1,5-Diphenylpentane (**3a**) was prepared by reaction of 4-phenylbutylmagnesium bromide with benzaldehyde, followed by catalytic hydrogenolysis of the carbinol,[10a] bp 83–87° (0.1 mm) (lit.[12] bp 190–192°). The product was purified by preparative glpc (16 ft × 0.25 in. 30% XF-1150 column with helium carrier gas at 190°, 40 psi); the ir and nmr spectra were consistent with the assigned structure.

2-Methyl-1,5-diphenylpentane (**3b**) was synthesized starting with phenylacetone and 3-phenylpropylmagnesium bromide. The 2-benzyl-5-phenyl-2-pentanol so obtained had bp 110° (0.12 mm) and ir and nmr spectra consistent with its formulation. The alcohol was dehydrated by means of pyridine and phosphorus oxychloride,[13] and the mixture of alkene isomers was catalytically hydrogenated as before[10a] to give the title hydrocarbon, bp 102–108° (0.14 mm). It was purified by preparative glpc (16 ft × 0.25 in. 30% XF-1150 column with helium carrier gas at 190°, 40 psi): ir (film) 3080 (m), 2950 (s), 1500 (s), 1462 (s), 1390 (m), 1098 (m), 1035 (m), 912 (m), 745 (s), 700 cm^{-1} (s); nmr (CCl_4) δ 0.86 (d, 3 H, J = 6.0 Hz, CH_3), 1.11–2.00 (m, 5 H, $C^4H_2C^3H_2C^2H$), 2.52 (apparent q, 4 H, benzylic), and 7.10 ppm (s, 10 H, aromatic); mass spectrum (70 eV) m/e (rel intensity) 77 (5), 91 (100), 105 (15), 149 (9), 147 (30), 238 (22), 239 (5), 240 (0.7); mass, calcd. for $C_{18}H_{22}$, 238.1721 (found, 238.1728).

2-Phenylbenzosuberane (**6a**).—2-Benzosuberone[14] reacted with phenylmagnesium bromide to give 2-phenyl-2-benzosuberol: mp 82–83°; 60% yield; ir (Nujol) 3500 (s), 1495 (s), 1460 (s), 1390 (s), 1180 (m), 1100 (m), 1075 (s), 1015 (s), 778 (m), 725 (s), and 702 cm^{-1} (s); nmr (CCl_4) δ 1.66 [s, 1 H, OH (exchangeable with D when treated with D_2O)], 1.50–2.18 (m, 4 H, C^3H_2-C^4H_2), 2.74–2.98 (m, 2 H, C^5-benzylic), 2.88–3.60 (AB pattern, 2 H, J = 14 Hz, C^1H_2), 6.93–7.63 (m, 4 H, aromatic), and 7.10 ppm (s, 5 H, aromatic). 2-Phenyl-2-benzosuberol was subjected to catalytic hydrogenolysis as before[10a] and the product 2-phenylbenzosuberone (**6a**) was purified by preparative glpc (20 ft × 0.25 in. 30% SE-30 silicone gum rubber column operated at 255° with helium carrier gas at 60 psi) to give a viscous oil: $n^{24}D$ 1.5844 (lit.[15] mp 37–38°); nmr (CCl_4) δ 1.30–2.33 (m, 4 H, $C^3H_2C^4H_2$), 2.42–3.43 [m (ABC pattern), 5 H, benzylic], 7.02 (s, 4 H, aromatic), and 7.16 ppm (s, 5 H, aromatic).

1-Benzyl-3,3-dimethylindan (**7b**) was synthesized by reaction of 3,3-dimethyl-1-indanone[3] with benzylmagnesium chloride followed by catalytic reduction of the intermediate carbinol so obtained by hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid:[10a] bp 180–190° (11 mm); $n^{26.8}D$ 1.5672; nmr (CCl_4) δ 1.07 and 1.28 (both singlets, 6 H, gem methyls), 1.43–3.75 (unresolved, 5 H, all other nonaromatic), and 7.02–7.15 ppm (both singlets in a ratio of 5:4, 9 H, aromatic); mass, calcd for $C_{18}H_{20}$, 236.1565 (found, 236.1570).

1,1-Dimethyl-3-phenyltetralin (**8b**).—This was prepared by H_2SO_4-catalyzed cyclization of the previously obtained 2-methyl-4,5-diphenylpent-1-ene: bp 132–135° (0.27 mm); $n^{26.8}D$ 1.5702; nmr (CCl_4) δ 1.30 and 1.13 (both singlets, 6 H, gem methyls), 1.84 (an apparent doublet, 2 H, C^2H_2), 2.70–3.38 [m with strong singlet at 2.90, 3 H, $CH_2CH(Ph)$], and 6.85–4.70 ppm (m with strong singlet at 7.18, 9 H, aromatic); mass, calcd for $C_{18}H_{20}$, 236.1565 (found, 236.1563).

