THE MECHANISM OF THE PARA-CLAISEN REARRANGEMENT

by

ROY TERANISHI

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1954
APPROVED:

Assistant Professor of Chemistry
In Charge of Major

Chairman of Chemistry Department

Chairman of School Graduate Committee

Dean of Graduate School

Date thesis is presented April 21, 1954
Typed by Mary Willits
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>History</td>
<td>3</td>
</tr>
<tr>
<td>Discussion</td>
<td>9</td>
</tr>
<tr>
<td>Experimental</td>
<td>19</td>
</tr>
<tr>
<td>Tables</td>
<td>22</td>
</tr>
<tr>
<td>Summary</td>
<td>27</td>
</tr>
<tr>
<td>Bibliography</td>
<td>28</td>
</tr>
</tbody>
</table>
THE MECHANISM OF THE PARA-CLAISEN REARRANGEMENT

INTRODUCTION

The mechanism of the Claisen rearrangement to the para position has not been satisfactorily explained or proved, although that postulated for the rearrangement to the ortho position is in good agreement with experimental data.

D. Stanley Tarbell (22, p.497) suggested that the rearrangement to the para position involved a dissociation of the allyl group, either as an ion or a radical, although he mentions that serious objections can be raised to both. Hurd and Pollack (10, p.550) have suggested that rearrangement to the para position might go by two steps: first, a shift of the allyl group to the ortho position with inversion, as described for the ortho rearrangement, followed by another shift to the para position with inversion. Very recently, in view of new data presented, there has been a tendency to accept this mechanism.

In this mechanism, first postulated by Hurd and Pollack (10, p.550), the intermediate formed in the first step would be a dienone, III.
In our studies a rearrangement of a phenyl allyl ether containing allyl groups in both ortho positions was observed. Thus, if the mechanism suggested by Hurd and Pollack (10, p.550) is assumed, the intermediate, III, would have two allyl groups in one ortho position, and the final product would result from one of the allyl groups migrating to the para position. In order to show that the allyl group in the ortho position migrated to the para position, an allyl ether with an $\alpha$-phenylallyl group in the ortho position was rearranged.
HISTORY

Claisen (1, p.3157), in 1912, discovered that allyl ethers of enols and phenols undergo a rearrangement on heating, the products being the isomeric C-allyl compounds. A large amount of data about this change has been accumulated through extensive investigations by Claisen and other workers, this work being stimulated by (a) the usefulness of the Claisen rearrangement in synthetic work, (b) its application as a tool in the study of the bond structures of aromatic compounds, (c) and its intrinsic interest as a molecular rearrangement. D. Stanley Tarbell has compiled and presented this information in Chemical Review (22, pp.495-546) and in "Organic Reactions" (23, pp.1-48).

The generally accepted mechanism of the rearrangement is based essentially on the following observations: (a) the Claisen rearrangement is a first order reaction, (b) in the arylallyl ether series the rearrangement is always accompanied by an inversion of the allyl group moving to the ortho position and by a lack of inversion of the group moving to the para position.

C. D. Hurd and L. Schmerling (9, pp.107-109) showed that the reaction process was intramolecular by heating a mixture of allyl \(\alpha\)-naphthyl ether and cinnamyl phenyl ether and obtaining 1-allyl-2-naphthol and \(o-(\alpha\)-phenylallyl)-phenol, but no cross products. This intramolecularity of the reaction was further verified by A. S. Fomenko,
G. P. Miklukhin, and E. A. Sadovnikova (7, pp.91-92), who found that in the rearrangement of allyl phenyl ether in the presence of 3,5-dideuterophenol, that the product was practically free of deuterium. That the H-atom moves as a proton to the oxygen has been shown by experiments by G. B. Kistiakowsky and R. L. Tichenor (13, pp.2303-2304) with deuterium compounds.

The information obtained by Kincaid and Tarbell (12, p.3086) that the rate of reaction was not appreciably affected by adding 10% of dimethylaniline or 1% of acetic acid to a solution of allyl 5-methylphenyl ether shows that the rearrangement does not go by a mechanism which requires catalysis by acids or bases. This evidence supports the conclusion of Hurd and Schmerling (9, pp.108-109).

