benzoic acid no depression in melting point was observed, m.p. 170–171°. The infrared spectra were also superimposable.

Oxidation of 3-carbomethoxy-4-(3',4'-methylenedioxyphenyl) 6,7,8-trimethoxy-1-tetralone, (Vb). The oxidations of 0.5 g. (0.0012 mole) of tetralone, Vb, was conducted in a manner identical to the oxidation of compound II. Difficulties were encountered in the purification of the oily oxidation product as it resisted all attempts at purification by fractional crystallization and column chromatography. Sublimation of the oil at 100°/0.01 mm. afforded a quantity of crystalline material. Recrystallization from ether gave needles, m.p. 144–146°, which did not depress the melting point of 3,4,5-trimethoxyphthalic anhydride on admixture. The infrared spectra were superimposable.

Attempted epimerization of 3-carbomethoxy-4-(3',4',5'-trimethoxyphenyl) - 6,7 - methylenedioxy - 1 - tetralone, (Va). The tetralone (0.20 g.) was dissolved in 5 ml. of dry pyridine and heated for 24 hr. at 100°. The pyridine was removed and after crystallization from ethyl acetate, 0.19 g. of tetralone, m.p. 183–183.5°, was recovered. When admixed with starting material no melting point depression was observed.

Attempted epimerization of 3-carbomethoxy-4-(3',4'-methylenedioxyphenyl)-6,7,8-trimethoxy-1-tetralone, (Vb). The tetralone IVb (0.20 g.) was subjected to the same conditions as compound IVa. The material was crystallized from benzene-ether. The recovered tetralone, 0.18 g., m.p. 135–135.5° produced no melting point depression when admixed with starting material.

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LAWRENCE, KAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The *ortho*-Claisen Rearrangement. V. The Products of Rearrangement of Allyl *m*-X-Phenyl Ethers[1]

WILLIAM N. WHITE AND CARL D. SLATER[2,3]

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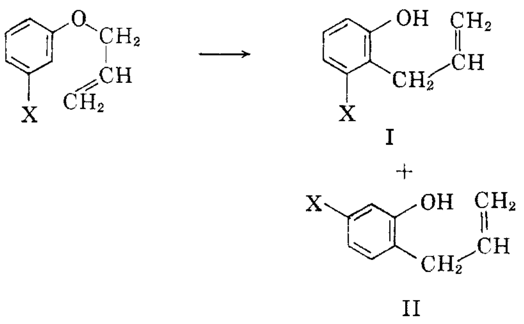
Isotope dilution analysis has been applied to determine the percentages of 2-allyl-5-X-phenol formed during the Claisen rearrangement of six allyl *m*-X-phenyl ethers.

The effect of substituents on the rearrangement of allyl aryl ethers has been investigated extensively.[4–7] These studies have led to a definition of the stereochemical[7] and electrical[6] nature of the transition state of this rearrangement. However, the isomerization of allyl *m*-X-phenyl ethers has not been systematically examined, and the scanty information which is available[5] indicates these compounds may behave somewhat anomalously. Therefore, it seemed probable that an investigation of the Claisen rearrangement of allyl *m*-X-phenyl ethers would lead to information more clearly delineating the electronic character of this reaction.

As a first phase of this study, it was deemed desirable to determine the distribution of isomers resulting from reaction of an allyl *m*-X-phenyl ether. This question has been investigated only superficially in the past. Previous results are summarized in Table I.



In the case of the methoxy, hydroxy and trifluoromethyl substituents the structure of the product indicated was established. The yields, however, are not sufficiently high to exclude the possibility of significant quantities of the other isomer having been formed, but lost in the work-up. Some work with allyl *m*-acetamidophenyl ether is interesting in this respect. Arnold and co-workers[8] report that only the 5-acetamido product was obtained. The structure was proven and its melting point was given as 160.5–162°. On the other hand, Budesinsky and Rockova[9] performed the rearrangement under identical condi-

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[2] Monsanto Fellow, 1959–60; Ethyl Corp. Fellow, 1958–59.

[3] From the thesis submitted by Carl D. Slater in partial fulfillment of the requirements for the Doctor of Philosophy Degree at the Ohio State University.

[4] W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

[5] H. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3278 (1958).

[6] W. N. White and W. K. Fife, *J. Am. Chem. Soc.*, **83**, 3846 (1961).

[7] (a) E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, **25**, 676 (1960); (b) A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 4681 (1960); (c) W. N. White and B. E. Norcross, *J. Am. Chem. Soc.*, **83**, 1968 (1961); (d) L. D. Huestis and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 1963 (1961).

[8] R. T. Arnold, J. McCool, and E. Schultz, *J. Am. Chem. Soc.*, **64**, 1023 (1942).

[9] Z. Budesinsky and R. Rockova, *Chem. Listy*, **48**, 427 (1954); *Chem. Abstr.*, **49**, 3880 (1955).

TABLE I

PRODUCTS OF REARRANGEMENT OF ALLYL *m*-X-PHENYL ETHERS REPORTED IN THE CHEMICAL LITERATURE

X	Allyl Subst.[a]	Solvent	Isomer[b]	Yield, %
OCH$_3$[c]	None	DMA[j]	II	—
CH$_3$[d]	None	None	I + II	70
OH[e]	None	None	II	45
NHCOCH$_3$[f]	None	DMA[j]	II	67
NHCOCH$_3$[g]	None	DMA[j]	I	46
			II	40
CH$_3$[h]	β-CH$_3$	None	II	—
CF$_3$[i]	None	None	II	75
CF$_3$[i]	α-CH$_3$	None	No reaction	