Registry No.—**1a,** 31444-33-4; **1b,** 31444-34-5; **2b,** 31444-35-6; **3b,** 31444-36-7; **6a,** 2979-01-3; **7b,** 31489-88-0; **8b,** 31444-38-9; **10b,** 31444-39-0; 2-methyl-4,5-diphenylpentan-1-ol, 31489-89-1.

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[12] G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 20 (1958).

[13] K. L. Rinehart, Jr., and E. G. Perkins in "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 444.

[14] T. A. Crabb and K. Schofield, *J. Chem. Soc.*, 4276 (1958).

[15] H. Nozaki, M. Yamabe, and R. Noyori, *Tetrahedron*, **21**, 1657 (1965).

Cyclialkylation of Phenol with 1,5-Hexadiene

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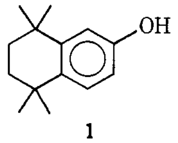
Received February 10, 1971

Phenol and 1,5-hexadiene (**6**) in carbon disulfide (4:1 mole ratio) at 30° react in the presence of boron trifluoride etherate to produce 5,6,7,8-tetrahydro-5,8-dimethyl-1- and -2-naphthol (**7** and **8**) and 2,5-diphenoxyhexane (**9**). A study of this reaction suggests that 5-phenoxy-1-hexene (**12**) and 2-(1-hexen-5-yl)phenol (**13**) are initially formed and react further to produce **9** and **7**, respectively. At longer reaction times, $C_{18}H_{26}O$ products are formed by reaction of **9** with **7** or $C_{12}H_{16}O$ ethers formed from **7**. Direct para alkylation by olefins **6** or **12** is excluded. The major para-alkylated product is formed from the alkylation of phenol with diether **9**.

The Lewis acid catalyzed reaction of phenol with cyclialkylating agents has been characterized by a diversity of products;[1,2] compounds **1–4** have been obtained starting with 2,5-dimethyl-1,5-hexadiene while **2** and **5** have been obtained from 2,5-dichloro-2,5-dimethylhexane.



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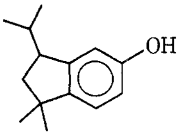

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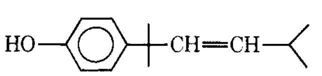

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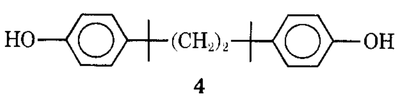

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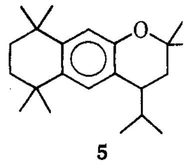

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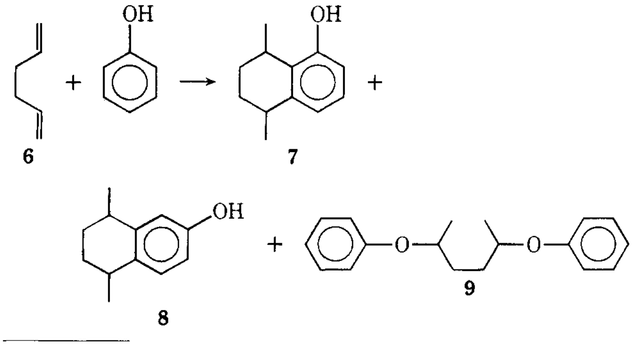
When phenol and 1,5-hexadiene (**6**) (4:1 mole ratio) at 30° reacted in the presence of boron trifluoride etherate for 3 hr, cycliadducts **7** and **8** were recovered in 27 and 8% yields, respectively, based on starting **6**. When the reaction was terminated after 15 min, **7** and diether **9** (25% yield) were the major products.[3] The



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[1] H. A. Bruson and J. W. Kroeger, *J. Amer. Chem. Soc.*, **62**, 36 (1940).

[2] D. G. Jones and P. E. Schick, British Patent 706424 (1954); *Chem. Abstr.*, **49**, 9036*g* (1955).

[3] The identification of new compounds is based on ir and proton nmr spectra in addition to microanalyses: see the Experimental Section.

