The ortho-Claisen Rearrangement. III. The Rearrangement of β-Alkylallyl Aryl Ethers[1,2]

BY WILLIAM N. WHITE AND BRUCE E. NORCROSS[3,4]

A series of β-alkylallyl phenyl ethers and β-alkylallyl p-methoxyphenyl ethers, in which the steric requirements of the alkyl group varied greatly have been synthesized. The rates of rearrangement of these ethers were determined and it was found that all the β-alkylallyl phenyl ethers reacted at nearly the same speed. The same result was obtained with the series of β-alkylallyl p-methoxyphenyl ethers. This indicates that the transition state of the Claisen rearrangement must have the atoms of the allyl group the ether oxygen, and the 1- and 2-carbons of the aromatic ring in a distorted chair conformation.

Introduction

The Claisen rearrangement has been extensively investigated.[5] Most studies have been concerned with demonstrating the intramolecularity of the reaction, the nature of the intermediate or the inversion of the allyl group. Few, however, have been concerned with the electronic[6,7] or stereochemical[8-11] nature of the transition state for rearrangement.

Two extreme conformations are possible for the transition state of the Claisen rearrangement. These involve different orientations of the allyl chain with respect to the aromatic portion of the molecule. In both conformations (Fig. 1) the allyl group is in a plane nearly parallel to the plane of the aromatic ring with the α-carbon atom of the allyl group over the ether oxygen to which it is bonded and the γ-carbon atom over the ortho atom of the ring to which it will become bonded. Conformations I and II differ only in the orientation of the β-carbon atom of the allyl group. In conformation I, it is projected away from the rest of the molecule to form a "distorted chair" or "elbowed out" conformation, while in conformation II the β-atom of the allyl group is superposed over the 1-atom of the aromatic nucleus resulting in a "distorted boat" or "elbowed-in" conformation. Conformations intermediate between these two in which the planes of the allyl group and the aromatic ring are non-parallel are conceptually possible but are deemed unlikely to be transition states for rearrangement for two reasons. First,

as the allyl group's plane is tilted from a position parallel to the aromatic ring, the substituents on the γ-carbon atom of the allyl radical become interposed between this atom and the ortho atom of the ring (or its attached substituent). Thus, the distance between these two atoms which must become bonded is increased. In addition, if the planes of the allyl group and the ring are non-parallel, the orbital being generated at the α-carbon atom by the rupture of the ether linkage will be orthogonal to and thus not overlap with the double-bond orbital of the allyl group. Thus, conformations I and II appear to be the best representations of possible transition states for the Claisen rearrangement.

Steric interactions associated with the distorted boat-form conformation II would make it quite a bit less stable than the chair-form conformation I[13] unless there were compensating electronic interactions in II which were not possible in I. This might be the case if π-bonding between the p-orbitals on the β-carbon of the allyl group and the 1-atom of the aromatic ring resulted in considerable stabilization of the activated complex.[14] If π-bonding of this nature is to occur to any appreciable extent, then the β-carbon of the allyl group and the 1-atom of the ring must not be separated by a distance of greater than about 3.0 Å.[15]

In the light of these considerations, a decision could be reached regarding the most likely transition state conformation by a kinetic study of β-alkylallyl aryl ethers in which the steric bulk of the alkyl group was varied. Reference to Fig. 2 shows that in conformation I the alkyl group is projected away from the rest of the molecule so that a change in its size should have little effect on the ability of the β-alkylallyl aryl ether to attain this conformation. On the other hand, the alkyl group in conformation II lies across the face of the ring so that increases in the bulk of the alkyl group will severely increase the steric interactions between the alkyl group and the aromatic nucleus and thus increase the energy for reaching the transi-

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(2) Presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 5, 1960.

(3) National Science Foundation Predoctoral Fellow, 1958–1960.

(4) From the thesis submitted by Bruce E. Norcross in partial fulfillment of the requirements for the Doctor of Philosophy Degree at The Ohio State University.

(5) Excellent reviews on this subject are to be found in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1945, pp. 1–48; M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, 1956, pp. 295–303; and E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, 1959, pp. 644–649.