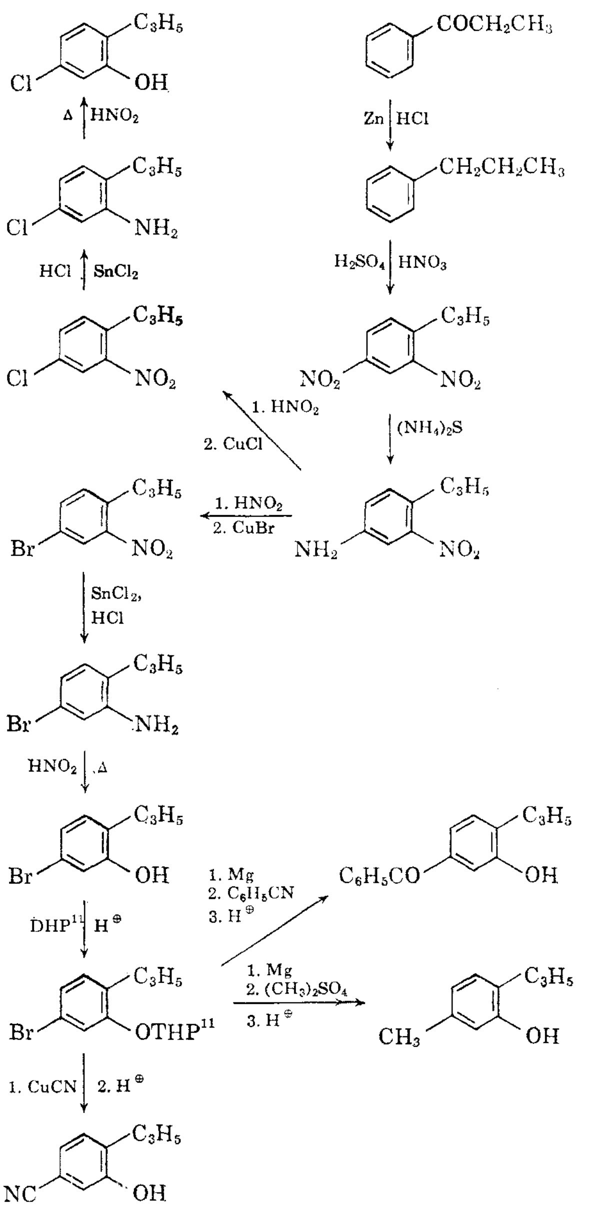
[a] Substituent in allyl group. [b] I = 2-allyl-3-X-phenol, II = 2-allyl-5-X-phenol. [c] Ref. 13. [d] L. Claisen and O. Eisleb, *Ann.*, 401, 57 (1913). [e] C. D. Hurd, H. Greengard, and F. D. Pilgrim, *J. Am. Chem. Soc.*, 52, 1700 (1930). [f] Ref. 8. [g] Ref. 9. [h] Q. R. Bartz, R. F. Miller, and R. Adams, *J. Am. Chem. Soc.*, 57, 371 (1935). [i] E. T. McBee and E. Rapkin, *J. Am. Chem. Soc.*, 73, 2375 (1951). [j] DMA = *N,N*-dimethylaniline.

tions and isolated both the 5-isomer and the 3-isomer in yields of 40% and 46%, respectively. The melting points were 164–165.5° and 158–159°, respectively. It can be inferred from this example that the quantitative nature of the data given in Table I is doubtful.

RESULTS AND DISCUSSION

The amount of 2-allyl-5-X-phenol formed in the rearrangement of allyl *m*-X-phenyl ethers was determined by isotopic dilution analysis[10] with carbon-14. The procedure adopted required the preparation of a series of 2-*n*-propyl-5-X-phenyl *p*-bromobenzenesulfonates. The syntheses of the 2-*n*-propyl-5-X-phenols, except for 2-*n*-propyl-5-methoxyphenol, are summarized as follows.

To carry out the isomer distribution analyses samples of allyl *m*-X-phenyl ether were dissolved in pure Carbitol, and heated for one to four half-lives in a constant temperature bath. The rearrangement products were isolated and subjected to quantitative hydrogenation of the allyl group double bond. The phenol was converted to the *p*-bromobenzenesulfonate by means of *p*-bromobenzenesulfonyl-C^{14} chloride and the crude mixture of isomeric *p*-bromobenzenesulfonates was then admixed with a weighed portion of inactive 2-*n*-propyl-5-X-phenyl *p*-bromobenzenesulfonate. The resulting material was recrystallized to constant activity as ascertained by activity determinations after five and seven recrystallizations. In summary the procedure was as shown on p. 3633.



The results obtained in this way are summarized in Table II.

The determination of the ratio of isomers formed in the rearrangement of allyl *m*-methoxyphenyl ether was slightly different from that already described. The synthesis of 2-*n*-propyl-3-methoxyphenyl *p*-bromobenzenesulfonate was accomplished by esterification of the hydrogenated product of rearrangement of allyl *m*-methoxyphenyl ether. Mauthner[13] showed that 2-allyl-5-methoxyphenol was obtained by rearrangement of allyl *m*-methoxyphenyl ether in refluxing *N,N*-dimethylaniline, but no yields were stated. When allyl *m*-methoxyphenyl ether was rearranged, hydrogenated, and converted to the *p*-bromobenzenesulfonate, a 31% yield of a crystalline compound, m.p. 106.4–107.9° was obtained. The remainder was a viscous oil, b.p. 220° at 2 mm. Both gave correct analyses for the desired *p*-bromobenzenesulfonate. The solid product was

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(10) V. J. Linnenbom in A. C. Wahl and N. A. Bonner, *Radioactivity Applied to Chemistry*, J. Wiley and Sons, Inc., New York, N. Y., 1951, p. 96.

(11) DHP = dihydropyran, THP = tetrahydropyranyl.

