The Effect of Pressure on the Allylation of Hindered Phenoxides[1]

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The allylations of all 4, 2,6, and 3,5 methyl-, ethyl-, isopropyl-, and *tert*-butyl-substituted phenols have been carried out in alkaline aqueous medium. The 4-alkylphenols give rise to 2-allylphenols and the allyl phenyl ethers as well as products resulting from further allylation. The 2,6-dialkylphenoxide ions yield allyl ethers, 4-allylphenols, and *o*-dienones as well as products containing more than one allyl group, and similar results were obtained with the 3,5-dialkylphenols. Some of these products are sensitive to thermal rearrangements. The product distributions have been measured over a pressure range of 1 atm to several kilobars, and the difference in partial molal volume of the isomeric transition states has been calculated in each reaction. In all cases, the transition states leading to ether formation are larger than those on the way to the ortho-substituted products, which in turn are larger than the transition states leading to the *p*-allylphenols; thus, massive support is provided for the contention that solvation of the O atom in hydroxylic media is of crucial importance in determining the allylation ratios. No systematic correlation with steric hindrance was found, however; the postulate, so well documented in the case of the Menshutkin reaction, that crowded transition states become favored at high pressure is not borne out in this reaction, so that its general validity must be questioned.

If the effect of pressure on a rate constant is known, the activation volume of the reaction can be calculated by means of the expression

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^*}{RT}$$

where k is expressed in concentration units at 1 atm. ΔV^*_o can be predicted for most mechanisms with fair accuracy on the basis of (a) comparisons with pressure data for reactions of well-known mechanisms, (b) volume changes in equilibria, and (c) densities and parachor data of stable substances. This ability allows one to use the pressure coefficient of a rate constant as a mechanistic criterion in many cases. Several features make important contributions to ΔV^*_o. Paramount among these are bond formation and cleavage, and charge separation and neutralization. Displacements in which there is no net change in the number of charges have small negative volumes of activation (~ -5 to -10 cm^3/mol), suggesting that bond formation is more advanced in the transition state than the concurrent bond fission.[3]

A factor of great potential interest is that of steric hindrance. Crowded compounds usually have somewhat greater densities than their unhindered isomers, and it would seem reasonable to suppose that hindered transition states would similarly have smaller volume requirements than the unhindered substrates from which they are formed. If this is so, hindered reactions should be accelerated to a greater degree than their unhindered analogs, clearly a possibility of much interest. Evidence for it has been reported by several groups. The first such claim was made by Perrin and Williams[4] in 1937 and quite recently Gonikberg[5] concluded that "the more sterically hindered a chemical reaction, the greater the degree to which it should be accelerated with increasing pressure."

In spite of the evidence,[6] it is probably still too early for such a generalization. Almost all of the examples that have been found are Menshutkin reactions, and even in that reaction the evidence is sometimes more apparent than real since one is often forced to compare data gathered in different solvents, at different temperatures and over different pressure ranges. Also, while it is true that crowded compounds are more dense than their unhindered isomers, the differences in molar volume seem rarely to be more than a cm^3 or two; but the $\Delta\Delta V^*$ values reported are often much larger than that. The potential of this phenomenon, a selective increase of the rate of sterically hindered reactions, appeared to us great enough to warrent a systematic investigation. We report here our results for the alkylation of substituted phenoxide ions in aqueous medium.

Discussion

Allyl chloride was chosen as the alkylating agent and water as the solvent because it is known[7] that, at least with phenoxide ion itself, initially three products form in reasonable amounts under such conditions: allyl phenyl ether, and *o*- and *p*-allylphenol. Since those mixtures can be readily analyzed, it appeared that the effect of pressure on the competition of those three reactions, already known in the case of phenoxide itself, might provide us with a well-documented example of the relation between that effect and steric hindrance in a displacement reaction.

In its execution, the problem was complicated somewhat by the possibilities of further alkylation of the phenolic products, and of rearrangements. Secondary alkylation (see Scheme I) was not found to present serious analytic difficulties in any case; thus, any allyl *o*-allylphenyl ether formed is simply considered *o*-allylphenol, since it must have arisen from that phenol. Any *o*- or *p*-diallylphenol was considered to be formed from both allylphenols; the ratio of the contributions was crudely calculated on the assumption that the rates of allylation at these positions are not affected by the presence of the *m*-allyl group already there. In nearly

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[3] W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967); *Cf.* also the several excellent reviews and books referred to in the opening paragraph of that paper.

