

A REINVESTIGATION OF THE  
CLAISEN REARRANGEMENT OF  
ALLYL o-TOLYL ETHER

by

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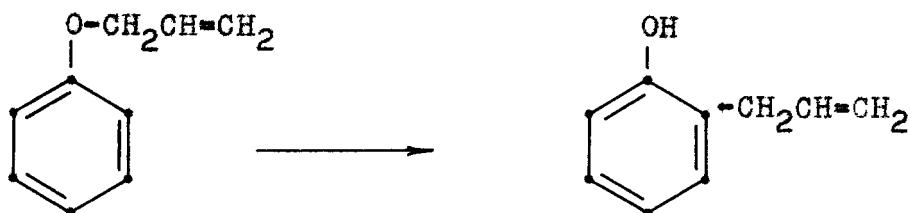
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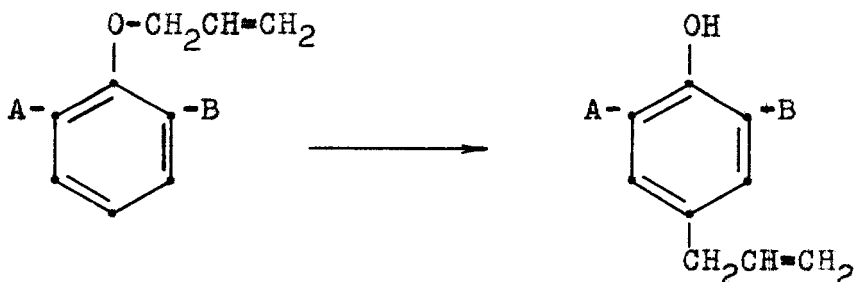
A REINVESTIGATION OF THE CLAISEN  
REARRANGEMENT OF ALLYL o-TOLYL ETHER

INTRODUCTION

In its most familiar form, the Claisen rearrangement is exemplified by the rearrangement of phenyl allyl ethers under sufficient thermal activation in the absence of any catalyst. When neither ortho position is occupied by a substituent other than hydrogen, the allyl group migrates exclusively to an ortho position:



However, if both ortho positions are blocked by a non-displaceable group, the allyl group then becomes attached para to the hydroxyl function.



These might be considered to be the two extreme cases, and the rules predicting such results hold almost invariably. If, however, only one ortho position were blocked, it can be seen that the allyl group may rearrange to the

ortho or the para position, and indeed, in a few cases both isomers have been observed. A general rule has been put forward, however, that whenever a single unsubstituted ortho position is available, the allyl group normally migrates exclusively to it (58, p. 4). Moreover, with but one exception (50, p. 1082), when this ortho group is alkyl, only the product predicted by that rule has been observed.

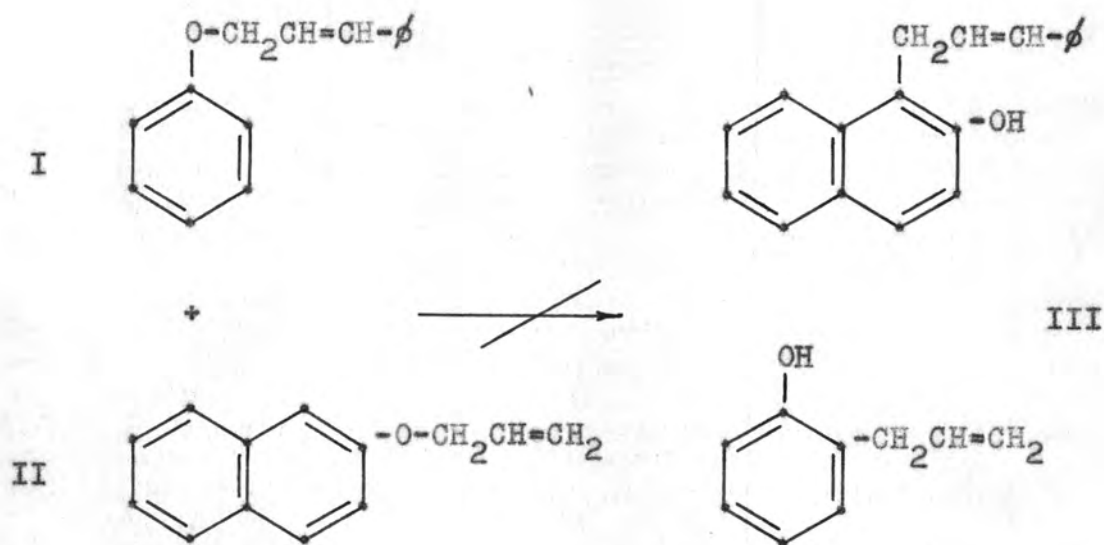
Recent studies have culminated in a satisfactory mechanistic basis for both the ortho and para rearrangements which predicts for the case in question an inevitable competition between rearrangement to the ortho and para positions. While it may be presumed, then, that the observed results with most mono-substituted phenyl ethers may be due to an extremely low rate of para rearrangement, it seems safer to conclude that the analytical methods previously employed were not sufficiently sensitive to permit identification of both products. The advent of chromatography, especially the gas chromatograph, has now changed this picture, but while mixtures have been observed, no coherent investigation has been reported.

As the initial case in a study aimed at elucidating the influence of ortho substituents on the para rearrangement, the rearrangement product from allyl o-tolyl ether has been re-examined. The results of that investigation are the subject of this thesis.

## HISTORICAL

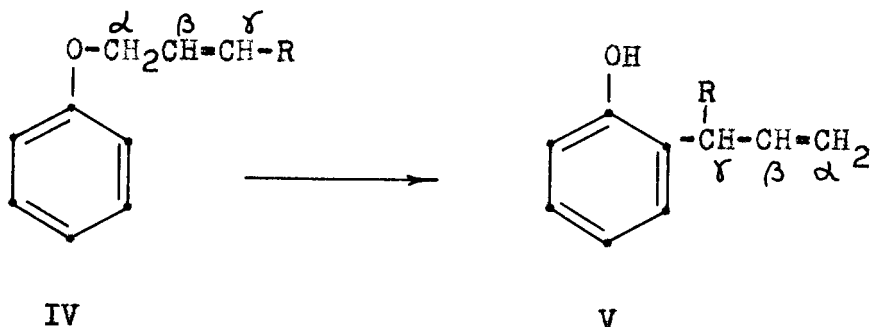
The development of insight into the nature of the Claisen rearrangement during the first several decades following its discovery in 1912 progressed primarily along three main routes of investigation: kinetic measurements, demonstrations of intramolecularity, and study of the phenomenon of inversion. Kinetically, both the ortho and para rearrangements have been shown by many workers to be strictly unimolecular, depending only upon the concentration of ether. In a recent work on the ortho rearrangement, allylic ethers of fifteen different phenols exhibited first order kinetics during thermal rearrangement. This might be cited as perhaps the most convincing single piece of evidence of the generality of that reaction order (20, p. 3281).

The question of intramolecularity was approached by simultaneous rearrangement of a mixture of two ethers, substituted differently so that the migration of the allylic grouping from one molecule to another could be readily determined from analysis of the reaction product. Thus, when a mixture of cinnamyl phenyl ether (I) and allyl  $\beta$ -naphthyl ether (II) was heated, no intermolecular or cross-products (III) were obtained, indicating the reaction to be intramolecular (25, p. 107).