Kincaid and Tarbell (12, pp.3085-3087) found that the reaction was strictly first order over a fivefold change of concentration in diphenyl ether solution, and that the initial rate in the pure liquid was the same as the rate in solution. This was verified for the para rearrangement by Schmid and Schmid (19, pp.439).

The conflicting results presented by Mumm and co-workers (14, p.1523; 15, p.100) on the rearrangement of α- and γ-ethylallyl ethers of methyl cresotinate have been eliminated by the work of Rhoads, Raulins and Reynolds (16, pp.2531-2532). As illustrated in Plate 1, these latter workers have found that the reaction of sodio-methyl
\[ \text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{-CH}_2\text{-CH-CH=CH}_2 \]

\[ \text{W} \]

\[ \text{C}_2\text{H}_5 \]
\[ \text{O-CH-CH=CH}_2 \]
\[ \text{CH}_3\text{CO}_2\text{CH}_3 \]

\[ \text{III} \]

\[ \text{O-CH}_2\text{-CH=CH-C}_2\text{H}_5 \]
\[ \text{CH}_3\text{CO}_2\text{CH}_3 \]

\[ \text{IV} \]

\[ \text{CR} \]
\[ \text{OH} \]
\[ \text{CH}_3\text{CO}_2\text{CH}_3 \]

\[ \text{CH-CH=CH}_2 \]
\[ \text{C}_2\text{H}_5 \]

\[ \text{CH}_2\text{-CH=CH-C}_2\text{H}_5 \]

\[ \text{CR} \]

\[ \text{OH} \]
\[ \text{CH}_3\text{CO}_2\text{CH}_3 \]

\[ \text{CH}_2\text{-CH=CH-C}_2\text{H}_5 \]

\[ \text{W} = \text{Williamson Ether Synthesis} \]

\[ \text{CR} = \text{Claisen Rearrangement} \]

PLATE 1
cresotinate, I, with α-ethylallyl chloride, II, in methanol gives rise to a mixture of III and IV as well as a phenolic fraction containing both possible C-allylated phenols. It was also shown that both ethers, III and IV, yielded rearranged compounds in which the allyl group had not inverted in migrating to the para position.

In addition to these works mentioned, Conroy and Firestone (6, pp.2530-2531) have presented some interesting data. In their publication they claim to have isolated some material which appears to be the Diels-Alder addition product resulting from the reaction of maleic anhydride and the postulated intermediate dienone III (see page 2). If this claim can be proved conclusively to be correct, then it can be used for further data in favor of the Hurd and Pollack mechanism.

The three recently published articles by Schmid and Schmid (18, pp.1879-1890; 19, pp.489-500; 20, pp. 687-690) are in agreement with the Hurd and Pollack mechanism. The first and second articles are very similar to the one by Ryan and O'Connor (17, pp.5866-5869). Both groups of authors verify inversion to the ortho position and no inversion to the para position in quantitative experiments with C-14. This series of experiments with C-14 in the allyl group show also that the allyl group is never free at any time in the thermal rearrangement as a free ion or free radical. If the allyl group did become a free ion or
where * denotes C-14 radical, then the radioactivity would be spread between the two end positions by resonance, as is shown by:

\[ \text{CH}_2=\text{CH}-\text{CH}_2 \quad \text{or} \quad \text{CH}_2=\text{CH}-\text{CH}_2^* \]

where * denotes C-14

+ denotes a positive charge

\cdot denotes an unpaired electron

Both groups of authors found to the limit of the experimental error that all the radioactivity was in the predicted positions.

M. S. Kharasch and co-workers (11, p.309) found that ultraviolet radiation of phenyl allyl ether at 20° leads to equal parts of phenol and p-allyl phenol, and they
postulated an allyl free radical as an intermediate. In the third article by Schmid and Schmid (20, pp.687-690) a rearrangement brought about by ultraviolet radiation of an allyl phenyl ether with C-14 in γ-position was reported; and, as predicted, the radioactivity was divided in approximately the same amount in the α- and γ-C-atoms. In the thermal rearrangement to the para position (the para-Claisen rearrangement), there was no activity distribution or inversion.

