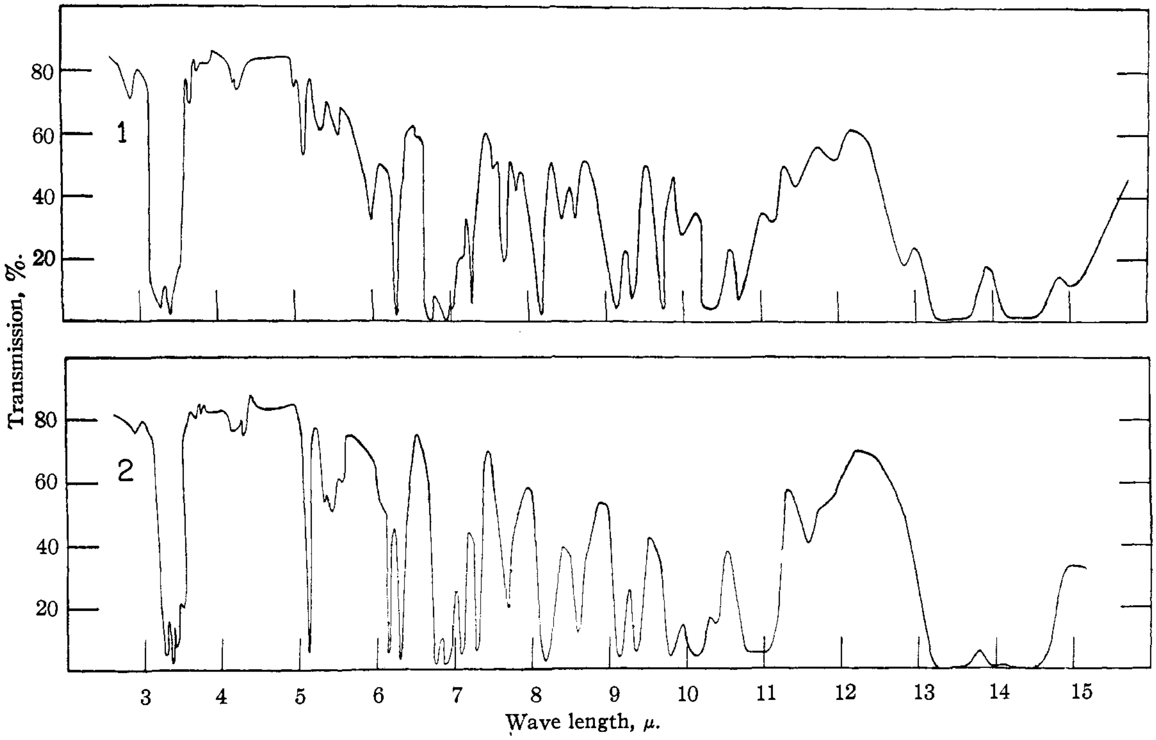
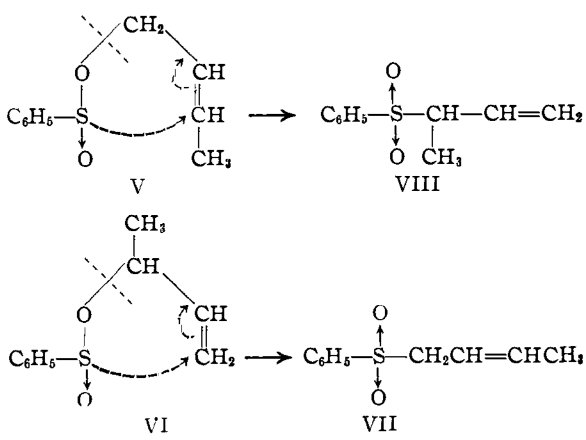


Fig. 1.—Infrared absorption spectra of crotyl phenyl sulfide (IX) (Curve 1) and α-methylallyl phenyl sulfide (X) (Curve 2).

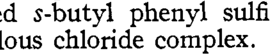
molecular cyclic process would result in inversion of the crotyl and α-methylallyl groups and lead to the isomeric sulfones VII and VIII, unless these sulfones were interconverted at the temperature of the rearrangement. Independent syntheses of the two sulfones VII and VIII were attempted by oxidation of the corresponding sulfides, in order to examine the thermal stabilities of both isomers.



Crotyl phenyl sulfide (IX) and α-methylallyl phenyl sulfide (X) were prepared by reaction of crotyl chloride and α-methylallyl chloride, respectively, with the sodium salt of thiophenol. The two sulfides

$$C_6H_5—S—CH_2—CH=CH—CH_3$$

IX



$$\underset{CH_3}{C_6H_5—S—CH—CH=CH_2}$$

X

(IX and X) had different physical properties, and appeared to be quite stable; X was recovered with little change in physical properties after heating at 150° for seven hours. The structure of X was established by hydrogenation in the presence of a large amount of palladium on charcoal catalyst, which yielded *s*-butyl phenyl sulfide, identified as the palladous chloride complex. The infrared absorption spectra of IX and X were different, consistent with the structures assigned to them, and indicated that neither isomer was contaminated with the other one, as shown by the absence of the 10.3 μ band of IX from the spectrum of X and the absence of the 10.9 μ band of X from the spectrum of IX (Fig. 1). Upon oxidation with hydrogen peroxide in a mixture of acetic acid and acetic anhydride at 0–5°, IX and X were converted to sulfones which were shown to be identical rather than isomeric by comparison of their physical properties and infrared absorption spectra (Fig. 2). The sulfones obtained by oxidation of both IX and X on catalytic hydrogenation yielded *n*-butyl phenyl sulfone. The infrared absorption spectrum of the saturated sulfone prepared from X by oxidation followed by catalytic hydrogenation was compared with the infrared spectra of *n*-butyl phenyl sulfone and *s*-butyl phenyl sulfone (Fig. 3). This comparison indicated the presence of 10% of

