cording to the procedure described earlier.[4] The properties were in accord with those reported.

Allyl 2,6-Diethylphenyl Ether.—A sample of 2,6-diethylphenol, m.p. 35–36°, was prepared essentially by the method of von Auwers.[16] This was treated with allyl bromide in *t*-butyl alcohol according to the procedure of Rhoads, Raulins, and Reynolds.[17] The ether was separated from unreacted phenol by extraction with Claisen alkali and isolated by distillation, b.p. 40° (0.03 mm.), $n^{22.5}\text{D}$ 1.4990.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.92; H, 9.76.

Allyl 2,6-Diisopropylphenyl Ether.—A sample of 2,6-diisopropylphenol[18] was converted to its allyl ether as described for allyl 2,6-diethylphenyl ether above. The clear liquid was distilled, b.p. 54–57° (0.05 mm.), $n^{23}\text{D}$ 1.4972, $\bar{\nu}$ 1640 and 920 cm.$^{-1}$, 73%.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.61; H, 10.16. Found: C, 82.35; H, 10.02.

Kinetics.—All rates were measured by the ampoule method using sealed Pyrex tubes suspended in a bath maintained at the desired temperature ±0.5°. Allyl *o*-cresyl ether was run in decalin solution[19] and the analysis was carried out by gas chromatography using a 20% Reoplex 400 on Chromosorb column. Allyl 2-ethylphenyl ether, allyl 2-isopropylphenyl ether, and allyl 2,6-diisopropylphenyl ether were rearranged neat and the reaction was followed by the change in refractive index. A Zeiss Abbe-type refractometer was used at 20.0° and the relation between refractive index and composition was shown to be linear in each case. Allyl 2,6-diethylphenyl ether and allyl 2,6-diisopropylphenyl ether were rearranged neat; the reaction was followed by n.m.r. Allyl 2,6-diethylphenyl ether has an n.m.r. band at τ 3.10 which represents the aromatic protons on carbons 3, 4, and 5, while 2,6-diethyl-4-allylphenol exhibits a band due to the aromatic protons at C-3 and C-5 at τ 3.31. The relevant bands for the diisopropyl case lie at τ 2.90 and 3.12, respectively. The relative areas under the peaks were corrected for the protons involved and the data were used directly to follow the progress of the rearrangement.[20]

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[16] K. von Auwers and W. Mauss, *Ann.*, **460**, 224 (1928); K. von Auwers and G. Wittig, *Ber.*, **57**, 1275 (1924).

[17] S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Am. Chem. Soc.*, **76**, 3456 (1954).

[18] We are indebted to the Ethyl Corp. for a generous sample of 2,6-diisopropylphenol and are pleased to acknowledge their courteous aid to our research.

[19] We are indebted to Dr. Richard Anderson who carried out this determination, which was made in 1961 in connection with another problem.

[20] The authors are indebted to the National Science Foundation for financial assistance toward the purchase of the Varian A-60 n.m.r. spectrometer.

Claisen Rearrangement of Allyl 2-Alkylphenyl Ethers[1]

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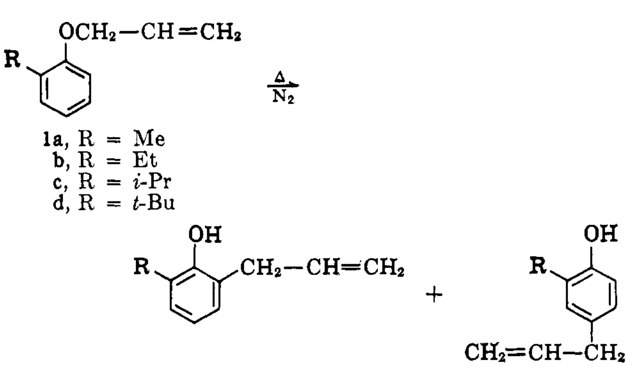
A series of allyl 2-alkylphenyl ethers with the alkyl group varied from methyl to *t*-butyl has been prepared and rearranged. The relative amounts of 6-allyl-2-alkylphenol and 4-allyl-2-alkylphenol were determined in each case by gas chromatography. For all but the *t*-butyl case the nature of the products was verified by synthesis. All rearrangements gave predominantly the 6-allyl-2-alkylphenol accompanied by smaller amounts (*ca.* 10%) of the 4-allyl-2-alkylphenol.