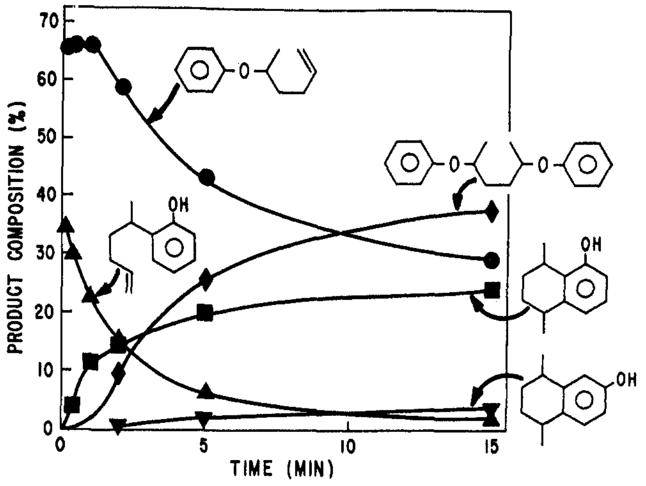
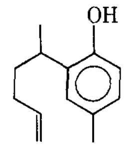


Figure 1.—Product composition from the reaction of phenol and 1,5-hexadiene (6): 0–15 min.

only previously reported cyclialkylation using **6** was performed on *p*-cresol, and led to the formation of **10** in addition to cycliadduct **11**.[4] In view of the com-



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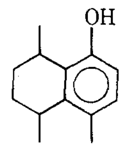
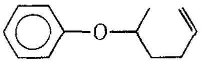


11

plexity of previous cyclialkylations and the fact that the *p*-cresol–**6** reaction is not comparable to the phenol–**6** reaction because of the blocked para position, we have studied the reaction of phenol with **6** in greater detail.

The initial step in elucidating the mechanism of the cyclialkylation was to determine the product distribution *vs.* time. When the reaction was followed by glpc, two substances, one compound **12**[3] and the other probably **13**, were shown to be the initial products formed in a ratio of 1.94 ± 0.20 while additional $C_{12}H_{16}O$ and $C_{18}H_{26}O$ compounds appear later in the reaction.



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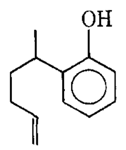


13

The identification of **13**, which is not present in sufficient quantities for isolation, is based on that fact that it is generated from phenol and **6**, it is the precursor of **7** but not **8** (*vide infra*), the glpc retention time is similar to that of **7** and 2-(2-hexyl)phenol, its formation is analogous to that of **10** from *p*-cresol and **6**,[4] and the fact that phenol and 1-hexene under similar conditions produce 2-phenoxyhexane and 2-(2-hexyl)phenol as the initial products[3] in a ratio of 1.56 ± 0.22 with no para-substituted or rearranged products observed.

A plot of product composition *vs.* time is shown in Figures 1 and 2 and, in more detail, in Table I in the Experimental Section. Scheme I depicts the reaction pathways observed in the study of the product composition *vs.* time and studies in which the individual reaction components are isolated and independently reacted with phenol and boron trifluoride etherate in carbon disulfide.

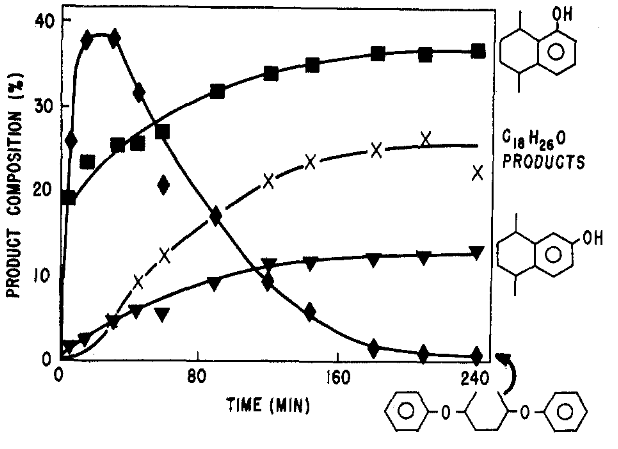
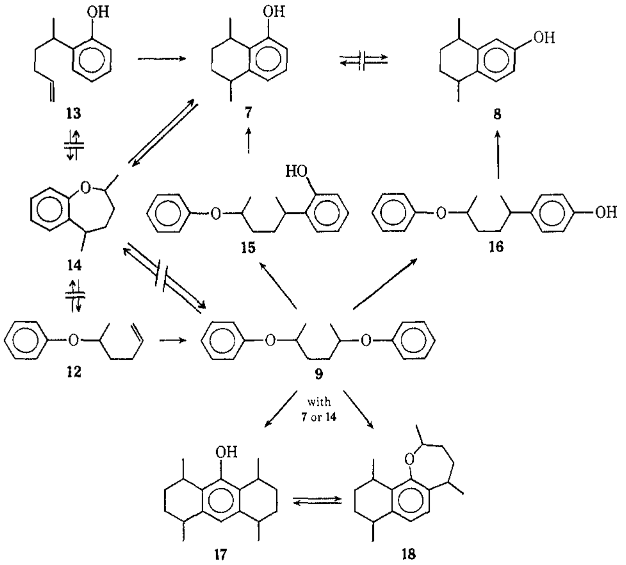


Figure 2.—Product composition from the reaction of phenol and 1,5-hexadiene (6): 0–240 min.