[4] M. W. Perrin and E. G. Williams, *Proc. Roy. Soc., Ser. A*, **159**, 162 (1937).

[5] M. G. Gonikberg, *Russ. J. Phys. Chem.*, **37**, 248 (1963).

[6] Summarized by W. J. le Noble and Y. Ogo, *Tetrahedron*, **26**, 4119 (1970).

[7] N. Kornblum, P. J. Berrigan, and W. J. le Noble, *J. Amer. Chem. Soc.*, **82**, 1257 (1960).

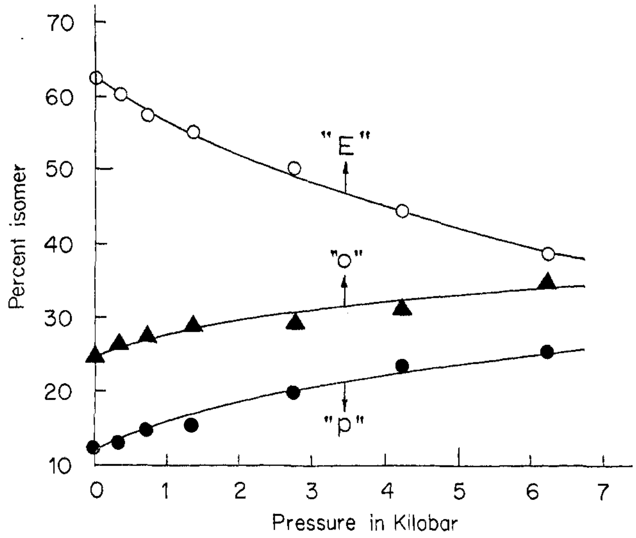
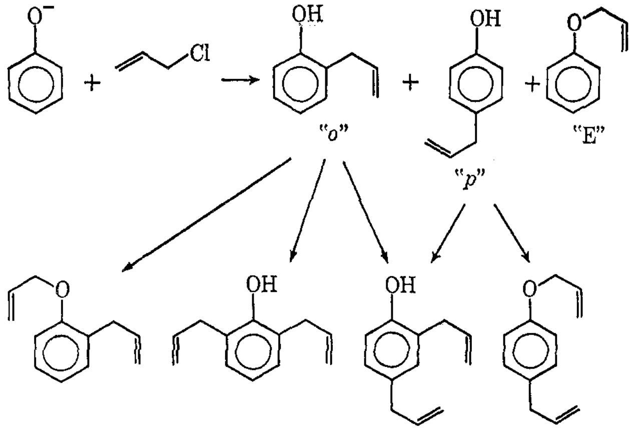


Figure 1.—*Primary product distribution in the allylation of 3,5-diisopropylphenoxide ion in water at 25° as a function of pressure.*

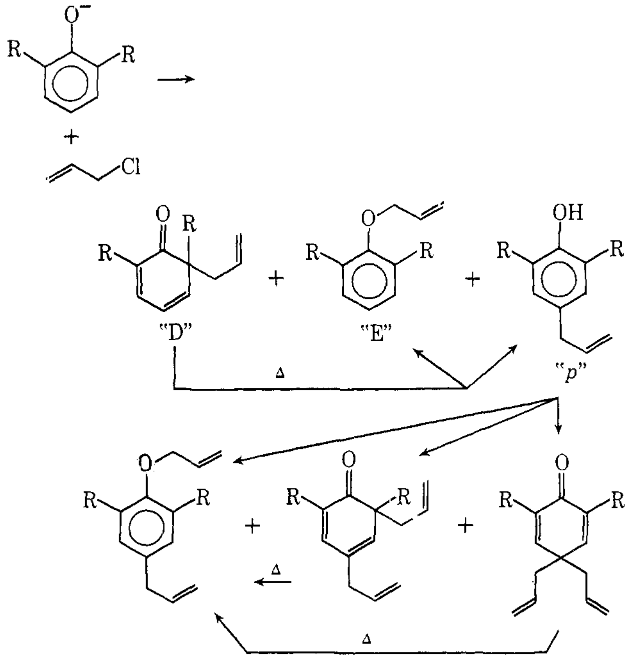
SCHEME I



all cases, however, it was possible by means of some preliminary experiments to choose conditions under which this side reaction constituted only a very minor nuisance.