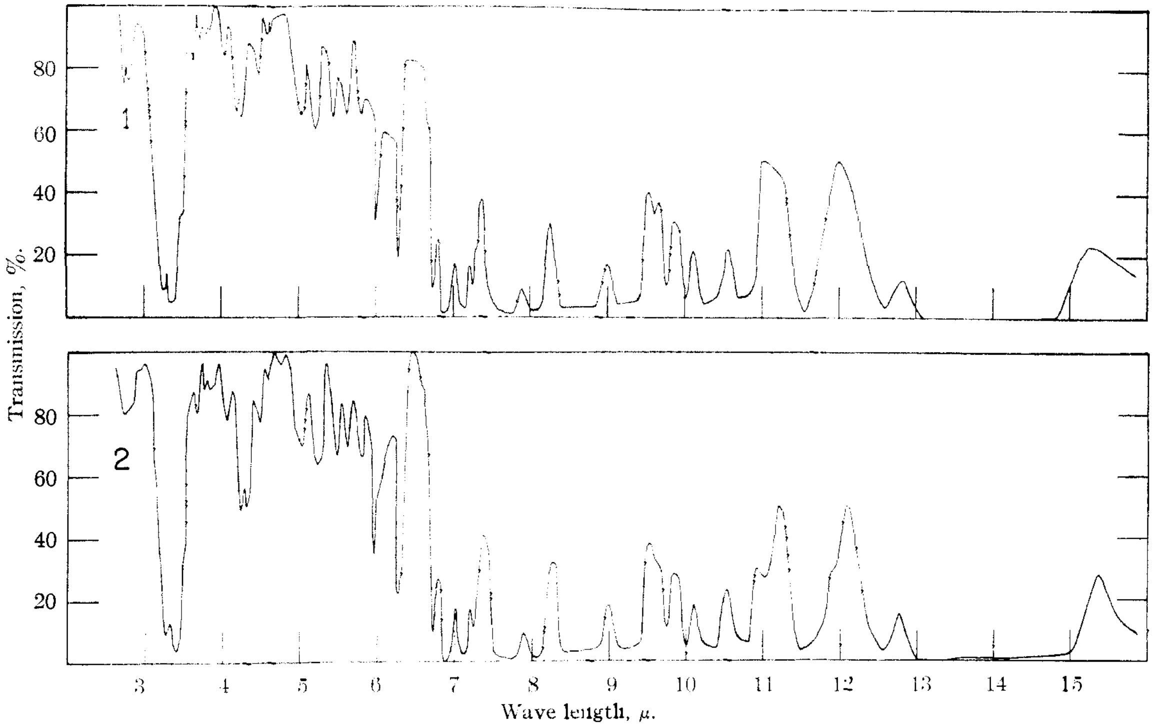


Fig. 2.—Infrared absorption spectra of the sulfone obtained by oxidizing crotyl phenyl sulfide (IX) (Curve 1) and the sulfone obtained by oxidizing α-methylallyl phenyl sulfide (X) (Curve 2).

s-butyl phenyl sulfone in approximately 90% of *n*-butyl phenyl sulfone in the sample derived from X, as shown by the close similarity of curves 1 and 3 (Fig. 3) and the intensity of the 11.76 μ band belonging to *s*-butyl phenyl sulfone in curve 3. This result, and the fact that infrared spectra and physical constants of the samples of sulfone obtained by oxidation of IX and X were identical, leads to the conclusion that oxidation of both sulfides produces a mixture containing approximately 90% of VII and 10% of VIII. The sulfone samples obtained by rearrangement of the two sulfinates V and VI had physical constants similar to the mixture of VII and VIII obtained by oxidizing IX and X, and as noted above were identified chemically as containing crotyl phenyl sulfone by reduction and conversion to a solid derivative of *n*-butyl phenyl sulfone. It is probable that both samples contained small amounts of α-methylallyl phenyl sulfone (see the section entitled "Infrared Spectra").

Possible interpretations of the route by which the isomeric sulfinates V and VI rearrange to a product composed largely of the same sulfone, VII, include the following: intramolecular rearrangement with inversion, leading to VII and VIII, which might in turn rearrange to a product containing predominately crotyl phenyl sulfone; interconversion of V and VI by an allylic rearrangement, followed by isomerization of the resulting mixture of sulfinates to a product containing predominately crotyl phenyl sulfone; rearrangement by an ionic mechanism, in which both esters could lead to the same product through formation of the same resonance-stabilized transitory carbonium ion, which on recombination with the benzenesulfinate anion could form the same product. Rearrangement by a combination of these mechanisms also is possible.

$$\begin{array}{l} \mathrm{V} \searrow \\ \qquad C_6H_5\overset{-}{S}O_2 + [\overset{+}{C}H_2{-}CH{=}CHCH_3 \longleftrightarrow \\ \mathrm{VI} \nearrow \\ \qquad\qquad CH_2{=}CH{-}\overset{+}{C}HCH_2] \longrightarrow \mathrm{VII} \end{array}$$

There is reason to believe that VII would be formed in larger amount than VIII, if the two were formed by an ionic process or were in equilibrium by an anionotropic mechanism, for an equilibrium mixture of the isomeric butenyl bromides contains over 80% of crotyl bromide.[10]

Acknowledgment.—We are indebted to Dr. R. C. Lord and Mr. R. S. McDonald for the measurement and interpretation of infrared spectra.

Experimental[11]

Allyl Phenyl Sulfide.—Allyl phenyl sulfide was prepared by the method of Hurd and Greengard[12]; b. p. 48–49°

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[10] Young and Lane, This Journal, **60**, 847 (1938).

[11] Melting points and boiling points are uncorrected except where otherwise specified. In the calculation of molecular refractions the Eisenlohr values were used (Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911), together with values of 7.80 for S in sulfides, 8.59 for SO in sulfoxides, 8.61 for SO_2 in sulfones and 1.25 for O in the S–O–C linkage (M_{He} values reported by Strecker and Spitaler, *Ber.*, **59B**, 1775 (1926)). An approximate M_D for the SO_2 group in sulfinic esters was obtained by addition of the value for SO in sulfoxides and for O in the S–O–C linkage.

[12] Hurd and Greengard, This Journal, **52**, 3357 (1930).

