filter which transmits wavelengths >490 nm. A 4:1 4-*Z*/4-*E* mixture was obtained from 4-*Z* and a 3:1 4-*E*/4-*Z* mixture was obtained from 4-*E*.

Determination of the Dipole Moments. The dipole moments were determined in cyclohexane by Smith's and Palit's modifications[14] of the Guggenheim method.[13] Six or seven solutions of each isomer with a weight fraction between 0.5×10^{-3} and 5×10^{-3} were studied, and the changes in the dielectric constant and the refraction index as compared with pure cyclohexane were determined at 33 °C.

Kinetic Procedure. Due to the low solubility, the substrate was weighed separately for each kinetic point into a pressure (Pyrex) ampule (Sovirel), and a 5-mL solution of the base or the nucleophile was added. The ampules were shaken after 1 min at the reaction temperature in order to facilitate dissolution and then kept in the dark in a thermostated bath with a temperature reading accurate to ±0.1–0.2 °C. The ampules were then cooled with ice–water, and their content was either titrated or analyzed spectrally.

The solvolysis was followed by potentiometric titration of the Cl^- with $AgNO_3$ using a calomel electrode immersed in a K_2SO_4/agar-agar solution. In the presence of 2,6-lutidine or NaOAc the kinetic samples were diluted with water (15 mL) before the titration. In the presence of CF_3CH_2ONa, water (15 mL) and AcOH (3–4 mL) were added before the titration, and for the product analysis studies the acid was neutralized with dilute aqueous NaOH after the titration.

In the experiments in the presence of thiolate ions the sample was diluted by water (20 mL) and a solution of 9.8 M of $Cu(NO_3)_2 \cdot 2H_2O$ (5 mL). The excess thiolate ions were precipitated as the cupric salts together with the starting material and the product. The solution was filtered, and the Cl^- ion was titrated. The precipitate was dissolved in CH_2Cl_2 and analyzed spectrally. Control experiments showed that the addition of the cupric salt had no effect on the relative proportions of the products.

Product Analysis. At the end of the reaction the mixture was poured into a mixture of CH_2Cl_2 (15 mL) and water (15 mL). The organic layer was separated and washed with dilute HCl in the reactions in the presence of 2,6-lutidine, NaOAc, or $NaOCH_2CF_3$. In the presence of thiolate ions the mixtures were first washed with NaOH and then with water. The organic solution was dried ($MgSO_4$), the solvent was evaporated, and the product distribution was analyzed by NMR and occasionally by IR.

4-*E* ⇌ 4-*Z* Isomerization. The positions of the Me, MeO, and aromatic signals of 4-*E* and 4-*Z* are sufficiently separated for a convenient follow-up of the 4-*E* ⇌ 4-*Z* isomerization. The methyl signals of the products are sufficiently away from those of 4-*E* and 4-*Z*, enabling a concurrent follow-up of the isomerizations and the solvolysis.

Registry No. (*E*)-4, 74684-45-0; (*Z*)-4, 74684-46-1; 5, 20765-22-4; 6, 74684-47-2; 7, 74684-48-3; (*E*)-9, 74684-49-4; (*Z*)-9, 74684-50-7; 10, 100-19-6; (*E*)-11, 74684-51-8; (*Z*)-11, 74684-52-9; (*E*)-12, 74684-53-0; (*Z*)-12, 74684-54-1; 13, 103-19-5; (*E*)-14, 74684-55-2; (*Z*)-14, 74684-56-3; 15, 7605-48-3; *p*-nitrophenylacetic acid, 104-03-0; anisole, 100-66-3; sodium *p*-toluenethiolate, 10486-08-5; sodium *p*-*tert*-butylbenzenethiolate, 54166-35-7.

Supplementary Material Available: Table I, 4-*E* ⇌ 4-*Z* isomerization data; Table II, solvolysis products of 4 in EtOH; Table IV, solvolysis products of 4 in 60% TFE; Table VI, product and precursor distributions in the solvolysis of 4-*E* and 4-*Z*; Table IX, data for the reaction of 4-*E* with sodium *p*-toluenethiolate; Table X, 4-*E* ⇌ 4-*Z* isomerization data during solvolysis in 80% EtOH/RS^- (6 pages). Ordering information is given on any current masthead page.

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. 9. Reaction of Phenol with 1-Propanol[1a]

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At 250–350 °C in the presence of alumina, phenol (1) reacts with excess 1-propanol to give mainly (>90%) C-alkylation to form mono- to penta-*n*-propylphenols plus some O-alkylation to form *n*-propyl aryl ethers. The principal component of the product mixture from 1 is 2,6-di-*n*-propylphenol (26–50 mol % yield). With 4-*n*-propylphenol as substrate (instead of 1), tri-, tetra-, and penta-*n*-propylphenols are formed in 48–79% combined yield. On the average, only 3% of the total C_3H_7 groups in the product mixture are isopropyl ones. Deoxygenation is not observed. It is proposed that the principal products result from an S_N2-type reaction mechanism which involves nucleophilic attack (variously by C-2, C-4, C-6, or O) of an adsorbed ambident phenoxide ion onto C-1 of an adsorbed *n*-propoxide group. *n*-Propylation at C-3 and C-5 of the phenol ring results from surface-catalyzed dienone–phenol rearrangement. Isopropylation may occur via a side reaction of S_N1 type.

Previous papers in this series[2-7] concerned alumina-catalyzed reactions of methanol with naphthols, indanol, hydroxybiphenyls, and hydroaromatic ketones of the benzene and naphthalene systems in a flow apparatus at 220–550 °C. In general terms, processes of (a) O-alkylation to give alkyl aryl ethers, (b) C-alkylation to give alkylarenols and alkylated hydroaromatic ketones, and (c) alkylation–deoxygenation to form alkylarenes variously occurred with the hydroxyarene substrates. Analogous interactions between phenol and methanol were reported by other investigators.[8] On the basis of mechanisms proposed in our studies,[2,3] one would expect that any primary or secondary alcohol should undergo processes b and c without skeletal rearrangement of the alkyl group. This paper and the following one[9] report the results of inter-

(1) (a) This investigation was supported by Research Grant No. CA-5969 from the National Cancer Institute, U.S. Public Health Service. (b) Research Assistant, 1964–1967.

(2) L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480, 1489, 1494 (1968).

(3) L. H. Klemm, C. E. Klopfenstein, and J. Shabtai, *J. Org. Chem.*, **35**, 1069 (1970).

(4) J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **35**, 1075 (1970).

(5) L. H. Klemm and D. R. Taylor, *J. Org. Chem.*, **35**, 3216 (1970).

(6) L. H. Klemm, R. Zell, and J. S. Shabtai, *J. Org. Chem.*, **39**, 698 (1974).

(7) L. H. Klemm and D. R. Taylor, *Org. Prep. Proced. Int.*, **8**, 163 (1976).