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

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

(8) S. J. Rhoads, R. Raulins and R. D. Reynolds, ibid., 76, 3456 (1954).

(9) H. Hart, ibid., 76, 4033 (1954).

(10) A. W. Burgstahler, ibid., 82, 4681 (1960).

(11) E. N. Marvell and J. L. Stephenson, J. Org. Chem., 25, 676 (1960).

(12) In this representation, a heavy angular line is used to indicate the allyl side chain, which is in a plane above and nearly parallel to that of the benzene ring.

(13) W. G. Dauben and K. S. Pitzer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 13–15.

(14) This might occur if a π-complex mechanism was involved (cf. M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 229–230, and for a more recent viewpoint, M. J. S. Dewar in "Theoretical Organic Chemistry— Papers Presented to the Kekulé Symposium," Butterworth's Scientific Publications, London, 1959, p. 190).

(15) This is the average distance between donor and acceptor in weakly bonded molecular complexes (cf. L. E. Orgel, Quart. Revs., 8, 422 (1954); L. J. Andrews, Chem. Revs., 54, 713 (1954); and S. P. McGlynn, ibid., 58, 1113 (1958)).
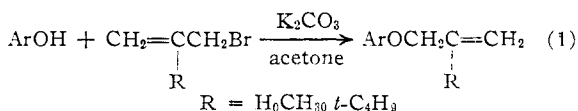
Fig. 1.

Fig. 2.

tion state.[16] In summary, increasing the bulk of the alkyl group in β-alkylallyl aryl ethers should decrease the rate of rearrangement if conformation II resembles the transition state and have essentially no effect upon the rate if the transition state of the rearrangement is similar to conformation I.
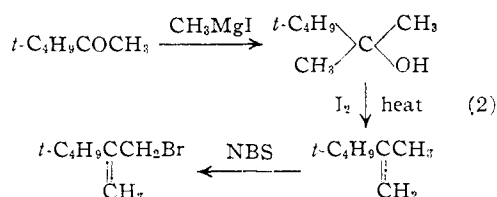
Results

The β-alkylallyl aryl ethers selected for this study were allyl, β-methylallyl, and β-t-butylallyl phenyl ethers and allyl, β-methylallyl, and β-t-butylallyl p-methoxyphenyl ethers. This choice was based upon the enormous increase in steric requirements of the β-substituent in the allyl group as it is changed from hydrogen to methyl to t-butyl and upon the difference in rates of rearrangement of allyl phenyl ethers and allyl p-methoxyphenyl ethers.[6,7]

The β-substituted allyl aryl ethers were synthesized by the reaction between the substituted phenol and the appropriately β-substituted allylic halides in the presence of potassium carbonate (eq. 1). The only allylic bromide commercially

$$\text{ArOH} + \underset{\overset{|}{R}}{\text{CH}_2{=}\text{CCH}_2\text{Br}} \xrightarrow[\text{acetone}]{\text{K}_2\text{CO}_3} \underset{\overset{|}{R}}{\text{ArOCH}_2\text{C}{=}\text{CH}_2} \quad (1)$$

$$R = H, CH_3, t\text{-}C_4H_9$$

unavailable was β-t-butylallyl bromide which was prepared as shown in eq. 2. Many allyl and β-methylallyl aryl ethers have been reported in the

$$t\text{-}C_4H_9\text{COCH}_3 \xrightarrow{\text{CH}_3\text{MgI}} \underset{\text{CH}_3}{\overset{t\text{-}C_4H_9}{>}}\text{C}\underset{\text{OH}}{\overset{\text{CH}_3}{<}}$$

$$\qquad\qquad\qquad\qquad\qquad\Big\downarrow \text{I}_2 \text{ heat} \quad (2)$$

$$\underset{\overset{|}{\text{CH}_2}}{t\text{-}C_4H_9\text{CCH}_2\text{Br}} \xleftarrow{\text{NBS}} \underset{\overset{|}{\text{CH}_2}}{t\text{-}C_4H_9\text{CCH}_3}$$

literature, so that no proof of structure beyond infrared absorption in the 885–895 cm.$^{-1}$ region indicative of a 1,1-disubstituted olefin and a correct analysis was necessary. In addition, for the β-t-butylallyl aryl ethers, additional structural