The phenomenon of inversion has probably been both the most intriguing and most extensively studied. As mentioned earlier, thermal rearrangement of allylic ethers of phenols having two open ortho positions gives rise to an ortho Claisen rearrangement, i.e., the allylic chain becomes attached ortho to the hydroxyl group. It was discovered, however, that the carbon atom of the allylic group which becomes attached to the benzene nucleus was not the one originally attached to the oxygen function. In the case of a simple allyl group, such inversion would, of course, be unobservable, but if the allylic group were unsymmetrical in some way so that one end might be distinguished from the other, inversion would be detectable. This lack of symmetry could be made manifest in two ways, the first being the introduction of a substituent onto the

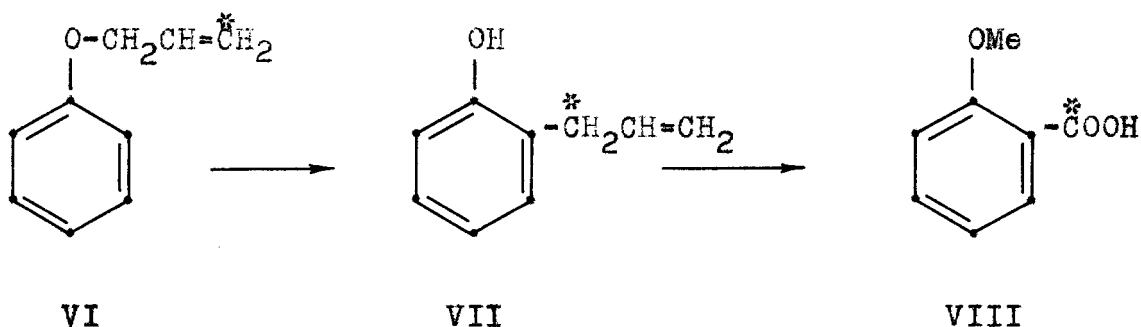
allyl chain at the alpha or gamma position. Thus investigators found that the rearrangement of (IV) yielded (V), showing the gamma carbon to have attached itself to the ring.



Specifically, with "R" as methyl or phenyl, this type of compound was obtained (9, p. 278; 10, p. 2345; 25, p. 107). Moreover, an inverted product is always obtained whether the allyl group be substituted at the alpha or gamma position, although "abnormal" inversion products have been observed. Where "R" is an ethyl group, the usual product was accompanied by appreciable amounts of a second compound in which the beta instead of the gamma carbon had become attached to the ortho position (26, p. 381; 32, p. 1393).

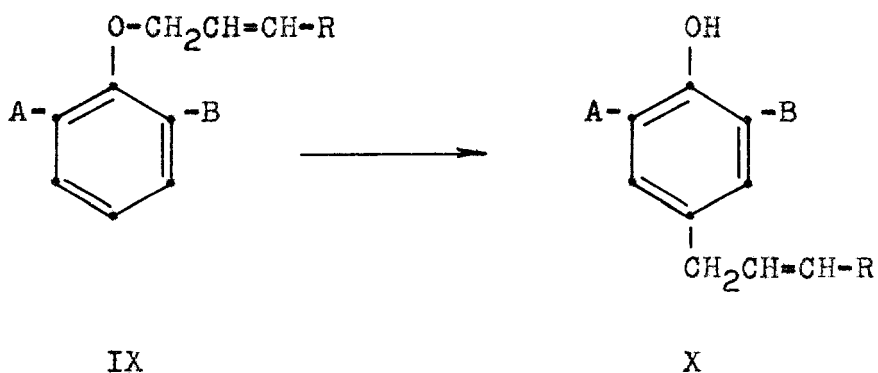
Further convincing evidence for inversion was acquired via a second route through labeling of a simple allyl group with  $\text{C}^{14}$ . Allyl- $\gamma$ - $\text{C}^{14}$  phenyl ether (VI) was rearranged, and after methylation and oxidation, all of the radioactivity was found to be present in the compound (VIII) (47, p. 5867). Such results could best be explained by assuming





the steps depicted above. Thus the phenomenon of inversion was again borne out. Para migration does not occur (at least less than 1%) when two ortho hydrogens are available to the rearrangement (33, p. 3042).

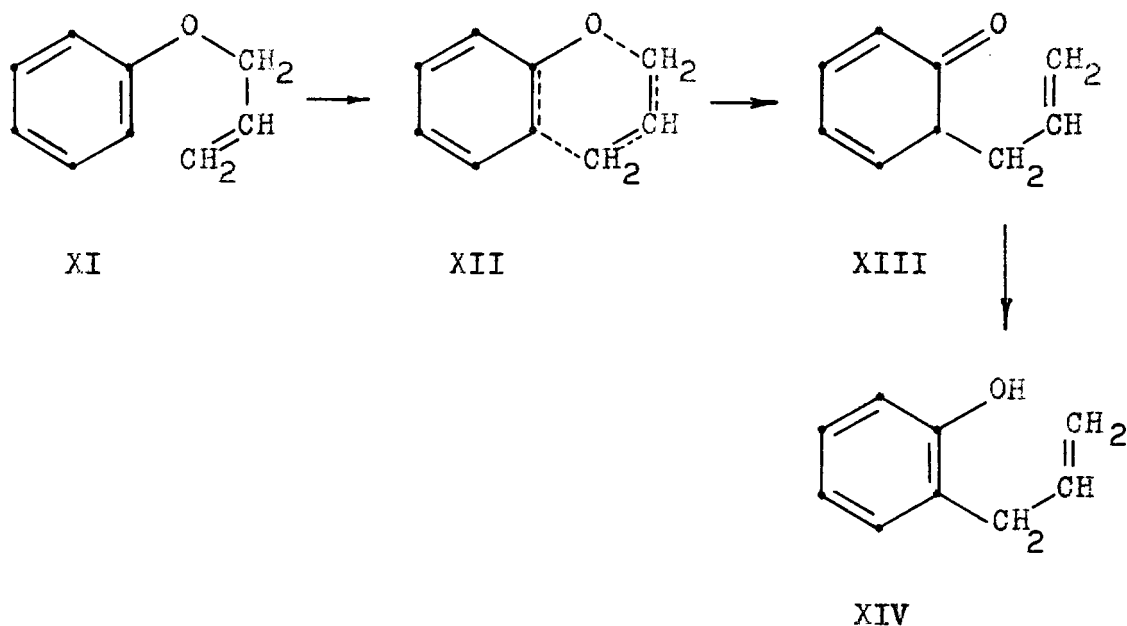
But when these observations were extended to the para rearrangement, non-inversion of the allylic grouping was found to prevail just as faithfully as did inversion with the former case. For example, with methyl and carbomethoxy



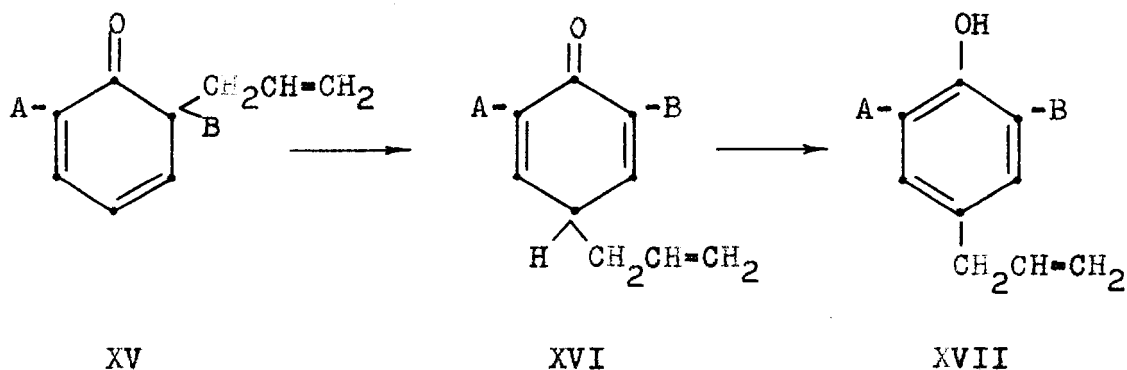
groups in the ortho positions, the rearrangement product was found to be of a non-inverted nature, i.e. where the alpha carbon becomes attached to the aromatic ring. Such

results have been reported when "R" is methyl, ethyl or phenyl (36, p. 2217; 37, p. 104; 38, p. 1525). Furthermore, radioactive tracer studies paralleling those for the ortho rearrangement have again supported this observation (47, p. 5867; 49, p. 491). Indeed, non-inversion has been found to occur no matter where the allylic function might be substituted and independent of the nature of the groups in the ortho positions. Meta migration has never been observed.