More serious is the problem of rearrangement. The best known of these is of course the Claisen rearrangement; fortunately, the room temperature conditions of our experiments preclude this rearrangement. The allyl 2,6-dialkylphenyl ethers did in some instances rearrange to phenols to a minor extent during injection into the vpc apparatus; however, this occurred in a highly reproducible way, and a correction could be made for it. The 2,6-dialkylphenoxides also gave rise to fair amounts of the cyclohexadienones, which readily rearrange to mixtures of the isomeric allyl phenyl ethers and *p*-allylphenols, as was first described by Curtin.[8] The neutral dienones and ether products could be separated from the phenols by means of extractions with Claisen's alkali. A study of the neutral products showed the dienones to be stable under the conditions of their generation, their separation from the phenols and subsequent concentration to small volume, but during vpc analysis they rearranged quantitatively and reproducibly as shown in Scheme II. This permitted their assay by monitoring of the 4-allylphenols formed in the neutral fraction. *p*-Dienones were observed only in the allylation of the 2,6-disubstituted *p*-allylphenols and not in the allylation of *p*-alkylphenols (one example of the latter reaction is known[9]).

SCHEME II



After the appropriate corrections had been applied for dialkylation, Claisen rearrangement, and dienone rearrangement, the ratios *r* of the three main products were calculated. Allowance is made for the fact that two ortho positions are available. The slopes of ln *r vs.* *p* permitted $\Delta\Delta V^*_o$ to be computed. Table I shows the results, considered to have a precision of better than 1 cm^3/mol. The individual data are too numerous for a complete recording here; however, Table I shows the product distribution at 1 atm as well as the $\Delta\Delta V^*_o$ values and Figure 1 shows the effect of pressure in the case of 3,5-diisopropylphenoxide ion as a typical example.

Results

The most obvious result is that V^*_E is always larger than V^*_o or V^*_D and that V^*_o, with one minor exception, is always larger than V^*_p. This was first observed with phenoxide itself, and it may be considered to be the result of desolvation; whereas alkylation of the oxygen atom requires substantial desolvation, reaction at the ortho sites requires this to a much smaller degree, and attack at the para carbon atom not at all.[7,10]

As far as steric hindrance is concerned, the $\Delta\Delta V^*$ values are remarkably insensitive to it. Large alkyl groups in the 2 and 6 positions cause a decrease in $V^*_E - V^*_p$, but the effect is small, and in the wrong direction when the individual alkyl groups are considered. Since the substituent effect on the product distribution itself is fairly small and irregular, one might question

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[8] D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, **80**, 1391 (1958).

[9] R. Barner, A. Boller, J. Borgulya, E. G. Herzog, W. von Philipsborn, C. von Planta, A. Fürst, and H. Schmid, *Helv. Chim. Acta*, **48**, 94 (1965).

[10] (a) W. J. le Noble, *J. Amer. Chem. Soc.*, **85**, 1470 (1963); (b) K. R. Brower, R. L. Ernst, and J. S. Chen, *J. Phys. Chem.*, **68**, 3814 (1964). The solvation (or desolvation) volume itself does not appear to be very sensitive to steric bulk; we have been unable, for instance, to find such an effect in the Menshutkin reaction,[6] and it is known that the ionization volumes of many week acids and bases are virtually independent of their structures.[8]

TABLE I

PRODUCT DISTRIBUTIONS AND THE DIFFERENCES IN ACTIVATION VOLUME IN CM^3/MOL FOR THE AQUEOUS ALLYLATION OF THE THREE POSITIONS IN VARIOUS PHENOXIDE IONS[a]