In agreement with earlier works (21, p.517; 23, p.9), this series of experiments with C-14 indicate that the Claisen rearrangement to the para position does not involve dissociation of the migrating allyl group to a free ion or free radical. In addition, the work presented in this paper, together with the indications published by Conroy and Firestone (6, pp.2530-2531) strongly favor the Hurd and Pollack mechanism.
DISCUSSION

The purpose of this work was to determine whether at any point in the rearrangement the allyl group migrating from the ether oxygen becomes equivalent to an allyl group in an ortho position. This data was obtained by rearranging allylic ethers of 2,6-diallylic phenols. The desired compounds were made by a series of Williamson syntheses, hydrogenations, and Claisen rearrangements, as shown by Plates 2, 3, and 4. In all cases, yields were sacrificed for purity of material.

The proof of structure of the various compounds depends on the following points: (a) in the Williamson ether syntheses, ethers must be obtained pure, free from C-alkylation products, (b) in the Claisen rearrangement to the ortho position, there is inversion of the allyl group, whereas there is no inversion of the allyl group migrating to the para position (6, pp.2530-2531; 18, p.1879; 19, p.489; 20, p.687), (c) although aldehyde, carboxyl and halogen groups have been displaced (22, p.495; 23, p.1), there has been no case reported in which a saturated alkyl group has been displaced in a Claisen rearrangement.

The conditions used in preparing the ethers shown in Plates 2, 3, and 4 were those of Claisen (2, p.275). The ethers were dissolved in petroleum ether and extracted with Claisen's alkali. This was done to remove all phenolic
material, starting material or C-alkylation product, from the neutral ether. It was imperative that the C-alkylation product be completely removed. It has been shown by Claisen (3, p.210) that the C-alkylation product of phenol and cinnamyl bromide was 2-cinnamylphenol; whereas, the rearranged product from cinnamyl phenyl ether was 2-(α-phenylallyl)-phenol.

Plate 2 illustrates the first parallel series of rearrangements observed. The reason for the parallel series of compounds with allyl and propyl groups is that the allylic groups will migrate but the saturated groups will not. Claisen (1, p.3157; 5, p.69) showed that methyl C-propylacetoacetate and n-propyl phenyl ether are stable to heat. If both of the ortho-positions and the para position of an allyl phenyl ether are blocked by saturated groups, a complex decomposition occurs on heating, but there is no displacement or migration of the allyl group to the meta position (22, p.496).

The starting compound of the series, 2,6-diallylphenol (compound 6) was made according to the method given by Claisen (5, p.69). The melting point of its phenylurethan derivative and the physical properties of compound 6 agreed with those reported by Claisen (5, p.69). The cinnamyl 2,6-diallylphenyl ether (compound 6) was prepared and rearranged to 2,6-diallyl-4-(γ-phenylallyl)-phenol (compound 7).
CA = C-Alkylation
CR = Claisen Rearrangement
H = Hydrogenation
W = Williamson Synthesis

A = -CH₂-CH=CH₂
A' = -CH₂-CH=CH-

P = -CH₂-CH₂-CH₃
P' = -CH₂-CH₂-CH₂-
In the attempt to recover 2,6-diallyphenol, very little of the starting material was recovered, but phenolic material with physical properties similar to compound 7 was obtained. The phenylurethan derivatives had the same melting points, and the mixed melting points showed no depression. From these data, it was concluded that the recovered phenolic material was the C-alkylation product. This is in accord with previous data since there is no inversion of the allyl group migrating to the para position, and thus the product from para-Claisen rearrangement and the C-alkylation in the para position should be identical. The reaction of C-alkylation was first reported by Claisen (4, p.119; 5, p.70).