These interesting observations led to the formulation of a mechanism for the reaction which, during its evolution, underwent modification and expansion until it finally included both the ortho, para, and as will be seen, can accommodate the ortho-para Claisen rearrangement. Although other mechanisms have received attention, the evidence is such that today this theory is almost universally accepted. This mechanism postulates a cyclic, concerted process involving a quasi six-membered ring (XII), commonly referred to as the Hurd-Pollack mechanism (28, p. 558). The illustration on the following page exemplifies the proposed steps for the ortho rearrangement. If the original ether had substituents other than hydrogen in

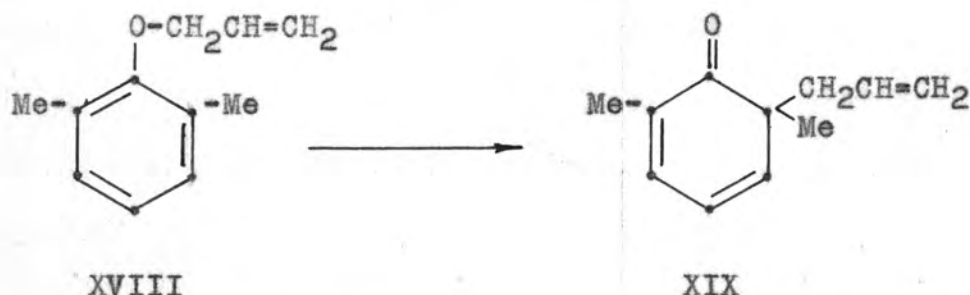


both ortho positions, the situation shown below occurs where (XV) cannot enolize but instead must rearrange once again.



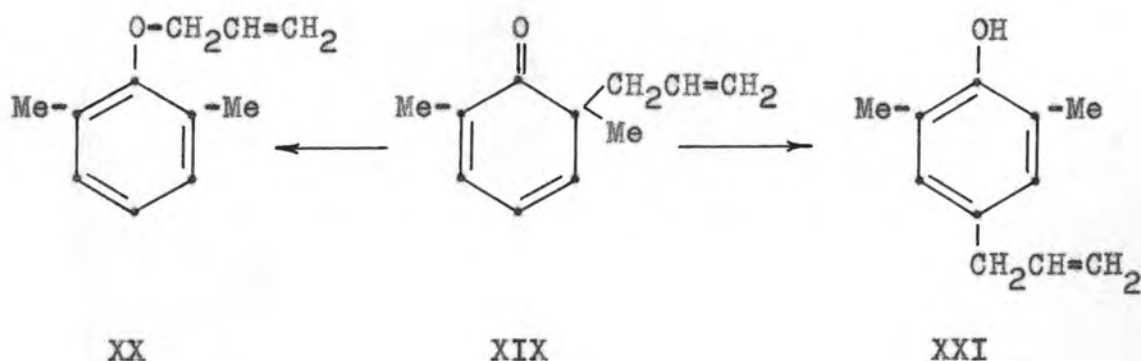
The isolation in 1953 of the Diels-Alder addition product of the dienone (XIX) with maleic anhydride during the Claisen rearrangement of allyl 2,6-dimethylphenyl ether

(11, p. 2531) lent considerable support to this mechanism, although only very small yields were realized.



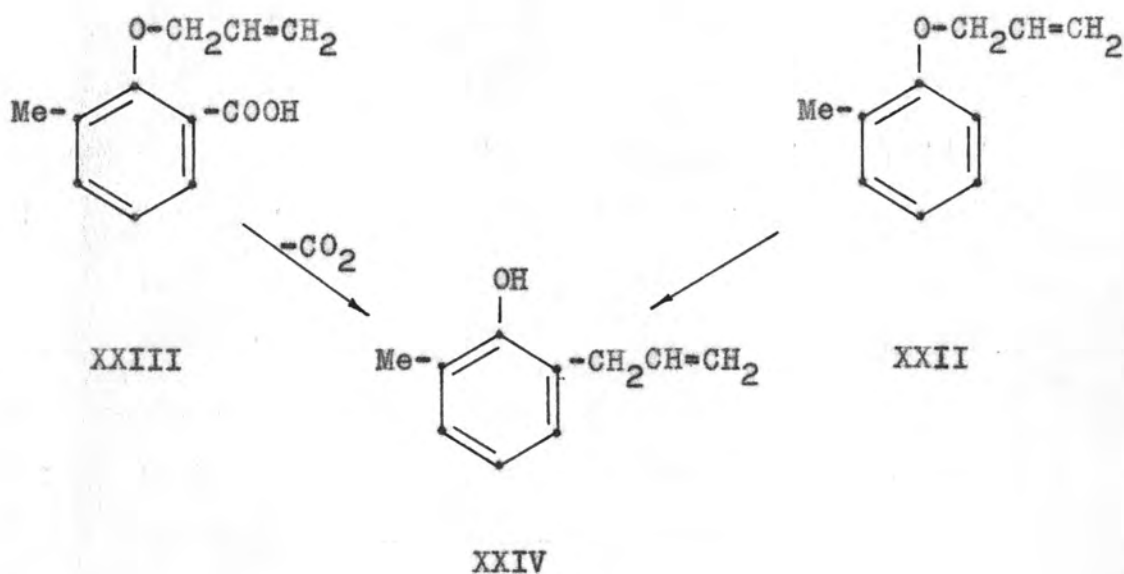
Afterwards, similar adducts were obtained in excellent yields (12, p. 2292), 87% of the dienone from allyl 2,4,6-trimethylphenyl ether being obtained (30, p. 780). This substantiates the presence of the dienone in at least the para rearrangement, and at the same time demonstrates the complete reversibility possible in a compound where no open positions for migration are available (18, p. 1112).

The last and perhaps most conclusive piece of evidence for the reaction mechanism came in 1957 with the independent synthesis of the dienone (XIX) (14, p. 3157). It was found to be identical with that obtained earlier as a maleic anhydride adduct (11, p. 2531), and upon warming to 84° the dienone rearranged to the phenol (XXI) 2.7 times as fast as to the ether (XX).



Thus the products resulting from this rearrangement have been well defined when both of the ortho positions are either open or blocked. However, considerable question has recently arisen concerning the nature of such products when only one ortho position is occupied, for as can be shown, this case should permit the formation of two isomers. Claisen himself originally assigned the ortho structure to the rearrangement product from allyl *o*-tolyl ether (XXII) because it appeared to be identical with that obtained from the allyl ether of 2-carboxy-6-methylphenol (XXIII) where concurrent decarboxylation occurred (8, p. 56).

Numerous subsequent workers also reported only an ortho isomer in yields approximating 80%, where again only one ortho position was occupied by such substituents as methyl, halogen, allyl, carbethoxy, etc. (37, p. 104; 38, p. 1525). Unfortunately, Claisen and subsequent investigators were plagued with the lack of sufficiently sensitive methods for detecting and separating substances



possessing closely similar physical properties.

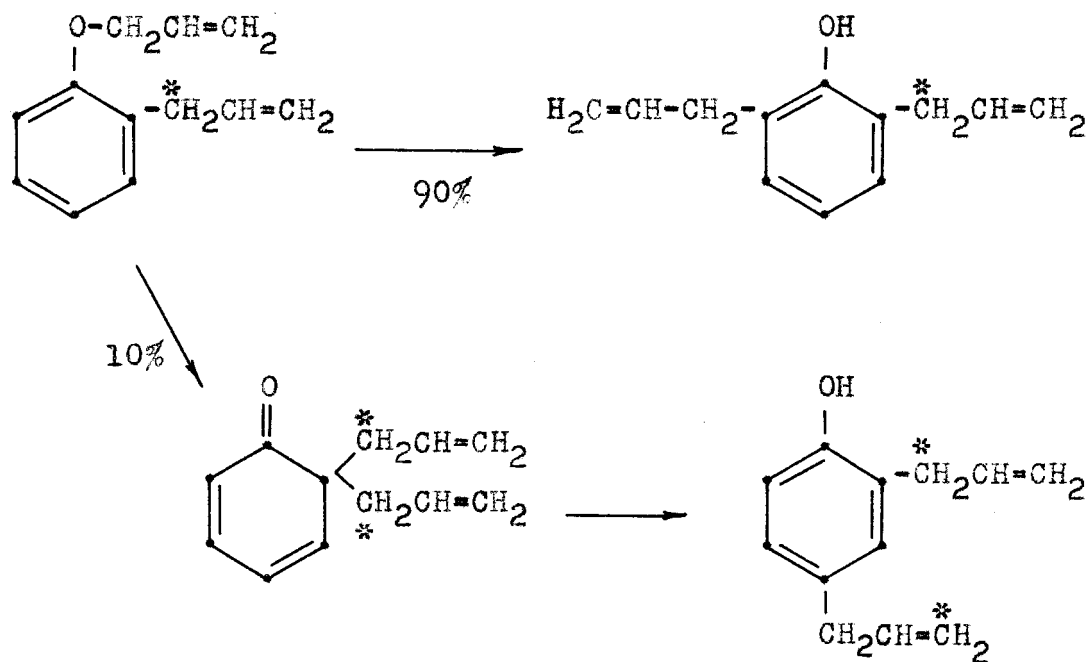
A few cases of para migration have been reported for this special case involving mono-ortho substituted phenols. The first such para migration was reported in 1922 for the rearrangement of  $\beta$ -methallyl 2-methoxyphenyl ether (54, p. 747). In this example a 40% yield was obtained of only the para isomer after fractionation and crystallization of the product. The observations of subsequent investigators came unexpectedly, and one group of workers discovered that they did not have a pure product only upon comparison of their synthetic substance with the naturally occurring one (5, p. 440). The cited "anomalies" are grouped in table 1.