SCHEME I



It appears from an examination of Figure 1 that monoether–monoolefin **12** is the precursor of diether **9** and that the 2,3 cycliadduct **7** is formed from the compound tentatively assigned structure **13**. When **12** is isolated and treated with phenol and boron trifluoride etherate, **9** is the only observable product; small amounts of **7** (*ca.* 0.1% of the amount of **9** after 11% reaction) can be explained as being derived from phenol and **9** (*vide infra*). Therefore, **12** is not a direct precursor of **7**, and a route involving the intermediacy of **14** in a "walk-around" mechanism can be eliminated. By default, **13** is the sole intermediate in the formation of **7** which is observed in the early stages of the reaction.

A similar experiment performed on **7** reveals that it does not isomerize to **8**, but slowly equilibrates with at least four $C_{12}H_{16}O$ ethers (glpc retention times comparable to, but not identical with, that of **12**). While one likely structure is **14**, the structure of these ethers was not investigated further. The fact that 15% of **7** rearranges after 2.5 hr while 22% is isomerized after

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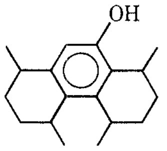
[4] E. A. Viktorova, E. A. Karakhanov, A. N. Shuikin, and N. I. Shuikin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 523 (1966); *Chem. Abstr.*, **65**, 8802a (1966).

20 hr indicates that the conversion to ethers is reversible and that the **7**:**14** equilibrium ratio under these conditions is *ca.* 3.5:1. Compound **8** was shown to be stable in the presence of phenol and boron trifluoride etherate over a period of 20 hr.

When diether **9** is treated with phenol and boron trifluoride etherate, two high-boiling transient products are observed in the ratio of 3.5:1. Subsequently, **7** and **8** are formed in a comparable ratio as the high-boiling compounds diminish. The fact that **7** and **8** are formed from **9** in what must reasonably be a two-step reaction, coupled with the preliminary appearance and subsequent disappearance of the high-boiling compounds, indicates that these transient products probably are intermediates in the conversion of **9** to **7** and **8**. Although isolation was not possible, reasonable tentative structures for these intermediates are **15** and **16**. It should be noted that diether **9** is the only source of the 3,4-cycliadduct **8** in the system.

Two $C_{18}H_{26}O$ products were also observed in this reaction. These compounds were identified as **17** and **18** based on spectral evidence[3] and evidence that (1) **17** equilibrates with **18** on treatment with boron trifluoride etherate in a manner similar to the equilibration of **7** and **14**, (2) **17** and **18** are formed from **7** and/or **14**, and (3) ortho alkylation predominates in this system.

The fact that **19** and **20** would exhibit ir and nmr spectra similar to those of **17** and **18**, coupled with the possibility that they could equilibrate, does not permit their exclusion as possible alternatives to **17** and **18**. It should be noted, however, that in related experiments we have detected steric retardation to 2,3-cyclialkylation when *p*-cresol is used in place of phenol,[5] and this would also argue for the formation of **17** instead of **19**.



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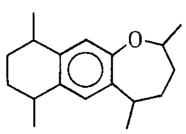

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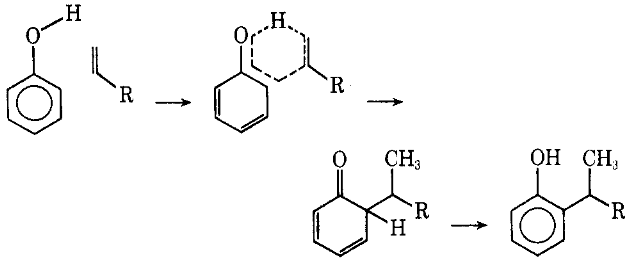
Data from the treatment of **9** with phenol and boron trifluoride etherate also indicates that the availability of **7** and/or **14** appears necessary for the formation of **17** and **18** because the (**7** + **14** + **15**):(**8** + **16**) ratio decreases with time as **17** and **18** are formed.

Although there is no need to invoke the alkylation of **8** in the formation of **17** and **18**, this experiment does not rule out the possibility of such a path, but indicates that the **9**–**7** and/or **14** reaction is the major secondary reaction leading to $C_{18}H_{26}O$ products.

The observation of exclusive ortho alkylation of the phenol ring by an olefin may appear unusual only because little work has been done on the kinetic alkylation which would separate direct alkylation by an olefin and secondary alkylation by an alkyl phenyl ether. Direct ortho alkylation by an olefin has been reported for thermal reactions[6] and reactions catalyzed by boron trifluoride[7] and aluminum phenolate.[8] The mechanism previously suggested[6,8] pictures the reaction proceeding through a six-center transition state assisted by Lewis acid coordination at oxygen and possibly at the double bond.