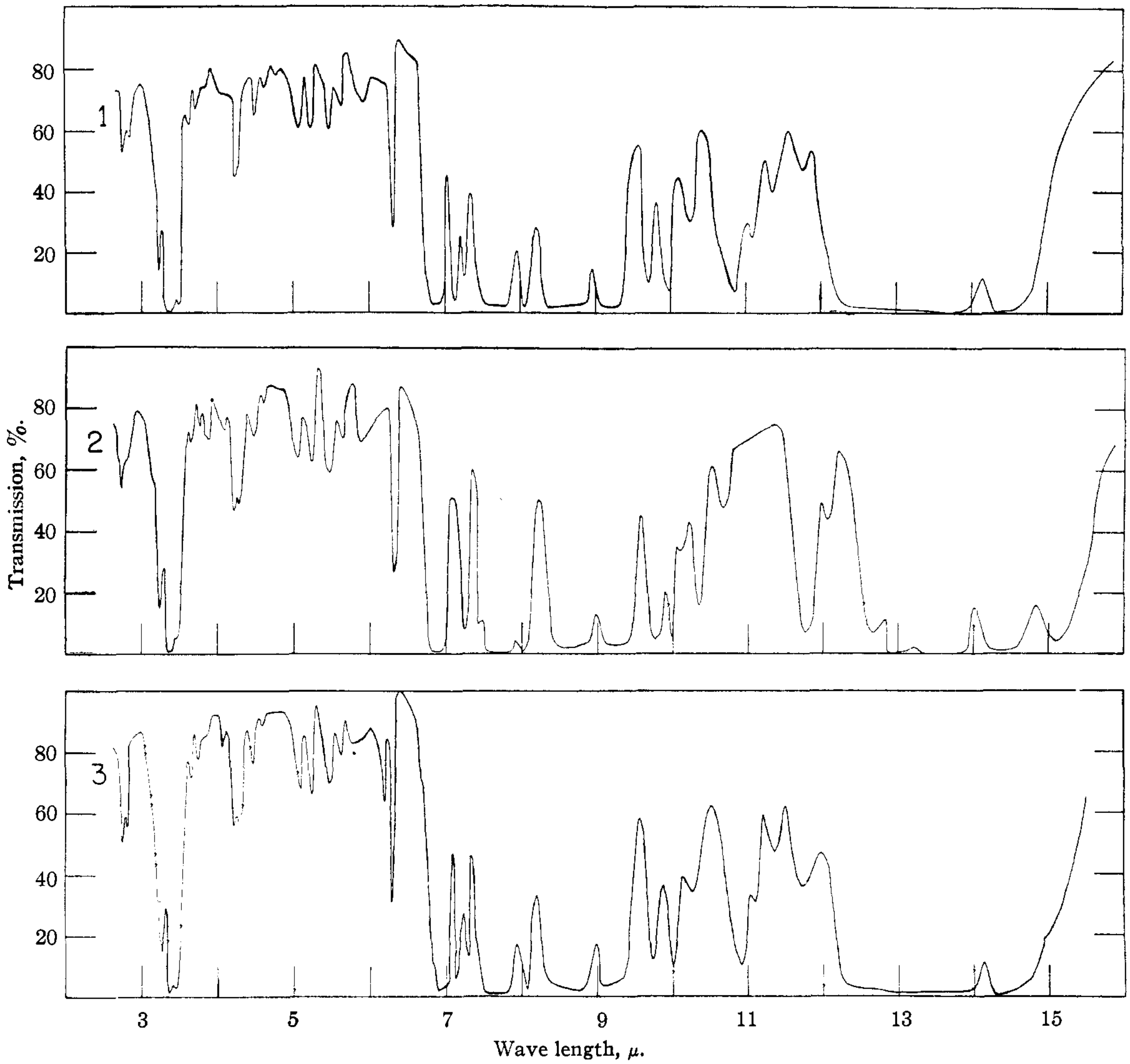

Fig. 3.—Infrared absorption spectra of *n*-butyl phenyl sulfone (Curve 1), *s*-butyl phenyl sulfone (Curve 2) and the saturated sulfone prepared from α-methylallyl phenyl sulfide (X) by oxidation followed by catalytic hydrogenation (Curve 3).

(0.43 mm.); n^{25}D 1.5732; d^{25}_4 1.0220; *M*D calcd. 47.49, found 48.46 (exaltation 0.97).

A solution of allyl phenyl sulfide in a mixture of equal parts of glacial acetic acid and acetic anhydride was ozonized at 5°, treated with water, and oxidized with 35% hydrogen peroxide. After decomposition of the excess hydrogen peroxide with manganese dioxide, acidification of the filtrate, and recrystallization of the extracted product, phenylsulfonylacetic acid was obtained, m. p. 111.5–112.5° (cor.).[13]

Allyl Phenyl Sulfoxide (I).—Compound I was prepared essentially by a method described by Hinsberg[14] for oxidizing formaldehyde diphenyl mercaptal to the disulfoxide. A solution of 38.8 g. of allyl phenyl sulfide in 400 ml. of glacial acetic acid was cooled to 0° in an ice-salt-bath. Hydrogen peroxide (30 g. of a 30% solution) was added with occasional shaking during twenty minutes and the mixture was allowed to stand at 0° for twenty hours. About two-thirds of the acetic acid was neutralized with sodium hydroxide, a large quantity of water was added, and the solution was extracted with chloroform. The combined extracts were washed with dilute sodium bicarbonate and hydrochloric acid, and then with water until the washings were neutral to litmus. The chloroform solution was dried over anhydrous potassium carbonate and distilled through a Vigreux column. The yield of I was 21.4 g. (64%), b. p. 103–104° (0.36 mm.); n^{25}D 1.5765; d^{25}_4 1.1205; *M*D calcd. 48.28, found 49.13 (exaltation 0.85).

Anal. Calcd. for $C_9H_{10}OS$: C, 65.03; H, 6.06. Found: C, 64.98; H, 6.28.

Compound I (10 g.) was heated at 100° for ten hours under a nitrogen atmosphere in a 50-ml. Claisen flask. Distillation separated 1.5 g. of allyl phenyl sulfide, b. p. 50° (0.4 mm.), n^{25}D 1.5684, and 1.9 g. of allyl phenyl sulfoxide, b. p. 102° (0.3 mm.), n^{25}D 1.5718. A higher boiling fraction of 2.4 g. partially solidified to give 0.84 g. of diphenyl disulfide as golden yellow needles, m. p. 57.5–60°. After recrystallization from ethanol, the diphenyl disulfide had m. p. 59–60°, which was not depressed by an authentic sample.[15]

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(13) Tröger and Vasterling, *J. prakt. Chem.*, [2] **72**, 338 (1905), report m. p. 112.5°.

(14) Hinsberg, *ibid.*, [2] **85**, 344 (1912).