ring substituent on phenyl allyl ether	% para product	isolation method	reference
2-hydroxy	44	crystallization & distillation	41, p. 1664
2,3-methylenedioxy	20	oxid. to benzoic acid derivative	5, p. 440
2-amino	33	fractional crystallization	60, p. 593
2-acetamido	13	fractional crystallization	60, p. 592
2-allyl- $\alpha$ -C <sup>14</sup>	16*	radiochemical analysis	50, p. 1082

\*Although the authors quoted 10-12% para isomer, the approximate value of 16% seems more readily to follow from the radiochemical data reported.

Table 1. Observed para products from phenols with a single open ortho position.

In the last example, the only such case with a hydrocarbon substituent, the workers utilized the rule of inversion at an ortho position and non-inversion at the para position. By labeling the allyl group as indicated, 7.5 - 9.5% of the activity was found in the terminal allylic carbon atom after rearrangement. These results were tentatively explained by assuming para migration.



This last investigation in 1954 completes the number of such cases discovered to date. It is still desirable to establish clearly that both ortho and para products are generally obtained when only a single ortho substituent is present, and show that both isomers are indeed a direct consequence of the mechanism.

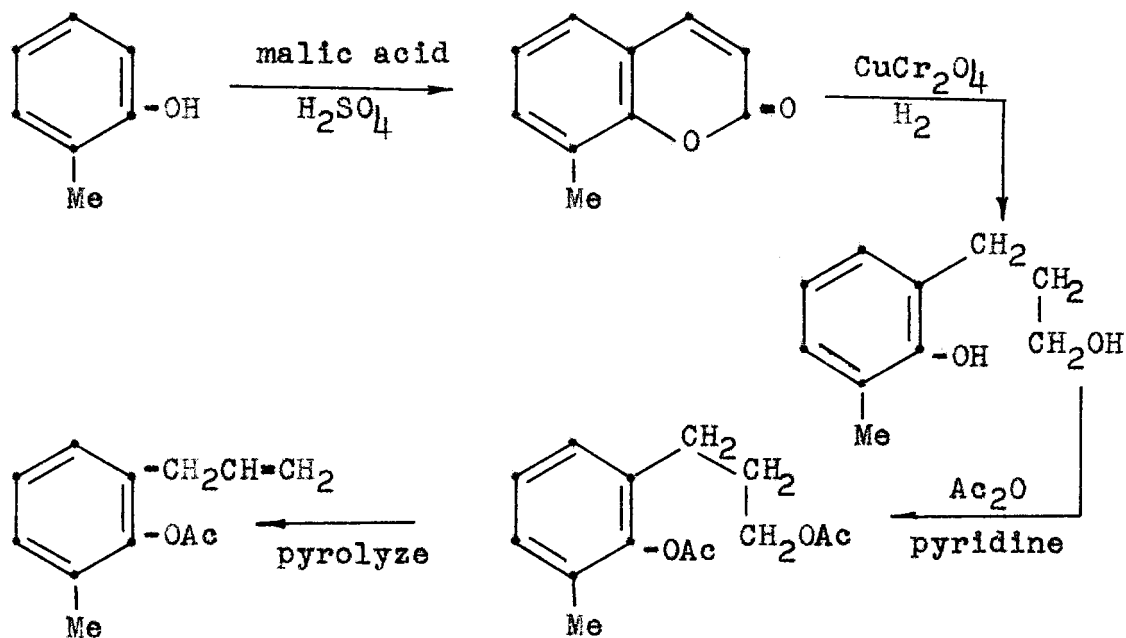
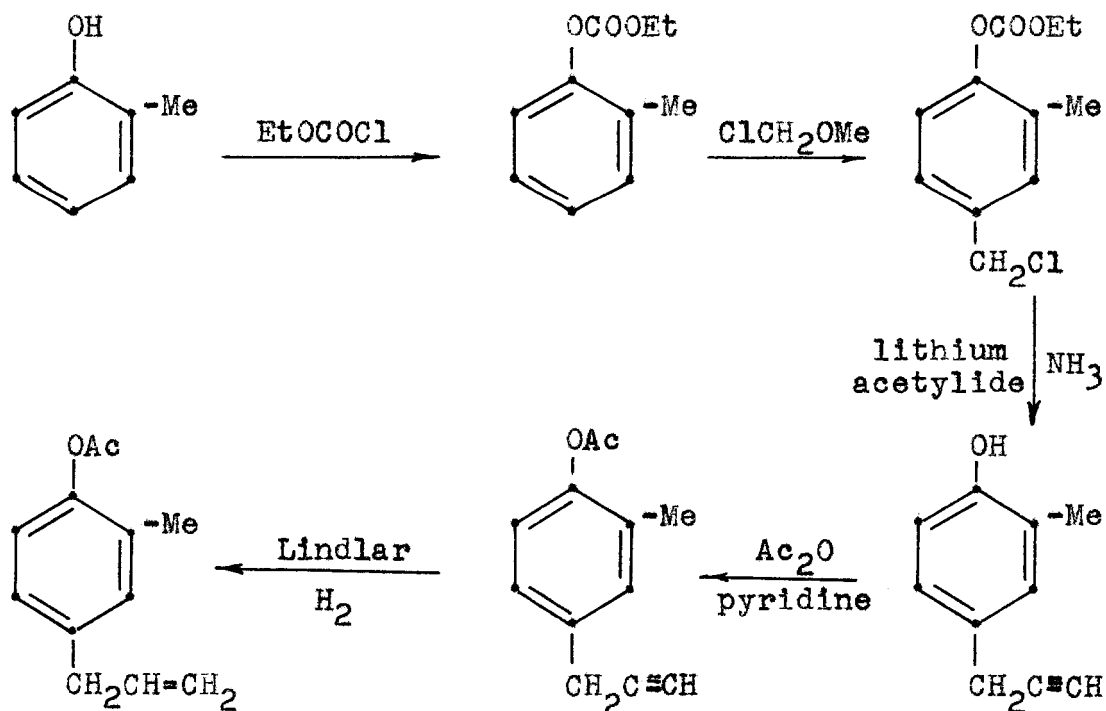


## DISCUSSION

A study of the mechanism of the Claisen rearrangement and of the reported cases of ortho-para rearrangement leads to the conclusion that two isomers should be formed during the rearrangement of allyl o-tolyl ether. This hypothesis was verified via a careful examination of this rearrangement product. Discussion of the results of that examination comprise the first part of this section.

A. The nature of the rearrangement product: An attempt was initially made to resolve the isomers predicted by theory by careful fractionation of the rearranged material through a very efficient column. The physical constants and infrared spectra of numerous fractions were found, however, to be virtually identical. This could mean that the rearrangement product is either essentially homogeneous, or that the two isomers have almost identical boiling points.