(8) (a) E. Briner, W. Plüss, and H. Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924); (b) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, 821 (1945); (c) N. M. Cullinane, S. J. Chard, and C. W. C. Dawkins, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 520. See also ref 14.

0022-3263/80/1945-4320$01.00/0

Table I. Alumina-Catalyzed Reactions of Phenol (1), *n*-Propyl Phenyl Ether (2), and 4-*n*-Propylphenol (3) with 1-Propanol (4)

parameter	expt no. 1	2	3	4	5	6	7	8	9	10	11
reaction temp, °C	250	300	300	300	300	350	350	300	250	300	350
substrate[a]	1	1	1	1	1	1	1	2	3	3	3
catalyst[b]	E	E	F	F	F	F	F	F	F	F	F
molar ratio used (4/substrate)	40	40	10	20	40	20	40	40	57.5	57.5	57.5
product component, mol %[c]											
n-propyl phenyl ether (2)	5.8	0.3	2.1	2.1	4.7	1.4					
n-propyl 2-*n*-propylphenyl ether (5)	6.5	0.6	1.9	2.1	3.5	0.7	1.6	2.6			
n-propyl 4-*n*-propylphenyl ether (6)	0.3	0.5	0.7	0.8		0.2		0.3	14.3	3.5	0.8
n-propyl 2,4-di-*n*-propylphenyl ether (7)		0.6					0.6		6.8	2.0	0.8
2-*n*-propylphenol (8)	3.1	4.9	6.6	5.9	5.7	9.4	10.4	7.1			
4-*n*-propylphenol (3)	1.4	0.6	0.5	1.1	0.7		2.1	0.7			
2-isopropylphenol (9)	0.7	0.9	1.6	0.8	0.7	1.8	0.2	1.3			
2,4-di-*n*-propylphenol (10)	4.1	1.5	1.2	1.3	1.7	0.2	2.2	1.9	11.9	3.1	2.0
2,6-di-*n*-propylphenol (11)	49.5	34.3	47.5	42.2	35.6	42.8	26.4	36.8	1.1		
2,5(or 3,4)-di-*n*-propylphenol (12)		1.2					7.5		1.6		2.0
2-isopropyl-6-*n*-propylphenol (13)	9.2	4.2	11.2	8.4	5.7	5.0	1.4	5.9	1.1		
2,3(or 4),6-tri-*n*-propylphenol (14)[d]	5.1	16.2	8.9	10.6	11.0	12.7	15.1	10.3	30.4[e]	28.8[e]	28.9[e]
2,6-di-*n*-propyl-4-isopropylphenol (15)[f]	1.0	4.2	2.3	1.5	1.2	2.0	3.1	1.3	1.6	1.1	2.3
2,3,4(or 5),6-tetra-*n*-propylphenol (16)[d,g]	5.1	17.5	8.1	14.6	14.2	16.0	12.9	10.4	15.9	22.1	31.3
2,3,4,5,6-penta-*n*-propylphenol (17)		1.7	4.2	5.7	12.2	3.7	0.4	17.0	2.2	28.2	14.2
unidentified (wt %)[h]	(5.0)	(11.8)	(2.7)	(3.9)	(3.7)	(4.1)	(16.1)	(4.7)[i]	(13.1)	(11.3)	(15.3)
extent of propylation[j]	2.1	2.6	2.3	2.5	2.7	2.5	2.4	2.7[i,k]	2.0[l]	2.9[l]	2.8[l]

[a] The conversion of substrate into liquid product was 96–100% in each experiment. [b] Catalyst E was prepared by hydrolysis of aluminum isopropoxide. Catalyst F was Houdry HA-100 alumina containing 0.4% sodium ion (see Experimental Section). [c] Based on total moles of substrate converted. [d] This mixture gives a single peak on VPC (cf. Experimental Section). [e] Only 2,4,6-tri-*n*-propylphenol (14b) is present. [f] No 2,4-di-*n*-propyl-6-isopropylphenol was identified in these product mixtures. [g] Partially oxidized to 2,3,5,6-tetra-*n*-propyl-1,4-benzoquinone (18) on exposure to air. [h] Includes all unidentified VPC peaks, of which the largest is <5% (by weight) of the total product. In a few cases small amounts of carbon deposits and nondistillable residues were also formed. [i] Excludes phenol (3.4%) produced. [j] Average number of propyl groups added per molecule, for identified products only. [k] Excluding *n*-propyl ether groups. [l] Excluding 4-*n*-propyl groups (cf. Experimental Section for isomeric compositions of 12 and 16).

actions between phenol (1) and the alcohols 1-propanol (4) and 2-propanol, respectively, in an effort to test our proposed mechanism under conditions which foster process b. For comparison, reactions were also conducted with *n*-propyl phenyl ether (2) and 4-*n*-propylphenol (3) as substrates, instead of 1. Experimental data are presented in Table I.

Results

In these experiments a solution of the substrate in excess 1-propanol (10–57.5 molar ratio) was added dropwise to a column of alumina catalyst maintained at a constant temperature of 250, 300, or 350 °C. Under these conditions conversion of substrate is essentially complete, and combined yields of isolated, identified products are 82–99 mol %. Only oxygen-bearing compounds, specifically ethers and phenols, are formed. Notably, neither hydroaromatic ketones nor alkyl-substitued benzenes are observed. However, as in previous investigations with methanol and various substrates, the total yield of ethers decreases with increasing reaction temperature under otherwise constant conditions (cf. expt 1 and 2, 4 and 6, 5 and 7, and 9–11). In each experiment the extent of propylation (i.e., the average number of propyl groups introduced into a molecule of substrate) is 2–3; but for all runs except no. 1, some pentapropylated compound is produced. For substrates 1 and 2, the dominant product (26–50%) is 2,6-di-*n*-propylphenol (11); while for substrate 3 at 300–350 °C, 2,4,6-tri-*n*-propylphenol (14b, 29%, again from propylation in positions 2 and 6 of the ring) as well as tetra- and penta-*n*-propylphenols (16 and 17; combined yields 46–50%) are significant components of the reaction mixture. Only three (9, 13, and 15) of the identified products bear isopropyl groups. In fact, just 0.4–6.8% of the total propyl groups introduced into the substrate in the various experiments occurs as isopropyl groups, while the remainder (an average of 97% for the 11 runs) occurs as normal propyl groups.