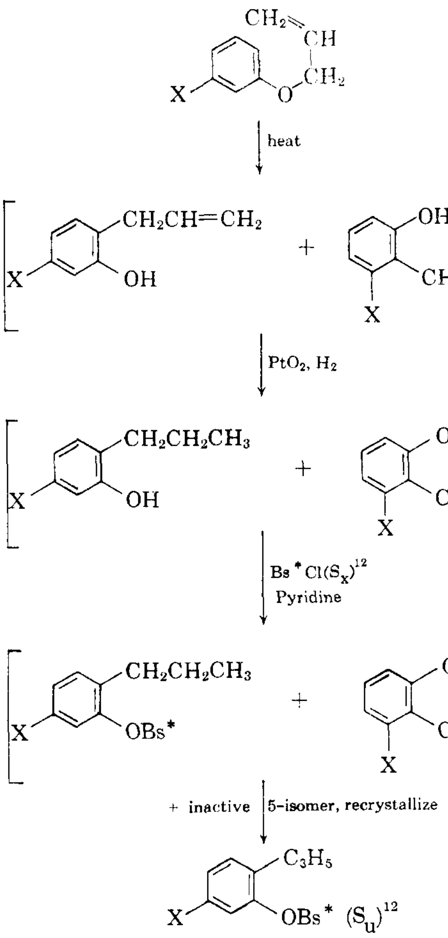

TABLE II

PERCENTAGE OF 2-ALLYL-5-X-PHENOLS FORMED IN THE REARRANGEMENT OF ALLYL *m*-X-PHENYL ETHERS

X	Temp.[a]	Mmole Sample	Mmole Diluent[b]	S_u[c] × 10^{-5}	Percent 5-Isomer[d]	Ratio of Isomers
OCH_3[e]	200	0.258	2.20	2.74	66[e]	1.94
OCH_3[e]	160	0.249	1.87	2.83	69[e]	2.22
CH_3	200	0.197	2.52	2.19	40	0.67
CH_3	160	0.242	2.87	2.50	43	0.75
CH_3	160	0.206	3.33	1.64	38	0.61
Br	200	0.310	1.84	4.10	36	0.56
Br	200	0.298	2.89	2.52	35	0.54
Br	160	0.192	1.54	2.57	29	0.41
Cl	200	0.322	2.16	3.56	35	0.54
Cl	200	0.209	2.58	1.90	33	0.49
Cl	160	0.191	1.41	3.17	34	0.52
COC_6H_5	200	0.279	2.06	2.15	23	0.30
COC_6H_5	160	0.214	3.32	0.99	21	0.26
CN	200	0.214	2.10	2.14	30	0.43
CN	160	0.219	2.18	2.20	31	0.45

[a] Temperature of rearrangement. [b] Inactive aryl *p*-bromobenzenesulfonate. [c] Specific activity of dilute, recrystallized 2-allyl-5-X-phenyl-*p*-bromobenzenesulfonate in mv./min./mole. [d] Calculated using S_x (activity of *p*-bromobenzenesulfonyl chloride) value of 7.24 × 10^6 mv./min./mole. [e] The diluent was 2-allyl-3-methoxyphenyl *p*-bromobenzenesulfonate. The fraction of 5-isomer was obtained by difference (see text).

hydrolyzed with base and demethylated with hydrobromic acid in acetic acid to give 2-*n*-propylresorcinol, as shown by the melting points of both 2-*n*-propylresorcinol and its bis-*p*-nitrobenzoate ester. The solid ester was therefore 2-*n*-propyl-3-methoxyphenyl *p*-bromobenzenesulfonate. The liquid was presumed to be the impure 5-methoxy isomer.

Because of this, the amount of 2-allyl-3-methoxyphenol formed in the rearrangement of allyl *m*-methoxyphenyl ether was determined by isotope dilution analysis using the crystalline 2-*n*-propyl-3-methoxyphenyl ester as diluent. The amount of the 5-isomer formed was obtained by difference.

Because of the extremely small quantities (from 4 to 8 ml.) of hydrogen involved in the hydrogenation step, it was felt that not too much significance could be attached to the measured percentages of theoretical hydrogen consumption. However, the hydrogen uptake fell in the range of 100±11% in all cases except for the product of rearrangement at 160° of allyl *m*-methoxyphenyl ether and one run on the product of rearrangement at 160° of allyl *m*-methylphenyl ether. These samples consumed 84 and 78%, respectively.

The hydrogenation of the rearrangement products of allyl *m*-cyanophenyl ether and allyl *m*-benzoylphenyl ether require special mention because of the nature of the substituents. It was shown in both cases that only the allyl group was affected. The compounds consumed 100 ± 10% of the theoretical amount of hydrogen. No further uptake was noted for periods of up to two hours. The infrared spectrum of the benzoyl substituted product contained a band at 6.0 μ which was also present and of equal intensity in the spectrum of the starting material. This is indicative of a carbonyl group located between two aromatic nuclei.[14] The band at

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[12] Bs‡ = radioactive *p*-bromobenzenesulfonyl derivative of activity S_x or S_u.

[13] F. Mauthner, *J. prakt. Chem.*, [2] **102**, 41 (1921).

[14] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., J. Wiley and Sons, Inc., New York, 1958.

10.9 μ present in the spectrum of the starting material and due to the vinyl group was missing in the spectrum of the product. Likewise, for the cyano substituent, there were equal intensity bands present in the spectra of both starting material and product at 4.5 μ, characteristic of a nitrile, whereas the vinyl absorption was present only in the spectrum of the starting material.

The per cent conversion of the hydrogenated phenols to *p*-bromobenzenesulfonates could be easily assayed. It was shown that the phenols could be recovered from ligroin in 100 ± 6% yield by thorough washing with sodium hydroxide solution. The wash solution was diluted to an appropriate volume. The optical density was determined at the λ_{max} for the phenoxide ion and used to determine the amount of phenol recovered by utilization of the extinction coefficient.

For this purpose the mother liquor from the first crystallization of the *p*-bromobenzenesulfonate esters was treated as described. Any unchanged 2-*n*-propyl-5-X-phenol would thus be recovered. In all cases, the conversion to the ester proved to be greater than 94%. Minor modifications of this procedure, as noted in the Experimental section, were employed for the rearrangement products of allyl *m*-cyanophenyl ether and allyl *m*-benzoylphenyl ether.

To test the accuracy of this method of determining isomer distribution a sample of 2-*n*-propyl-5-bromophenol was treated as described above for the allyl *m*-X-phenyl ethers. The product had 91% of the calculated activity. A subsidiary, although speculative, indication of the accuracy of the method is the precision of the results obtained (Table II).

The data summarized in Table II tend to indicate that the steric effect of substituents in allyl *m*-X-phenyl ethers have very little effect upon the isomer distribution observed in the rearrangement of these ethers. On the other hand, the electrical nature of the substituent appears to have a small influence on the ratio of isomers. The table shows that the ratio of 2-allyl-5-X-phenol to 2-allyl-3-X-phenol varies from 0.28 to 2.1. This variation does not follow any systematic pattern with respect to the expected steric bulk of the substituents. Thus, the benzoyl group would be expected to be the largest of the groups examined, but allyl *m*-benzoylphenyl ether gives the highest proportion of the most hindered isomer (2-allyl-3-X-phenol) of any of the ethers studied. This type of result is not very surprising. The fact that the allyl chain is bound to the ether oxygen makes it extremely improbable that its other end could approach a *meta* substituent on the ring sufficiently closely to cause appreciable steric interaction.

The ratio of isomers obtained from rearrangement of allyl *m*-X-phenyl ethers appears to vary roughly with the electrical nature of the *meta* substituent. Thus, electron-donating substituents (CH_3O and CH_3) appear to favor formation of the unhindered 5-isomer while the electron-withdrawing groups (CN and COC_6H_5) favor formation of the hindered 2-allyl-3-X-phenol. The explanation for this trend is not readily apparent.