(15) Taboury, *Ann. chim. phys.*, [8] **15**, 47 (1908).

Allyl Phenyl Sulfone (II).—II was prepared by the method of Otto.[16] After distillation through a Widmer column, II was obtained in 53% yield, b. p. 110–113° (0.5 mm.); n^{25}_{D} 1.5460; d^{25}_{4} 1.1844; M_D calcd. 48.30, found 48.72 (exaltation 0.42).

Catalytic hydrogenation of 9.1 g. of II dissolved in 40 ml. of absolute ethanol containing 1.5 g. of palladinized charcoal catalyst[17] (added in two portions) yielded 8.7 g. (95%) of *n*-propyl phenyl sulfone, m. p. and mixed m. p. with an authentic sample 44.5–46°.[18]

Heating II at temperatures varying from 150° (seven and one-half hours) to 250° (one and one-half hours) produced no detectable rearrangement. Partial decomposition occurred at the higher temperatures, but material was recovered in each instance which was identified as allyl phenyl sulfone by b. p., refractive index and in one case by hydrogenation in the presence of palladinized charcoal[17] to *n*-propyl phenyl sulfone, m. p. and mixed m. p. with an authentic sample[18] 44.5–46°.

Allyl β-Chloroethyl Sulfone.—Allyl β-chloroethyl sulfide[19] (27.3 g.) was oxidized with 50 ml. of 30% hydrogen peroxide by a procedure used by Pomerantz and Connor.[20] The yield of allyl β-chloroethyl sulfone after distillation through a Widmer column was 26.4 g. (78%), b. p. 105–109° (0.5 mm.); n^{25}_{D} 1.4970; d^{25}_{4} 1.2874; M_D calcd. 38.30, found 38.32.

Anal. Calcd. for $C_5H_9O_2SCl$: C, 35.58; H, 5.38. Found: C, 35.76; H, 5.33.

Allyl Vinyl Sulfone (IV).—IV was prepared by treating allyl β-chloroethyl sulfone (18.6 g.) with 11.3 g. of triethylamine in 130 ml. of anhydrous benzene, according to a procedure used by Alexander and McCombie[21] for the preparation of divinyl sulfone. After twenty-four hours, the precipitated triethylamine hydrochloride was separated by filtration and the benzene solution was washed with water and distilled. The yield of IV was 9.3 g. (63%), b. p. 118–120° (9.5 mm.), 80–83.5° (0.7 mm.); n^{25}_{D} 1.4815; d^{25}_{4} 1.1427; M_D calcd. 32.97, found 32.94.

Anal. Calcd. for $C_5H_8O_2S$: C, 45.41; H, 6.10. Found: C, 45.51; H, 6.28.

A 10.5-g. sample of IV was heated at 125° under nitrogen for twenty-four hours. On distillation 7.5 g. of IV was recovered. A 13.1-g. sample of IV heated at 150° for eighteen hours largely decomposed and polymerized, and the recovery of IV after distillation was only 2.6 g. To confirm the identity of the distillate, 1.78 g. was hydrogenated in alcohol solution in the presence of portions of palladinized charcoal[17] totaling 3 g. After separation of the catalyst, concentration and several recrystallizations of the residue from a mixture of pentane and methylene chloride 0.3 g. of ethyl *n*-propyl sulfone was obtained, m. p. 22–24°.[22] Another sample of IV heated at 175° for two hours decomposed and polymerized extensively, but 10% of IV was recovered.

Allyl Benzenesulfinate (III).—Benzenesulfinyl chloride was prepared and converted to III by modification of a procedure described for the preparation of ethyl *p*-toluenesulfinate.[23] Benzenesulfinyl chloride (42.5 g.) was allowed to react with allyl alcohol (23.1 g.) in anhydrous ether (120 ml.) over anhydrous potassium carbonate (55 g.) during twelve hours. III was isolated by adding water, separating the ether layer, extracting the ether layer several times with water, and washing the combined aqueous layers with ether. After drying the combined ether extracts over anhydrous potassium carbonate, distillation through a Widmer column yielded 23.7 g. (49%) of III, b. p. 81–82° (0.2 mm.); n^{25}_{D} 1.5430; d^{25}_{4} 1.1434; M_D calcd. 49.53, found 50.17 (exaltation 0.64).

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.04; H, 5.70.

Rearrangement of III.—III rearranged on heating at temperatures of 100 to 175°. Decomposition and polymerization were more extensive at the higher temperatures and the yields of allyl phenyl sulfone (II) were low. After 30.3 g. of III had been heated at 100° for twenty-nine hours, the dark product was dissolved in chloroform, washed with aqueous sodium bicarbonate and water, and dried over anhydrous potassium carbonate. Distillation yielded 21.3 g. (70%) of recovered III, b. p. 82–87° (0.3 mm.), n^{25}_{D} 1.5420–1.5423 and 6.1 g. (20%) of II, b. p. 110–113° (0.25 mm.), n^{25}_{D} 1.5448.

The identity of II prepared by rearrangement was established by reduction. A solution of 4.1 g. of the redistilled rearrangement product (II) in 50 ml. of ethanol containing 1 g. of palladinized charcoal[17] absorbed 104% of one molar equivalent of hydrogen during four and one-half hours. After concentration of the filtered solution, addition of water and recrystallization of the solid obtained from aqueous ethanol, there was obtained 2.1 g. (51%) of *n*-propyl phenyl sulfone, m. p. 43–44°, mixed m. p. with an authentic sample[18] 44–45.5°.

Crotyl Benzenesulfinate (V).—V was prepared in the same manner as III from benzenesulfinyl chloride and crotyl alcohol. It was found advisable to distil no more than 25 g. of V at a time in order to minimize decomposition. The yield of V was 29%, b. p. 66° (0.025 mm.), 100–102° (0.23–0.28 mm.), n^{25}_{D} 1.5388; d^{25}_{4} 1.1161; M_D calcd. 54.15, found 55.08 (exaltation 0.93).

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17; saponification equivalent, 196. Found: C, 61.20; H, 6.48; saponification equivalent, 195.

In order to verify the structure of the ester V a small amount was saponified. The alcohol produced was identified as crotyl alcohol by conversion to the 3,5-dinitrobenzoate, m. p. (after recrystallization from ethanol and pentane) and mixed m. p. with a known sample[24] 68–69.5°.