Mechanistic Interpretations

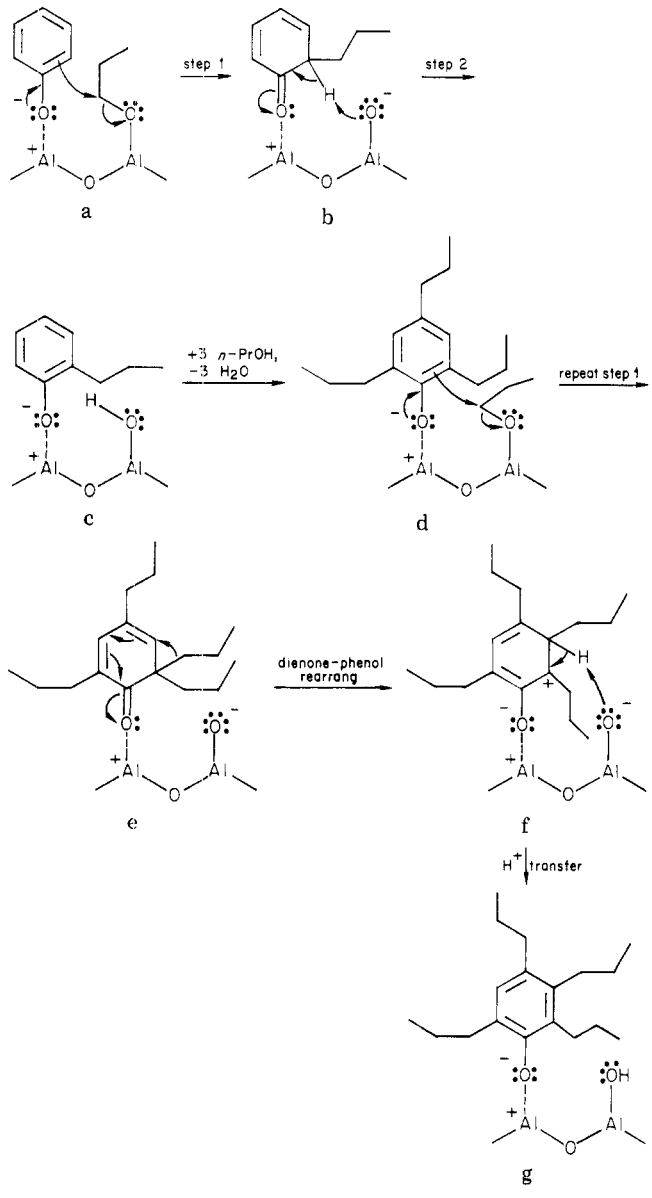
It is proposed that *n*-propylation occurs by means of a nucleophilic attack either by a ring carbon atom (C-alkylation) or by the oxygen atom (O-alkylation) of a chemisorbed ambident phenoxide ion onto C-1 of a neighboring chemisorbed *n*-propoxy group (S_N2-type mechanism). For C-alkylation, nucleophilic attack by the phenoxide ion is electronically preferred at ortho and para positions of the benzene ring. Thus, 3-propylphenol (or its propyl ether) is not found. However, there is a strong preference for substitution at C-2 and C-6, as compared to substitution at C-4. We ascribe this preference to surface adsorption of the phenoxide ion (with anchoring by means of the oxygen atom) in an edgewise or a tilted configuration, whereby C-2 and C-6 of the ring readily come within bonding distances of C-1 of adsorbed propoxy groups, while C-4 of the ring more commonly remains too remote from C-1 of the propoxy groups to give reaction.[10]

Scheme I depicts a likely mechanistic pathway from phenol to 2,3,4,6-tetra-*n*-propylphenol (16a). The overall reaction involves an ensemble of at least four adsorption sites on the catalyst surface. However, for simplicity, only two of these sites are shown in the scheme. First, both phenol and 1-propanol are dissociatively adsorbed (as protons, phenoxide ions, and propoxide ions). The protons bond to surface basic sites (oxide ions), phenoxide groups

(9) L. H. Klemm and D. R. Taylor, *J. Org. Chem.*, following paper in this issue.

(10) D. R. Taylor and K. H. Ludlum, *J. Phys. Chem.*, 76, 2882 (1972).

Scheme I

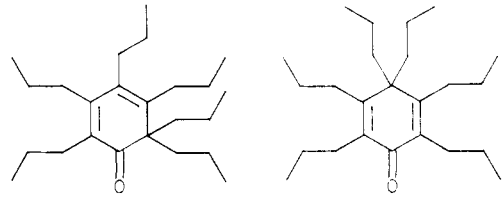


bind largely ionically[10] to Lewis acidic sites (incompletely coordinated aluminum ions), and propoxide groups bind covalently[11] to Lewis acidic sites. Structure a of Scheme I shows phenoxide and propoxide groups chemisorbed to adjacent acidic sites and undergoing (effectively via an eight-membered transition state)[4] nucleophilic attack by C-2 of the former onto C-1 of the latter (step 1). The resultant basic site (or another nearby one) abstracts a proton from C-2 of the adsorbed cyclohexadienone intermediate (see b and step 2) to yield chemisorbed 2-*n*-propylphenol (8 and c). Successive adsorptions of three more molecules of 1-propanol (with loss of three molecules of H_2O) plus repetition of steps 1 and 2 at C-6 and C-4 will give configuration d. A second alkylation at C-2 to give e[12] (or alternatively alkylation at C-4) followed by dienone–phenol rearrangement plus proton transfer will yield g, i.e., an adsorbed molecule of **16a**. Modifications and extension of Scheme I (plus desorption of appropriate compounds from the surface) thereby readily account for the appearance of **3**, **8**, **10**, **11**, **14**, **16**, and **17** in the product mixtures. Compound **12** is shown as either 2,5- or 3,4-di-*n*-propylphenol. While the structure of **12** has not been clearly established, it is more likely the latter isomer (cf. Experimental Section), which can also form by the same general pathway.

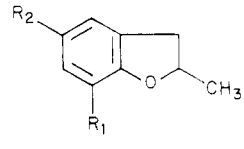
Ether formation, as for **2**, can proceed by the same general scheme, but by means of a six-membered transition state involving nucleophilic attack by the phenoxide oxygen atom onto C-1 of the propoxy group. With C-alkylation prior to O-alkylation, one can also obtain compounds **5**–**7**. It might be noted that the combined yield of ethers formed decreases rapidly with increasing reaction temperature (12.6% in expt 1 vs. 2% in expt 2; cf. also expt 4 and 6, as well as 9–11). This change is consistent with a higher energy of activation for C-alkylation as compared to O-alkylation.