Another interesting feature of the results in Table II is the insensitivity of the ratio of isomers to the temperature of rearrangement. The largest change in this ratio, 0.41 to 0.55 over a temperature range of 40° (160° to 200°), was observed in the rearrangement of allyl *m*-bromophenyl ether. These small or nonexistent changes in isomer ratio with temperature indicate that there must be little difference in the activation enthalpy for rearrangement of the allyl *m*-X-phenyl ether to 2-allyl-3-X-phenol or to 2-allyl-5-X-phenol.

EXPERIMENTAL

Preparation of allyl m-X-phenyl ethers. A mixture of 0.1 mole of substituted phenol, 0.1 mole of allyl bromide and 0.2 mole of powdered anhydrous potassium carbonate in 100 ml. of anhydrous acetone was stirred and refluxed for 8 or more hours. Water (250 ml.) was then added and the organic matter removed by extraction with three 50-ml. portions of ether. The combined ether extracts were washed with two 50-ml. portions of 2% potassium hydroxide solution and once with 100 ml. water. The ether solution was dried by filtration through anhydrous magnesium sulfate and the ether removed on the steam bath. The residue was then distilled at reduced pressure. The ethers prepared in this manner are listed in Table III.

n-Propylbenzene. To 900 g. of amalgamated zinc,[15] 750 ml. of water and 900 ml. of concd. hydrochloric acid was added 243.0 g. (1.81 moles) of propiophenone. After refluxing vigorously for 5 hr., the organic layer was separated, dried over anhydrous calcium chloride, and distilled to give 170.4 g. (78%) of *n*-propylbenzene, b.p. 155–160° (lit.[16] b.p. 155–160°).

2,4-Dinitro-n-propylbenzene. To a stirred solution of 1500 ml. of concd. sulfuric acid and 800 ml. of concd. nitric acid at 40° was added dropwise during 1 hr. 345 g. (2.86 moles) of *n*-propylbenzene. After addition was complete, stirring was continued and the temperature maintained at 40° for 30 min. The stirred mixture was then heated for 45 min. on the steam bath, during which time the temperature rose to 90°. The acid was separated and the organic layer was taken up in 1.5 l. of ether. The ether was washed with 500 ml. of water, 500 ml. of 7% sodium carbonate solution and 500 ml. of water. Evaporation of the ether and distillation of the residue gave 481 g. (80%) of product, b.p. 154–160° at 2.5 mm. (lit.[17] b.p. 170–173° at 11 mm.).

3-Nitro-4-n-propylaniline. In a 5-l., three-neck flask equipped with addition funnel, stirrer, and reflux condenser was placed 388 g. (1.85 moles) of 2,4-dinitro-*n*-propylbenzene and 400 ml. of 95% ethanol. The solution was brought to reflux and then 1713 ml. of 22% ammonium sulfide solution was added over 0.5 hr. The solution was refluxed an additional 40 min. and was then poured into 4 l. of ice water. After standing for 3 hr., the solid was collected by filtration and pressed dry. It was then taken up in 800 ml. of 95% ethanol and decolorized with activated charcoal. The ethanolic solution was poured slowly with stirring into 3.5 l. of ice water, and after standing 3 hr. the solid was again

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(15) E. L. Martin in R. Adams, *Org. Reactions*, Vol. I, J. Wiley and Sons, Inc., New York, 1942, p. 163.

(16) E. Clemmensen, *Ber.*, **46**, 1837 (1913).

(17) O. L. Brady and R. N. Cunningham, *J. Chem. Soc.*, 121 (1934).

TABLE III

PREPARATION OF ALLYL *m*-X-PHENYL ETHERS

X	Yield, %	B.P. (mm.)	Calcd. C	Calcd. H	Found C	Found H
OCH_3	87	73.0–73.5(1)[a]				
CH_3	81	64.5–65.0(4)[b]				
Br	92	105–106(5.5)	50.73	4.21	50.56	4.46
Cl	87	79–80(2.5)	64.10	5.38	64.39	5.22
COC_6H_5	64	163–164(1)	80.64	5.92	80.49	5.72
CN	90	128.5(6)	75.45	5.69	75.27	5.51

[a] Ref. 5 gives b.p. 66.0–66.1° at 0.5 mm. [b] L. Claisen and O. Eisleb (*Ann.*, **401**, 57 (1913)) report b.p. 92–94° at 12 mm

collected and dried. Crystallization from benzene-petroleum ether (b.p. 60–68°) mixture followed by crystallization from petroleum ether (b.p. 60–68°) alone gave 145 g. (44%) of bright orange crystals, m.p. 57.6–59.0° (lit.[8] m.p. 59.0–59.5°).

2-n-Propyl-5-chloronitrobenzene. To 40 ml. of concd. hydrochloric acid and 25 ml. of water was added 17.4 g. (0.097 mole) of 3-nitro-4-*n*-propylaniline. The mixture was heated and stirred until a fine slurry resulted. It was then cooled with stirring to 0° by immersion in an ice bath. While the temperature was kept at 0° a solution of 6.76 g. (0.097 mole) of sodium nitrite in 20 ml. of water was added dropwise. The resulting clear solution was stirred an additional 15 min. and then added dropwise to a stirred cuprous chloride solution at 27°. (The cuprous chloride solution was prepared by dissolving 29.9 g. of hydrated copper sulfate and 11.0 g. of sodium chloride in 100 ml. of water, adding 5.0 g. of sodium bisulfite in 15 ml. of water at 55°, filtering off the solid quickly and dissolving it in 47 ml. of concd. hydrochloric acid and 25 ml. of water.)

The resulting solution was stirred overnight, then allowed to stand for 4 days, and finally heated on the steam bath for 45 min. with stirring. The solution was cooled and extracted three times with 75-ml. portions of benzene. The benzene extract was washed twice with 50-ml. portions of 5% sodium hydroxide solution and twice with 100-ml. portions of water. It was then dried by filtration through anhydrous magnesium sulfate and the benzene was stripped off. Distillation of the residue gave 15.2 g. (79%) of pale yellow liquid, b.p. 104–106° at 2 mm. or 131–132° at 7 mm.

Anal. Calcd. for $C_9H_{10}ClNO_2$: C, 54.14; H, 5.05. Found: C, 54.31; H, 5.13.