In conclusion, it has been shown that phenol and 1,5-hexadiene (**6**) react in the presence of boron trifluoride etherate to produce 5-phenoxy-1-hexene (**12**) and a transient intermediate tentatively identified as 2-(1-hexen-5-yl)phenol (**13**) which further react to give 2,5-diphenoxyhexane (**9**) and 5,6,7,8-tetrahydro-5,8-dimethyl-1-naphthol (**7**), respectively. Direct para alkylation by olefins **6** or **12** is excluded; the major para-alkylated product (**8**) is formed from the alkylation of phenol with diether **9**.

Experimental Section

Methods.—Proton nmr spectra were recorded on a Varian A-56/60 spectrometer and chemical shifts are reported in parts per million downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer. Spectra and elemental analyses were obtained from the Analytical Laboratory of Corporate Chemical Research, Allied Chemical Corp.

All reagents were obtained from Baker and Adamson or Aldrich, and were used as received.

Unless specifically mentioned, no evidence was obtained to indicate the presence of more than one stereoisomer or diastereoisomer in any structure mentioned; on the other hand, the presence of more than one isomer, or isomer fractionation during work-ups, cannot be discounted.

Phenol and 6 (3 Hr).—A solution of 376 g (4.00 mol) of phenol, 82 g (1.00 mol) of **6**, and 20 ml of boron trifluoride etherate in 500 ml of carbon disulfide was stirred at 30° for 3 hr and then poured onto ice water. The organic phase was separated and dried (Na_2SO_4), and the products were fractionated by distillation through a 15-cm Vigreux column. In addition to recovered phenol, there was obtained 20 g, bp 45–70° (0.4 mm), 51 g, bp 70–100° (0.4 mm), and 29 g, bp 100–150° (0.4 mm).

Redistillation of the first fraction afforded 14 g (7% yield based on starting 1,5-hexadiene) of clear liquid, bp 56–62° (0.4 mm), identified as isomeric $C_{12}H_{16}O$ ethers (*e.g.*, **14**): nmr ($CDCl_3$) δ 0.8–1.9 (m, 10, CH_3 and CH_2, characterized by a pair of d centered at 1.23 and 1.27; J = 7.0 and 6.0 Hz, respectively, indicating the predominance of a seven-membered ring as in **14**), 2.40–3.08 (m, 1, ArCH), 3.35–4.15 (m, 1, ArOCH), and 6.65–7.20 ppm (m, 4, ArH); ir (neat) 750 (1,2-disubstituted aromatic) and 1238 cm^{-1} (Ar–O); no O–H was observed.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.84; H, 9.35.

Redistillation of the 70–100° (0.4 mm) fraction afforded 47.5 g (27% yield based on starting **6**) of clear liquid, bp 85–86° (0.4 mm), identified as 5,6,7,8-tetrahydro-5,8-dimethyl-1-naphthol (**7**): nmr (CCl_4) δ 1.2 (pair of d, 6, J = 7 Hz, CH_3), 1.3–2.2 (m, 4, CH_2), 2.6–3.3 (m, 2, ArCH), 5.16 (s, 1, OH), and 6.2–7.0 ppm (m, 3, ArH);[9] ir (neat) 740, 790 (1,2,3-trisubstituted aromatic), 1270 (Ar–O), and 3400 cm^{-1} (O–H).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.67; H, 8.91.

The 100–150° (0.4 mm) fraction was dissolved in 200 ml of

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[5] J. M. Balquist, unpublished results.

[6] R. G. Anderson and S. H. Sharman, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, **15**, (2), E-27 (1970).

[7] F. J. Sowa, H. D. Hinton, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **54**, 3694 (1932).

[8] R. Stroh, R. Seydel, and W. Hahn, "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press, New York, N. Y., 1963, p 337.

[9] Aromatic pattern similar to that of 5,6,7,8-tetrahydro-1-naphthol; Sadtler nmr spectrum 2694M.

TABLE I

PRODUCT COMPOSITION FROM PHENOL AND 1,5-HEXADIENE (**6**)