For many years the idea that the migratory allyl group in the Claisen rearrangement would enter an *ortho* position exclusively when at least one was available was an important rule.[2] Use of the rule has been made frequently in synthetic work,[3] but recent studies on the mechanism of the Claisen rearrangement have shown that the idea is generally untenable.[4] In fact there exists a considerable collection of examples which attests to the common formation of both *ortho* and *para* products in the rearrangement of *ortho*-substituted phenyl allyl ethers.[5] Aside from the apparently general inference that the ratio of *ortho* to *para* product is distinctly lower when the *ortho* substituent is hydroxyl or amino than when it is alkyl, no generalizations concerning the factors which influence the partitioning of the allyl group between the *ortho* and *para* positions have been developed. The work reported here will show that the size of the *ortho* substituent has a surprisingly small influence on that partitioning.

The series of allyl 2-alkylphenyl ethers **1a–d** was prepared from the 2-alkylphenols by etherification in *t*-butyl alcohol.[6] These were rearranged neat under nitrogen and the product was analyzed by gas chromatography. The results are shown in Table I. As expected, the separation between the peaks due to *ortho* and *para* product decreased with increasing size of the alkyl group. However, in every case except *t*-butyl the



1a, R = Me
b, R = Et
c, R = *i*-Pr
d, R = *t*-Bu

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[1] A preliminary account of this work was presented at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960; *cf.* Abstracts, p. 85P. Published with the approval of the Monographs Publication Committee, Oregon State University, as Research Paper No. 470, School of Science, Department of Chemistry. The authors are pleased to acknowledge partial financial support from the National Science Foundation under Grant G 7432, the Sigma Xi-RESA Research Fund, and the General Research Grants of Oregon State University. Paper no. 6 on the Claisen Rearrangement; paper no. 5: *J. Org. Chem.*, **27**, 1109 (1962).

[2] D. S. Tarbell, *Org. Reactions*, 2, 8 (1944).

[3] Note, for example, the use of Claisen rearrangements of *ortho*-substituted phenyl ethers to prepare 2,6-dialkylphenols as model compounds for analytical procedures: (a) E. N. Marvell, A. V. Logan, L. Friedman, and R. Ledeen, *J. Am. Chem. Soc.*, **76**, 1922 (1954); (b) D. Y. Curtin and M. W. Johnson, Jr., *ibid.*, **78**, 2611 (1956); (c) M. J. S. Dewar and N. A. Putnam, *J. Chem. Soc.*, 4080 (1959).

[4] For an excellent review, see S. J. Rhoads, "Molecular Rearrangements," part I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 655.

[5] References to these are listed by P. Fahrni, W. Haegele, K. Schmid, and H. Schmid [*Helv. Chim. Acta*, **38**, 783 (1955)].

[6] S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Am. Chem. Soc.*, **76**, 3456 (1954).

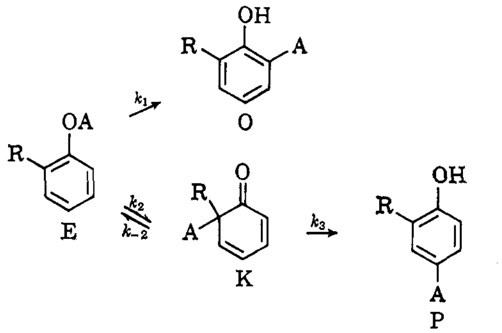
Table I

Products from the Rearrangement of *o*-Alkylphenyl Allyl Ethers

R	% *ortho*	% *para*	*ortho* : *para*
Me	85	15	5.6
Et	90	10	9
i-Pr	90	9	10
t-Bu	91	6	15

peaks were well separated and the analyses are reasonably accurate. For the *t*-butyl case the peaks were not completely separated and the value given represents a minimum figure.