2-n-Propyl-5-chloroaniline. To a solution of 23.0 g. (0.115 mole) of 2-*n*-propyl-5-chloronitrobenzene in 200 ml. of 95% ethanol was added over 5 min. with swirling a solution of 79.0 g. (0.35 mole) of hydrated stannous chloride in 150 ml. of concd. hydrochloric acid. Swirling was continued until the temperature began to fall. The solution was then heated on the steam bath for 15 min. and finally cooled to room temperature. A solution of 200 g. of sodium hydroxide in 500 ml. of water was added and the resulting warm mixture was allowed to cool to room temperature. It was extracted four times with 100-ml. portions of ether. The combined extracts were dried over anhydrous potassium carbonate, the ether was evaporated, and the residue was distilled. There was obtained 18.1 g. (92%) of colorless oil, b.p. 104–105° at 1.5 mm.

Anal. Calcd. for $C_9H_{12}ClN$: C, 63.71; H, 7.13. Found: C, 63.59; H, 7.21.

2-n-Propyl-5-chlorophenol. A fine slurry was prepared from 15.1 g. (0.089 mole) of *2-n*-propyl-5-chloroaniline, 20 ml. of concd. sulfuric acid and 150 ml. of water. To this slurry was added with rapid stirring at 5° a solution of 6.13 g. (0.089 mole) of sodium nitrite in 20 ml. of water. After an additional stirring period of 15 min., the solution was filtered. The bulk of this solution was kept in an ice bath while small portions were added dropwise to a solution of 50 ml. of concd. sulfuric acid and 100 ml. of water at 135–140° in a 500-ml. three-neck flask equipped with addition funnel, thermometer, and steam-distillation take-off condenser. The addition of the diazonium solution required 1.5 hr. Distillate was collected until no more oil passed over. The distillate was extracted with three 75-ml. portions of ether. The combined ether extracts were dried by filtration through anhydrous magnesium sulfate, the ether was evaporated, and the residue distilled. The distillate was taken up in anhydrous ether and passed through a short column of Woelm alumina. Distillation, after removal of ether, gave 10.9 g. (72%) of product, b.p. 103–104° at 3 mm.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.71; H, 6.54. Found: C, 63.96; H, 6.60.

2-n-Propyl-5-bromonitrobenzene. To a solution of 130 ml. of concd. sulfuric acid in 1500 ml. of water was added 152.0 g. (0.85 mole) of 3-nitro-4-*n*-propylaniline. The resulting slurry was cooled to 5° and rapidly stirred while a solution of 58.3 g. (0.85 mole) of sodium nitrite in 150 ml. of water was added. The temperature was maintained at 5° during this addition and for an additional 15 min. The cold diazonium solution was then slowly (0.5 hr.) poured with stirring into a solution of 129 g. (0.90 mole) of cuprous bromide in 800 ml. of 48% hydrobromic acid and 200 ml. of water while the temperature was kept at 25–30°. The solution was stirred overnight, then extracted four times with 150-ml. portions of ether. The combined ether extracts were dried by filtration through anhydrous magnesium sulfate and the ether was evaporated. The residue was distilled at reduced pressure, then taken up in anhydrous ether and passed through a short column of Woelm alumina. The solvent was removed and the product distilled to give 159.6 g. (77%) of pale yellow liquid, b.p. 99–101° at 0.5 mm. or 105° at 1 mm.

Anal. Calcd. for $C_9H_{10}BrNO_2$: C, 44.21; H, 4.17. Found: 44.18; H, 4.03.

2-n-Propyl-5-bromoaniline. To a solution of 45.8 g. (0.188 mole) of 2-*n*-propyl-5-bromonitrobenzene in 200 ml. of 95% ethanol was added with swirling during 5 min. a solution of 135.3 g. (0.600 mole) of hydrated stannous chloride in 200 ml. of concd. hydrochloric acid. The resulting solution was allowed to stand for 1 hr. and was then cooled in an ice bath. After the addition of 300 g. of sodium hydroxide in 1 l. of water the suspension was cooled and extracted four times with 150-ml. portions of ether. The combined extracts were dried over anhydrous potassium carbonate. The ether was evaporated and the residue distilled to give 36.9 g. (92%) colorless oil, b.p. 134–136° at 6 mm.

Anal. Calcd. for $C_9H_{12}BrN$: C, 50.48; H, 5.65. Found: C, 50.75; H, 5.43.

2-n-Propyl-5-bromophenol. A fine slurry prepared from 50.3 g. (0.235 mole) of 2-*n*-propyl-5-bromoaniline, 40 ml. of concd. sulfuric acid and 750 ml. of water was cooled to 5°. A solution of 16.1 g. of sodium nitrite in 50 ml. of water was added to this stirred suspension during 0.5 hr. After an additional 15 min. at 5°, the diazonium solution was treated in the same manner as described above in the preparation of 2-*n*-propyl-5-chlorophenol. Approximately 1 l. of distillate was collected in 2 hr. This distillate was extracted three times with 75-ml. portions of ether. The combined extracts were dried by filtration through anhydrous magnesium sulfate and the ether was evaporated. Distillation of the residue gave 38.3 g. (76%) of colorless oil, b.p. 108–110° at 2 mm.

Anal. Calcd. for $C_9H_{11}BrO$: C, 50.24; H, 5.15. Found: C, 50.18; H, 4.95.

2-(2-n-Propyl-5-bromophenoxy)tetrahydropyran. To 49.5 ml. (0.500 mole) of dihydropyran containing 4 drops concd. hydrochloric acid was added 73.5 g. (0.342 mole) of 2-*n*-propyl-5-bromophenol. The solution was swirled for 5 min. then kept overnight. Ether (150 ml.) was added and the ethereal solution was washed three times with 80-ml. portions of 10% sodium hydroxide solution and twice with 100-ml. portions of water. The ether layer was dried by filtration through anhydrous magnesium sulfate and the solvent was evaporated. Double distillation of the residue gave 82.5 g. (81%) of pale yellow oil, b.p. 130–135° at 0.5 mm.

Anal. Calcd. for $C_{14}H_{19}BrO_2$: C, 56.20; H, 6.40. Found: C, 56.53; H, 6.38.

2-n-Propyl-5-cyanophenol. To a solution of 30.7 g. (0.103 mole) of 2-(2-*n*-propyl-5-bromophenoxy)tetrahydropyran in 100 ml. of freshly distilled *N*-methylpyrrolidone was added 16.1 g. (0.18 mole) of cuprous cyanide. The mixture was refluxed for 1 hr. 45 min., cooled, and poured into 240 ml. of water containing 48 g. of ferric chloride hexahydrate and 50 ml. of concd. hydrochloric acid. The resulting mixture was heated, with stirring, for 10 min. on the steam bath. After cooling, it was extracted three times with 75-ml. portions of ether, and the combined ether extracts were washed with water and dried by filtration through anhydrous magnesium sulfate. Evaporation of the solvent, followed by distillation of the residue gave 15.0 g. (91%) of crude material, b.p. 135–155° at 1 mm., which solidified upon standing. Two additional distillations followed by two crystallizations from petroleum ether (b.p. 30–60°), gave 4.17 g. (25%) of colorless crystals, m.p. 54.6–56.4°.