Time, min	Unreacted phenol, %	Product composition, %, excluding phenol							
		7	**8**	**9**	**12**	**13**	**17** and **18**	$C_{12}H_{16}O$ ethers	Higher boiling products
0.08	99.9	0.0	0.0	0.0	65.5	34.5	0.0	0.0	0.0
0.33	99.4	4.1	0.0	0.0	66.0	29.8	0.0	0.0	0.0
1	97.8	11.5	0.0	0.0	66.2	22.4	0.0	0.0	0.0
2	91.2	14.0	0.1	9.5	58.5	15.6	0.0	2.3	0.0
5	82.3	19.8	1.8	25.9	43.3	6.2	0.0	3.0	0.0
15	81.5	23.7	2.7	37.7	29.2	2.0	0.0	4.0	0.0
30	79.0	25.7	4.7	38.3	17.0	0.0	4.7	4.2	3.3
45	76.2	25.5	6.0	31.7	14.0	0.0	9.8	4.7	6.7
60	74.1	28.2	5.6	20.5	11.5	0.0	12.6	5.8	6.8
90	78.0	31.9	9.2	17.7	9.6	0.0	17.1	5.6	6.7
120	78.7	34.0	11.2	9.2	8.9	0.0	21.8	6.5	5.6
150	81.0	34.6	11.4	6.3	7.8	0.0	23.0	7.8	6.6
180	80.3	36.7	12.0	1.5	8.5	0.0	25.0	7.8	6.5
210	79.0	36.0	12.5	1.4	7.6	0.0	26.6	8.3	3.8
240	81.0	36.8	13.2	0.9	7.3	0.0	22.2	8.4	8.4
1260	79.0	39.6	13.2	0.0	4.3	0.0	26.1	6.5	8.4

ether and extracted with five 100-ml portions of 10% aqueous sodium hydroxide. The aqueous phase was acidified with hydrochloric acid and the acidic water layer was extracted with two 100-ml portions of ether. The ether solution was dried (Na_2SO_4) and distilled to give 15.8 g (8%) of clear liquid, bp 108–109° (0.4 mm) identified as 5,6,7,8-tetrahydro-5,8-dimethyl-2-naphthol (**8**): nmr (CCl_4) δ 1.2 (paired d, 6, J = 7 Hz, CH_3), 1.3–2.2 (m, 4, CH_2), 2.4–3.1 (m, 2, ArCH), 6.0 (s, 1, OH), and 6.4–7.1 ppm (m, 3, ArH);[10] ir (neat) 813 (1,2,4-trisubstituted aromatic), 1242 (Ar–O), and 3370 cm^{-1} (O–H).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.06; H, 9.21.

2,5-Diphenoxyhexane (9).—When the above reaction (0.25 scale) was terminated after 15 min and the organic phase extracted with five 500-ml portions of 10% aqueous sodium hydroxide, distillation of the dried (Na_2SO_4) organic phase afforded 13.2 g of yellow liquid, bp 140–150° (0.5 mm). Recrystallization of this liquid from methanol afforded 8.1 g (25%) of white crystals, mp 68–72°, identified as 2,5-diphenoxyhexane (**9**). Further purification afforded an analytical sample: mp 74–76°; nmr ($CDCl_3$) δ 1.3 (d, 6, J = 7 Hz, CH_3), 1.8 (m, 4, CH_2), 4.1–4.6 (m, 2, CH), and 6.7–7.5 ppm (m, 10, ArH); ir (KBr) 685, 750 (monosubstituted aromatic), and 1240 cm^{-1} (Ar–O); no O–H was observed.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.78; H, 8.34.

5-Phenoxy-1-hexene (12).—A solution of 32.5 g (0.35 mol) of phenol, 20.7 g (0.25 mol) of **6**, 6 ml of boron trifluoride etherate, and 40 ml of carbon disulfide was stirred at 30° for 5 min and poured onto ice water; the organic phase was separated and extracted with five 100-ml portions of 10% aqueous sodium hydroxide solution. The organic phase was dried (Na_2SO_4) and distilled to give 2.5 g (6%) of clear liquid, bp 55° (0.4 mm), identified as 5-phenoxy-1-hexene (**12**): nmr ($CDCl_3$) δ 1.2 (d, 3, J = 6 Hz, CH_3), 1.5–1.9 (m, 2, aliphatic CH_2), 1.9–2.4 (m, 2, allylic CH_2), 4.3 (hextet, 1, J = 6 Hz, OCH), 4.7–5.2 (m, 2, $CH{=}CH_2$), 5.4–6.2 (m, 1, $CH{=}CH_2$), and 6.6–7.4 ppm (m, 5, ArH); ir (neat) 690, 750 (monosubstituted aromatic), 1240 (Ar–O), and 910, 995, 1643, 3020, and 3070 cm^{-1} (vinyl).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.99; H, 9.32.

1,2,3,4,5,6,7,8-Octahydro-1,4,5,8-tetramethyl-9-anthranol (17) and $C_{18}H_{26}O$ Ethers.—A solution of 164 g (2.00 mol) of 1,5-hexadiene and 94 g (1.00 mol) of phenol in 350 ml of carbon disulfide was treated with 20 ml of boron trifluoride etherate and stirred at 25–30° for 6 hr. The solution was cooled, diluted with 500 ml of ether, and extracted with five 250-ml portions of 10% aqueous sodium hydroxide solution; the organic phase was separated, dried (Na_2SO_4), and distilled. The 56-g fraction, bp 100–160° (1.0 mm), was carefully redistilled to give 42 g of yellow liquid, bp 120–130° (0.1 mm).