This same product was then subjected to gas chromatographic analysis, and the eluate indeed gave two peaks. Due to the results of the fractional distillation, it seemed reasonable to assume that these two peaks were attributable to the suspected isomers, thus giving a concrete basis for their existence. It next remained to identify these isomers, and an independent synthesis of

Ortho scheme:Para scheme:

each isomer was carried out by unequivocal means as shown by the reaction schemes on page 15.

To ensure the unequivocal nature of the synthesis two essential criteria must be met: the problem of orientation on the ring, and that of preparing the terminal double bond. For the ortho isomer, 8-methylcoumarin is a starting material par excellence because it is a crystalline solid, hence readily purified and identified, and it guarantees the required 1,2,3 orientation. While the 8-methylcoumarin was obtained via the usual von Pechmann synthesis, only low yields were realized (3, p. 905; 43, p. 3826; 59, p. 2557). Because of this, the possibility that isomeric methylcoumarins might have resulted from small amounts of m- or p-cresol contamination due to the much higher yields obtained from these compounds cannot be ignored. However, all have melting points considerably different from that of the 8-methylcoumarin as table 2 shows (43, p. 3826).

cresol	coumarin	m. p.
ortho	8-methyl	109°
meta	5-methyl	66
	7-methyl	126
para	6-methyl	75

Table 2. Melting points of isomeric methylcoumarins

To assure a terminal double bond the 8-methylcoumarin must be transformed into a substance with a terminal functional group on a propyl chain. The coumarin was hydrogenated over copper chromite (6, p. 3069) followed by acetylation, and the resulting 2-( $\gamma$ -hydroxypropyl)-6-methylphenyl acetate subjected to pyrolysis over glass wool, a reaction known to give unrearranged olefins (22, p. 782). The general procedure was essentially that of Wibaut, Houtman and co-workers (62, p. 1057). Contrary to the opinion of Bailey (4, p. 74), these authors found a fresh carbon coating on the glass wool actually to be necessary for the reaction to occur. The unusually brief contact time of ten seconds at 495-500° sufficed.

That the terminal double bond is the exclusive product from this reaction is substantiated by the fact that the product from pyrolysis, showing only a single peak by GPC, exhibits no conjugated double bond absorption in the infrared at 965  $\text{cm}^{-1}$  while giving good evidence for the terminal double bond at 915  $\text{cm}^{-1}$ . None of the phenolic acetate underwent cleavage since this requires more drastic conditions (27, p. 2420). The 2-methyl-6-allylphenyl acetate exhibits the expected absorption at 780  $\text{cm}^{-1}$  for the 1,2,3 tri-substituted aromatic system. Thus the identity of this isomer appears to be indisputable.

Unfortunately, no such ideal starting material is available in the para case, and direct substitution of o-cresol is a necessity. Here it is necessary not only to provide the proper orientation, but the group introduced must permit the formation of the terminal double bond. While several routes are available, that starting with the introduction of a chloromethyl group proved most satisfactory.

A modification of the procedure of Sommelet (53, p. 257) was the only one of several (39, p. 1013; 44, p. 103; 45, p. 2200) which gave acceptable results. Both ortho and para chloromethyl derivatives were formed but were readily separated by fractional distillation. That the higher melting and boiling one is the expected para isomer is corroborated by comparison with the physical constants reported by Sommelet. In addition to the predicted infrared absorption for a 1,2,4 tri-substituted aromatic compound at  $820\text{ cm}^{-1}$ , this isomer shows via its subsequent reactions that it is definitely not the ortho one. The assignment of the para orientation to this isomer seems quite well justified.

The proper orientation having been established, the chloromethyl derivative was coupled with lithium acetylide according to the procedure of Raphael (46, p. 193). This

product, showing strong absorption in the infrared for a terminal triple bond at  $3150\text{ cm}^{-1}$ , was acetylated, the acetate giving only a single peak to gas chromatography. The terminal position of the triple bond was confirmed by reaction with alcoholic silver nitrate (24, p. 143). Finally, semi-hydrogenation over the Lindlar catalyst (35, p. 450) gave the 2-methyl-6-allylphenyl acetate containing the desired double bond ( $908\text{ cm}^{-1}$ ).

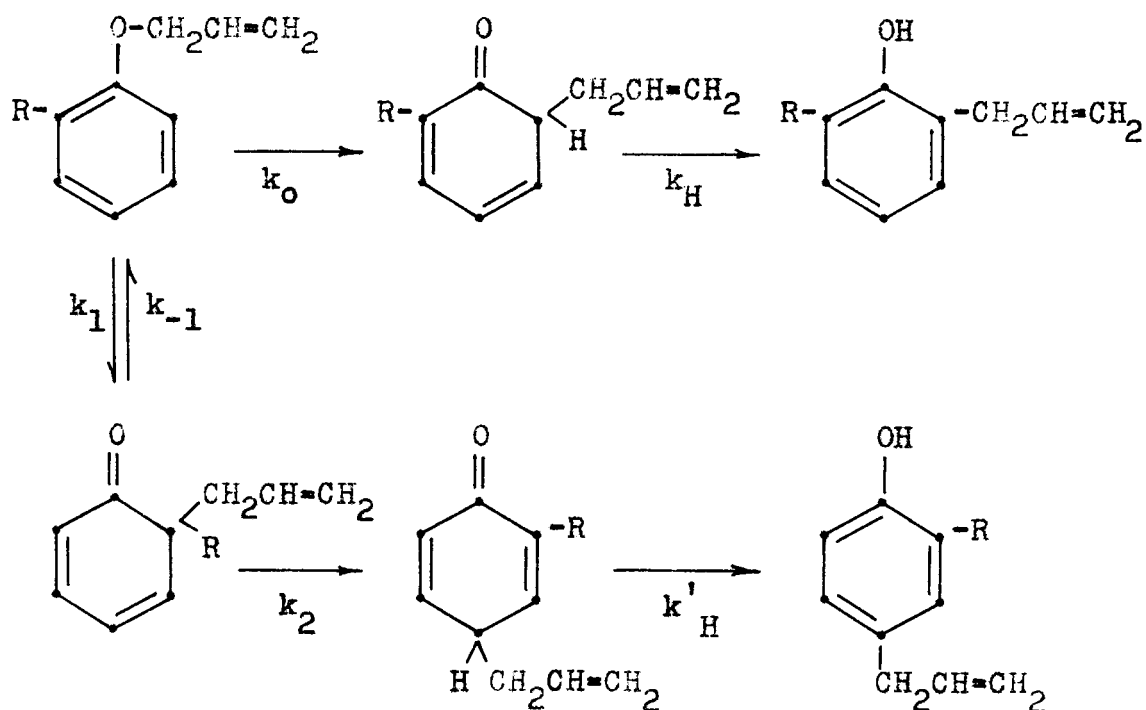
The synthetic and rearrangement mixtures, giving superimposable IR spectra, were submitted to gas chromatographic analysis, the results from which appear in table 3. A value of 6.6% was obtained for the para isomer, the accuracy of which is excellently substantiated by the comparative analysis shown for a known ortho-para mixture. Similar GPC analysis of the rearrangement product after base extraction but before acetylation exhibited closely paralleling behavior, yielding two peaks, the smaller comprising 6.8% of the total. Direct analysis of the rearrangement product gave a higher value (see table 4) which indicates that the Claisen's alkali exerts a partitioning effect favoring the ortho isomer. But these results give indisputable evidence for the formation of two products in the reaction studied, and are convincing indeed that the minor constituent is actually the hitherto unidentified 4-allyl-2-methylphenol.

	rearrangement mixture		synthetic mixture	
	ortho	para	85% ortho	15% para
retention time (minutes)	14.5	18.8	14.4	18.8
% of total	93.4	6.6	85.1	14.9

Table 3. GPC analysis of 2-allyl- and 4-allylphenyl acetates.

B. Conclusions: The initial part of this work demonstrated the separation of the expected Claisen rearrangement isomers from allyl o-tolyl ether by fractional distillation to be impractical if not impossible. It is thus readily understandable how earlier workers with limited - in the modern sense - analytical tools at their disposal, thought their respective Claisen products to be homogeneous.