R_2	R_3	R_4	R_5	R_6	*o*	*p*	E	$V^*_E - V^*_{o(D)}$	$V^*_E - V^*_p$
H	H	H	H	H[b]	17	21	62	2.2	7.6
H	H	Me	H	H	41	0	59	3.5	
H	H	Et	H	H	43	0	57	3.3	
H	H	*i*-Pr	H	H	33	0	67	2.5	
H	H	*tert*-Bu	H	H	28	0	72	2.2	
H	Me	H	Me	H	37	45	18	2.0	3.6
H	Et	H	Et	H	34	37	29	5.7	7.6
H	*i*-Pr	H	*i*-Pr	H	25	12	63	3.5	7.5
H	*tert*-Bu	H	*tert*-Bu	H	22	0	78	6.2	
Me	H	H	H	Me	19	61	20	3.0	2.4
Et	H	H	H	Et	27	62	11	2.0	3.0
i-Pr	H	H	H	*i*-Pr	16	66	18	1.9	4.9
tert-Bu	H	H	H	*tert*-Bu	0	100	0		

[a] The temperatures were between 25 and 45°, as detailed in the Experimental Section. [b] See ref 10a.

how severely hindered O-allylation is. With 3,5 substitution, the product distributions give a clear indication of steric hindrance but again any trends in ($V^*_E - V^*_o$) and in ($V^*_E - V^*_p$) are small and irregular at best. The reasons for the difference in pressure sensitivity between hindered Menshutkin reactions and phenoxide allylations are not yet clear, and we can only conclude that claims of the generality of a correlation between hindrance and ΔV^* must be regarded with reservation at present.

Experimental Section

Where possible, the commercial parent phenols were employed after suitable purification. All of the new compounds mentioned below (*i.e.*, where no literature reference is given) except those referred to as trace products were subjected to elemental analysis and found to have a C and H per cent within 0.4% of the calculated values. Identification was carried out by nmr in all cases, and the analysis of mixtures was done by vpc. At least four samples were injected in every case, and the areas of the vpc peaks obtained were related to the composition by means of curves constructed by the use of synthetic mixtures.

***p*-Cresol.**—2-Allyl-4-cresol[11] and allyl *p*-cresyl ether[12] were prepared at 45° by allylation, separated by means of Claisen alkali,[13] and isolated by fractional vacuum distillation; small samples were further purified by means of vpc. The small scale analytical experiments were carried out at 40° for 48 hr in syringes;[10a] 4.3 mmol of cresol, 0.5 cm^3 of 5 *N* sodium hydroxide, and 19 ml of water saturated at room temperature with allyl chloride were used. The excess phenol served to suppress the formation of dialkylated products. After the reaction the contents of the syringe were transferred with 30 ml of benzene to a separatory funnel containing 3 g of sodium chloride and 1 ml of concentrated hydrochloric acid. After the extraction the aqueous part was treated with two more portions of benzene. The combined organic layers were distilled through a 30-cm Vigreux column until 1–3 cm^3 remained. This residue was analyzed by means of vpc. A 2-m Chromosorb W column impregnated with Carbowax 20M was used at 167° for all *p*-allylphenol product mixtures.

***p*-Ethylphenol.**—The large scale alkylation was carried out as above to give allyl *p*-ethylphenyl ether[12] and 2-allyl-4-ethylphenol.[12] The small scale reactions were also carried out as those with *p*-cresol.

***p*-Isopropylphenol.**—The large scale reaction was carried out with 0.15 mmol of the phenol, 0.24 mol of sodium hydroxide, and 0.25 mol of allyl chloride in 150 ml of water at 60° for 80 hr. The products obtained were allyl *p*-isopropylphenyl ether ($n^{25}D$ 1.5074), 2-allyl-4-isopropylphenol ($n^{25}D$ 1.5250), and traces of allyl 2-allyl-4-isopropylphenyl ether and 2,6-diallyl-4-isopropylphenol. The small scale reactions were carried out at 50° for 48 hr; an excess of 0.5 cm^3 allyl chloride was used to compensate for evaporation during assembly.

***p-tert*-Butylphenol.**—Both the large and small scale reactions were done as with *p*-isopropylphenol to give allyl *p-tert*-butylphenyl ether,[14] 2-allyl-4-*tert*-butylphenol,[14] and a trace of allyl 2-allyl-4-*tert*-butylphenyl ether.