(16) A construction of transition state conformation II with Dreiding models in such a way that the bonds being formed and broken are each 2.0 Å. long and perpendicular to the plane of the benzene ring results in a distance of 2.5 Å. between the allyl β-carbon and the 1-atom of the ring and a distance of 3.2 Å. between the ring and the β-substituent. Since the half-thickness of the aromatic ring is 1.9 Å. and the van der Waals radii of the hydrogen atom, methyl radical and t-butyl group are, respectively, 1.2, 2.0 and 3.5 Å., this model predicts that steric interactions due to the β-substituent will be weak in allyl aryl ethers, strong in β-methylallyl aryl ethers, and very strong in β-t-butylallyl aryl ethers if transition state conformation II is involved.

evidence was obtained by ozonolysis which yielded formaldehyde and an α-aryloxy pinacolone (synthesized independently). These carbonyl compounds were isolated and characterized as their 2,4-dinitrophenylhydrazone derivatives.

The substituted allyl aryl ethers in diphenyl ether solution were heated in sealed tubes under the conditions used in the kinetic studies, and the base-soluble fraction isolated. The products of rearrangement were shown to be the expected o-allyl-phenols through their infrared absorption characteristics, analyses and other properties.

The rates of rearrangement of the β-alkylallyl aryl ethers were determined dilatometrically and the results are summarized in Table I. These rate constants agree with those determined by Goering and Jacobson[7] in those cases in which a comparison is possible. Furthermore, the magnitude of

TABLE I

SUMMARY OF KINETICS OF REARRANGEMENT OF β-ALKYLALLYL ARYL ETHERS

Substituents					
Ring	Chain[a]	T, °C.	$k \times 10^5$, sec.	$H^{\ddagger\,b}$	$S^{\ddagger\,c}$
None	None	184.85	1.52[d]	32.3	−11.1
		197.29	3.85[d]		
None	β-CH$_3$	183.96	1.19	31.1	−14.0
		184.85	1.32[d]		
		197.29	3.29[d]		
None	β-t-C$_4$H$_9$	185.27	1.52	35.0	− 5.2
		195.11	3.27		
		197.22	4.00		
p-CH$_3$O	None	184.85	4.58[d]	33.0	− 7.3
		197.29	12.2[d]		
p-CH$_3$O	β-CH$_3$	183.88	3.23	36.2	− 0.9
		184.48	3.33		
		194.37	8.15		
		194.37	8.20		
		204.57	18.0		
p-CH$_3$O	β-t-C$_4$H$_9$	184.87	6.48	31.6	− 9.7
		194.38	13.3		
		204.52	27.9		

^{a} The allyl group. ^{b} Kcal., per mole. ^{c} Entropy units per mole. ^{d} Rates determined by Goering and Jacobson.[7]

the values for allyl phenyl ether, allyl p-methoxyphenyl ether, β-methylallyl phenyl ether and β-methylallyl p-methoxyphenyl ether are consistent with rates determined spectrophotometrically[6] for these substances in Carbitol solution when these rates are extrapolated for solvent effects. The activation parameters are also in accord with those obtained in other studies.[6,7] However, in our experience, the dilatometric measurements did not give rate constants to a precision better than ±5%. This corresponds to an error[17] in $\Delta H^{\ddagger}$ of ±2 kcal./mole and in $\Delta S^{\ddagger}$ of ±4 e.u./mole.

The data collected in Table I show that the rates and activation parameters of the β-alkylallyl phenyl ethers are all about the same within experimental error. However, in the series of β-alkylallyl p-methoxyphenyl ethers, the unsubstituted isomer rearranges a little faster than the β-methyl compound and the β-t-butylallyl isomer reacts

(17) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, J. Am. Chem. Soc., 77, 837 (1955).

about twice as fast. These differences are reflected in the enthalpies of activation.