That two isomers should result from the heating of all mono-ortho substituted phenyl allyl ethers has recently been recognized by H. Schmid, who first worked out the complete kinetics for the ortho-para Claisen rearrangement (17, p. 783; 29, p. 21). In the normal para rearrangement where both ortho positions of the phenol are occupied by some group other than hydrogen, the intermediate has been conclusively proven to be that depicted in XV, where the allyl group has attached itself to one of the substituted



Ortho-para rearrangement scheme

ortho positions. Thus, in the analysis of the ortho-para case, an attack on the ortho carbon attached to hydrogen to the complete exclusion of attack at the one holding the methyl group does not seem likely. Consequently, the process for the case in question may best be shown to follow two paths, depending upon which ortho position is attacked. The intermediate obtained from  $k_o$  can proceed directly to the final ortho product due to the high mobility of a proton, whereas the intermediate from  $k_1$  must again rearrange along  $k_2$  before giving rise to a hydrogen which can enolize, resulting in the final para product. The enolization is fast, so that  $k_o$  and  $k_2$  would



be expected to be essentially non-reversible steps.

In light of the known faster rate for the para rearrangement (29, p. 21), it might be expected that the para isomer should have been the predominant product from allyl o-tolyl ether. If the Claisen products are formed reversibly, however, the observed ortho-para ratio of 9:1 could possibly reflect the thermodynamic stability of the isomers rather than kinetic control. While this is quite unlikely since all of the observed ortho-para rearrangements (table 1) have yielded predominantly ortho products, this possibility was nevertheless investigated. Any isomer equilibration during heating would evidence itself through a change in the ortho-para ratio during the course of the reaction. The results from such an examination appear in table 4.

sample	time (min.)	temperature	% ortho	% para
-	0	198	-	-
1	20	203	90.8	9.2
2	45	212	89.3	10.7
3	65	222	88.3	11.7
4	110	224	89.2	10.8
5	5.2 hr.	225	86.5	13.5
6	25 hr.	226	89.2	10.8

Table 4. Direct GPC analysis of the Claisen rearrangement mixture.

The figures show the ortho-para ratio to remain relatively constant during the course of the reaction and consequently attest to the final mixture being kinetically rather than thermodynamically controlled. The amount of para isomer here is somewhat higher than was found earlier for the acetate esters, but the above approximate value of 11% is undoubtedly more reliable since the rearrangement product here underwent no chemical treatment prior to analysis.

But the proof of irreversibility in the overall Claisen rearrangement still leaves open the question as to why, from comparison with other rate data, the ortho isomer forms the bulk of the product. A comparison of existing rate results for various substituted phenyl allyl ethers might lead one to suspect just the opposite, as was indeed concluded by H. Schmid in some of his discussions on the Claisen rearrangement (29, p. 21). In the case of 2,4-dimethylphenyl allyl ether, he reasoned that since the rate of rearrangement of allyl 2,6-dimethylphenyl ether was much greater than that in allyl phenyl ether itself, the allyl group would attack the ortho carbon bearing the methyl group in preference to the other ortho position. This meant, then, that most of his rearrangement product, 2-allyl-4,6-dimethylphenol, had

resulted from migration of the allylic function via the two and four positions rather than directly to the open ortho position in a single step.

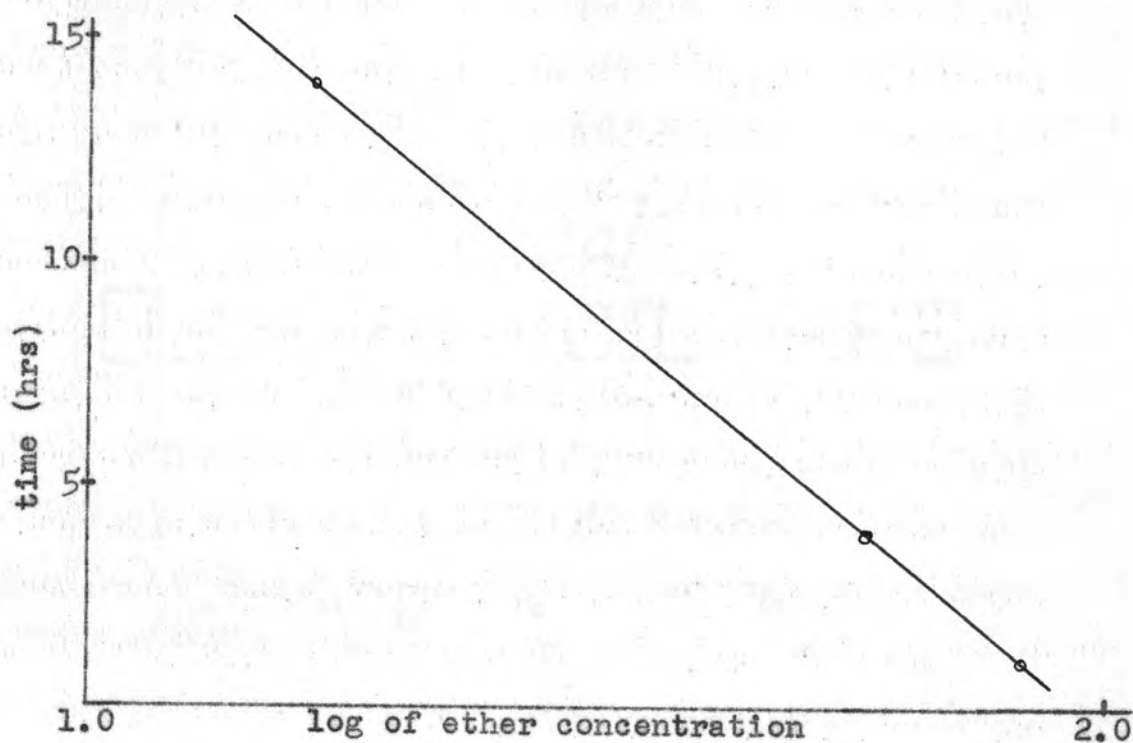
However, Schmid had no rate data available for mono-ortho substituted phenyl allyl ethers since none have been reported heretofore. Thus it was especially desirable to determine the kinetics for the rearrangement of allyl o-tolyl ether. This would be of particular interest also because it permits an examination of the proportionate influence of individual ortho and para methyl groups on the rate. Consequently, the rearrangement of a dilute solution of the ether was followed in decalin, a completely inert, high boiling hydrocarbon which should place at a minimum the known solvent effects on the reaction (20, p. 3287). The data for this kinetic study appears below.

sample	hrs.		ether	ortho	para	other	o/p
-	0	reten. time <sup>*</sup> %	4.4 100	-	-	-	-
1	1	reten. time %	4.3 85.8	16.2 12.8	36.5 0.9	13.2 0.5	12.6/1
2	4	reten. time %	4.3 57.4	16.1 37.2	36.3 3.8	13.1 1.6	9.4/1
3	14	reten. time %	4.3 16.0	16.2 74.8	36.3 7.6	13.1; 8.5 1.4; 0.2	9.8/1

\*Retention times given as minutes from air peak.

Table 5. Kinetic data for the rearrangement of allyl o-tolyl ether.

Here again, the ortho-para ratio is demonstrated to remain fairly constant throughout the reaction, although the value of roughly 9.5% para product is about 1.5% lower than that obtained by refluxing of the pure ether given in table 3. But since the para isomer is the less energetically favored one, it might be expected that higher temperatures - as encountered with refluxing of the pure ether - would favor its formation. Both of these values are in reasonable agreement with that of 16% para indicated from radiochemical analysis of the thermal product from allyl 2-allyl- $\gamma$ -C<sup>14</sup>-phenyl ether (50, p. 1082).



Kinetics exhibited by the rearrangement of allyl o-tolyl ether.

A plot of time against the logarithm of the ether concentration gave virtually a straight line, thus verifying the adherence of the reaction to clean, first order kinetics. The half life was found to be 5.2 hours, from which the reaction rate  $k_{\text{total}}$  was readily calculated to be  $3.7 \times 10^{-5} \text{ sec}^{-1}$  at  $190^{\circ}$ . Since for such a reaction the ortho-para ratio will be the same as the ratio of their specific rearrangement velocities, the individual rate constants for the competing ortho and para rearrangements were found to be respectively  $k_o = 3.4 \times 10^{-5} \text{ sec}^{-1}$  and  $k_p = 0.35 \times 10^{-5} \text{ sec}^{-1}$ . This value is in accord with the known catalysis of the rearrangement by electro-positive substituents (20, p. 3281) and the observations of investigators examining electronic influences on the Claisen rearrangement (61, p. 3273).