An analytical sample, prepared by two additional crystallizations from petroleum ether (b.p. 30–60°) had m.p. 56.4–57.8°.

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.50; H, 6.88. Found: C, 74.79; H, 6.60.

3-Hydroxy-4-n-propylbenzophenone. In a dry, three-neck, 500-ml. flask equipped with stirrer, reflux condenser, and addition funnel were placed 1.22 g. (0.050 mole) of magnesium turnings and 50 ml. of purified tetrahydrofuran. There was added a small crystal of iodine, 1 drop of bromobenzene and 14.95 g. (0.050 mole) of 2-(2-*n*-propyl-5-bromophenoxy)tetrahydropyran in 20 ml. of purified tetrahydrofuran. The mixture was refluxed, with stirring, for 0.5 hr. after the iodine color had disappeared. Then 5.16 g. (0.050 mole) of benzonitrile in 10 ml. of purified tetrahydrofuran was added with rapid stirring, and refluxing was continued for 100 min. At the end of this time a negative test for Grignard reagent was obtained with Michler's ketone reagent. The condenser was removed and the tetrahydrofuran was evaporated until only a viscous red oil remained. After addition of 200 ml. of 1:3 hydrochloric acid, the stirred mixture was heated for 20 min. on the steam bath and cooled. The resulting liquid was extracted three times with 80-ml. portions of ether and the combined ether extracts were evaporated until the volume was 75 ml. To this solution was added 125 ml. of petroleum ether (b.p. 60–68°) and it was shaken twice with 50-ml. portions of 8% sodium hydroxide solution and once with 50 ml. of water. The combined washings were acidified with hydrochloric acid, cooled, and extracted four times with 40-ml. portions of ether. The ether solution was dried with magnesium sulfate and passed through a small column of Woelm alumina. The ether was evaporated and the residue was crystallized twice from petroleum ether (b.p. 90–100°) to give 6.65 g. (55%) of white crystals, m.p. 106.8–107.6°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.27; H, 6.97.

2-n-Propyl-5-methylphenol. In a dry, three-neck, 500-ml. flask equipped with stirrer, reflux condenser, and addition funnel were placed 2.84 g. (0.119 mole) of magnesium turnings, 75 ml. of purified tetrahydrofuran, a small crystal of iodine, and about one-fourth of a solution composed of 29.9 g. (0.100 mole) of 2-(2-*n*-propyl-5-bromophenoxy)tetrahydropyran and 50 ml. purified tetrahydrofuran. The mixture was refluxed, with stirring, until the iodine color disappeared, and the remaining solution of the bromide was added. Refluxing was continued an additional 15 min. After the reaction mixture was cooled to 10°, there was added during 10 min. 23.6 ml. (0.25 mole) of dimethyl sulfate. The solution was then allowed to warm to room temperature and was stirred an additional 8 hr. Following this it was diluted with 200 ml. of ether and shaken with 12.5 ml. of 1:6 hydrochloric acid. The ether layer was separated and washed four times with 100-ml. portions of water and then evaporated. The residue was heated on the steam bath for 30 min. with 200 ml. of 1:6 hydrochloric acid. The hydrolysis mixture was cooled and extracted five times with 40-ml. portions of ether. The combined ether extracts were evaporated, and the residue was taken up in 200 ml. of petroleum ether (b.p. 60–68°). This solution was washed twice with 50-ml. portions of 10% sodium hydroxide solution and twice with 50-ml. portions of water. The combined washings were first treated with activated charcoal, and then acidified with hydrochloric acid and extracted three times with 50-ml. portions of ether. Following drying by filtration through anhydrous magnesium sulfate, the ether solution was evaporated. Distillation of the residue gave 6.45 g. (42%) of liquid, b.p. 95–103° at 4 mm. An analytical sample boiled at 97° at 5 mm.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.76; H, 9.16.

Preparation of 2-n-propyl-5-X-phenyl p-bromobenzenesulfonates. A solution of 0.050 mole of *p*-bromobenzenesulfonyl chloride and 0.025 mole of 2-*n*-propyl-5-X-phenol in 20 ml. of pyridine was heated on the steam bath for 3 hr. and then poured into a mixture of 25 ml. of concd. hydrochloric acid and 150 ml. of crushed ice. The product was collected either by filtration or extraction with ether and recrystallized several times from petroleum ether (b.p. 60–68°).

TABLE IV

2-*n*-PROPYL-5-X-PHENYL *p*-BROMOBENZENESULFONATES

X	Yield, %	M.P.	Calcd. C	Calcd. H	Found C	Found H
CH_3	59	57–68[a]	52.04	4.64	52.04	4.58
COC_6H_5	75	69.1–70.5	57.52	4.17	57.52	4.20
CN	84	94.8–96.2	50.54	3.71	50.35	3.87
Br	78	56.5–57.4	41.49	3.25	41.64	3.34
Cl	64	57.3–58.6	46.11	3.61	46.33	3.86

[a] The melting point was found to be dependent on the rate of heating indicating that this compound must go through a phase transition near its melting point. When a sample was immersed in a bath at 60° it rapidly melted completely, then partially solidified and remelted at a higher temperature.

2-Allyl-5-methoxyphenol and 2-allyl-3-methoxyphenol. A solution of 67.5 g. (0.46 mole) of allyl-3-methoxyphenyl ether in 46.4 g. of *N*,*N*-dimethylaniline was refluxed for 225 min. After cooling, the solution was diluted with 300 ml. of petroleum ether (b.p. 60–68°) and washed twice with 125-portions of 10% sulfuric acid. The organic layer was then washed twice with 75-ml. portions of 13% sodium hydroxide solution and twice with 100-ml. portions of water. The combined basic washings were then acidified in the cold with concentrated hydrochloric acid and extracted three times with 50-ml. portions of ether. The ether solutions were dried by filtration through anhydrous magnesium sulfate and evaporated. Double distillation gave 44.0 g. (65%) of colorless liquid, b.p. 142–145° at 15 mm. (lit.[18] b.p. 143–144° at 15 mm.)