The yellow liquid was dissolved in 200 ml of hexane and chromatographed on a 4.2 × 60 cm column of silica gel and eluted with 10% chloroform in hexane. The first 300-ml fraction was discarded; the next 1500 ml was concentrated to dryness and crystallized from 25 ml of hexane at −20° to afford 5.3 g (2.1%) of a yellow powder, mp 141–144° after filtration. Further recrystallization afforded an analytical sample, mp 144–145°, identified as 1,2,3,4,5,6,7,8-tetrahydro-1,4,5,8-tetramethyl-9-anthranol (**17**): nmr (CCl_4) δ 1.18 (d, 12, J = 7.0 Hz, $CHCH_3$), 1.30–2.18 (m, 8, CH_2), 2.55–3.14 (m, 4, ArCH), 4.44 (s, 1, OH), and 6.40 ppm (s, 1, ArH); ir (KBr) 868 (pentasubsituted aromatic), 1120–1235 (several absorptions which could be ascribed to Ar—O), and 3160 cm^{-1} (O–H).

Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.64; H, 10.25.

The mother liquor from the initial crystallization of **17** was concentrated and redistilled to give 6.2 g (3.0%) of a pale yellow liquid identified as an isomeric mixture of $C_{18}H_{26}O$ ethers: nmr ($CDCl_3$) δ 1.15–2.20 (m, 20, CH_2 and CH_3), 2.6–3.1 (m, 3, ArCH), 3.3–4.2 (m, 1, ArOCH), and 6.7–7.2 ppm (m, 2, ArH); ir (neat) 810 (1,2,3,4-tetrasubstituted aromatic) and 1200–1250 cm^{-1} (several absorptions which could be Ar–O); a medium band at 863 cm^{-1} might be due to 1,2,4,5-tetrasubstituted aromatic absorptions. The aliphatic nmr pattern and the glpc peak width indicate that this fraction probably is a mixture.

Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.60; H, 10.04.

Compound **17** is soluble in Claisen's alkali,[11] and extraction of a hexane solution of **17** and $C_{18}H_{26}O$ ethers represents another method of separating **17** from the ethers.

Phenol and 6. Product Composition *vs.* Time.—A solution of 31.6 g (0.336 mol) of phenol, 6.9 g (0.084 mol) of **6**, and 40 ml of carbon disulfide was heated to 30° by means of an oil bath, and 6 ml of boron trifluoride etherate was added; 2 ml aliquots were periodically removed, poured onto 20 ml of water, and shaken; and the organic phase was separated and analyzed by glpc on a 5 ft × 0.25 in. copper tube packed with 5% Triton X-100 on 45–50 mesh Chromosorb W inserted into an F & M Model 720 dual column gas chromatograph programmed at 8°/min starting at 60°. A type W weight-sensitive thermal conductivity detector was used, and therefore the reported percentages are weight per cent. Using a He flow of 60 cc/min, the following retention times (compound) were obtained: 5.5–8.0 ($C_{12}H_{16}O$ ethers), 6.5 (**12**), 9.2 (phenol), 18.6 (**13**), 20.3 (**7**), 22.2 (**8**), 24.3 (**9**), and 25.0–26.1 min (**17** and **18**).

The results are shown in Table I; peak areas are normalized to 100% after excluding phenol and carbon disulfide. In cases where there are traces of additional compounds, the products shown would not total 100%. For the purpose of this experiment

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(10) Aromatic pattern similar to that of 3,4-dimethylphenol; Sadtler nmr spectrum 193M.

(11) For previous observations of the solubility of hindered ortho-disubstituted phenols in Claisen's alkali (*ca.* 35% aqueous methanolic potassium hydroxide, see ref 8, p 354. We thank a referee for suggesting this experiment.

all observable peaks with retention times longer than 26.1 min are listed as "higher boiling products."

Reactions at times shorter than 1 min were performed individually in a 25-ml beaker using 0.8 g of **6**, 3.0 g of phenol, and 5 ml of carbon disulfide. T_0 was taken as the time at which 1 ml of boron trifluoride etherate was added rapidly; the reaction was quenched when 10 ml of water was added rapidly. The reaction was then worked up as before.

Treatment of 7, 8, 9, 12, and 17 with Phenol and Boron Trifluoride Etherate.—A solution of 1.0 g of either **7**, **8**, **9**, **12**, or **17**, 5.0 g of phenol, and 15 ml of carbon disulfide was heated to 30°; 1 m of boron trifluoride etherate was added, and 2 ml aliquots were removed, quenched, and analyzed as before. The compounds tentatively identified as **15** and **16** were observed at 29.9 and 32.2 min, respectively, under the glpc conditions previously described. The percentages of the products from **7–9** and **12**, excluding phenol and carbon disulfide, are shown in Table II.