Rearrangement of V.—Preliminary trials showed that V decomposed exothermically after a variable induction period on heating at temperatures above 80°. By using an inert solvent, decomposition was minimized and it was possible to isolate the rearrangement product, crotyl phenyl sulfone (VII).

A solution of 10.0 g. of V in 25 ml. of anhydrous toluene was heated at 100° for six and one-half hours. The toluene was removed under reduced pressure, and the residual oil was refluxed with 400 ml. of 0.1 *N* sodium hydroxide solution in order to saponify any unchanged V. A benzene extract of the resulting mixture was washed with water, dried over sodium sulfate and distilled. There was obtained 1.8 g. (18%) of crotyl phenyl sulfone (VII), b. p. 111° (0.2 mm.), n^{25}_{D} 1.5490.

In order to determine the structure of the rearrangement product, an ethanol solution of 1.8 g. was heated with Norite under reflux, filtered and hydrogenated in the presence of palladinized charcoal.[17] The saturated sulfone was converted to a derivative by a procedure described by Ipatieff and Friedman,[9] by nitration and reduction, followed by reaction with *m*-bromobenzoyl bromide in the presence of 10% aqueous sodium hydroxide. Crystallization from ethanol separated two derivatives, both identifying the reduction product as *n*-butyl phenyl sulfone: (1) *n*-butyl *m*-(3-bromobenzoylamino)-phenyl sulfone, m. p. and mixed m. p. with a known sample 130–131.5°; (2) *n*-butyl *m*-(di-3-bromobenzoylamino)-phenyl sulfone, m. p. and mixed m. p. with a known sample 198–199.5°.

Crotyl Phenyl Sulfide (IX).—Thiophenol (25.0 g.) was added to a solution of sodium ethoxide prepared from 5.2 g. of sodium and 150 ml. of absolute ethanol. The solution was cooled in an ice-bath and 22.5 g. of crotyl

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[16] Otto, *Ann.*, **283**, 183 (1894).

[17] Hartung, THIS JOURNAL, **50**, 3372 (1928).

[18] Prepared from *n*-propyl iodide and sodium benzenesulfinate by the procedure of Otto, *Ber.*, **21**, 998 (1888), m. p. 44–45°.

[19] Scherlin and Wasilewsky, *J. prakt. Chem.*, [2] **121**, 174 (1929).

[20] Pomerantz and Connor, THIS JOURNAL, **61**, 3388 (1939).

[21] Alexander and McCombie, *J. Chem. Soc.*, 1916 (1931).

[22] Fenton and Ingold, *ibid.*, 2340 (1929), report m. p. 25°.

[23] Phillips, *ibid.*, **127**, 2569 (1925).

[24] Young and Andrews, THIS JOURNAL, **66**, 424 (1944).

chloride[25] was added dropwise with stirring during about one-half hour. The ice-bath was removed after about five and one-half hours and stirring was continued for one hour. Part of the solvent was removed under reduced pressure and water was added to the residue. The precipitated oil was separated, the water layer extracted with ether and the combined oil and extracts washed with water and dried over calcium chloride. Distillation through a Widmer column gave 27.9 g. (75%) of IX, b. p. 62.5–69° (0.5 mm.), n^{25}_{D} 1.5664–1.5676. Fractionation using a 1.3 × 23 cm. column packed with glass helices gave material having b. p. 69.6–70.0° (1.3 mm.); n^{25}_{D} 1.5680; d^{25}_{4} 1.0045; M_{D} calcd. 52.11, found 53.50 (exaltation 1.39).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.12; H, 7.37. Found: C, 72.98; H, 7.41.

In order to determine the amount of α-methylallyl phenyl sulfide (X) which was present in this product, the infrared spectrum was determined.

Differences between the infrared spectra of crotyl phenyl sulfide and α-methylallyl phenyl sulfide (described below) (Fig. 1) occur throughout the region studied (3–15 μ). The best absorption bands for determination of the concentration of the two isomers were those occurring at 10.90 μ for α-methylallyl phenyl sulfide and 10.33 μ for crotyl phenyl sulfide. The intensity of these bands allows the detection of as little as 0.5% of either isomer as an impurity in the other. On the basis of the intensities of these bands in the samples studied it was concluded that IX contained less than 1% of α-methylallyl phenyl sulfide (X) after the first distillation.

Crotyl Phenyl Sulfone (VII).—Following the procedure of Pomerantz and Connor[20] for the oxidation of sulfides to sulfones, a solution of 31.2 g. of IX in 200 ml. of a glacial acetic acid–acetic anhydride mixture was cooled to 0° and oxidized with 52 ml. of 30% hydrogen peroxide, which was added with shaking during thirty minutes. After the mixture had warmed to room temperature and stood for about three days, a small amount of manganese dioxide was added, the solution was filtered, and the solvent was removed under reduced pressure. Water was added to the residue, the oil separated, and the aqueous layer extracted with benzene. Distillation separated 16.0 g. (43%) of VII, b. p. 106–109° (0.1 mm.); n^{25}_{D} 1.5421; d^{25}_{4} 1.1581; M_{D} calcd. 52.92, found 53.34 (exaltation 0.42).

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17. Found: C, 61.07; H, 6.23.

Crotyl phenyl sulfone prepared in this manner was characterized by hydrogenation of an ethanol solution of 9.0 g. in the presence of 1.5 g. of palladinized charcoal catalyst[17] added in two portions. The reduction was slow but 98% of the theoretical one molar equivalent of hydrogen was absorbed. The solution was filtered and concentrated and the residue was diluted with water and extracted with benzene. The benzene solution was washed with water and dried over sodium sulfate. Distillation gave 7.6 g. (83%) of *n*-butyl phenyl sulfone, b. p. 105–108° (0.2 mm.), n^{25}_{D} 1.5240. The *n*-butyl phenyl sulfone so obtained was identified by conversion to *n*-butyl *m*-(3-bromobenzoylamino)-phenyl sulfone,[9] m. p. and mixed m. p. with the known sample described below 131–133°.

A small sample of the crotyl phenyl sulfone prepared by oxidizing IX was fractionated through a 0.6 × 31 cm. unpacked column and the spectrum of the distillate, n^{25}_{D} 1.5427, was determined in the range from 3–15 μ (Fig. 2). The identification of the major component of the sample as crotyl phenyl sulfone was confirmed by the intensity of the double bond stretching band at 6.11 μ; this band is much weaker than would be expected for the terminal double bond in α-methylallyl phenyl sulfone (VIII).