It should be noted that the gross preponderance of *n*-propyl groups in the total product mixtures of the catalyzed reactions is inconsistent with the intermediate formation of free propyl carbonium ions on the catalyst surface. If such ions were regularly formed, one would expect to obtain extensive conversion of *n*-propyl groups into isopropyl ones prior to the alkylation step (S_N1-type mechanism), though it is conceivable that such conversion would be strongly repressed if *n*-propyl carbonium ions were to effect alkylation at a rate which is much greater than that of rearrangement. In fact, three isolated products (**9**, **13**, and **15**) do contain one isopropyl group apiece. We ascribe this isopropylation process to a side reaction which does involve propyl carbonium ions. This will be discussed in more detail in the succeeding paper.[9]

Shine and Schoening[13] investigated the migration of an *n*-propyl group in the dienone–phenol rearrangement. They found that *n*-propyl migrates more readily than methyl and without isomerization to isopropyl. In the reaction of phenol with methanol in the presence of alumina, mono-[8b] to pentamethylphenols[14] have been isolated. However, only after pentamethylphenol is formed is the dienone–phenol rearrangement inhibited sufficiently as to permit isolation of geminal dimethylcyclohexadienones.[14a] Adapting our scheme and that of Krysin and Koptyug[14a] to the reaction of 1-propanol with phenol, one would expect penta-*n*-propylphenol (**17**) to undergo further alkylation at temperatures of 300–350 °C to form intermediates **29** and **30**. These intermediates should, in turn, be converted



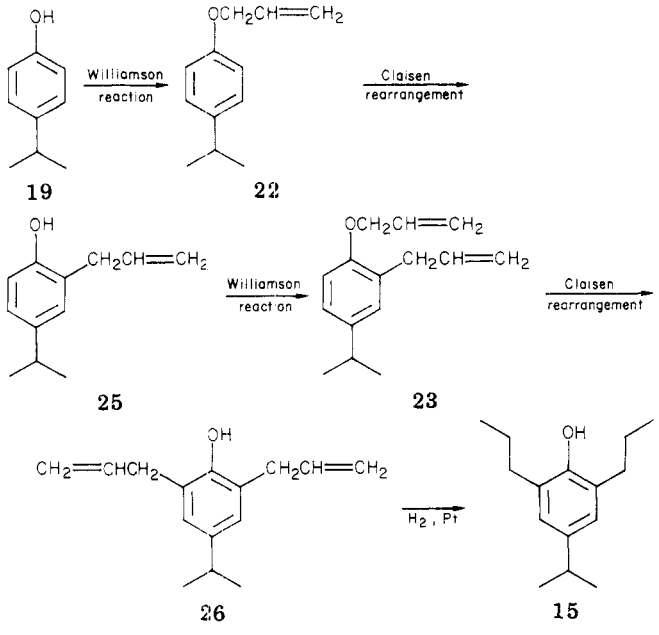
29 **30**



33, R_1 = *n*-Pr; R_2 = H
34, R_1 = H; R_2 = *i*-Pr
35, R_1 = *i*-Pr; R_2 = H

(11) R. O. Kagel, *J. Phys. Chem.*, **71**, 844 (1967).
(12) Intermediates resulting from ipso alkylation[14b] have been isolated and identified in studies on catalytic reductive methylation of phenol[14a] and naphthols.[2,3]
(13) H. J. Shine and C. E. Schoening, *J. Org. Chem.*, **37**, 2899 (1972).
(14) (a) A. P. Krysin and V. A. Koptyug, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1596 (1969); *Chem. Abstr.*, **71**, 112540 (1969); (b) B. E. Leach, *J. Org. Chem.*, **43**, 1794 (1978).

Scheme II



into hexa-*n*-propylbenzene (**31**) with or without the action of propanol as a reducing agent.[5] However, careful search by VPC of our reaction mixtures failed to show the presence of even traces of **31**. It is, therefore, very likely that under our reaction conditions propylation of the phenol ring ceases at the pentaalkylated stage of **17**, perhaps due to steric hindrance to formation of **29** or **30** because of the buttressing effect of the vicinal propyl groups. However, an effort to run reactions at temperatures >350 °C in order to check on this possibility proved unsuccessful because it gave markedly lower total product yields and very complex mixtures.

Synthetic Aspects

Sixteen new compounds (**5**, **6**, **12–17**, and **20–27**; see the Experimental Section) were isolated in analytically pure form from catalytic reaction mixtures by vapor-phase chromatography and/or synthesized for use as reference substances. *n*-Propyl and allyl aryl ethers were prepared from the corresponding phenols by the Williamson synthesis. Claisen rearrangement of the allyl aryl ethers produced allylalkylphenols, which were converted into propyl-substituted phenols by catalytic hydrogenation. An example of these various synthetic transformations is shown in Scheme II.

Structural Assignments

In general, structural assignments of compounds isolated from catalytic reaction mixtures were made by means of elemental analyses, spectra, and (wherever reasonably feasible) comparison with reference samples or literature data. Distinction between *n*-propyl and isopropyl groups was easily made by ^{1}H NMR spectrometry (see Table II), while ethers ($ArOCH_2$ stretching band at 1240 ± 20 cm^{-1})[15a] were distinguished from phenols, which showed OH signals in both infrared (3490–3630 cm^{-1})[15b] and NMR spectra. Out-of-plane CH deformation vibrations[15c] (see Table III), the presence of a sharp OH stretching band for a 2,6-disubstituted phenol,[15b] and NMR splitting patterns aided in the assignment for the arrangement of substituents on the benzene ring. The isolation of a bright yellow artifact which fits the ultraviolet, infrared, and NMR criteria (cf. Experimental Section) for 2,3,5,6-tetra-*n*-propyl-1,4-benzoquinone (**18**) implied the presence of 2,3,5,6-tetra-*n*-propylphenol (**16b**) in the unresolved mixture (**16**) of tetra-*n*-propylphenol isomers. Likewise, artifacts were produced when the intermediates 2-allyl-6-*n*-propylphenol (**24**), 2-allyl-4-isopropylphenol (**25**), and 2-allyl-6-isopropylphenol (**32**)[16] were subjected to VPC at an injection-port temperature >270 °C. Thus, cyclizations to the dihydrobenzofurans **33–35**, respectively, occurred and confirmed the location of the allyl group at C-2 in each case.

Experimental Section[17]

Apparatus, Catalysts, and Procedure. Reactions were carried out in a flow system consisting essentially of a vertically mounted Pyrex reactor tube (2.7 cm o.d.) packed to a height of 28 cm with fresh alumina catalyst (45 g), on which was superposed a narrow layer of Pyrex glass wool (to prevent splashing of influent solution). The tube was heated by a surrounding Cenco combustion furnace (30 cm in length). The reaction temperature (measured by a fixed thermocouple near the midpoint of the furnace but external to the reactor tube) was maintained at ±2 °C throughout each experiment. Two catalysts, E (*ex* aluminum isopropoxide) and F (Houdry hard alumina, grade HA-100), were used.[18] The catalyst bed was activated in situ prior to the experiment proper by being heated at the reaction temperature for 16 h in a stream of dry nitrogen gas (>99.99% pure).[18,19] A solution of phenol (2–5 g) in 1-propanol (32–129 g) was added dropwise to the top of the reactor at a constant rate over a period of 5 h, while a flow of nitrogen gas was maintained at 30–40 mL/min (measured at ambient conditions). The effluent, collected in ice- and air-cooled traps, was combined with acetone washings (three or four 100-mL portions) of the cooled catalyst and evaporated. An ether extract of the resultant residue was dried and analyzed by VPC at 168–200 °C (programmed) on a 1 cm × 2.4 m column of Chromosorb W (60–80 mesh) impregnated with 10% DC-550 silicone oil. Repeated analyses of product and synthetic mixtures showed an accuracy of ±0.9% (absolute error). The reproducibility of results from duplicative experiments was ±1.5% (absolute) for any identified component. Unless otherwise noted, preparative quantities of the various products were also isolated by VPC and identified by chemical and/or physical methods. Data for the various experiments are presented in Table I.