The starting material, 2,6-diallyphenol (compound 6), was hydrogenated to 2,6-dipropylphenol (compound 9). The phenylurethan of this compound had the same melting point as that reported by Claisen (5, p.71). In the hydrogenations of the allylic groups the amount of hydrogen taken up was used as verification of the number of allylic double bonds present in the molecule.

Cinnamyl 2,6-dipropylphenyl ether (compound 10), prepared by a Williamson ether synthesis with cinnamyl bromide and 2,6-dipropylphenol (compound 10), was rearranged to 2,6-dipropyl-4-(γ-phenylallyl)-phenol (compound 11), which was hydrogenated to 2,6-dipropyl-4-(γ-phenylpropyl)-phenol (compound 8). The phenylurethan of compound 8 obtained in
this manner was identical with those obtained from the hydrogenation of (a) the rearranged product from cinnamyl 2,6-diallylphenyl ether and (b) the C-alkylation product from 2,6-diallylphenol and cinnamyl bromide. The mixed melting points were not depressed. Thus it was concluded that the three methods yielded the same product. The C-alkylation path and the hydrogenated path indicate the structure of compound 8 to be 2,6-dipropyl-4-(γ-phenyl-propyl)-phenol.

From this series of rearrangements, it is concluded that the unsubstituted allyl group in the ortho position is not displaced by the cinnamyl group migrating to the para position.

Plate 3 illustrates the two paths of synthesis used to prepare 2-allyl-6-(α-phenylallyl)-phenol.

The first method utilized 2-allylphenol (compound 3), a compound reported by Claisen (5, p.69). This compound 3 was converted to the cinnamyl 2-allylphenyl ether (compound 12), which was in turn rearranged to 2-allyl-6-(α-phenyl-allyl)-phenol (compound 13).

The identity of this compound was checked by starting with cinnamyl phenyl ether (compound 2-a), which was rearranged to 2-(α-phenylallyl)-phenol (compound 3-a). The melting point of the phenylurethan of compound 3-a agreed with that reported by Claisen (3, p.210) and Hurd and Schmerling (9, p.107). Allyl 2-(α-phenylallyl)-phenyl
CR = Claisen Rearrangement
W = Williamson Synthesis

A = \(-\text{CH}_2-\text{CH}=-\text{CH}_2\)
A' = \(-\text{CH}_2-\text{CH}=-\text{CH}-\text{C}_6\text{H}_5\)
A'' = \(-\text{CH}-\text{CH}=-\text{CH}_2\)
ether (compound 12-a) was formed by a Williamson ether synthesis, and the compound 12-a was rearranged to 2-allyl-6-(α-phenylallyl)-phenol. The melting points of the phenylurethans of the material made by the two methods were identical, and the mixed melting point showed no depression. Thus it was concluded that 2-allyl-6-(α-phenylallyl)-phenol was the correct structure for compound 13.

Plate 4 illustrates the most important of the series of rearrangements. Compound 13, 2-allyl-6-(α-phenylallyl)-phenol, was allowed to react with allyl bromide, and the allyl 2-allyl-6-(α-phenylallyl)-phenyl ether (compound 15-a) obtained was insoluble in Claisen's alkali. Compound 15-a was rearranged (compounds 7 and 16-a), and the reaction mixture was hydrogenated (compounds 8 and 17). Fractional crystallization of the phenylurethan of the hydrogenated mixture (compounds 8 and 17) yielded two sharp melting fractions, with melting points of 108-109° and 136.5-137.5°.

Compound 13 was hydrogenated to 2-propyl-6-(α-phenylpropyl)-phenol (compound 14). This was done to obtain a pure sample of compound 17. It was assumed that the α-phenylpropyl group in the ortho position would not migrate under Claisen rearrangement conditions (see page 10). The allyl ether of compound 14 (compound 15) was rearranged to 2-propyl-4-allyl-6-(α-phenylpropyl)-phenol (compound 16), which was hydrogenated to form 2,4-dipropyl-6-
CR = Claisen Rearrangement
H = Hydrogenation
W = Williamson Synthesis

A = -CH₂-CH=CH₂
A' = -CH₂-CH=CH-[C₆H₅]
A'' = -CH-CH=CH₂
P = -CH₂-CH₂-CH₃
P' = -CH₂-CH₂-CH₂-[C₆H₅]
P'' = -CH-CH₂-CH₃

PLATE 4
(α-phenylpropyl)-phenol (compound 17). The phenylurethan of compound 17 melted at 136-137°C. The melting point of a mixture of this phenylurethan and the higher melting phenylurethan from the fractional crystallization showed no depression.