2-n-Propyl-5-methoxyphenol and 2-n-propyl-3-methoxyphenol. To a solution of 23.5 g. (0.159 mole) of the mixture obtained from the rearrangement of allyl *m*-methoxyphenyl ether in 150 ml. of 95% ethanol was added 0.22 g. of Adam's catalyst. The mixture was hydrogenated under 32 p.s.i.g. hydrogen until no further uptake was noted. The platinum was filtered off and the filtrate was diluted with 300 ml. of ether.The ether solution was washed five times with 100-ml. portions of water, dried by filtration through anhydrous magnesium sulfate, and distilled to give 20.4 g. (86%) of colorless liquid, b.p. 140–148° at 15 mm. An analytical sample boiled at 140° at 15 mm.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.43. Found: C, 72.37; H, 8.42.

2-n-Propyl-3-methoxyphenyl p-bromobenzenesulfonate. The mixture of 2-*n*-propyl-3-methoxyphenol and 2-*n*-propyl-5-methoxyphenol was treated as described above to prepare the *p*-bromobenzenesulfonate. The residue from the ether extraction was crystallized four times from methanol to give 2-*n*-propyl-3-methoxyphenyl *p*-bromobenzenesulfonate (31%) as colorless crystals, m.p. 107–108.2°.

Anal. Calcd. for $C_{16}H_{17}BrO_4S$: C, 49.88; H, 4.45. Found: C, 49.66; H, 4.40.

The mother liquors from these crystallizations yielded 24% of viscous, pale yellow oil, 2-*n*-propyl-5-methoxyphenyl-*p*-bromobenzenesulfonate (?), b.p. 220° at 2 mm.

Anal. Calcd. for $C_{16}H_{19}BrO_4S$: C, 49.88; H, 4.45. Found: C, 50.02; H, 4.43.

2-n-Propylresorcinol. A mixture of 10.56 g. (0.027 mole) of 2-*n*-propyl-3-methoxy *p*-bromobenzenesulfonate and 32 g. of 25% aqueous sodium hydroxide was refluxed for 50 hr. After the first 25 hr. an additional 4 g. of solid sodium hydroxide was added. The solution was cooled, acidified with dilute hydrochloric acid, and extracted five times with 30-ml. portions of ether. The ether solution was dried by filtration through anhydrous magnesium sulfate and evaporated. The residue (3.52 g.) was dissolved in a mixture of 4 ml. of 48% hydrobromic acid and 4 ml. of glacial acetic acid and was refluxed 4 hr. The solution was cooled, taken up in 75 ml. of ether and washed twice with 100-ml. portions of water. Following filtration of the ether solution through anhydrous magnesium sulfate, the ether was evaporated. The residue was crystallized from benzene-petroleum ether (b.p. 60–68°) mixture to give 1.87 g. (45%) of 2-*n*-propylresorcinol as brown crystals. A small portion of this solid was sublimed to give colorless crystals of m.p. 99.0–101.5° (lit.[18] m.p. 100–102°).

2-n-Propylresorcinol bis-p-nitrobenzoate. To a solution of 1.86 g. (0.01 mole) of *p*-nitrobenzoyl chloride in 5 ml. of dry pyridine was added 0.50 g. (0.0033 mole) of 2-*n*-propylresorcinol. The solution was boiled for 5 min. and poured into 50 ml. of water. The solid was filtered off and crystallized first from methanol and then from petroleum ether (b.p. 90–100°) to give 1.12 g. (76%) fine, pale yellow needles, m.p. 160.1–161.8° (lit.,[19] m.p. 163°).

p-Bromobenzene-C^{14}-sulfonyl chloride. An ampoule containing 0.050 mc. of bromobenzene-C^{14} was crushed under 31.4 g. (0.200 mole) of bromobenzene. This active bromobenzene was then added dropwise during 10 min. to 40 ml. of 7% fuming sulfuric acid. (The temperature was held between 60° and 75° during the addition.) The mixture was then kept at 85° for 10 min. It was cooled and poured into 125 ml. of cold water and the resulting solution was warmed to 65° and filtered. The filtrate was heated to 85° and 50 g. of sodium chloride was added with stirring. This suspension was maintained at 90° for 5 min., and then cooled to 10°. The salt was filtered off, pressed, and dried overnight in an oven at 75°.

The dried salt was mixed with 41.6 g. (0.200 mole) of phosphorus pentachloride in a dry, 500-ml. Erlenmeyer flask and heated until a melt resulted. The mixture was maintained molten for 20 min., after which it was cooled and petroleum ether (b.p. 60–68°) was added and brought to a boil. The residue was filtered off and the filtrate was concentrated to 100 ml. under vacuum. After thorough cooling, the product was collected by filtration and recrystallized twice from petroleum ether (b.p. 60–68°). There was obtained 22.9 g. (45%) colorless crystals, m.p. 74.5–75.4° (lit.,[20] m.p. 75–76°).

Determination of isomer ratios. The rearrangement sample was prepared by sealing a solution of 3 to 5 g. of allyl *m*-X-phenyl ether in 10 g. of Carbitol in a 30-ml. Kjeldahl flask. The flask was immersed in a constant temperature bath for one to three reaction half-lives, after which it was removed, cooled and opened. The contents were taken up in 150 ml. of petroleum ether (b.p. 60–68°) (150 ml. of petroleum ether and 50 ml. of ether were used for the rearrangement products of allyl *m*-benzoylphenyl ether and allyl *m*-cyanophenyl ether) and the solution was washed with five 100-ml. portions of water. The organic layer was then washed twice with 50-ml. portions of 4% sodium hydroxide solution and once with 50 ml. of water. The combined basic washings were acidified with cold 1:6 hydrochloric acid and the mixture was extracted with two 30-ml. portions of ether. The combined ether extracts were dried by filtration through anhydrous magnesium sulfate. The ether was then removed on the steam bath and the flask containing the residue was evacuated to 0.5 mm. for 1 to 2 hr.

The hydrogenation was carried out in an apparatus consisting of a 50-ml. reaction chamber and a 10-ml. hydrogen reservoir. In the reaction chamber were placed 10.0 (or 20.0) ml. of cyclohexane and 0.002 to 0.004 g. of platinum oxide. The chamber was flushed thoroughly with hydrogen and closed off from the rest of the system by means of a stopcock. Agitation with a magnetic stirrer was begun and the catalyst was saturated with hydrogen for 4 hr. or longer. A weighed amount of sample was then introduced. This was done by weighing a hypodermic syringe filled with sample, injecting the compound through a serum bottle cap on a side-arm of the reaction chamber, and reweighing the empty syringe. In this manner samples of 0.0200 to 0.0600 g. (2×10^{-4} mole) could be conveniently handled. (A modification of this procedure for the rearrangement products of allyl *m*-cyanophenyl ethyl and allyl *m*-benzoylphenyl ether consisted of dissolving a weighed amount of the product in a weighed amount of pre-reduced pyridine and treating this solution as the sample.) When no further uptake of hydrogen was noted the solvent was evaporated under a stream of dry air.