Kinetic analysis of the formation of the *ortho* and *para* products shows that $d(P)/dt = (k_2k_3/k_{-2} + k_3)(E)$ and $d(O)/dt, = k_1(E)$. It is apparent that the ratio of *ortho* to *para* product should remain constant throughout the rearrangement; this was verified for the ether **1a**. The ratio of *ortho* to *para* product is dependent on two factors: the relative rates of rearrangement to the two *ortho* positions, k_1 and k_2, and the partitioning of the dienone between return to the ether and migration to the *para* position. The partitioning ratio k_3/k_{-2} has been ascertained for two cases.[7] It appears to be nearly independent of temperature,[7a] and proved quite insensitive to the nature of the alkyl group in the *ortho* position. The rate of the Claisen rearrangement generally appears to be quite insensitive to the nature of the alkyl group when this is in a *para* position.[8] Thus the change from a methyl to an ethyl group alters the rate by only 4%. Based on these data it seems quite reasonable to assume that both k_3/k_{-2} and the various k_1 values will be nearly independent of the nature of the alkyl group present in the *ortho* position.[9] If this is indeed a valid assumption, then the small change noted in the *ortho* to *para* ratio reflects the rather slight effect of bulk on the k_2 values.



A = allyl

We would not have predicted this result on the basis of our present knowledge of the transition-state geometry.[10] This is probably best represented by a chair-like six-membered ring (Figure 1). In the present case the alkyl group must take up an axial-like position. Clearly the results where R = Me, Et, and *i*-Pr are readily rationalized in terms of this transition state. If the replacement of a hydrogen by a methyl group had no effect, the *ortho* to *para* ratio should be unity, and the value 5.6 therefore reflects the influence of the methyl group. As Allinger and Hu[11] have pointed out, the steric effect of methyl, ethyl, and isopropyl groups should be very similar in an axial position since the major effect of the change should be to freeze out certain of the rotational states available to the methyl group. Therefore, the largest effect was made with the introduction of the methyl group and further alteration to the isopropyl substituent caused little further change.

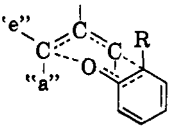


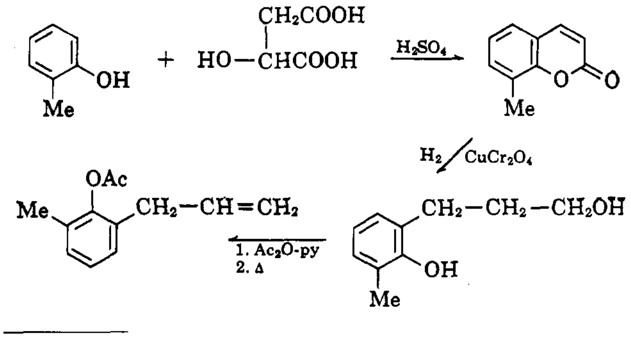
Figure 1.—Transition state geometry for the Claisen rearrangement.

The same reasoning does not apply to the results with an *o*-*t*-butyl group. These results seem to point to a considerable flexibility in the transition state. In particular it may be suggested that the two planes generated by the three carbons of the allyl group and by the benzene ring and its attached oxygen atom can deviate from their expected parallel position without a serious energy gain.

Up to this point we have tacitly assumed that the products obtained when an allyl 2-alkylphenyl ether is heated are 6-allyl-2-alkylphenol and 4-allyl-2-alkylphenol, and that these are the major and minor products, respectively. A direct experimental proof that this is indeed a proper assumption was made for allyl *o*-cresyl ether. The two expected products were synthesized by alternate routes as is illustrated in Schemes I and II. These products were used as internal standards to ascertain the identity of the rearrangement products *via* gas chromatography. It is interesting that a careful fractionation of the rearrangement product using an efficient distillation column effected no separation of the two isomers.