The phenylurethan of 2,6-dipropyl-4-(α-phenylpropyl)-phenol (compound 8) melted at 108-109°C (see Plate 2 for unequivocal synthesis). The mixed melting point of this phenylurethan and the lower melting phenylurethan from the fractional crystallization showed no depression.

Thus the observations of the series of reactions illustrated by Plate 4 suggest (a) that an allylic group in the ortho position can migrate to the para position and (b) that not only does the allyl group migrating from the oxygen atom to the ortho position undergo inversion, but also that it goes from the ortho position to the para position with inversion. Both suggestions are in agreement with the requirements of the Hurd-Pollack mechanism.

The preferential migration of the substituted allyl group over the non-substituted group is in agreement with previous data. Tarbell and Wilson (24, p.607) found that O-allyl-3,5-dichlorosalicylic acid rearranged more slowly than the crotyl compound, and that allyl 2,4-dichlorophenyl ether also rearranged more slowly than the crotyl 2,4-dichlorophenyl ether. Also Rhoads, Raulins and Reynolds (16, pp.2531-2532) found that at 120°C, α-ethylallyl methyl
cresotinate ether rearranged; whereas, under the same conditions, the \( \gamma' \)-ethylallyl methyl cresotinate ether did not rearrange.
EXPERIMENTAL

The experimental conditions and procedures of preparation of allyl ethers and of their rearrangements are well discussed by Tarbell in his article in "Organic Reactions" (23, pp.22-28). Therefore, the experimental data were summarized and presented in Table 1, 2, and 3. Only representative reactions of Williamson ether synthesis, hydrogenations and Claisen rearrangement will be discussed. The phenylurethans were made by the procedure given by Shrinor and Fuson (21, p.21).

Preparation of allyl 2-(α-phenylallyl)-phenol ether (compound 12-a)

A solution of 24 g. (0.115 moles) of 2-(α-phenylallyl)-phenol in 50 ml. of methanol was added to a solution of sodium methoxide prepared by adding 2.7 g. (0.115 moles) of sodium to 100 ml. of methanol. Then 13.9 g. (0.115 moles) of allyl bromide was added, and the reaction mixture was stirred for two days. The ethers were formed at room temperatures in order to eliminate insofar as possible any rearrangement after formation of the ether. At the end of this time, the reaction mixture was diluted with 100 ml. of water and extracted with one 50 ml. portion, then with three 25 ml. portions of low boiling petroleum ether. The petroleum ether solution was extracted with one 50 ml. portion, followed by four 25 ml. portions of Claisen's alkali to remove any phenolic material.
The petroleum ether solution was washed with 25 ml. portions of water, dilute sulphuric acid, and water. The wash with water was repeated until all traces of acid were removed. The petroleum ether solution was dried over 1-2 g. of anhydrous magnesium sulfate, the dried solution filtered and the petroleum ether distilled under diminished pressure. The allyl 2-(α-phenylallyl)-phenyl ether was isolated as a white, crystalline solid which was recrystallized from methanol. Yield 13.6 g. (47%). M. P. 40-41°.

Preparation of 2,6-dipropyl-4(γ-phenylpropyl)-phenol (compound 8)

A solution of 8.32 g. (0.029 moles) of 2,6-diallyl-4-(γ-phenylallyl)-phenol in 100 ml. of 95% ethanol was placed in the hydrogenator bottle with 0.5 g. of 10% palladium on charcoal. The material absorbed the theoretical amount of hydrogen. The hydrogenated mixture was filtered to remove the catalyst, and the ethanol was distilled under reduced pressure. The product was distilled under reduced pressure, B. P. 170-180° (0.5-1.0 mm.). Yield 7.90 g. (95%).