TABLE II

Compound **7**

Time, min	**7**	$C_{12}H_{16}O$ ethers[a]
150	84.8	15.2
1200	78.2	21.8

Compound **8**

Chromatographs recorded at 5, 15, 30, 90, 180, and 1200 min revealed **8** as the only compound excluding phenol

Compound **9**

Time, min	**7**	**8**	**9**	**15**
5	1.0	0.2	94.8	3.5
15	5.2	1.5	85.7	5.5
30	15.2	4.8	79.3	0.0
150	41.6	19.9	20.0	0.0

Time, min	**16**	**17** and **18**	$C_{12}H_{16}O$ ethers[b]
5	0.5	0.0	0.0
15	1.8	0.0	0.6
30	0.0	0.0	0.7
150	0.0	8.8	5.9

Compound **12**

Time, min	**7**	**9**	**12**
1	0.1	10.9	89.0
2	0.4	20.5	79.1
5	1.2	32.6	66.2

[a] A minimum of four peaks were observed; the peak corresponding to **12** was not observed. [b] Compound **12** is not present.

Compound 17.—Treatment of **17** leads to an equilibration of **17** with $C_{18}H_{26}O$ ethers in a reaction comparable to the equilibration of **7** with $C_{12}H_{16}O$ ethers. The appearance of a new ir absorption at 810 cm^{-1} indicates that the predominant substitution pattern of the ethers is 1,2,3,4 (as shown in **18**) although a band at 868 cm^{-1} could obscure the 1,2,4,5-tetrasubstitution pattern. The compounds could not be resolved by glpc.

Phenol and 1-Hexene.—A solution of 94 g (1.00 mol) of phenol, 28 g (0.33 mol) of 1-hexene, 6 ml of boron trifluoride etherate, and 100 ml of carbon disulfide was stirred at 30° for 30 min, and poured onto 200 ml of ice water; the organic phase was separated, washed with three 200-ml portions of 10% aqueous sodium hydroxide solution, and dried (Na_2SO_4). Distillation of the organic phase afforded 15 g of clear liquid, bp 71–73° (0.8 mm), 11.5 g, bp 74–92° (0.8 mm), and 3.6 g of clear liquid, bp 93–94° (0.8 mm).

The fraction with bp 71–73° (0.8 mm) is identified as 2-phenoxyhexane: nmr (neat) δ 0.7–1.1 (m, 3, CH_2CH_3), 1.1–1.8 (m, 9, aliphatic H with $OCHCH_3$ at 1.16, d, J = 6 Hz), 3.9–4.4 (sextet, 1, J = 6 Hz, OCH), and 6.6–7.3 ppm (m, 5, ArH); ir (neat) 692, 750 (monosubstituted aromatic), and 1235 cm^{-1} (Ar–O).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.92; H, 10.30.

The fraction with bp 93–94° (0.8 mm) is identified as 2-(2-hexyl)phenol: nmr (CCl_4) δ 0.7–1.0 (m, 3, CH_2CH_3), 1.0–1.8 (m, 9, aliphatic H with $ArCHCH_3$ at 1.27, d, J = 7 Hz), 2.8–3.3 (q, 1, J = 7 Hz, ArCH), 5.55 (broad s, 1, OH), and 6.7–7.2 ppm (m, 4, ArH); ir (neat) 750 (1,2-disubstituted aromatic), 1220 (Ar–O), and 3400 cm^{-1} (O–H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.86; H, 10.28.

Phenol and 1-Hexene. Product Composition *vs.* Time.—A solution of 15.8 g (0.17 mol) of phenol, 3.4 g (0.04 mol) of 1-hexene, and 40 ml of carbon disulfide was heated to 30°; 3 ml of boron trifluoride etherate was added and 2-ml aliquots were periodically removed, quenched, and analyzed as before. 2-Phenoxyhexane and 2-(2-hexyl)phenol (retention times 6.2 and 15.4 min, respectively, under conditions previously described) were the only products observed over a period of 10 min.

Time, min	2-Phenoxyhexane, %	2-(2-Hexyl)phenol, %
1	57.0	43.0
2	60.5	39.5
10	65.4	34.6

Registry No.—**6**, 592-42-7; **7**, 31382-69-1; **8**, 31382-70-4; **9**, 31382-71-5; **12**, 31382-72-6; **13**, 31382-73-7; **14**, 31376-80-4; **17**, 31428-90-7; **18**, 31376-81-5; phenol, 108-95-2.

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