The residue was taken up in 5.0 ml. of dry pyridine and approximately 1×10^{-3} mole *p*-bromobenzenesulfonyl-C^{14} chloride was added. The solution was refluxed for 6 to 9 hr., cooled, poured into 120 ml. of 1:5 hydrochloric acid containing 50 g. of crushed ice and extracted three times with 30-ml. portions of ether (the first portion of ether was used to wash into the mixture an appropriate weighed amount of the corresponding inactive *p*-bromobenzenesulfonate ester). The combined ether extracts were dried by filtration through anhydrous magnesium sulfate and the ether was evaporated on the steam bath. The residue was crystallized repeatedly and the activity was determined (*vide infra*).

To show the extent of the conversion of the hydrogenated rearrangement mixture to the *p*-bromobenzenesulfonate ester, the ultraviolet absorption of the sodium 2-*n*-propyl-5-X-phenoxide was utilized. The wave length of maximum absorption (λ_{max}) and the molecular extinction coefficient (ϵ) for the sodium 2-*n*-propyl-5-X-phenoxide were determined by dissolving the appropriate amount of 2-*n*-propyl-

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[18] D. B. Limaye and I. Ghate, *Rasayanam*, **1**, 39 (1936); *Chem. Abstr.*, **31**, 2182 (1937).

[19] J. P. Brown, D. H. Johnson, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 2019 (1951).

[20] H. Huebner and J. Alsberg, *Ann.*, **156**, 326 (1870).

5-X-phenol in 0.1*N* sodium hydroxide and examining the solution with a Beckman Model DU spectrophotometer. The extinction coefficient was obtained as the average of three determinations. The results are shown in Table V.

TABLE V

ULTRAVIOLET ABSORPTION MAXIMA OF SODIUM 2-*n*-PROPYL-5-X-PHENOXIDES

X	λ_{max} (mμ)	$\epsilon \times 10^{-3}$
OCH_3[a]	287	2.96
CH_3	291	3.85
Br	296	4.57
Cl	295	4.13
COC_6H_5	374	2.75
CN	321	5.11

[a] A mixture of the 3- and 5-isomer.

The analytical procedure was tested using samples of the 2-*n*-propyl-5-X-phenols. The phenol was taken up in 150 ml. of petroleum ether (b.p. 60–68°) (ether was used for 2-*n*-propyl-5-cyanophenol and cyclohexane for 2-*n*-propyl-5-benzoylphenol). This solution was washed with five 20-ml. portions of 4% sodium hydroxide and with two 25-ml. portions of water. The combined washings were diluted volumetrically to obtain a solution with a conveniently read optical density. From this optical density the amount of material recovered was calculated. The percentage recovery varied from 98–106%.

In the isomer distribution experiments, the crude *p*-bromobenzenesulfonate esters were first crystallized from petroleum ether (b.p. 60–68°). The mother liquor was diluted to 150 ml. and washed with dilute base and water as described below.

The *p*-bromobenzenesulfonates from the rearrangement of allyl *m*-benzoyl- and *m*-cyanophenyl ethers were treated somewhat differently in that the ester was first dissolved in cyclohexane and ether, respectively. This solution was then extracted with base and water and the aqueous solution was analyzed. The organic phase was evaporated and the ester was recrystallized.

Data concerning the percentage conversion in hydrogenation and in the formation of the *p*-bromobenzenesulfonates are shown in Table VI.

TABLE VI

EXTENT OF HYDROGENATION AND CONVERSION TO *p*-BROMOBENZENESULFONATES OF THE REARRANGEMENT PRODUCTS OF ALLYL *m*-X-PHENYL ETHERS

X	Rearrmt. Temp.	H_2 Uptake, %	Sulfonate, %
OCH_3	200	95	95
OCH_3	160	84	97
CH_3	200	97	97
CH_3	160	78	98
CH_3	160	90	98
Br	200	99	99
Br	200	97	99
Br	160	94	95
Cl	200	94	99
Cl	200	109	96
Cl	160	111	97
COC_6H_5	200	105	98
COC_6H_5	160	96	99
CN	200	100	99
CN	160	107	94

After the recovered *p*-bromobenzenesulfonates had been crystallized several times, usually alternately from petroleum ether (b.p. 60–68°) and methanol, they were thoroughly dried and the activity was determined. This was done by burning samples to carbon dioxide, collecting the carbon dioxide in an ionization chamber, and measuring the "rate of drift" by means of a Cary Model 31 vibrating reed electrometer and a Cary Multi-Range recorder. This procedure has been described in detail by Neville[21] and by Raaen and Ropp.[22]

The combustion train employed was that of Neville[21] modified by inclusion of a stannous chloride trap, as described by Raaen and Ropp.[22] The procedure was to weigh from 5 to 20 mg. sample into a platinum boat, place the boat in a combustion tube, and cover it with 200 to 400 mg. of potassium iodate. An evacuated ionization chamber was than placed in position, and 10 ml. of Van Slyke[23] oxidizing solution was added to the sample. This was heated cautiously to boiling (3 to 10 min.), and then allowed to cool for 5 min. Another 5 ml. of oxidizing solution was added, and the solution was once again boiled. After a 5-min. cooling period, inactive carbon dioxide was slowly swept through the train until the ionization chamber was filled. The ionization chamber was then attached to the vibrating reed electrometer and five "rates of drift" were recorded and averaged. This procedure led to slopes in terms of mv./min.

These values were corrected for background by measuring the "rate of drift" when the ionization chamber contained only inactive carbon dioxide. The corrected activities were converted to specific activities by dividing the slope for a sample by the number of moles in the sample.

From these specific activities the percentage of 2-allyl-5-X-phenol present in the original mixture was calculated from the equation:

$$\% = \frac{bS_u}{a(S_x - S_u)} \times 100$$

where

a = moles of rearrangement mixture used
b = moles of inactive *p*-bromobenzenesulfonate used
S_x = specific activity of *p*-bromobenzenesulfonyl-C^{14} chloride
S_u = specific activity of *p*-bromobenzenesulfonate

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