hexanone-2,2,6,6-d_4. Both the preparation of the p-toluenesulfonate ester and lithium aluminum deuteride reduction of the ester were accomplished as described above for **1e**.

Mass-spectrometric analysis showed 0.5% d_0 and 3.7% d_1 compounds as contaminants.

Thermal Rearrangement of o-Methyldiaryl Ethers

ARNOLD FACTOR, HERMAN FINKBEINER, ROBERT A. JERUSSI, AND DWAIN M. WHITE

General Electric Research and Development Center, Schenectady, New York 12301

o-Methyldiaryl ethers have been found to rearrange to o-benzylphenols at elevated temperatures. For example, 2,6-dimethylphenyl phenyl ether (**1**) cleanly rearranges at 370° under vacuum to 2-benzyl-6-methylphenol (**2**) with 4-methylxanthene (**3**) as a minor side product. The reaction may have general synthetic utility for the production of o-benzylphenols. These o-benzylphenols appear to be formed by an intramolecular free-radical reaction in which the benzyl methylene group occupies the aryl position originally attached to oxygen. The formation of both o-benzylphenols and xanthenes was catalyzed by oxidizing agents such as sulfur. A chain mechanism is proposed for this rearrangement reaction.

The ether linkage of aryl ethers is considered one of the more stable chemical bonds. Phenyl ether is unaffected by hydrogen iodide at 250°[1] and only slowly attacked by sodium hydroxide at 300°.[2] Effective cleavage of the ether bond requires such vigorous reagents as alkali metals in refluxing pyridine[3] or sodium in liquid ammonia.[4] In fact, the extreme stability of phenyl ethers has made them important heat-exchange fluids and high-temperature lubricants.[5]

Recent studies[6-9] indicate that this thermal stability is also characteristic of poly(2,6-dimethyl-1,4-phenylene ether). However, at very high temperatures (>400°), poly(2,6-dimethyl-1,4-phenylene ether) undergoes an exothermic decomposition.[6] In the course of studying this decomposition, changes in the nuclear magnetic resonance spectrum were observed that suggested the formation of diphenyl methylene groups. Since structural characterization of high polymers is notoriously difficult, model compounds were studied.

The model compound initially chosen was 2,6-dimethylphenyl phenyl ether (**1**). When **1** was heated at 370° for 23 hr, changes in the nmr spectrum similar to those observed with polymer occurred. The two products detected by vapor phase chromatography were identified as 2-benzyl-6-methylphenol (**2**) and 4-methylxanthene (**3**) (eq 1). Further investigation

was warranted, since the migration of a phenyl group from oxygen to a saturated carbon had not previously been reported and the study of rearrangement reactions has often been significant in revealing new mechanistic paths.

Results

A series of aryl ethers have been examined to determine the scope of the rearrangement and to obtain information about the mechanism of the reaction. Table I shows the results obtained with six of the aryl ethers that have been examined. This reaction appears to be in a unique class, since prolonged reactions at high temperatures usually produce such a myriad of products that they have no synthetic utility. However, in these cases, the reaction mixture consisted of only three components: starting material, the corresponding phenol from rearrangement, and the xanthene.

The structures of the o-benzylphenols reported in Table I were confirmed by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. These compounds show a characteristic band at 3520–3540 cm⁻¹ in their infrared spectra due to a π-bonded phenolic OH, and, except for the major product from **7**, an nmr peak at τ 6.2–6.4 (diaryl methane group). The 2-diphenylmethyl-6-methylphenol (**14**) derived from **7** showed an nmr peak at τ 4.4 (triarylmethyl proton). The products from **5**, **6**, **7**, and **8** are new compounds and their structures were confirmed by comparison with authentic compounds synthesized by alkylation of the appropriate phenols with benzyl chlorides.

1

   2   **3**   (1)
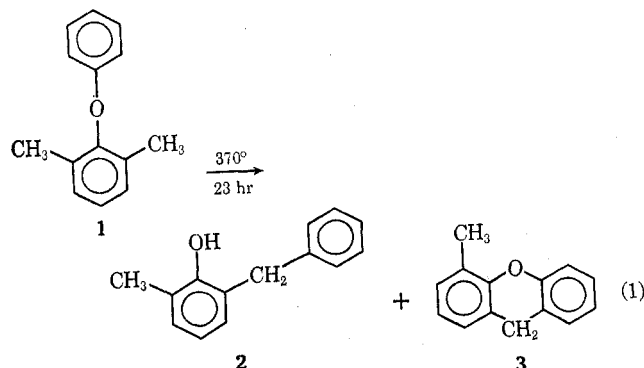
(1) N. Orlon and W. Ipatieff, *Chem. Ber.*, **60**, 1966 (1927).
(2) K. H. Meyer and F. Bergius, *ibid.*, **47**, 3158 (1914).