Discussion

The data in Table I show there is not much difference in the rates of rearrangement of allyl, β-methylallyl and β-t-butylallyl aryl ethers. This may be interpreted as being indicative of any of three possibilities: (1) the transition state of the Claisen rearrangement has a preferred conformation like that designated I in Fig. 1, (2) the Claisen rearrangement is not subject to steric changes in the allyl group or (3) the variation of electrical influence of the β-substituent as it is changed from hydrogen to methyl to t-butyl is such as to just balance out the decrease in reactivity expected from the increasing steric interactions demanded by conformation II. Possibilities 2 and 3 can be readily eliminated.

There is ample evidence that the Claisen rearrangement is influenced considerably by the steric requirements of groups in the allyl chain. Thus, Alexander and Kluiber[18] demonstrated that asymmetric induction must operate in the rearrangement of optically active trans-α,γ-dimethylallyl phenyl ether to optically active 2-(α,γ-dimethylallyl)-phenol. In addition, Burgstahler[10,19] showed that both cis- and trans-α,γ-dimethylallyl vinyl ether rearranged to only the trans product, a result that can be explained by the unfavorable crowding in the transition state leading to cis product. A somewhat similar study by Marvell and Stephenson[11] with cis- and trans-α,γ-dimethylallyl phenyl ethers also supports the contention that the steric interaction of groups in the allyl chain are effective in determining the relative favorability of various possible transition states. Thus, the proposition that the Claisen rearrangement is not influenced by steric changes in the allyl side chain seems untenable.

It is probable that electrical effects due to substituent change at the β-position in the allyl chain are unimportant in determining rates of the Claisen rearrangement since the rates of rearrangement of β-methyl allylphenyl ether[20] ($k_{181}^0 = 2.08 \times 10^{-5}$ sec.$^{-1}$) and β-chloroallyl phenyl ether[20] ($k_{181}^0 = 1.95 \times 10^{-5}$ sec.$^{-1}$) are practically identical. The van der Waals radii[21] of the methyl group (2.0 Å.) and the chlorine atom (1.8 Å.) are nearly the same but the electrical effects of these two radicals are quite different. The similarity in rates of rearrangement of these two β-substituted allyl aryl ethers must, therefore, indicate that the electrical effects of β-substituents in the allyl chain do not influence to any appreciable extent the rate of the Claisen rearrangement.

Evidently, it is necessary to conclude from the above that any difference in the rates of rearrangement of β-alkylallyl aryl ethers (caused by variation of the β-substituent only) must be di-

agnostic of important changes in the steric environment of the β-substituent in going from the initial state to the transition state. Conversely, the absence of any rate effect with change in spatial properties of the alkyl group in β-alkylallyl aryl ethers indicates that there must be little change in the steric interactions of the β-substituent in going from the initial state to the transition state.

In order to assign a meaning to the rate data in terms of the nature of the transition state, it is therefore necessary to define the nature of the initial state as a point of reference. Certainly, the initial reactant molecule has a preferred conformation in which the bulky groups are as far from one another as possible. It is probably safe to assume that highly hindered conformations corresponding to possible transition states (I and II in Fig. 1) are present in extremely low concentrations[22] so that the initial state of the ether consists for all practical purposes only of extended molecules. Therefore, the β-substituent in the β-alkylallyl aryl ethers must be in a relatively unobstructed environment in the reactant molecules.

The combination of this unhindered initial state with the possible transition states (I and II) results in three mechanistic possibilities. They are:

Case I: Conformation II (Fig. 1) Best Represents the Transition State.—If this was true, then as one varied the β-alkyl group from hydrogen to methyl to t-butyl, one would expect to find that the rates of rearrangement decreased in the same order since it would be necessary to overcome the increasing steric interaction of substituent and aromatic ring in the transition state as the size of the alkyl group was increased.

Case II: Conformation I (Fig. 1) Represents the Transition State.—In this case no decrease in the rate of rearrangement would be expected, since the β-carbon of the allyl side chain is removed from the steric environment of the aromatic ring and is in an unhindered position as it is in the initial state.