When comparing these figures with those for other Claisen ethers, it is somewhat difficult to view all such studies on a common footing. The rate is dependent not only upon temperature, but is also affected by the nature of the solvent and even the concentration of starting ether, two not unrelated conditions. These effects, however, are fortunately not large, and for an approximate comparison several rate constants appearing in the literature have been re-calculated at  $190^{\circ}$  by means of the Arrhenius equation,  $k = Ae^{-E_a/RT}$ . This comparative data

allyl ether	ring group(s)	$k_{190} \times 10^5$	solvent	adjusted $k \times 10^5$	reference
1	none	2.2	DPE	0.8	20, p. 3281
2	4-methyl	2.3*	decalin	1.2	20, p. 3281
		3.1	DPE		20, p. 3281
		3.7*	DMA		20, p. 3281
		3.8	DPE		31, p. 3087
3	2-methyl	3.7	decalin	3.4	this thesis
		3.4 ( $k_o$ )			
		0.35 ( $k_p$ )			
4	2,4-dimethyl	7.4	DMA	4.5-5	29, p. 21
5	2,6-dimethyl	29.5	DPA	10-13	56, p. 729
		30.2	DEA		21, p. 664

\*Extrapolated from 185° by comparison to data in DPE since no  $E_a$ 's available. Abbrev: DPE, diphenyl ether; DMA, dimethyl aniline; DEA, diethyl aniline.

Table 6. Comparative kinetic data for substituted phenyl allyl ethers.

is presented above in table 6. The "adjusted k" represents an attempt to correct for probability and solvent differences. While the probability correction is readily made, that for solvent differences can only be estimated in the absence of experimental results directly pertaining to the solvents and reactions in question. Here it is assumed that since the transition states in the ortho rearrangement of ethers 1-4 would be expected to be very similar, the solvent effects will likewise be similar.

This estimate of the relative specific rate constants in decalin permits a rough correlation of the effect of location and number of methyl groups on the rate of the ortho rearrangement to a single open ortho position for ethers 1-4. Such a comparison reveals that a para methyl group causes a 50% increase in reaction rate, whereas an ortho methyl results in a 400% increase; i.e., an ortho methyl group is eight times as effective as one in the para position. Apparently, then, the unexpectedly high rate constant for 2,6-dimethylphenyl allyl ether, interestingly four times that for allyl o-tolyl ether, is a consequence of some special effect of ortho methyl groups on the rearrangement. The exact nature of the factors contributing to this effect is not at present clear.

## EXPERIMENTAL

o-Cresol: Technical o-cresol distilled through a 3 ft. Fenske column was used in all work. The physical constants, b.p. 77.2-78.0° (11-12 mm),  $n_{D}^{41}$  1.5359-1.5361 and m.p. 30.5° (corr. from m.p. curve) are all in excellent agreement with accepted values (16, p. 2877; 40, p. 596).

Allyl o-tolyl ether: One hundred and seventeen grams (1.08 moles) of o-cresol in 200 ml. of anhydrous acetone was allowed to react in the usual manner (58, p. 26) with 135 g. (1.08 moles) of allyl bromide in the presence of 55 g. of anhydrous potassium carbonate. After fractionation through a Fenske column, 97.1 g. (61%) of a colorless oil was obtained, b.p. 87-88° (13-14 mm);  $n_{D}^{15.4}$  1.5202;  $n_{D}^{20}$  1.5188. The literature lists b.p. 85° (12 mm) (8, p. 56);  $n_{D}^{15.4}$  1.5188 (2, p. 174).

Rearrangement of allyl o-tolyl ether: The ether, 14.8 g. (0.10 mole), was refluxed under nitrogen for 1 hr., the vapor temperature rising from 196° to 232°. After refluxing for an additional half hour, the product was taken up in petroleum ether and extracted with Claisen's alkali. After acidification, the aqueous fraction was shaken with ethyl ether, the organic phase washed free of acid and dried over Drierite. Distillation yielded 11.6 g. (79%) of a colorless oil, b.p. 100-108° (10 mm)(Lit. b.p.



106-107° (12 mm))(8, p. 56);  $n^{20}_D$  1.5378 (Lit.  $n^{20}_D$  1.538) (2, p. 176).

Analysis of the rearrangement product: Ten grams of the rearrangement product and 30 g. of acetic anhydride was refluxed in 70 ml. of pyridine (distilled from BaO) for 20 hrs. The acetic acid, acetic anhydride and pyridine were removed in vacuo and the residue completely distilled. The yield was 11.9 g. (93%) of a colorless oil, b.p. 116-118° (9 mm)(Lit. b.p. 128° (14 mm))(1, p. 662);  $n^{20}_D$  1.5076 (Lit.  $n^{20}_D$  1.507)(1, p. 662). This material was fractionated through a Podbielniak Mini-Cal column, all fractions had b.p. 103° (6 mm),  $n^{20}_D$  1.5074-1.5078.

8-Methylcoumarin: Concentrated sulfuric acid (745 g.) was placed in a 3-l. three-necked flask fitted with a stirrer, dropping funnel, and condenser with a thermometer suspended inside. The acid was heated to 105° whereupon heating was discontinued while 456 g. (4.22 moles) of o-cresol was added at a rate which maintained the temperature between 105° and 110° (20 min.), the solution becoming dark red. The solution was then heated to 135° (10 min.) and 565 g. (4.22 moles) of dl-malic acid added over a period of 2 hrs., the temperature being kept below 140°. The flask contents became black and viscous, and a vigorous evolution of carbon monoxide was observed after each addition.

After the reaction mixture had been stirred for an additional half hour, it was submitted to steam distillation. Unreacted cresol was removed from the coumarin by rapid extraction with ice-cold 5% sodium hydroxide, and the crude coumarin recrystallized thrice from 95% ethanol. The product was obtained as white needles, 36 g. (5.3%), m.p. 109.6-109.9°, in excellent agreement with the literature values of 109-110° (7, p. 80; 55, p. 338).

2-( $\beta$ -Hydroxypropyl)-6-methylphenol: The 8-methylcoumarin, 36.7 g. (0.23 mole), 5.8 g. of copper chromium oxide, and 75 ml. of purified dioxane (19, p. 284) were shaken in a Parr high pressure bomb at 250-260° under a pressure of 1500-2400 psi. After 4.5 hrs. the calculated amount of hydrogen had been absorbed and the uptake rate had become quite slow. The catalyst was filtered from the solution, the dioxane removed by distillation, and a benzene solution of the residue extracted with 5% sodium hydroxide. Acidification of the aqueous extracts with glacial acetic acid gave an oil which was taken up in benzene and washed with bicarbonate, water and dried over Drierite. Recrystallization of the crude product from dry benzene yielded 27.0 g. (71%) of white needles, m.p. 61.4-61.8°.

Anal. Calc'd. for  $C_{10}H_{14}O_2$ : C, 72.2; H, 8.44.

Found: C, 72.2; H, 8.34.

Calc'd. hydroxyl content: 20.5%.

Found: 20.4%; 20.7%; 20.8%. Aver: 20.6%.

2-Methyl-6-( $\beta$ -hydroxypropyl)phenyl acetate: Forty-five grams (0.271 mole) of the above phenol in 400 ml. of dry pyridine was acetylated with 170 g. of acetic anhydride in the manner described on page 30. Distillation through a small Fenske column gave 64.3 g. (95%) of a clear oil, b.p.  $111^{\circ}$  (0.25 mm);  $n_D^{20}$  1.4952.

Anal. Calc'd. for  $C_{14}H_{18}O_4$ : C, 67.3; H, 7.22.

Found: C, 70.0; H, 7.30.