The tedious synthesis of each of the two isomeric rearrangement products for the cases **1b** and **1c** was avoided

Scheme I



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[7] (a) D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957); (b) W. Haegele and H. Schmid, *Helv. Chim. Acta*, **41**, 658 (1958).

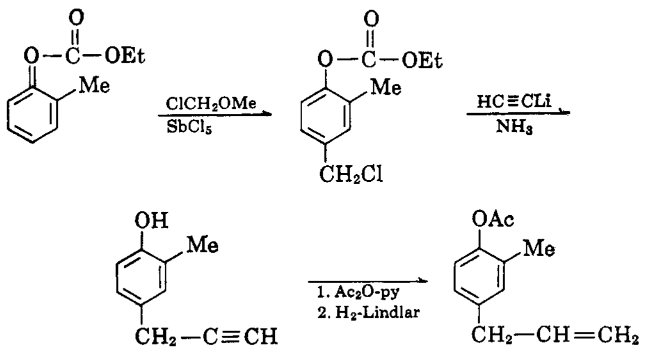
[8] (a) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958); (b) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. K. Fife, *ibid.*, **80**, 3271 (1958).

[9] This is probably not strictly true but a more careful analysis shows that the k_1 values will probably increase as the size of the R group increases owing to increasing strain in the ground state. Simultaneously the same steric factors will tend to increase the energies of the activated complex for k_2 and k_{-2} as well as that of the dienone intermediate. In our opinion this effect will be larger in the ground states (phenol and dienone) than in the activated complexes. Thus as R increases in size k_{-2}/k_3 will decrease. Since $o/p = k_1/k_2(1 + k_{-2}/k_3)^{-1}$, as R increases in size both k_1 and the factor $(1 + k_{-2}/k_3)^{-1}$ will increase and these effects tend to cancel. Thus we feel that the major factor influencing the change in *ortho* : *para* ratio is k_2. This more complex analysis leads to the same conclusion as the simpler one given in the discussion.

[10] E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, **25**, 676 (1960); A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 4681 (1960); W. N. White and B. E. Norcross, *ibid.*, **83**, 1968, 3265 (1961).

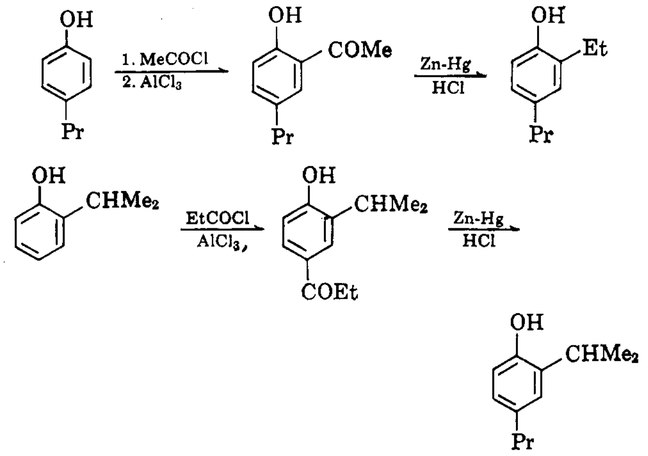
[11] N. L. Allinger and S-E. Hu, *J. Org. Chem.*, **27**, 3417 (1962).

SCHEME II



by reducing the double bond in the rearranged material and comparing the *para* products with authentic samples obtained synthetically as illustrated in Scheme III. The products from **1d** were assigned purely by analogy with the other examples.

SCHEME III



One problem which plagued the analytical scheme deserves a brief comment. Direct analysis of the reaction product always gave a higher percentage of *para* product than analysis of a purified product. It was shown that this was due to preferential oxidation of the *para* product during extraction with Claisen alkali. All of the rearrangement products are sensitive to oxidation and, if the analysis was carried out on products stored in stoppered containers for a few days, the *para* product was found to have been preferentially oxidized and several new products appeared. Fresh samples of all the rearranged products were shown *via* thin layer chromatography to contain only two components. In each case the R_f value for the major product was larger than that for the minor one.