Case III: Conformation II is Preferred Energetically but Conformation I Can Be Attained Under Conditions Unfavorable for II.—Conformation II will then define the transition state only in the case of the unsubstituted allyl aryl ether and conformation I will represent the transition state for more highly hindered molecules. If this is so a rate decrease would still be expected with increasingly bulky substituents due to the added energy or decreased entropy necessary to convert the preferred but hindered conformation II to the alternate but less likely or less energetically favored conformation I. In other words the preference of II only when there is no hindrance would imply an energetic or entropic favoring of II, so that a change of mechanism to I with increasing non-bonding interactions would mean that the change to I must be accompanied by a less favorable energy or entropy situation, which would be reflected in a lower rate. Thus, if a decrease in rate corresponding to increasingly bulky β-sub-

(18) E. R. Alexander and R. W. Kluiber, J. Am. Chem. Soc., **73**, 4304 (1951); see also H. Hart, ibid., **76**, 4033 (1954).

(19) A. W. Burgstahler, Abstracts of Papers, 137th Meeting of the American Chemical Society, April 5–14, 1960, p. 10-O.

(20) W. N. White, D. Gwynn and R. Schlitt; unpublished observations.

(21) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, p. 189.

(22) In the much less hindered n-butane molecule the skew form is present to the extent of only 0.3% at 180° (cf. W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 7–9, 26).

stituents was observed, the data would not have an unambiguous interpretation and could not be used to distinguish between the two possibilities designated case I and case III.

Fortunately, this is not the case. Reference to Table I shows there is very little change in rate with increasing steric requirements of the β-substituents in the allyl chain. In fact, the change is not a decrease as required by cases I and III but a very slight increase. This strongly indicates that case II applies and conformation I (Fig. 1) best represents the transition state of the Claisen rearrangement. This is the "elbowed-out" or "chair-form" conformation.

Experimental

Preparation of Allyl Aryl Ethers.—A mixture of 0.2 mole of substituted phenol, 24.2 g. (0.23 mole) of allyl bromide, 28.0 g. (0.20 mole) of potassium carbonate and 200 ml. of acetone was refluxed for 10 hours. This slurry was cooled, treated with 200 ml. of water, and extracted with three 25-ml. portions of ether. The combined ether extracts were washed with three 25-ml. portions of 10% aqueous sodium hydroxide, three 25-ml. portions of saturated brine, dried over magnesium sulfate, and distilled.

Allyl phenyl ether, b.p. 119.5–120.5° (30.2 mm.), $n^{25}D$ 1.5210, ν_{max} 882 cm.$^{-1}$, was available from previous work in this Laboratory.[6]

Allyl p-methoxyphenyl ether, b.p. 76–76.5° (1.5 mm.), $n^{25}D$ 1.5265, ν_{max} 885 cm.,$^{-1}$ (reported[6] b.p. 130.0–131.5° (6 mm.)) was obtained in 80% yield.

Preparation of β-Methylallyl Aryl Ethers.—A mixture of 0.41 mole of substituted phenol, 36.4 g. (0.4 mole) of β-methylallyl chloride, 60.8 g. (0.44 mole) of potassium carbonate and 400 ml. of acetone was refluxed for 10 hours. This slurry was cooled, treated with 400 ml. of water, and extracted with four 100-ml. portions of ether. The combined ether extracts were washed with three 50-ml. portions of 10% aqueous sodium hydroxide, three 50-ml. portions of saturated brine, dried over magnesium sulfate, and distilled.

β-Methylallyl phenyl ether, b.p. 54.0–54.5° (2 mm.), $n^{25}D$ 1.5148, ν_{max} 890 cm.,$^{-1}$ (reported[7] b.p. 75.2–75.8° (10 mm.)) was obtained in 46% yield.

β-Methylallyl p-methoxyphenyl ether, b.p. 90–90.5° 2 mm.), $n^{25}D$ 1.5210, ν_{max} 888 cm.,$^{-1}$ was obtained in 30% yield.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.31; H, 7.91.