Starting Materials and Reference Compounds. Phenol (**1**), 2- and 4-*n*-propylphenols (**8** and **3**), 2- and 4-isopropylphenols (**9** and **19**), *n*-propyl phenyl ether (**2**), and 1-propanol (**4**) were available from commercial sources.

n-Propyl 2- and 4-*n*-propylphenyl ethers (**5** and **6**) were synthesized according to a general procedure,[20] wherein a solution of 0.1 mol of **8** or **3**, respectively, in anhydrous acetone was refluxed first with 0.086 mol of anhydrous K_2CO_3 for 2.5 h and then with 1-bromopropane (0.18 mol) for 24 h. Processing in the usual

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 3rd ed., Chapman and Hall, London, 1975, (a) pp 131–133, (b) pp 108–115, (c) pp 84–91.

(16) E. N. Marvell, B. Richardson, R. Anderson, J. L. Stephenson, and T. Crandall, *J. Org. Chem.*, **30**, 1032 (1965); W. Kawai and S. Tsutsumi, *Kogyo Kagaku Zasshi*, **63**, 1412 (1960); *Chem. Abstr.*, **57**, 11074c (1962).

(17) Elemental analyses were performed by Micro-Tech Laboratories. ^{1}H NMR spectra were obtained by means of a Varian Associates A-60 instrument, infrared spectra by means of a Beckman IR-7 spectrophotometer, and ultraviolet spectra by means of a Cary Model 15 instrument.

(18) Catalysts E and F are distinguished from A and C, respectively, used in earlier papers[2] only by the temperature (and its possible effect on crystalline structure, chemical composition, and catalytic activity) used in preheating (activation). Thus E and F were not preheated at 650 °C (as were A and C) in our experiments.[19]

(19) According to information supplied by Alcoa Research Laboratories [A. Russell et al., Technical Paper No. 10, Alcoa Research Laboratories, Pittsburgh, PA, 1956, Table 12, p 34] α-alumina monohydrate shows onset of decomposition to γ-alumina at 250 °C (upon heating for 1 h in dry air). Thus, it is believed that the catalytic activity of E may be ascribed to the presence of γ-alumina therein.

(20) W. M. Lauer and D. W. Wujciak, *J. Am. Chem. Soc.*, **78**, 5601 (1956).

Table II. ^{1}H NMR Spectral Data[a] for Various Phenol Derivatives

compd[b]	aliphatic protons[c]	aromatic protons[c]	phenolic proton[c]
5	0.7-1.2 (m, 2 CH_3), 1.2-2.0 (m, 2 CH_2Me), 2.60 (t, J = 7, benzylic CH_2), 3.76 (t, J = 6.5, OCH_2)	6.5-7.2 (m, 4 H)	
6	0.7-1.2 (m, 2 CH_3), 1.2-2.2 (m, 2 CH_2Me), 2.47 (t, J = 7.5, benzylic CH_2), 3.75 (t, J = 6.5, OCH_2)	6.70 and 6.98 (2 d, J = 9, 4 H)	
10	0.88 (t, J = 7, 2 CH_3), 1.2-2.0 (m, 2 CH_2Me), 2.2-2.8 (m, 2 CH_2Et)	6.3-7.1 (m, 3 H)	5.78 (s)
11	0.92 (t, J = 6.5, 2 CH_3), 1.2-2.0 (m, 2 CH_2Me), 2.50 (t, J = 7, 2 CH_2Et)	6.5-7.0 (m, 3 H)	4.54 (s)
12	0.6-1.2 (m, 2 CH_3), overlaps 1.0-2.0 (m, 2 CH_2Me), 2.0-2.8 (m, 2 CH_2Et)	6.3-7.1 (m, 3 H)[d]	5.84 (br s)
13	0.92 (t, J = 6.5, CH_2CH_3), 1.19 (d, J = 7, $CH(CH_3)_2$), partially overlaps 1.3-2.0 (m, CH_2Me), 2.49 (t, J = 7, CH_2Et), 3.11 (6 peaks of septet, J = 7, CH)	6.6-7.2 (m, 3 H)	4.68 (s)
14[e]	0.7-1.2 (m, 3 CH_3), 1.2-2.0 (m, 3 CH_2Me), 2.2-2.8 (m, 3 CH_2Et)	6.59 and 6.80 (2 d, J = 8, H of **14a**), 6.71 (s, H of **14b**)[f]	4.48 (s, H of **14b**), 4.57 (s, H of **14a**)[f]
14b[g]	0.90 (t, J = 7.5, p-$CH_2CH_2CH_3$), overlaps 0.92 (t, J = 7.5, 2 o-$CH_2CH_2CH_3$), 1.2-2.0 (m, 3 $CH_2CH_2CH_3$), 2.45 (t, J = 7.5, p-$CH_2CH_2CH_3$), overlaps 2.48 (t, J = 7.5, 2 o-$CH_2CH_2CH_3$)	6.68 (s, 2 H)	4.41 (s)
15	0.91 (t, J = 6.5, 2 $CH_2CH_2CH_3$), 1.17 (d, J = 6.5, $CH(CH_3)_2$), overlaps 1.2-2.0 (m, 2 CH_2Me), 2.2-3.1 (m, 2 benzylic CH_2 plus CH)	6.73 (s, 2 H)	4.40 (s)
16[h]	0.6-1.2 (m, 4 CH_3), 1.2-1.9 (m, 4 CH_2Me), 2.2-2.8 (m, 4 CH_2Et)	6.49 (s of **16a**), 6.67 (s of **16b**)[i]	4.36 (s, H of **16b**), 4.48 (s, H of **16a**)[i]
17	1.01 (t, J = 6.5, 5 CH_3), overlaps 1.2-1.9 (m, 5 CH_2Me), 2.3-2.8 (m, 5 CH_2Et)		4.29 (s)
20	0.91 and 0.94 (2 overlapping, t, J = 6.5, 2 CH_2CH_3), 1.22 (d, J = 7, $CH(CH_3)_2$), 1.3-2.0 (m, 2 CH_2Me), 2.47 (br t, 2 CH_2Et), 3.12 (6 peaks of septet, CH)	6.68 and 6.77 (2 d, J = 2.3, 2 H)	4.38 (s)
21	0.93 (t, J = 7, CH_3), 1.2-2.0 (m, CH_2Me), 2.62 (t, J = 7.5, CH_2Et), 4.2-4.5 (m, CH_2CH=CH_2), 5.0-5.6 (m, CH=CH_2), 5.6-6.3 (m, CH=CH_2)	6.5-7.2 (m, 4 H)	
22	1.18 (d, J = 7, 2 CH_3), 2.79 (septet, $CHMe_2$), 4.3-4.5 (m, CH_2CH=CH_2), 4.9-5.6 (m, CH=CH_2), 5.6-6.3 (m, CH=CH_2)	6.6-7.3 (m, including d of d, J = 9, at 6.88, 4 H)	
23	1.18 (d, J = 7, 2 CH_3), 2.78 (m, $CHMe_2$), 3.30 (d, J = 6.5, benzylic CH_2), 4.3-4.5 (m, OCH_2), 4.8-5.6 (m, 2 CH=CH_2), 5.6-6.4 (m, 2 CH=CH_2)	6.5-7.1 (m, 3 H)	
24	0.91 (t, J = 6.5, CH_3), 1.2-2.0 (m, CH_2Me), 2.53 (t, J = 7.5, CH_2Et), 3.1-3.4 (m, CH_2CH=CH_2), 4.8-5.3 (m, CH=CH_2), 5.6-6.3 (m, CH=CH_2)	6.5-7.2 (m, 3 H)	4.82 (s, overlaps m at 4.8-5.3)
25	1.18 (d, J = 7, $CH(CH_3)_2$), 2.75 (5 peaks of septet, $CHMe_2$), 3.30 (d, J = 6, CH_2CH=CH_2), 4.8-5.2 (m, CH=CH_2), 5.6-6.3 (m, CH=CH_2)	6.4-7.0 (m, 3 H)	5.55 (s, overlaps m at 5.6-6.3)
26	1.18 (d, J = 7, $CH(CH_3)_2$), 2.75 (septet, $CHMe_2$), 3.2-3.5 (m, 2 CH_2CH=CH_2), 4.8-5.3 (m, 2 CH_2CH=CH_2), 5.6-6.4 (m, 2 CH_2CH=CH_2)	6.78 (m, 2 H)	4.83 (s, overlaps m at 4.8-5.3)
27	0.91 (t, J = 7, CH_2CH_3), 1.20 (d, J = 7, $CH(CH_3)_2$), overlaps 1.3-2.0 (m, CH_2Me), 2.2-2.7 (m, CH_2Et), 2.7-3.4 (m, CH_2CH=CH_2 plus $CHMe_2$), 4.7-5.2 (m, CH=CH_2), 5.5-6.3 (m, CH=CH_2)	6.72 and 6.79 (2 s, 2 H)	4.52 (s)
28	1.21 (d, J = 7, $CH(CH_3)_2$), 3.37 (septet, $CHMe_2$), 4.3-4.5 (m, CH_2CH=CH_2), 5.0-5.6 (m, CH=CH_2), 5.6-6.5 (m, CH=CH_2)	6.5-7.3 (m, 4 H)	