2,6-Dimethylphenol.—The bulk reaction was carried out at 25° with 0.050 mol of the phenol, 0.2 mol of sodium hydroxide, and 25 ml of allyl chloride. The resulting mixture was neutralized at 20° with 10% hydrochloric acid saturated with sodium chloride and extracted three times with 100 ml of benzene. The combined benzene solutions were extracted four times with 50 ml of cold Claisen alkali. The combined Claisen extracts were cooled, neutralized with concentrated hydrochloric acid, and extracted four times with 50 ml of benzene; these extracts were combined, dried, and reduced to a small volume (phenolic residue); the original benzene layer was washed with water, briefly dried over anhydrous magnesium sulfate, and flash evaporated at room temperature (neutral residue). The phenolic part was shown by both nmr and vpc to consist entirely of unreacted starting material and 4-allyl-2,6-dimethylphenol:[15] vpc was carried out for all of the 2,6-dialkylphenol experiments by means of a 4-m column charged with 40% Carbowax 20M absorbed on Chromosorb W (HMDS treated) at 185°. Vpc of the neutral fraction gave rise to allyl 2,6-dimethylphenyl ether,[15] allyl 4-allyl-2,6-dimethylphenyl ether,[16] and 4-allyl-2,6-dimethylphenol[15] (formed by rearrangement of dienone, see below). Ir and nmr spectra of the neutral fraction prior to vpc showed that 2,6-dimethylphenol and 4-allyl-2,6-dimethylphenol were absent (both have a strong band at 2.75 μ) and that the dienone was present, ir 6.05 μ (s); for nmr see below. The neutral fraction could be enriched in the dienone by means of either high vacuum distillation (0.06 mm, temperature below 43°), which gave a mixture of 64% dienone and 36% allyl ether as estimated by means of nmr or tlc. Allyl 2,6-dimethylphenyl ether, allyl 4-allyl-2,6-dimethylphenyl ether, and the dienone have R_f values of 0.94, 0.16, and 0.40, respectively, when a mixture of benzene and petroleum ether (2:1) is used to develop samples of the neutral mixture on an Eastman Chromagram Sheet No. 6060; preparative separation was achieved with a 2-mm layer of silica gel PF 254 (Merck). Samples of the dienone so enriched showed the vpc peaks of its two isomers and of allyl 4-allyl-2,6-dimethylphenyl ether; the latter arises from contamination of the dienone by dialkyldienones (see below). These enriched mixtures allow the following nmr assignments to be made for the monoallyldienone: τ 8.88 (s, 3, quaternary CH_3), 8.21 (s, 3, $=CCH_3$), 7.04–7.90 (m, 2, quaternary CH_2), 4.10–5.25 (m, 3, $CH=CH_2$), 3.14–3.95 ppm (m, 3, $=CH-CH=CH-$). It was confirmed[16] by means of these enriched mixtures that the dienone under the conditions of our vpc separations was completely converted into a mixture of the isomeric ether and phenol in the ratio of 23:77; it was also shown that allyl 2,6-dimethylphenyl ether itself rearranged to the phenolic isomer to the extent of 9% during vpc.

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[11] N. Kornblum, P. J. Berrigan, and W. J. le Noble, *J. Amer. Chem. Soc.*, **85**, 1141 (1963).

[12] H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

[13] L. Claisen, *Justus Liebigs Ann. Chem.*, **418**, 69 (1919); see p 96.

[14] A. B. Sen and R. P. Rastogi, *J. Indian Chem. Soc.*, **30**, 355 (1953).

[15] D. S. Tarbell and J. F. Kincaid, *J. Amer. Chem. Soc.*, **62**, 728 (1940).

[16] D. Y. Curtin and R. J. Crawford, *ibid.*, **79**, 3156 (1957).