2-Methyl-6-allylphenyl acetate: The ester was pyrolyzed over glass wool in a Vycor combustion tube mounted vertically through two furnances. Carbonization was effected on the packing in the pyrolysis zone by the introduction of a small amount of ethyl acetate with the bottom heater at  $650-700^{\circ}$ . In a representative run, the pre-heater was set at  $200^{\circ}$  and the pyrolysis heater at  $495-500^{\circ}$ , using a nitrogen flow rate to give a contact period in the pyrolysis zone of 10 sec. The di-acetate, 16.47 g. (0.066 mole), was diluted with an equal volume of dry benzene, two drops of acetic anhydride added, and the solution introduced into the pyrolysis tube at the rate of one drop every 10 sec. After all of the liquid had thus been added, a little dry benzene was similarly introduced to wash the tube and packing, the volatile components

removed under reduced pressure and the slightly yellow residue fractionated through a small Fenske column. The recovered starting material, 13.49 g., b.p.  $134^{\circ}$  (0.70 mm),  $n_D^{20}$  1.4954 was recycled through the apparatus. The lower boiling fraction, containing no phenol as indicated by the absence of infrared absorption at  $3400\text{ cm}^{-1}$ , was distilled through a Podbielniak Mini-Cal distillation column to yield 1.67 g. of a colorless oil, b.p.  $74-77^{\circ}$  (2.3-2.5 mm);  $n_D^{20}$  1.5078. This represents a 13.2% conversion per pass, or a 74% overall yield when corrected for recovered starting material.

Anal. Calc'd. for  $C_{12}H_{14}O_2$ : C, 75.8; H, 7.37.

Found: C, 75.8; H, 7.48.

o-Tolyl ethyl carbonate: One hundred and eight grams (1.00 mole) of o-cresol was treated with an equal weight of ethyl chlorocarbonate in a chloroform-pyridine solution as described by Sommelet (53, p. 257). Distillation of the base-insoluble crude product through a small Vigreux column gave 121 g. (67%) of a clear liquid, b.p.  $76^{\circ}$  (1.7 mm);  $n_D^{25}$  1.4861.

4-Chloromethyl-2-methylphenyl ethyl carbonate: The carbonate, 78.1 g. (0.434 mole), together with 36.7 g. (0.456 mole) of chloromethyl ether was dissolved in 500 ml. of carbon tetrachloride in a 1-l. three-necked flask equipped with a stirrer, dropping funnel and drying tube.

Then 20.5 ml. (48 g., 0.161 mole) of anhydrous antimony pentachloride was introduced dropwise into the stirred liquid over 1.5 hrs., keeping the temperature between  $0^{\circ}$  and  $-3^{\circ}$ . After stirring for an additional 3 hrs. at  $0^{\circ}$ , the flask contents were poured onto ice, washed with sodium bicarbonate and with water until no sulfide test was given for the antimony ion. Fractionation through a Fenske column yielded 21 g. of starting material, 5.5 g. of the ortho product, b.p.  $90-92^{\circ}$  (0.3 mm), m.p.  $28^{\circ}$ ,  $n^{23}_D$  1.5095, and 40 g. of the para isomer, b.p.  $104^{\circ}$  (0.35 mm), m.p.  $36^{\circ}$ ,  $n^{23}_D$  1.5112. Both the ortho and para isomers give a positive Beilstein test for halogen, and represent respectively 6% and 40% yields, corrected for recovered starting material. For the para isomer, the literature reports b.p.  $162^{\circ}$  (16 mm); m.p.  $35^{\circ}$  (53, p. 257).

2-Methyl-4-propargylphenol: A solution of lithium acetylide in 1700 ml. of liquid ammonia was prepared from 7.3 g. (1.05 moles) of lithium and acetylene gas purified by passage through an efficient Dry Ice-acetone cold trap (46, p. 193). The well-stirred grey suspension was cooled in a Dry Ice-acetone bath and 39.8 g. (0.175 mole) of the above chloromethyl ester, dissolved in 50 ml. of absolute ether, added over 1.5 hrs. while bubbling a slow stream of acetylene continuously into the slurry. After

the reaction mixture had been agitated at  $-35^{\circ}$  overnight, ammonium chloride was added and the ammonia permitted to evaporate. After acidification with phosphoric acid and filtration from polymeric substances, the product was taken up in 5% sodium hydroxide, the solution acidified and the product isolated by steam distillation. Fractionation through a Fenske column yielded 12.6 g. (50%) of a clear liquid giving a negative Beilstein test; b.p.  $134^{\circ}$  (13 mm);  $n_D^{26.5}$  1.5492.

Anal. Calc'd. for  $C_{10}H_{10}O$ : C, 82.2; H, 6.85.

Found: C, 81.7; H, 7.10.

2-Methyl-4-propargylphenyl acetate: Twelve and seven-tenths grams (0.087 mole) of the above phenol was acetylated in the manner described on page 30. Fractionation of the product through a Podbielniak Mini-Cal column gave 9.3 g. (57%) of a colorless liquid which rapidly turned brown upon standing and gave only a single peak via gas chromatography; b.p.  $113^{\circ}$  (4 mm);  $n_D^{25}$  1.5177.

Anal. Calc'd. for  $C_{12}H_{12}O_2$ : C, 76.6; H, 6.38.

Found: C, 76.0; H, 6.79.

4-Allyl-2-methylphenyl acetate: The propargyl acetate (7.21 g., 0.0384 mole), dissolved in 55 g. of ethyl acetate containing 20 drops of synthetic quinoline, was hydrogenated at room temperature and pressure over 0.5 g. of Lindlar catalyst (35, p. 450) until absorption of almost

the theoretical amount of hydrogen had been effected. The quinoline was removed by acid extraction, the product treated with 5% ethanoic silver nitrate and the excess silver nitrate removed by the addition of salt. The product was dried and slowly distilled through a Vigreux column. The yield was 4.8 g. (67%); b.p.  $77^{\circ}$  (0.8 mm);  $n_D^{21}$  1.5078.

Anal. Calc'd. for  $C_{12}H_{14}O_2$ : C, 75.8; H, 7.37.

Found: C, 75.3; H, 7.08.

Kinetics: One-half milliliter of a 0.60 M solution of allyl o-tolyl ether in decalin (at least 99% pure by GPC) was sealed under nitrogen in each of three 6 mm. tubes and placed into a constant temperature bath at  $190 \pm 0.5^{\circ}$ . The sample vials were removed at appropriate times and the contents injected directly into the gas chromatograph, the retention times of 1.2 and 1.6 minutes for cis and trans decalin not interfering in the overall product analysis. Only a small amount of rearrangement occurred on the GPC column as evidenced by a slight trailing of the ether peak.

Gas chromatography: Separations were performed at  $190^{\circ}$  in a Perkin-Elmer model 154 Vapor Fractometer over a 6 ft. column of firebrick coated with Reoplex 400 (20% by weight) using helium as the carrier gas. The phenolic acetates appeared as merging but completely resolved

peaks, while the free ortho and para phenols eluted from the column as widely separated peaks, having retention times of 17.0 and 38.4 minutes respectively.



## SUMMARY

A re-examination of the Claisen rearrangement product from allyl *o*-tolyl ether has revealed the anticipated formation of two isomers: the known 6-allyl-2-methylphenol, and appreciable amounts of the heretofore undetected 4-allyl-2-methylphenol. Moreover, there is no reason to believe that the thermal rearrangement of allylic ethers of all mono-ortho substituted phenols should not give rise to a mixture of ortho and para substituted phenols, the ratio of the two depending upon the nature of that ortho substituent. This must be borne in mind when employing synthetic procedures involving such intermediates, and some recent investigations merit reviewing in the light of these conclusions (13, p. 2613; 15, p. 4084).

The para isomer from the rearrangement of allyl *o*-tolyl ether was found to be produced to the extent of about 10%, although it could not be detected by either careful fractional distillation or infrared analysis. The isomers were successfully resolved and conclusively identified by gas chromatography. The rearrangement was shown to follow clean first-order kinetics,  $k_{\text{total}} = 3.7 \times 10^{-5} \text{ sec}^{-1}$ , and analysis of the rate data gave  $k_o = 3.4 \times 10^{-5} \text{ sec}^{-1}$  and  $k_p = 0.35 \times 10^{-5} \text{ sec}^{-1}$  at  $190^\circ$ . It was shown

that methyl groups in the ortho position are particularly effective in enhancing the rate of rearrangement.

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