Experimental

Allyl 2-Alkylphenyl Ethers.—Allyl *o*-cresyl ether was prepared according to Claisen and Eisleb.[12] The other ethers were made by treating equimolar quantities of potassium *t*-butoxide and the proper phenol with allyl bromide in refluxing *t*-butyl alcohol.[6] The alcohol was removed by distillation; the ether was extracted thoroughly with Claisens alkali, dried over magnesium sulfate, and distilled.

Allyl 2-Ethylphenyl Ether.—This ether, b.p. 52–54° (0.1 mm.), $n^{21}\mathrm{D}$ 1.5139, was obtained in 67% yield.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.36; H, 8.94.

Allyl 2-Isopropylphenyl Ether.—A sample of this ether was prepared from *o*-isopropylphenol[13] in 54% yield, b.p. 63–64° (0.4 mm.), $n^{27}\mathrm{D}$ 1.5050.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.04.

Allyl 2-*t*-Butylphenyl Ether.—This ether was obtained in 40% yield from *o*-*t*-butylphenol[13] as a clear liquid, b.p. 66–68° (0.1 mm.), $n^{24}\mathrm{D}$ 1.5080. Six analyses were carried out with the values scattered randomly about the theoretical, with none being acceptable. Two of these which were carried out on the same sample are given below by way of illustration.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.95, 81.17; H, 9.81, 9.38.

Rearrangement.—The allyl 2-alkylphenyl ethers were rearranged in two ways. Neat samples were heated at 195–200° under nitrogen until the refractive index remained constant. The crude material was distilled nearly to dryness and the distillate was analyzed by gas chromatography. The distillate was also taken up in Claisen alkali, the solution was extracted with petroleum ether, and the phenolic product was recovered by acidification of the alkaline solution. Analysis was repeated on the purified material. Alternatively, rearrangement was carried out in N,N-dimethylaniline solution under nitrogen. The cool solution was diluted with petroleum ether and extracted exhaustively with dilute hydrochloric acid. The wash solution was extracted several times with petroleum ether. The combined petroleum ether solutions were dried over anhydrous sodium sulfate and the solvent was removed. The product was distilled and analyzed by gas chromatography and by thin layer chromatography using silica gel G and a 5:4:1 mixture of hexane–chloroform–dimethylamine as eluent.

Product from Allyl *o*-Cresyl Ether.—The rearrangement product was treated with acetic anhydride and pyridine and the acetate was isolated by distillation, b.p. 116–118° (9 mm.), $n^{20}\mathrm{D}$ 1.5076, in 93% yield. The acetate was fractionally distilled using a Podbielniak "Mini-Cal" column rated at 175 theoretical plates. Thirteen fractions, all boiling at 103° (6 mm.), $n^{20}\mathrm{D}$ 1.5074–1.5078, were obtained. The infrared spectra were all indistinguishable. Gas chromatographic analysis showed two peaks with apparent retention volumes of 166 and 214 ml. at 212°. A synthetic sample of 2-methyl-6-allylphenyl acetate had an apparent retention volume of 163 ml. and 2-methyl-4-allylphenyl acetate, of 215 ml.

Product from Allyl 2-Ethylphenyl Ether.—The rearrangement product distilled at 60–66° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5308. It gave rise to two peaks on the gas chromatograph with apparent retention volumes of 225 and 420 ml. at 206°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.87; H, 8.96.

Product from Allyl 2-Isopropylphenyl Ether.—The rearranged material boiled at 60–65° (0.2 mm.), $n^{23}\mathrm{D}$ 1.5230. Two peaks, apparent retention volumes 200 and 360 ml., were observed at 206° on gas chromatographic analysis.

Anal. Calcd. for $C_{12}N_{16}O$: C, 81.77; H, 9.15. Found: C, 81.72; H, 9.42.

Product from Allyl 2-*t*-Butylphenyl Ether.—The rearranged product, b.p. 80–88° (0.3 mm.), $n^{26}\mathrm{D}$ 1.5186, gave two partially overlapping peaks with apparent retention volumes of 160 and 190 ml. at 222°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.04; H, 9.55.