Preparation of β-t-Butylallyl Aryl Ethers.—Into a 1-liter 3-necked flask equipped with stirrer and reflux condenser was placed 300 ml. of carbon tetrachloride, of which 50 ml. was distilled from the flask to effect drying. To this was added 51.7 g. (0.53 mole) of 1-methyl-1-t-butylethylene (prepared by the iodine-catalyzed dehydration of t-butyl-dimethylcarbinol,[23] 94 g. (0.54 mole) of N-bromosuccinimide and 1 g. (0.004 mole) of benzoyl peroxide. This solution was heated at reflux for 3 hours, cooled, and the succinimide[24] filtered off and washed with two 25-ml. portions of carbon tetrachloride. The combined carbon tetrachloride extracts were washed with two 50-ml. portions of saturated sodium thiosulfate, two 50-ml. portions of water, dried over calcium chloride, and distilled., 44 g. (47% yield) of β-t-butylallyl bromide, b.p. 109–111° (760 mm.), $n^{25}D$ 1.4668, was obtained.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40. Found: C, 47.32; H, 7.50.

A mixture of 0.17 mole of the substituted phenol, 23.7 g. (0.125 mole) of β-t-butylallyl bromide, 23.3 g. (0.17 mole) of potassium carbonate and 200 ml. of dry acetone was refluxed for 24 hours. The resulting slurry was cooled, treated with 300 ml. of water, and extracted with three 100-ml. portions of ether. The combined ether extracts were

washed with three 50-ml. portions of 10% aqueous sodium hydroxide, three 50-ml. portions of saturated brine, dried over magnesium sulfate, and distilled.

β-t-Butylallyl phenyl ether, b.p. 78–78.5° (1.5 mm.), $n^{25}D$ 1.5060, ν_{max} 894 cm.,$^{-1}$ was obtained in 42% yield.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.97; H, 9.66.

β-t-Butylallyl p-Methoxyphenyl ether, b.p. 117–118° (2 mm.), $n^{25}D$ 1.5112, ν_{max} 895 cm.,$^{-1}$ was obtained in 62% yield.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.48; H, 9.22.

Preparation of α-Aryloxypinacolones.—A mixture of 17.9 g. (0.1 mole) of α-bromopinacolone,[25] 15.2 g. (0.11 mole) of potassium carbonate, 0.11 mole of substituted phenol and and 100 ml. of dry acetone was refluxed for 10 hours. After cooling, the mixture was poured into 250 ml. of water, and extracted with three 50-ml. portions of ether. The combined ether extracts were washed with three 25-ml. portions of 10% aqueous sodium hydroxide, three 25-ml. portions of saturated brine, dried over magnesium sulfate, and distilled or evaporated to dryness and recrystallized to constant melting point.

α-Phenoxypinacolone, b.p. 115–117° (1 mm.), $n^{25}D$ 1.5065, was obtained in 91% yield. Its 2,4-dinitrophenylhydrazone. m.p. 142.3–143.1° (crystallized from Skellysolve B and ethyl acetate), was prepared for analysis.

Anal. Calcd. for $C_{18}H_{20}O_5N_4$: C, 58.05; H, 5.41; N, 15.05. Found: C, 58.35; H, 5.56; N, 15.09.

α-(p-Methoxyphenoxy)-pinacolone, m.p. 62.6–64.4° (crystallized from Skellysolve B and ethyl acetate), was obtained in 86% yield. Its 2,4-dinitrophenyl hydrazone, m.p. 152.8–153.8° (crystallized from Skellysolve B and ethyl acetate), was prepared for analysis.

Anal. Calcd. for $C_{19}H_{22}O_6N_4$: C, 56.71; H, 5.51; N, 13.92. Found: C, 56.51; H, 5.79; N, 13.80.

Ozonolysis of β-t-Butylallyl Aryl Ethers.—A stream of ozone–oxygen gas delivering about 9×10^{-4} mole of ozone per minute at the flow rate of 15 liters per hour was passed into a solution of 100 mg. (about 5×10^{-4} mole) of a β-t-butylallyl aryl ether in 10 ml. of chloroform at ice-acetone slurry temperature for 90 seconds. The time of exposure to ozone was critical, since longer periods resulted in the recovery of only tars. This ozonolysis mixture was then immediately poured into a freshly prepared solution of 1.39 g. (5×10^{-3} mole) of ferrous sulfate heptahydrate and 2 ml. (0.024 mole) of concentrated hydrochloric acid in 8 ml. of water.[26] This mixture was stirred for 1 hour, separated, and the chloroform layer was washed three times with 4-ml. portions of distilled water. The aqueous layer and the washes were combined, added to an equal volume of an aqueous ethanolic solution saturated with 2,4-dinitrophenyl-hydrazine hydrochloride[27] and allowed to stand for 24 hours. The resulting precipitate was filtered, taken up in benzene, and chromatographed through a 13×80 mm. column of Fisher acid-washed alumina with benzene as the eluting agent. This solution was then evaporated to dryness, and recrystallized from a Skellysolve B–ethyl acetate mixture to yield pure formaldehyde 2,4-dinitrophenylhydrazine, identified by the infrared spectra, and the melting point and mixed melting point.