These rearrangements did not affect the retention times or sharpness of the peaks and hence apparently occurred at the hot inlet port (280°). Both the dienone and ether were shown to be stable under the conditions of their formation (at all pressures used here) and work-up prior to vpc injection. When 4-allyl-2,6-dimethylphenol is further allylated, a neutral fraction can be isolated containing the allyl ether and a substantial amount of a 4:3 mixture of 4,6-diallyl-2,6-dimethylcyclohexa-2,4-dienone and 4,4-diallyl-2,6-dimethylcyclohexa-2,5-dienone (the nmr spectrum of the mixture contained methyl signals at τ 8.8 and 8.2 in a 2:5 ratio). Both compounds quantitatively rearranged to the ether during vpc. The analytical experiments were carried out for 48 hr at 25° with 0.0043 mol of 2,6-dimethylphenol, 0.017 mol of sodium hydroxide, 19 ml of water saturated with allyl chloride, and 0.8 ml of additional allyl chloride. The syringes were then emptied with the use of 10 ml of toluene into a separatory funnel containing 3 g of sodium chloride and 2 ml of concentrated hydrochloric acid. The mixture was extracted with three 30-ml portions of toluene, and the combined extracts were dried briefly over anhydrous magnesium sulfate. Diphenyl ether (0.060 g) was added as an internal standard; half of the resulting solution was concentrated by flash evaporation at room temperature and analyzed by means of vpc as described in the bulk reactions. Beside the two phenols and the two ether products, the diphenyl ether was observed in the chromatogram. The other half was treated with Claisen's alkali (four 10-ml portions), dried, concentrated by flash evaporation, and then analyzed by vpc; the starting phenol was absent from this mixture. The entire composition could then be related to the areas of the various peaks in the two chromatograms by means of the data obtained above for the rearrangements of the neutral products.

2,6-Diethylphenol.—A solution of 35 g of sodium nitrite in 100 ml of water is added to a cold, rapidly stirred solution of 75 g of 2,6-diethylaniline in 265 ml of 50% aqueous sulfuric acid during a 10-min period. This slurry is added to a hot mixture of 250 ml of water and 325 ml of 96% sulfuric acid in 30 min. After cooling to 100°, the oily layer is decanted on ice, which leads to the formation of a dark brown solid. Decolorization with carbon black and crystallization from 15% aqueous hydrochloric acid affords a 60–70% yield of 2,6-diethylphenol, mp 36–36.5° (lit.[17] 36–36.5°). The bulk allylation was carried out under the same conditions as those used for the dimethylphenol. Allyl 2,6-diethylphenyl ether (n^{25}D 1.5040), allyl 4-allyl-2,6-diethylphenyl ether (n^{25}D 1.5113), and 4-allyl-2,6-diethylphenol (n^{25}D 1.5268), were obtained. The mono- and diallylated ethers and 6-allyl-2,6-diethylcyclohexa-2,4-dienone could be separated on Chromagram sheets. Small samples of the latter compound (contaminated with 13% of diallylated dienones as shown by the presence of that much diallylated ether in vpc recordings) allowed its identification by nmr as before. During vpc the dienone decomposed completely into an 18–82 mixture of allyl 2,6-diethylphenyl ether and 4-allyl-2,6-diethylphenol. It was also found that pure monoallyl ether during vpc rearranged to the isomeric phenol to the extent of 10.5%, and that all products were stable to the conditions of their formation and subsequent work-up except vpc. The analytical experiments were entirely similar to those carried out with the dimethyl homolog; diphenyl ether was again used as an internal standard.

2,6-Diisopropylphenol.—The bulk reaction, similar to that of the dimethyl homolog, gave rise to allyl 2,6-diisopropylphenyl ether (n^{25}D 1.4970), allyl 4-allyl-2,6-diisopropylphenyl ether (n^{25}D 1.5068), and 4-allyl-2,6-diisopropylphenol (n^{25}D 1.5168). The mono- and diallylated ethers and 6-allyl-2,6-diisopropylcyclohexa-2,4-dienone were again separated on Chromagram sheets; small samples of the latter compound (contaminated with 3% diallyldienones as judged by the amount of the diallylated ether in the vpc recordings) were used for identification by nmr. During vpc the dienone decomposed quantitatively into a 17:83 mixture of allyl 2,6-diisopropylphenyl ether and 4-allyl-2,6-diisopropylphenol. The ether furthermore rearranges to the isomeric phenol to the extent of 15% during vpc; otherwise, all products proved to be stable to preparation and work-up. The analytical experiments were completely similar to those carried out with the dimethyl analog; diphenyl ether was again used as an internal standard.