Gas Chromatographic Analysis.—All analyses were performed on a Perkin-Elmer 154C vapor fractometer using helium as a carrier gas. The column contained 20% Reoplex 400[14] on Celite 545 which was used at the temperature specified under the various compounds. Quantitative analyses were determined from the relative areas under the peaks, and most peak assignments were made on the basis of internal comparisons with synthetic materials as described in the actual experiments.

8-Methylcoumarin.—*o*-Cresol (456 g., 4 moles) was warmed with 745 g. of concentrated sulfuric acid for 20 min. Then 565 g. (4.25 moles) of malic acid was added over a 2-hr. period with the

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[12] L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

[13] We are pleased to acknowledge our indebtedness to the Ethyl Corp. for their kindness in supplying both *o*-isopropyl and *o*-*t*-butylphenols for this work.

[14] We are indebted to the Geigy Co. for a generous sample of Reoplex 400.

temperature maintained at 130–140°. The product was isolated by steam distillation, taken up in chloroform, and washed with 5% sodium hydroxide and water. After recrystalliation from ethanol, the 8-methylcoumarin melted at 109.6–109.9° (lit.[15] m.p. 109–110°). A yield of 36 g. (5.6%) was obtained.

2-(3-Hydroxypropyl)-6-methylphenol.—A solution containing 36 g. (0.225 mole) of 8-methylcoumarin in purified dioxane was hydrogenated at 2400 p.s.i. and 250° over 5.8 g. of copper chromium oxide. The product was recrystallized from benzene and 27 g. (72%) of white needles, m.p. 61.4–61.8°, were obtained.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; OH, 20.5. Found: C, 72.20; H, 8.34; OH, 20.6.

2-Allyl-6-methylphenyl Acetate.—The above alcohol was treated with pyridine and excess acetic anhydride giving a diacetate, b.p. 111 (0.25 mm.), n^{20}D 1.4952, in 95% yield. The diacetate was pyrolyzed by passage through a Vycor tube heated at 490–500° using nitrogen as a carrier gas. A 15% conversion per pass was obtained and recycling gave an eventual 74% yield. The liquid product was subjected to fractional distillation on a Podbielniak column giving a colorless oil, b.p. 74–77° (2.3–2.5 mm.), n^{20}D 1.5078.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.81; H, 7.48.

Ethyl 2-Methyl-4-chloromethylphenyl Carbonate.—Ethyl *o*-cresyl carbonate (0.5 mole), b.p. 76° (1.7 mm.), n^{25}D 1.4861, was mixed with 1 mole equiv. of chloromethyl ether in 500 ml. of dry benzene. The solution was held at 0–5° while 50.0 g. of anhydrous antimony pentachloride was added over a 1.5-hr. period. The reaction mixture was stirred for 3 hr. at 0° and then poured onto ice. The organic layer was separated, washed with water until free of antimony, and dried over anhydrous magnesium sulfate. The product was distilled through a small Fenske column, b.p. 103–104° (0.3 mm.), n^{25}D 1.5112, m.p. 34.2–36.0°, yield 30–40%.

Anal. Calcd. for $C_{11}H_{13}ClO_3$: C, 57.77; H, 5.73. Found: C, 57.81; H, 5.67.

2-Methyl-4-propargylphenol.—A solution of lithium acetylide in liquid ammonia was prepared from 6.25 g. (0.9 mole) of lithium. To this was added 34.3 g. (0.15 mole) of ethyl 2-methyl-4-chloromethylphenyl carbonate. The solution was stirred overnight, an excess of ammonium chloride was added, and the ammonia was allowed to evaporate. The product was taken up in chloroform, the solution was extracted with 5% sodium hydroxide, and the product was recovered by chloroform extraction after acidification of the basic solution. After an initial steam distillation the product was distilled through a small Fenske column: b.p. 133–134° (13 mm.); n^{26}D 1.5492; ν 3400, 3270, 2150, 1270, 1115, and 820 cm.$^{-1}$; yield 50%. The product gave a negative Beilstein test.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.73; H, 7.10.