***n*-Butyl Phenyl Sulfone.**—This compound was prepared in the manner described by Baldwin and Robinson[26]; b. p. 117° (0.2 mm.); n^{25}_{D} 1.5242; d^{25}_{4} 1.1269; M_{D} calcd. 53.39, found 53.84 (exaltation 0.45).

Known derivatives which were prepared from this sample of *n*-butyl phenyl sulfone by the procedure of Ipatieff and Friedman[9] were *n*-butyl *m*-(3-bromobenzoylamino)-phenyl sulfone, m. p. 130.5–132° and *n*-butyl *m*-(di-3-bromobenzoylamino)-phenyl sulfone, m. p. 198–201°.

α-Methylallyl Benzenesulfinate (VI).—VI was prepared from benzenesulfinyl chloride and α-methylallyl alcohol by the procedure used for III and V. It was necessary to distil VI at low pressures in amounts not exceeding 10 g. in order to minimize decomposition. Yields of VI were about 12%; b. p. 64–68° (0.001 mm.); n^{25}_{D} 1.5312; d^{25}_{4} 1.1072; M_{D} calcd. 54.15, found 54.86 (exaltation 0.71).

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17. Found: C, 60.80; H, 6.14.

The structure of VI was verified by saponification with alkali and identification of the alcohol produced as α-methylallyl alcohol, m. p. of the 3,5-dinitrobenzoate (after crystallization from ethanol and methanol) and mixed m. p. with a known sample[24] 51.5–52.5°.

Rearrangement of VI.—VI was rearranged at low temperatures in toluene as a diluent in order to reduce the amount of decomposition. VI (10.0 g.) in 25 ml. of anhydrous toluene was heated at 80° for six and one-half hours. The product was isolated in the manner described under the rearrangement of V. Distillation yielded 2.0 g. (20%) of crotyl phenyl sulfone, b. p. 109–112° (0.2 mm.), n^{25}_{D} 1.5450. This product was hydrogenated with difficulty, presumably because of contamination with small amounts of decomposition products. The hydrogenation was completed as far as possible in ethanol solution by several additions of palladinized charcoal,[17] and boiling the solution with the catalyst at intermediate stages to remove catalytic poisons. The product was converted to a derivative by the procedure of Ipatieff and Friedman[9] as before. After recrystallization of the products from ethanol, there was obtained *n*-butyl *m*-(3-bromobenzoylamino)-phenyl sulfone (m. p. and mixed m. p. with a known sample 131–133°), and *n*-butyl *m*-(di-3-bromobenzoylamino)-phenyl sulfone (m. p. and mixed m. p. with a known sample, 200–201°).

***s*-Butyl Phenyl Sulfide.**—*s*-Butyl phenyl sulfide was prepared by the method of Taylor[27]; b. p. 63.5° (1 mm.); n^{25}_{D} 1.5395; d^{25}_{4} 0.9732; M_{D} calcd. 52.58, found 53.56 (exaltation 0.98).

The palladous chloride complex,[9,28] obtained by treatment with 2% aqueous palladous chloride solution, after recrystallization from aqueous acetone, had m. p. 141.5–142.5° (dec., cor.).

***s*-Butyl Phenyl Sulfone.**—Following the procedure of Pomerantz and Connor,[20] 30.0 g. of *s*-butyl phenyl sulfide was oxidized and yielded 28.0 g. (78%) of *s*-butyl phenyl sulfone, b. p. 113.5° (0.2 mm.); n^{25}_{D} 1.5271; d^{25}_{4} 1.1367; M_{D} calcd. 53.39, found 53.63 (exaltation 0.24).

Anal. Calcd. for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.45; H, 7.33.

s-Butyl *m*-(di-3-bromobenzoylamino)-phenyl sulfone, m. p. 170–172°, was prepared as a derivative.[9]

α-Methylallyl Phenyl Sulfide (X).—α-Methylallyl chloride[29] (45.3 g.) was added dropwise with stirring during one-half hour to a mixture, cooled in an ice-bath, prepared by adding 50.0 g. of thiophenol to a solution of sodium ethoxide (prepared by adding 10.4 g. of sodium to 300 ml. of absolute alcohol). The mixture was stirred at about 0° for four and one-half hours, allowed to stand overnight while the ice melted, concentrated under reduced

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(25) Prepared from a commercial mixture by the procedure of Roberts, Young and Winstein, THIS JOURNAL, **64**, 2163 (1942); b. p. 85–85.5° (767 mm.), n^{25}_{D} 1.4320.

(26) Baldwin and Robinson, *J. Chem. Soc.*, 1448 (1932).

(27) Taylor, THIS JOURNAL, **58**, 2650 (1936).

(28) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2731 (1938).

(29) Prepared from a commercial mixture according to the procedure of Roberts, Young and Winstein (ref. 25), except that a small amount of cuprous chloride was added during the first distillation (Lane, Fentress and Sherwood, THIS JOURNAL, **66**, 545 (1944)). Two distillations using a 110 cm. helix-packed column gave material having b. p. 63.6–65.0° (758 mm.), n^{20}_{D} 1.4161.

pressure to a volume of about 150 ml., and poured into 600 ml. of water. An ether extract of the mixture was washed with water and dried over magnesium sulfate. The pale yellow oil obtained upon concentration of the filtered solution was distilled twice through a Widmer column with a 15-cm. spiral. X was obtained in a yield of 40.1 g. (53%), b. p. 64-66° (1.7 mm.), n^{25}D 1.5540-1.5547. Fractionation of the higher boiling material through a 1.3 × 23 cm. helix-packed column afforded an additional 3.3 g. (4%). The two products were combined and fractionated through a 1.3 × 23 cm. helix-packed column. The yield of α-methylallyl phenyl sulfide (X) was 37.8 g. (51%), b. p. 56-58° (1.2 mm.); n^{25}D 1.5546; $d^{25}{}_4$ 0.9876; MD calcd. 52.11, found 53.34 (exaltation 1.23).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.12; H, 7.37. Found: C, 72.93; H, 7.61.