Preparation of 2-allyl-6-(α-phenylallyl)-phenol (compound 13)

A solution of 12.0 g. (0.048 moles) of allyl 2-(α-phenylallyl)-phenol in 50 ml. of dimethylaniline was heated on a Wood's metal bath at 200-210° for two hours.
The reaction mixture was diluted with 100 ml. of petroleum ether, and the dimethylaniline extracted with 150 ml. of dilute sulphuric acid. The acid extracts were washed with three 25 ml. portions of petroleum ether. The combined petroleum ether solution was extracted with a 50 ml. portion followed with four 25 ml. portions of Claisen's alkali. The phenolic fraction was isolated by carefully acidifying the alkaline solution with concentrated HCl, while cooling the reaction vessel in an ice bath. The acid mixture was extracted with a 100 ml. portion, then by four 25 ml. portions of petroleum ether. This petroleum ether solution was extracted with water until no more acid could be detected. The petroleum ether solution, after being dried with anhydrous magnesium sulphate, was distilled under reduced pressure. Yield 7.41 g. (62%). B. P. 155-158° (0.5-1.0 mm.).
<table>
<thead>
<tr>
<th>Product (compounds on Plate 2)</th>
<th>Yield (percent)</th>
<th>Boiling Point</th>
<th>$n^o$</th>
<th>Melting Point of Phenylurethan</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. 2,6-diallylphenol</td>
<td>62-73</td>
<td>106-107°C(5-6mm)</td>
<td>1.5376</td>
<td></td>
<td>(5, pp. 91-92)</td>
</tr>
<tr>
<td>6. cinnamyl 2,6-diallylphenyl ether rearranged on distillation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. 2,6-diallyl-4-(γ-phenylallyl)-phenol, from rearrangement</td>
<td>31</td>
<td>200-205°C(1-2mm)</td>
<td>1.5920</td>
<td>136-137°C</td>
<td></td>
</tr>
<tr>
<td>7. from C-alkylation</td>
<td>25</td>
<td>200-205°C(1-2mm)</td>
<td>1.5920</td>
<td>136-137°C</td>
<td></td>
</tr>
<tr>
<td>8. 2,6-dipropyl-4-(γ-phenylpropyl)-phenol</td>
<td>90</td>
<td>170-180°C(0.5-1mm)</td>
<td>1.5448</td>
<td>108-109°C</td>
<td></td>
</tr>
<tr>
<td>9. 2,6-dipropylphenol</td>
<td>90</td>
<td>130-140°C(10-11mm)</td>
<td>1.5448</td>
<td>130-131°C</td>
<td>(5, p. 93)</td>
</tr>
<tr>
<td>10. cinnamyl 2,6-dipropylphenyl ether rearranged on distillation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. 2,6-dipropyl-4-(γ-phenylallyl)-phenol</td>
<td>80</td>
<td>170-180°C(0.5-1mm)</td>
<td>1.5448</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1
<table>
<thead>
<tr>
<th>Product (compounds on Plate 3)</th>
<th>Yield (percent)</th>
<th>Boiling Point</th>
<th>n\textsuperscript{20}D Melting Point of Phenylurethan</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-a cinnamyl phenyl ether</td>
<td>71</td>
<td>(65-67°MP)</td>
<td></td>
<td>(2,p.279)</td>
</tr>
<tr>
<td>3-a 2-((\alpha)-phenylallyl)-phenol</td>
<td>67</td>
<td>145-155(^\circ)(0.5-1mm)</td>
<td>95.5-96.5(^\circ)</td>
<td>(2,p.280)</td>
</tr>
<tr>
<td>12 cinnamyl 2-allylphenyl ether</td>
<td>29</td>
<td>164-166(^\circ)(0.5-1mm)</td>
<td>1.5895</td>
<td></td>
</tr>
<tr>
<td>12-a allyl 2-((\alpha)-phenylallyl)-phenyl ether</td>
<td>47</td>
<td>(40-41°MP)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 2-allyl-6-((\alpha)-phenylallyl)-phenol</td>
<td>62</td>
<td>155-158(^\circ)(0.5-1mm)</td>
<td>1.5843  101-102(^\circ)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
<table>
<thead>
<tr>
<th>Product (compounds on Plate 4)</th>
<th>Yield (percent)</th>
<th>Boiling Point</th>
<th>$n_D^{20}$</th>
<th>Melting Point of Phenylurethan</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 2-propyl-6-(α-phenylallyl)-phenol</td>
<td>93</td>
<td>152-154°(0.5-1mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 allyl-2-propyl-6-(α-propyl)-phenyl ether</td>
<td>rearranged with distillation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 2-propyl-4-allyl-6-(α-phenylpropyl)-phenol</td>
<td>63</td>
<td>151-154°(0.5-1mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16-a 2,4-diallyl-6-(α-phenyl-allyl)-phenol</td>
<td>not isolated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 2,4-dipropyl-6-(α-phenyl-allyl)-phenol</td>
<td>81</td>
<td>145-150°(0.5-1mm)</td>
<td>136.5-137.5°</td>
<td></td>
</tr>
</tbody>
</table>