β-t-Butylallyl phenyl ether yielded 15 mg. (13%) of form-aldehyde 2,4-dinitrophenylhydrazone, m.p. 163.6–164.8°, mixed m.p. 165.0–165.8°, authentic sample m.p. 166.4–167.2°.

β-t-Butylallyl p-methoxyphenyl ether yielded 17 mg. (18%) of formaldehyde 2,4-dinitrophenylhydrazone, m.p. 159.8–161.2°, mixed m.p. 163.8–165.4°, authentic sample m.p. 166.4–167.2°.

The chloroform layer, containing the α-aryloxypinacolone resulting from ozonolysis, was evaporated to near dryness at the aspirator. The resulting sirup was dissolved in a minimum of grain alcohol, added to 50 ml. of 2,4-dinitro-phenylhydrazine stock solution, and allowed to stand for 24 hours. The resulting precipitate was filtered, taken up in benzene, and chromatographed through a 13×80 mm.

(23) R. C. Huston and W. T. Barett, *J. Org. Chem.*, **11**, 657 (1946).

(24) The density relationships of succinimide, N-bromosuccinimide and carbon tetrachloride (cold) are such that the starting reagent, N-bromosuccinimide, does not float in the solution; whereas the product, succinimide, floats on the surface of the reaction mixture, thus providing a convenient indication of reaction completion.

(25) O. Widman and E. Wahlberg, *Ber.*, **44**, 2067 (1911).

(26) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

(27) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Edition, Interscience Publishers, Inc., New York, N. Y., 1957, p. 264.

TABLE II

PRODUCTS OF REARRANGEMENT

Substituents		Yield, %	B.p.		$n^{25}D$	Carbon, %		Hydrogen, %	
Ring	Chain		°C.	Mm.		Calcd.	Found	Calcd.	Found
H	β-t-C₄H₉	44	79–83	1	1.5375	82.06	82.24	9.54	9.30
p-CH₃O	β-CH₃	45	104–105	1.5	1.5535	74.13	74.04	7.92	7.67
p-CH₃O	β-t-C₄H₉	56	88–90	1	1.5423	76.32	76.08	9.15	9.14

column of Fisher acid-washed alumina with benzene as the eluting agent. This solution was then evaporated to dryness, and recrystallized from a Skellysolve B-ethyl acetate mixture to yield a pure 2,4-dinitrophenylhydrazone which was identified by comparison of its infrared spectra, melting point and mixed melting point with a sample synthesized independently.

β-t-Butylallyl phenyl ether yielded 28 mg. (14%) of α-phenoxypinacolone 2,4-dinitrophenylhydrazone, m.p. 141.6–142.6°, mixed m.p. 142.0–143.0°, authentic sample m.p. 142.3–143.1°.

β-t-Butylallyl p-methoxyphenyl ether yielded 29.2 mg. (16%) of α-(p-methoxyphenoxy)-pinacolone 2,4-dinitro-phenylhydrazone, m.p. 152.0–153.2°, mixed m.p. 152.7–153.5°, authentic sample m.p. 153.4–154.0°.

Isolation of Rearrangement Products.—In the cases of those allyl aryl ethers used in this study which had not been previously shown to yield the expected phenols on thermal rearrangement, large scale rearrangements were made in diphenyl ether in order to isolate and characterize the phenol produced. In general, 2 g. of the allyl aryl ether dissolved in 20 g. of pure diphenyl ether was sealed under vacuum in a thick-walled tube after repeated degassing. These sealed tubes were then heated for 24 hours in boiling ethylene glycol (b.p. 195–197°), cooled, and opened.