[a] Obtained in CCl_4 solution. [b] The names of compounds **3-17** are given in Table I. Other compounds shown in Table II are as follows: **20**, 2-isopropyl-4,6-di-*n*-propylphenol; **21**, allyl 2-*n*-propylphenyl ether; **22**, allyl 4-isopropylphenyl ether; **23**, allyl 2-allyl-4-isopropylphenyl ether; **24**, 2-allyl-6-*n*-propylphenol; **25**, 2-allyl-4-isopropylphenol; **26**, 2,6-diallyl-4-isopropylphenol; **27**, 2-isopropyl-4-allyl-6-*n*-propylphenol; **28**, allyl 2-isopropylphenyl ether. [c] Chemical shifts are in δ values vs. tetramethylsilane as an internal standard; J values are in hertz; the symbols s, d, t, and m refer to singlet, doublet, triplet, and multiplet, respectively. [d] The splitting pattern of this multiplet is characteristic of a 1,2,4-trisubstituted benzene. [e] Mixture of 2,3,6-tri-*n*-propylphenol (**14a**) and 2,4,6-tri-*n*-propylphenol (**14b**) isolated from expt 8. This faintly yellow liquid solidifies at 0 °C. [f] Overlapping peaks which indicate an approximate ratio of **14b**/**14a** of 2. [g] Isomerically pure compound isolated from expt 9-11. [h] Mixture of 2,3,4,6-tetra-*n*-propylphenol (**16a**) and 2,3,5,6-tetra-*n*-propylphenol (**16b**). [i] Assignments are made on the assumption that more **16a** than **16b** will be formed from 4-*n*-propylphenol as substrate. On this basis, expt 8 gave the ratio of **16a**/**16b** as 2.3. With phenol as starting material this ratio was 0.8.

Table III. Infrared Spectral Absorption Bands[a] for Various Phenol Derivatives

compd[b]	solvent[c]	(OH) or Ar—O—CH_2 stretching[d]	other notable bands[e] for the range of 2000–1000 cm^{-1}	other notable bands[e] for the range of 1000–700 cm^{-1}
5	A	1240 s	1600 m, 1225 m, 1125 s, 1050 m	980 s, 750 s (4 vicinal arom H), 730 m
6	A	1250 s	1390 m, 1300 m, 1180 s, 1120 m, 1075 m, 1055 m, 1030 m	985 s, 850 m, 825 s (2 vicinal arom H), 810 m, 800 m
7	A	1250 s, 1230 s	1610, 1390, 1380, 1340, 1315, 1140 s, 1070, 1050, 1020	980 s, 880 (lone arom H), 805 m (2 vicinal arom H)
12	B	(3615 m, 3490)	1465 m, 1455 m, 1425 s, 1270 m, 1225 m, 1175 m, 1150 m, 1110 m	870 (lone arom H), 840 (2 vicinal arom H)
13	AB[f]	(3630 s)	1315 m, 1260 m, 1190 s, 1170 m, 1150 m, 1110 m	820 m, 790 m, 775 m, 750 s (3 vicinal arom H)
14[g]	A	(3620 m)	1380, 1270, 1240, 1220, 1190 s, 1155, 1110, 1095	
15	B	(3625 m)	1480 s, 1460 s, 1190 s, 1175 m	880, 870 (lone arom H)
16	B	(3620 s)	1470 vs, 1460 m, 1420 m, 1380 m, 1260 m, 1220 s, 1200 s, 1110 s, 1095 m	885–860 (br, lone arom H)
17	A	(3610 s)	1375 s, 1310 m, 1275 m, 1235 s, 1210 s, 1190 s, 1110 s, 1090 s	880, 735
20	A	(3620 s)	1200 vs, 1165 vs, 1135 s	
21	A	1240 vs, 1220 vs	1650, 1130 s	920 s, 750 vs (4 vicinal arom H)
22	A	1240 vs, 1220 vs	1645, 1610 s, 1285 s, 1180 vs, 1030 vs	1000 s, 985 s, 925 vs, 830 vs (2 vicinal arom H)
23	A	1250 vs, 1220 s	1650 m, 1640 m, 1030 s	995 s, 925 s, 910 s, 810 s (2 vicinal arom H)
24	A	(3620 s, 3560 s)	1640 m, 1255 vs, 1200 vs, 1190 vs, 1000 s	920 s, 750 vs (3 vicinal arom H)
25	A	(3610 s, 3560 s)	1640 s, 1265 vs, 1230 s, 1195 vs, 1170 s	910 s, 820 vs, 810 s (2 vicinal arom H)
26	A	(3540 s, br)	1640 s, 1205 vs, 1170 s, 1000 vs	910 vs (lone arom H)
27	A	(3605 s)	1640 m, 1195 vs, 1160 vs, 1130 s	910 vs (lone arom H)
28	A	1240 vs	1650, 1600 m, 1225 s	750 vs (4 vicinal arom H)