In addition to the 4% of X obtained from the fractionation of the higher boiling material, there was obtained 5.9 g. (8%) of crotyl phenyl sulfide (IX), b. p. 70.9-71° (1.3 mm.), n^{25}D 1.5676-1.5680.

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.12; H, 7.37. Found: C, 73.47; H, 7.55.

A 1-g. sample of X was heated at 150° for seven hours and then fractionated; 0.89 g. was recovered with little change in refractive index (n^{25}D 1.5542-1.5564).

Structure of X.—Palladium on Norite catalyst[30] (5 g.) was suspended in 20 ml. of 95% ethanol and shaken with hydrogen at atmospheric pressure until there was no further absorption.[31] A solution of 0.750 g. of α-methylallyl phenyl sulfide in 25 ml. of ethanol was then added, and the mixture was shaken with hydrogen. After five hours, 105% of one molar equivalent of hydrogen was absorbed. The catalyst was removed by filtration and digested twice with 25 ml. of boiling ethanol. The solvent from the combined filtrates was removed under reduced pressure and the oil was taken up in 100 ml. of ether, washed twice with 5% aqueous potassium hydroxide and then with five 10-ml. portions of water (until neutral) and dried over magnesium sulfate. The filtered solution after concentration under reduced pressure afforded 0.121 g. (16%) of a pale yellow oil, which was converted to the palladous chloride complex[9,23] by shaking with 3.8 ml. of 2% aqueous palladous chloride solution. Recrystallization of the solid thereby obtained from aqueous acetone gave 0.107 g. of the palladous chloride derivative of *s*-butyl phenyl sulfide as fine orange rods, m. p. and mixed m. p. with an authentic sample 140-142° (dec., cor.).

The infrared spectrum of X was determined in the range of 3-15 μ (Fig. 1). The double bond stretching band at 6.11 μ is at least a factor of three stronger in α-methylallyl phenyl sulfide (X) than in crotyl phenyl sulfide (IX). This is in agreement with the generally observed fact that terminal double bonds cause much stronger absorption in this region than internal double bonds, and affords confirmatory evidence that the product was α-methylallyl phenyl sulfide. From measurements of the intensities of the crotyl phenyl sulfide band at 10.33 μ in samples of X, as described above, it was concluded that they contained only 1-2% of crotyl phenyl sulfide.

Attempted Preparation of α-Methylallyl Phenyl Sulfone by Oxidation of α-Methylallyl Phenyl Sulfide.—Using essentially the procedure of Pomerantz and Connor,[20] a solution of 31.2 g. of α-methylallyl phenyl sulfide (n^{25}D 1.5544-1.5554) in 200 ml. of a glacial acetic acid-acetic anhydride mixture was cooled in an ice-salt-bath, and 52 ml. of hydrogen peroxide (35%) was added dropwise with stirring at 0-5° during one-half hour. The solution was stirred for one-half hour, freshly packed in ice and allowed to come to room temperature as the ice melted. After standing for three days, 5.5 g. of manganese dioxide was added in portions with cooling. When effervescence ceased, excess manganese dioxide was removed by filtration, and the filtrate was poured into 1500 ml. of water. An ether extract of the mixture was washed with 10% aqueous sodium bicarbonate and then with water until neutral. The solution, after drying over magnesium sulfate, was concentrated under reduced pressure at a temperature not exceeding 40°. There was obtained 26.5 g. (71%) of a yellow oil having n^{25}D of 1.5411, a portion of which was used for study of the infrared spectrum. Distillation of 19.9 g. of the oil yielded 15.6 g. (56%) of a colorless liquid, b. p. 110-113° (0.16 mm.); n^{25}D 1.5424; $d^{25}{}_4$ 1.1581; MD calcd. (for α-methylallyl phenyl sulfone or crotyl phenyl sulfone) 52.92, found 53.37 (exaltation 0.45).

Anal. Calcd. for $C_{16}H_{12}O_2S$: C, 61.19; H, 6.17. Found: C, 61.02; H, 6.24.

A solution of the sulfone (10.0 g.) prepared by oxidizing X, in 100 ml. of ethanol containing 1 g. of palladium on Norite catalyst[30] was hydrogenated at atmospheric pressure. Hydrogen absorption amounted to 92% of one molar equivalent in three and one-half hours. Addition of a further 0.5 g. of catalyst resulted in the absorption of an additional 4%. The catalyst was removed by filtration, and the filtrate after concentration under reduced pressure and distillation yielded 9.15 g. (91%) of a colorless liquid, b. p. approximately 95° (0.12 mm.); n^{25}D 1.5246; $d^{25}{}_4$ 1.1297; MD calcd. (for *n*- or *s*-butyl phenyl sulfone) 53.39, found 53.75, (exaltation 0.36). Another sample prepared in the same way was converted to a derivative by the procedure of Ipatieff and Friedman,[9] and gave *n*-butyl *m*-(3-bromobenzoylamino)-phenyl sulfone, m. p. 131.5-133°, which was not depressed on mixture with a known sample.

Infrared Spectra.—The spectra of crotyl phenyl sulfone obtained by oxidation of IX, and the product (before and after distillation) obtained by oxidizing X were identical in the range of 3-15 μ except for relatively weak absorption bands believed to be caused by small amounts of impurities (Fig. 2).

To determine the composition of the sulfone samples obtained by oxidizing IX and X the infrared spectrum of the saturated sulfone obtained by hydrogenating the sulfone prepared from X was compared with the infrared spectra of *n*-butyl phenyl sulfone and *s*-butyl phenyl sulfone (Fig. 3). The spectra of the latter two were sufficiently different to make the identification and analysis relatively simple. The spectrum of the reduction product contained all of the bands in the spectrum of a mixture of the two isomers and no additional bands. This is considered good evidence that the two components of the reduction product are *n*- and *s*-butyl phenyl sulfone. The amount of *s*-butyl phenyl sulfone was estimated as 10% on the basis of the intensity of the 11.76μ band of the *s*-butyl phenyl sulfone in the reduced sample. From this result, and the fact that the sulfone samples obtained by oxidizing IX and X have identical infrared spectra, it is inferred that the oxidations give a mixture composed of approximately 90% crotyl phenyl sulfone (VII) and 10% α-methylallyl phenyl sulfone (VIII).