The diphenyl ether solution was diluted by an equal volume of diethyl ether, and extracted with four 10-ml. portions of Claisen alkali. This basic solution was then extracted with three 10-ml. portions of ether to remove the diphenyl ether soluble in the methanolic alkali. The Claisen alkali solution was then neutralized with cooling with concentrated hydrochloric acid and extracted with four 10-ml. portions of ether. The ether solution was then dried over magnesium sulfate, and either distilled or evaporated to dryness and the resulting solid phenol recrystallized. The major difficulty in this method was in obtaining pure phenol, uncontaminated by traces of diphenyl ether.

The products were shown to be the expected o-allylphenols by their infrared absorption in the 885–895 cm.⁻¹ region indicative of a terminal double bond[28] and the absence of absorption in the 960–970 cm.⁻¹ region which is indicative of the absence of internal olefinic linkages.[28] The properties, yields and analyses of these allylphenols are summarized in Table II.

Kinetic Measurements.—Two dilatometers, A and B, were constructed as described by Goering and Jacobson.[7] Dilatometer B had a capillary volume about two-thirds that of A, and the same total volume as that of A. This feature allowed checks to be run on solutions of varying concentrations.

The constant temperature bath was also patterned after that of Goering and Jacobson,[7] and was capable of maintaining the temperature within 0.003°. However, initial experiments indicated that temperature fluctuations were introduced by the raising of the wooden door in the side of the insulated box. Therefore, the door was modified by introduction of a glass-ended rectangular tunnel, 12 inches by 2 inches, which permitted direct observation of the bath interior.

Concentrations of the allyl aryl ethers were adjusted to between 0.05 M and 0.15 M to give a volume change corresponding to a decrease of about 20 cm. in the height of the meniscus in the dilatometer capillary. This decrease in height was measured with a cathetometer on an arbitrary scale.

Specific first-order rate constants were determined by first plotting meniscus height against time and smoothing the curve. At convenient time intervals, points were picked from this smooth decay curve, and Guggenheim's procedure[29] was applied to these to obtain a first-order plot and rate constant. A typical kinetic run is summarized in Tables III and IV.

TABLE III

DILATOMETER READINGS DURING REARRANGEMENT OF β-t-BUTYLALLYL p-METHOXYPHENYL[a]

t[b]	H[c]	t[b]	H[c]	t[b]	H[c]
32	200.6	72	127.3	121	85.3
33	197.4	75	125.5	125	83.7
35	193.9	78	121.8	131	79.3
39	185.7	81	118.3	135	76.1
45	173.7	82	116.7	142	74.6
47	169.2	86	112.4	147	72.5
51	161.5	88	110.6	153	72.1
53	158.4	92	106.0	155	71.2
57	152.3	95	103.6	165	68.5
58	151.0	99	101.1	172	67.4
60	146.7	103	96.5	176	67.3
63	142.6	108	92.7	193	64.1
68	134.7	115	88.6	207	63.1
69	133.0	117	87.1		

[a] Run 33, $T = 204.52°$. [b] t in minutes. [c] H is height of liquid in dilatometer in mm.

TABLE IV

APPLICATION OF GUGGENHEIM METHOD TO RATE DATA FOR β-t-BUTYLALLYL p-METHOXYPHENYL[a]

H_1[b]	H_2[b,c]	$H_1 - H_2$	$\log(H_1 - H_2)$	t_1[d]
199.3	66.6	132.7	2.123	32.5
182.6	65.4	117.2	2.069	40.0
168.3	64.4	103.9	2.017	47.5
155.1	63.5	91.6	1.962	55.0
142.9	62.7	80.2	1.904	62.5
132.2	61.9	70.3	1.847	70.0

[a] Run 33, $T = 204.52°$, $k = 27.9 \times 10^{-5}$ sec.⁻¹. [b] Dilatometer reading in mm. [c] Δt between H_1 and H_2 was 145 min. [d] t_1 in min.

(28) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34 ff.

(29) (a) E. A. Guggenheim, Phil. Mag., 2, 538 (1926); (b) A. A Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 48–49.