2-Methyl-4-proparglyphenyl Acetate.—The above phenol was acetylated with pyridine and acetic anhydride. The acetate [b.p. 113° (4 mm.); n^{25}D 1.5177; ν 3270, 2150, 1750, 1368, 1115, and 820 cm.$^{-1}$] was a colorless oil which rapidly turned brown on standing.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 75.97; H, 6.79.

2-Methyl-4-allylphenyl Acetate.—Hydrogenation of 4.7 g. (0.025 mole) of 2-methyl-4-propargylphenyl acetate over Lindlar catalyst in ethyl acetate utilized 96% of 1 equiv. of hydrogen. The product [b.p. 80° (1 mm.); n^{21}D 1.5078; ν 1115, 995, 910, and 820 cm.$^{-1}$] was a clear liquid which gave no precipitate with alcoholic silver nitrate and gave only a single peak in the gas chromatogram.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42. Found: C, 75.49; H, 7.18.

2-Hydroxy-5-propylacetophenone.—Crude *p*-propylphenyl acetate (51 g., 0.285 mole) was added slowly to a well-stirred mixture of 38.3 g. (0.287 mole) of anhydrous aluminum chloride in 50 ml. of carbon disulfide. The mixture was heated until the evolution of hydrogen chloride ceased, the carbon disulfide was distilled, and the residue was heated for 3 hr. at 140°. To this was added 34 ml. of concentrated hydrochloric acid followed by 50 ml. of cold water. The insoluble oil was separated and dissolved in 10% sodium hydroxide; the solution was extracted with ether. The basic layer was made acidic and the organic product was separated and dried. The product, b.p. 80–85° (0.25 mm.), n^{20}D 1.5365, was a thick liquid.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.05; H, 7.78.

2-Ethyl-4-propylphenol.—Five grams of the above ketone was reduced in 24 hr. over amalgamated zinc using the directions of Read and Wood.[16] The product, b.p. 70–72° (0.25 mm.), n^{20}D 1.5194, was a colorless mobile oil.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.95; H, 9.69.

A phenylurethan prepared from this phenol melted at 144.5–145.4°.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47. Found: C, 76.59; H, 7.42.

A sample of the rearrangement product from allyl 2-ethylphenyl ether was hydrogenated over 10% palladium on charcoal in glacial acetic acid. Two peaks were observed in the gas chromatogram, the second of which was increased in size when a mixture of this product and 2-ethyl-4-propylphenol was chromatographed.

3-Isopropyl-4-hydroxypropiophenone.—A mixture of 4 g. (0.03 mole) of *o*-isopropylphenol and 2.75 g. (0.03 mole) of propionyl chloride was warmed for 1 hr. and the crude ester was dissolved in 25 ml. of nitrobenzene. The solution was cooled in an ice bath, 4.5 g. (0.033 mole) of anhydrous aluminum chloride was added, and the mixture was allowed to stand at room temperature for 3 days. It was then heated for 3–4 hr. at 50–60° and then decomposed with ice and dilute hydrochloric acid. The product was separated by extraction of the organic layer with 10% sodium hydroxide. Acidification gave a light yellow solid which was crystallized from a large volume of water, m.p. 123°, 3.6 g. (64%).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.74; H, 8.47.

2-Isopropyl-4-propylphenol.—The above ketone (2.2 g., 0.011 mole) was reduced with amalgamated zinc and hydrochloric acid for 48 hr. The product was distilled from an alembic at a bath temperature of 120° at 0.5-mm. pressure, n^{27}D 1.5097.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.70; H, 9.86.

A sample of the rearranged product from allyl *o*-isopropylphenyl ether was hydrogenated over palladium on charcoal in glacial acetic acid. The reduced product gave two peaks in its gas chromatogram, the second of which was shown to be produced by 2-isopropyl-4-propylphenol by comparison with an authentic sample.

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[15] Ph. Chint and Fr. Bolswig, *Bull. soc. chim. France*, [3] **35**, 78 (1906).

[16] R. R. Read and J. Wood, Jr., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 444.