[a] Obtained on 5 or 10% solutions. In general, all absorbances ≥60% are reported here. Symbols used to show relative intensities of absorption are m (medium, 60–70%), s (strong, 70–80%), vs (very strong, >80%). Selected pertinent bands of intensities <60% are shown without symbol. [b] The names of compounds 5–17 are given in Table I and those of 20–28 in footnote *b* of Table II. [c] A is CS_2; B is CCl_4. [d] In cm^{-1}. [e] Excludes absorptions in the region 3400–2000 cm^{-1}. [f] Solvent B was used for the range >2000 cm^{-1} and solvent A for that <2000 cm^{-1}. [g] The infrared spectrum of **14b** (expt 9–11) was identical with that reported in the literature for 2,4,6-tri-*n*-propylphenol. This sample was isolated from expt 8.

manner gave liquids: **5**, bp 104–106 °C (11 mmHg), 55%; **6**, bp 61–62 °C (0.6 mmHg), 63%. When the same procedure was followed but allyl bromide was employed instead of 1-bromopropane, there were obtained the following: allyl 2-*n*-propylphenyl ether (**21**), bp 45–46 °C (0.1 mmHg), 81% from **8**; allyl 2-isopropylphenyl ether (**28**) from **9**;[16] allyl 4-isopropylphenyl ether (**22**), bp 49–50 °C (0.3 mmHg), 82% from **19**; allyl 2-allyl-4-isopropylphenyl ether (**23**), bp 48–49 °C (0.3 mmHg), 35% from **25** (vide infra). Similarly, 2-isopropyl-6-*n*-propylphenol (**13**) was converted into allyl 2-isopropyl-6-*n*-propylphenyl ether (**36**) (not obtained analytically pure), but by means of NaOMe in EtOH[21] instead of K_2CO_3 in acetone.

Claisen rearrangement of the preceding allyl ethers was effected in an atmosphere of nitrogen at 280 °C for 45 min. The products obtained were as follows: 2-allyl-6-*n*-propylphenol (**24**), bp 59–61 °C (0.6 mmHg), 77% from **21**; 2-allyl-6-isopropylphenol (**32**);[16] 2-allyl-4-isopropylphenol (**25**) from **22**;[22] 2,6-diallyl-4-isopropylphenol (**26**), bp 76–80 °C (0.2 mmHg), 71% from **23**; 2-isopropyl-4-allyl-6-*n*-propylphenol (**27**) from **36**.[22] Catalytic hydrogenation (of all but **25**) was accomplished by shaking a solution of 5 g of substrate in 65 mL of absolute ethanol with 0.7 g of prereduced Adams platinum catalyst in the presence of hydrogen gas (at 1 atm pressure and 25 °C) until uptake of gas ceased (ca. 2 h). Removal of catalyst and evaporation of solvent left, respectively, the following liquid products: **11**, 94%;[23] **13**, bp 49–51 °C (0.3 mmHg), 95%; **15**, 100%;[22] **20**, 43%.[22] Hexa-*n*-propylbenzene was synthesized by the method of Hopff and Gati.[24]

^1H NMR spectra and some infrared spectral absorption bands for new compounds, as well as others for which the data are not reported in literature sources, are presented in Tables II and III, respectively.

Miscellaneous Compounds Isolated. 2,3,5,6-Tetra-*n*-propyl-1,4-benzoquinone (18). The tetrapropylphenol fraction from expt 9 was chromatographed on neutral alumina (Woelm). 2,6-Disubstituted phenols were eluted with benzene, and the remaining band was eluted with chloroform. The residue from evaporation of the $CHCl_3$ was separated by preparative VPC on a column of silicone at 200 °C to yield **18** as a bright yellow liquid: NMR (CCl_4) δ 0.96 (t, J = 7 Hz, 4 CH_3) which partially overlaps 1.1–2.0 (m, 20 H total, 4 CH_2Me), 2.46 (br t, J = 7 Hz, 8 H, 4 benzylic CH_2); IR (CCl_4) 2980 (s), 2950 (m), 2890 (m), 1645 (vs, quinone), 1470 (m), 1460 (m), 1290 (m) cm^{-1}; UV (EtOH) 264 nm (log ε 4.25), 272 (4.26). Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.97; H, 10.04.

The spectral data of **18** are consistent with those reported by Cookson et al.[25] for duroquinone: UV (EtOH) 258 nm (log ε 4.32), 265 (4.30); IR ($CHCl_3$) 1640 cm^{-1} (quinone).

Mixture **14** from expt 8 showed only one strong sharp OH band at 3620 cm^{-1}. Since it consisted of two components, (on the basis of NMR spectrometry) and one of them was shown to be 2,4,6-tri-*n*-propylphenol (**14b**),[23] the other must be 2,3,6-tri-*n*-propylphenol.

Compound **10**, isolated from expt 9–11, was partially identified by its infrared spectrum.[23]

Compound **12** may be a single isomer. The out-of-plane bending bands indicate that **12** has a 1,2,4-trisubstitution pattern, i.e., is either 2,5- or 3,4-di-*n*-propylphenol. On the basis of its retention time (32 min) on a 10% DC-550 silicone oil column, as compared to that of 2,4-di-*n*-propylphenol (16 min), it seems unlikely that **12** can have a substituent at C-2. Hence, it is highly probable that **12** is the 3,4-isomer (cf. the previous discussion).

(21) D. Y. Curtin and H. W. Johnson, *J. Am. Chem. Soc.*, 78, 2611 (1956).
(22) Purified by vapor-phase chromatography.
(23) P. Demerseman, J. P. Lechartier, R. Reynaud, A. Cheutin, R. Royer, and P. Rumpf, *Bull. Soc. Chim. Fr.*, 2559 (1963).
(24) H. Hopff and A. Gati, *Helv. Chem. Acta*, 48, 509 (1965).
(25) R. C. Cookson, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3043 (1964).

Compound 7, isolated as a liquid from expt 9, was tentatively identified as *n*-propyl 2,4-di-*n*-propylphenyl ether by its infrared spectrum (Table III) and the fact that relatively large amounts of both **6** and **10** were obtained in this experiment.