Table 3
### Analytical Data

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C (percent)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2,6-diallyl-4-(γ-phenylallyl)-phenol</td>
<td>86.85</td>
<td>86.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>7.64</td>
</tr>
<tr>
<td>8</td>
<td>2,6-dipropyl-4-(γ-phenylpropyl)-phenyl ether</td>
<td>85.09</td>
<td>85.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>9.52</td>
</tr>
<tr>
<td>12-a</td>
<td>allyl 2-(α-phenylallyl)-phenyl ether</td>
<td>86.37</td>
<td>86.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>7.25</td>
</tr>
<tr>
<td>13</td>
<td>2-allyl-6-(α-phenylallyl)-phenol</td>
<td>86.37</td>
<td>86.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>7.25</td>
</tr>
<tr>
<td>16-a</td>
<td>2,4-diallyl-6-(α-phenylallyl)-phenol</td>
<td>86.85</td>
<td>86.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>7.64</td>
</tr>
<tr>
<td>7</td>
<td>2,6-diallyl-4-(γ-phenylallyl)-phenol</td>
<td>86.85</td>
<td>86.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>7.64</td>
</tr>
</tbody>
</table>

Table 4
Analytical Data

<table>
<thead>
<tr>
<th>Phenylurethans of</th>
<th>Calculated C (percent)</th>
<th>Found C (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-allyl-6-(α-phenylallyl)-phenol</td>
<td>81.27  6.27</td>
<td>80.43  6.14</td>
</tr>
<tr>
<td>2,6-diallyl-4-(γ-phenylallyl)-phenol</td>
<td>82.12  6.65</td>
<td>81.87  6.59</td>
</tr>
<tr>
<td>2,6-dipropyl-4-(γ-phenylpropyl)-phenol</td>
<td>80.92  8.00</td>
<td>80.89  7.95</td>
</tr>
<tr>
<td>2,4-dipropyl-6-(α-phenylpropyl)-phenol</td>
<td>80.92  8.00</td>
<td>80.76  7.90</td>
</tr>
</tbody>
</table>

Table 5
SUMMARY

The Claisen rearrangement to the para position was studied to determine if at any point in the rearrangement the allyl group migrating from the ether oxygen becomes equivalent to an allyl group in an ortho position as suggested by the Hurd-Pollack mechanism. The results of the rearrangement of cinnamyl 2,6-diallylphenyl ether suggested that there is no observable migration of the unsubstituted allyl group from the ortho position. The rearrangement of allyl 2-allyl-6-\(\alpha\)-phenylallyl-phenyl ether gave results which suggest that (a) the allyl group migrating from the ether oxygen does become equivalent to an allyl group in an ortho position, (b) an allylic group in the ortho position can migrate to the para position, (c) there is inversion in the migration from the ortho to the para position, and (d) the \(\alpha\)-substituted allylic group migrates preferentially over the non-substituted allylic group.
BIBLIOGRAPHY