2,6-Di-*tert*-butylphenol.—Exploratory alkylation experiments were carried out with 50:50 aqueous methanol at 25° and at 1 as well as at 5000 atm for 72 hr; these indicated the formation of three products, the first of which was present in such small traces that it could not be further identified. Also obtained in about a 100:1 ratio were 4-allyl-2,6-di-*tert*-butylphenol (n^{25}D 1.5118), and 2,4-diallyl-6-*tert*-butylphenol, mp 32.5–33°.

3,5-Dimethylphenol.—Bulk allylation at 45° for 25 hr followed by a work-up based on Claisen's alkali and vpc afforded allyl 3,5-dimethylphenyl ether,[18] 2-allyl-3,5-dimethylphenol, mp 43–44°, 4-allyl-3,5-dimethylphenol, mp 63.5–64.5°, and traces of 2,4- and 2,6-diallyl-3,5-dimethylphenols. In the analytical experiments which lasted 24 hr, the temperature was 25°. Vpc was carried out at 200° with the same column as described above for the 2,6-dialkylphenol experiments.

3,5-Diethylphenol.—This material was prepared from commercially available 2,6-diethylaniline by successive *p*-bromination in glacial acetic acid at 15°, diazotation and reduction[19] to 3,5-diethylbromobenzene,[20] and oxidation in 26% yield of the Grignard reagent.[21] It was crystallized from ligroin, mp 75° (lit.[22] 77°). The bulk allylation was carried out for 80 hr as in the preceding case; the analytical experiments were carried out as before at 25°, but for 14 hr; the same vpc conditions were applied. The products are allyl 3,5-diethylphenyl ether (n^{25}D 1.5087), 2-allyl-3,5-diethylphenol (n^{25}D 1.5292), 4-allyl-3,5-diethylphenol (n^{25}D 1.5324), and traces of the 2,4- and 2,6-diallylphenols.

3,5-Diisopropylphenol.—This compound was prepared from *m*-diisopropylbenzene *via* nitration[23] in 95% yield to a mixture of 2- and 4-nitro-1,3-diisopropylbenzene, reduction of the crude mixture for 1 hr at 100° by tin and hydrochloric acid to the anilines (94%), bromination of these anilines as described in the preceding case in 94% yield, and deamination[19] of the mixture in 87% to give 3,5-diisopropylbromobenzene, bp 72.5–74° (1 mm), n^{25}D 1.5250. Oxidation of the Grignard reagent[21] gave a 61% yield of the phenol, which was purified by sublimation, mp 52–53° (lit.[24] 52°). The allylation was allowed to proceed at 25°, 2 days for the bulk reaction, and 3 hr for the analytical work. The products were allyl 3,5-diisopropylphenyl ether (n^{25}D 1.5006), 2-allyl-3,5-diisopropylphenol (mp 50–51°), and 4-allyl-3,5-diisopropylphenol (mp 82.5–83.5°).

3,5-Di-*tert*-butylphenol.—Allylation of this material gave only two products under all conditions, allyl 3,5-di-*tert*-butylphenyl ether (n^{25}D 1.4959), and 2-allyl-3,5-di-*tert*-butylphenol (mp 65–66°).

Registry No.—*p*-Cresol, 106-44-5; *p*-ethylphenol, 123-07-9; *p*-isopropylphenol, 99-89-8; *p*-*tert*-butylphenol, 98-54-4; 2,6-dimethylphenol, 576-26-1; 2,6-diethylphenol, 1006-59-3; 2,6-diisopropylphenol, 2078-54-8; 2,6-di-*tert*-butylphenol, 128-39-2; 3,5-dimethylphenol, 108-68-9; 3,5-diethylphenol, 1197-34-8; 3,5-diisopropylphenol, 26886-05-5; 3,5-di-*tert*-butylphenol, 1138-52-9.

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[22] P. Jannasch and A. Rathjen, *Chem. Ber.*, **32**, 2392 (1899).

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[24] Netherlands Patent Application 6,504,165; *cf. Chem. Abstr.*, **64**, 6561*g* (1966).