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Summary

A number of allyl-substituted sulfur compounds have been prepared and examined for susceptibility to rearrangement on heating. Allyl phenyl sulfoxide, allyl phenyl sulfone and allyl vinyl sulfone undergo decomposition and polymerization rather than isomerization at tempera-

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[30] "Organic Syntheses," Vol. 26, John Wiley and Sons, New York, N. Y., 1946, p. 32.

[31] Hydrogenation of compounds containing divalent sulfur by the use of a similar type of catalyst has been reported by Mozingo, Harris, Wolf, Hoffhine, Easton and Folkers, THIS JOURNAL, **67**, 2092 (1945).

tures which produce any change. Allyl benzenesulfinate yields allyl phenyl sulfone on heating and both crotyl benzenesulfinate and α-methylallyl benzenesulfinate rearrange on heating to a product which is principally crotyl phenyl sulfone, and probably contains small amounts of α-methylallyl phenyl sulfone.

The oxidation of crotyl phenyl sulfide yields crotyl phenyl sulfone, and the oxidation of α-methylallyl phenyl sulfide also yields crotyl phenyl sulfone. The product obtained by oxidizing α-methylallyl phenyl sulfide was characterized chemically and by infrared analysis. The spectral analysis confirmed its identity as crotyl phenyl sulfone and indicated the presence in the sample of about 10% of the secondary isomer, α-methylallyl phenyl sulfone.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Decomposition of *p*-Methoxy-*p*′-nitrobenzoyl Peroxide

BY JOHN E. LEFFLER[1]

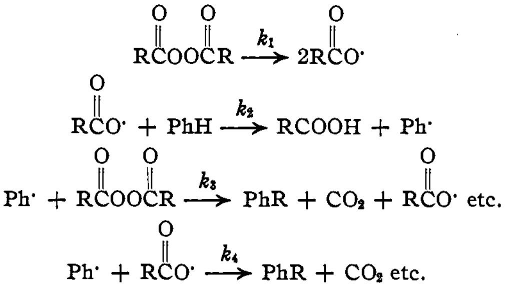
Part I. The Free Radical Decomposition

The present paper is part of a program of research on the mechanisms of peroxide decomposition and certain related oxidation reactions.[2] In particular it is desired to know: (a) the ionic or radical nature of the reaction mechanisms, (b) the role of the structure of the compound and the nature of the reaction medium in determining whether the reaction will be of radical or ionic type and (c) the extent to which a change in the ionic or radical character of the reaction changes the products.

Benzoyl peroxide has been shown to decompose by a free radical mechanism under most circumstances.[3] The reaction is of mixed first and higher order depending on the solvent and the nature of the processes by which chains of radical-induced decomposition are broken.[3] Evidence of the radical nature of the reaction is provided by the following facts: it is inhibited by oxygen; it goes at the same rate in the non-polar solvent benzene as it does in the polar solvent nitrobenzene; it initiates the polymerization of styrene. The reaction continues to be mainly radical in nature even under conditions favoring an ionic mechanism. Benzoyl peroxide acts as a polymerization initiator for the highly polar monomer acrylonitrile without any added solvent. Its decomposition. is only weakly catalyzed by acids and then only by the strongest acids in fairly high concentrations.[4] Such behavior is not surprising in view of the symmetrical structure of benzoyl peroxide.

The unsymmetrical analog, *p*-methoxy-*p*′-nitrobenzoyl peroxide, however, acts quite differently. Although it can decompose by a radical mechanism, a moderate change in the conditions of the reaction leads to decomposition by an ionic path.

The reaction in benzene at 70° is first order, the rate constant being $7.5 \pm 0.2 \times 10^{-2}$ hours^{-1}. The difference in rate constants between two runs differing in starting concentration by a factor of twelve is less than the experimental error. Unlike the decomposition of benzoyl peroxide the reaction is first order with no observable contribution from higher order terms. Figure 1 shows the kinetic runs in benzene at 70°, the black circle above the top curve shows the deviation from that curve caused by not removing oxygen from the ampoule containing the decomposing peroxide before sealing it. Since the reaction is slower in the presence of oxygen it is likely that the mechanism is similar to that of benzoyl peroxide decomposition, the oxygen inhibiting the reaction by combining with chain carrying radicals.



$$\mathrm{R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R} \xrightarrow{k_1} 2\mathrm{R\overset{O}{\overset{\|}{C}}O\cdot}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\cdot} + \mathrm{PhH} \xrightarrow{k_2} \mathrm{RCOOH} + \mathrm{Ph\cdot}$$

$$\mathrm{Ph\cdot} + \mathrm{R\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R} \xrightarrow{k_3} \mathrm{PhR} + \mathrm{CO_2} + \mathrm{R\overset{O}{\overset{\|}{C}}O\cdot}\ \text{etc.}$$

$$\mathrm{Ph\cdot} + \mathrm{R\overset{O}{\overset{\|}{C}}O\cdot} \xrightarrow{k_4} \mathrm{PhR} + \mathrm{CO_2}\ \text{etc.}$$

The observed kinetics will be first order if attack by radicals from the solvent is so much faster than attack by radicals from the peroxide that the former accounts for nearly all the induced decomposition. In such a case we have the equations[5]

(1) $-\mathrm{d[P]/d}t = k_1[\mathrm{P}] + k_3[\mathrm{Ph^\cdot}][\mathrm{P}]$

(2) $0 = 2k_1[\mathrm{P}] - k_2[\mathrm{RCOO^\cdot}] + k_3[\mathrm{P}][\mathrm{Ph^\cdot}] - k_4[\mathrm{Ph^\cdot}][\mathrm{RCOO^\cdot}]$

(3) $0 = k_2[\mathrm{RCOO^\cdot}] - k_3[\mathrm{Ph^\cdot}][\mathrm{P}] - k_4[\mathrm{Ph^\cdot}][\mathrm{RCOO^\cdot}]$

It can be shown that equations (2) and (3) are solvable for [Ph·] and that the expression obtained is not a function of [P]. It then follows that equation (1) is first order in [P].

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(2) J. E. Leffler, "Cleavages and Rearrangements of Oxygen Radicals and Cations," to appear in *Chemical Reviews*.

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(4) J. E. Leffler. Thesis, Harvard University, 1948.

(5) [P] stands for the peroxide concentration. Equations (2) and (3) are the steady state assumptions for the radicals RCOO· and Ph·.