Thermal Cyclizations. 2-Allylphenols **24**, **25**, and **32** were cyclized to 2-methyl-2,3-dihydrobenzo[*b*]furans (**33**, **34**, and **35**,[26] respectively) when they were chromatographed in the vapor phase at an injection port temperature >270 °C. In each case there was a loss of the OH function as evidenced by both infrared and NMR spectra on the effluent product: NMR (CCl_4) for **33** δ 0.92 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.2–2.0 (m, 5 H, CH_2Me plus $CHCH_3$), 2.3–3.9 (m, 4 H, 2 benzylic CH_2), 4.4–5.1 (m, 1 H, OCHMe), 6.3–7.2 (m, 3 H, aromatic); for **34** δ 1.17 [d, J = 7 Hz, $CH(CH_3)_2$] which overlaps 1.32 (d, J = 6.5 Hz, 9 H total, $OCHCH_3$), 2.3–3.5 (m, 3 H, $CHMe_2$ plus benzylic CH_2), 4.3–5.0 (m, 1 H, OCHMe), 6.4–7.0 (m, 3 H, aromatic); for **35** δ 1.0–1.5 (2 overlapping d, J = 7 Hz, 9 H, 3 Me), 2.3–3.4 (m, 3 H, $CHMe_2$ plus benzylic CH_2), 4.4–5.1 (m, 1 H, OCHMe), 6.4–7.1 (m, 3 H, aromatic).

(26) This compound was reported by Kawai and Tsutsumi[16] from refluxing **32** with HBr–HOAc.

Registry No. **1**, 108-95-2; **2**, 622-85-5; **3**, 645-56-7; **4**, 71-23-8; **5**, 74663-45-9; **6**, 74663-46-0; **7**, 74463-47-1; **8**, 644-35-9; **9**, 88-69-7; **10**, 23167-99-9; **11**, 6626-32-0; **12**, 74741-50-7; **13**, 74663-48-2; **14a**, 74663-49-3; **14b**, 74663-50-6; **15**, 74663-51-7; **16a**, 74663-52-8; **16b**, 74663-53-9; **17**, 74663-54-0; **18**, 74663-55-1; **19**, 99-89-8; **20**, 74663-56-2; **21**, 74663-57-3; **22**, 71029-37-3; **23**, 74663-58-4; **24**, 73295-87-1; **25**, 74663-59-5; **26**, 74663-60-8; **27**, 74663-61-9; **28**, 942-58-5; **32**, 3354-56-1; **33**, 74663-62-0; **34**, 74663-63-1; **35**, 74663-64-2; 1-bromopropane, 106-94-5; allyl bromide, 106-95-6.

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. 10. Reaction of Phenol with 2-Propanol[1a]

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At 300–350 °C in the presence of alumina, phenol (**1**) reacts with excess 2-propanol (**37**) to give mixed monopropyl-, dipropyl-, and 2,4,6-triisopropyl- (**42**) phenols. At 300 °C the principal components of the product mixture are 2-isopropylphenol (26–30 mol % yield) and 2,6-diisopropylphenol (44–52%); at 350–400 °C, they are the isomeric monoisopropylphenols (50–60%). With 3-isopropylphenol as substrate (instead of **1**), 2,5-diisopropylphenol is obtained (79%), while 4-isopropylphenol gives 2,4-diisopropylphenol and **42** (70% combined yield). In various runs, 0–20% of the propyl groups introduced are *n*-propyl ones. It is proposed that the principal products result from an S_N2-type reaction mechanism which involves nucleophilic attack (variously by C-2, C-4, and C-6) of an adsorbed ambident phenoxide ion onto C-2 of an adsorbed isopropoxide group. *n*-Propylation is ascribed to a side reaction of S_N1 type.

In the preceding paper[2] we reported the alumina-catalyzed reactions of phenol (**1**), *n*-propyl phenyl ether (**2**), and 4-*n*-propylphenol (**3**) with 1-propanol in the temperature range of 250–350 °C. Phenol underwent mainly (>90%) C-alkylation to form mono- to penta-*n*-propylphenols plus some O-alkylation to yield *n*-propyl aryl ethers. Substrates **2** and **3** gave similar results. On the average, 2–3 propyl groups were introduced per molecule and only 3% of these were isopropyl, instead of *n*-propyl ones. It was proposed that *n*-propylation of **1** involves an initial S_N2-type attack of an adsorbed ambident phenoxide ion onto C-1 of an adsorbed *n*-propoxide group, while isopropylation results from a side reaction of S_N1 type.

The present paper extends our study to the use of 2-propanol (**37**) or propene (**38**) as the propylating agent and to an investigation of the pathway for interconversion of *n*-propyl and isopropyl groups in the reactions. Phenol, 3-isopropylphenol (**36**), and 4-isopropylphenol (**19**) were used as substrates with **37** in the temperature range of 300–400 °C. Only **1** was reacted with **38**. A single alumina catalyst, F,[3] fresh for each experiment, was employed. Results with **37** and **38** are presented in Table I, while reactions of **2**, 2-*n*-propylphenol (**8**), and 2-isopropylphenol (**9**) in an inert solvent (benzene) without added propylating agent are shown in Table II.[5]

Results and Discussion

Inspection of Table I shows that under the reaction conditions used an average of 1–1.8 propyl groups were introduced into the benzene rings of substrates **1**, **19**, and **36**. No O-alkylation occurred, in contrast to the situation for reaction of **1** and 4-*n*-propylphenol (**3**) with 1-propanol.[2] In expt 1–4, phenol plus 2-propanol gave mono-, di-, and tripropylphenol products. Only isopropyl groups were found in the product mixture at 300 °C, but above this temperature significant quantities of *n*-propyl groups were also present (ca. 10% of the total propyl groups at 350 °C and 20% at 400 °C, expt 5). Changing the molar ratio of 2-propanol to phenol in the reaction mixture from 20:1 to 40:1 had relatively little effect on the product distribution. In contrast, changing the reaction temperature affected the positions of substitution markedly. At 300 °C isopropylation occurred with high selectivity for substitution ortho to the phenolic group. Thus, phenol (expt 1 and 2) gave **9** (26–30%) and **41** (44–52%), 3-isopropylphenol (expt 6) produced a particularly high yield of **40** (79%), and 4-isopropylphenol (expt 7) was largely converted into **39** (28%) and **42** (43%). Contrariwise, at 350 and 400 °C substitution occurred with far less discrimination to produce the isomerically mixed monosubstituted phenols **9**,

(1) (a) This investigation was supported by Research Grant No. CA-5969 from the National Cancer Institute, U.S. Public Health Service. (b) Research Assistant, 1964–1967.

(2) L. H. Klemm and D. R. Taylor, *J. Org. Chem.*, preceding paper in this issue.

(3) The same designation of F for this catalyst was used in the preceding paper[2] in this series. Both F and C (a catalyst employed in earlier studies)[4] were Houdry HA-100 alumina, but they differ from one another in the manner of pretreatment *in our laboratory*. Thus, C was preheated at 650 °C and then cooled to the reaction temperature, while F was not heated above the reaction temperature employed.

(4) L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480, 1489, 1494 (1968).

(5) To facilitate correlation with the preceding paper,[2] the same system of numbering compounds is used in both papers.

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