(3) V. Prey, *ibid.*, **76**, 156 (1943).
(4) P. A. Sartoretto and F. J. Sowa, *J. Amer. Chem. Soc.*, **59**, 608 (1937).
(5) C. L. Mahoney and E. R. Barnum, "Synthetic Lubricants," R. C. Gunderson and A. W. Hart, Ed., Reinhold Publishing Co., New York, N. Y., 1962, Chapter 11.
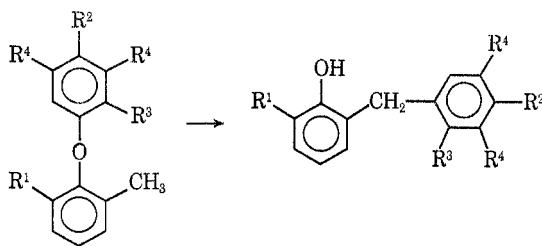(6) A. Factor, *J. Polym. Sci., Part A-1*, **7**, 363 (1969).
(7) F. E. Karasz and J. M. O'Reilly, *Polymer Lett.*, **3**, 561 (1965).
(8) H. E. Hoyt, B. D. Halpern, K. C. Tsou, M. Bodnar, and W. Tannar, *J. Appl. Polym. Sci.*, **8**, 1633 (1964).
(9) R. T. Conley and W. M. Alvino, Organic Coatings and Plastics Chemistry Preprints, No. 2, Vol. 25, 1965, p 149.

TABLE I

Starting ether	R¹	R²	R³	R⁴	Temp, °C	Time, hr	Yield, %	Conversion, %
1	CH_3	H	H	H	370	23	70	95
4	H	H	H	H	370	4	15	95
5	CH_3	OCH_3	H	CH_3	370	5	50	55
6	C_6H_5	H	H	H	370	18	50[a]	85
7	$CH_2C_6H_5$	H	H	H	320	15	50[b]	55
8	H	H	CH_3	H	370	4	40	80

[a] A trace of sulfur was used to initiate the reaction. [b] 50% 2-diphenylmethyl-6-methylphenol (14) and 10% 2,6-dibenzylphenol (15).

In all the reactions in Table I, vapor phase chromatography showed material at retention times where xanthenes were expected; however, only in the cases of the products from ethers 1, 4, and 8 were xanthenes isolated and identified. In the case of compound 4, xanthene was formed, as shown by comparison with an authentic sample. The xanthene from compound 8 was shown to be 4-methylxanthene (3), the same xanthene formed from 2,6-dimethylphenyl phenyl ether (eq 2).
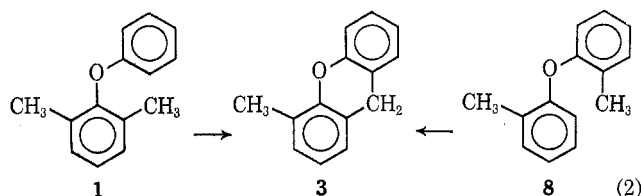

It was possible that these xanthenes were formed from 2-benzylphenols. The reaction of di-o-tolyl ether (8) rules out this possibility. If 2-(2-methylbenzyl)phenol (9) were an intermediate, 1-methylxanthene (10) rather than 4-methylxanthene (3) would have been found. (Compare eq 2 and 3.)
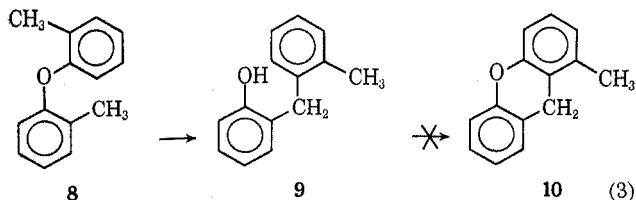
Since 4-methylxanthene (3) was a minor product in the rearrangement of 1, it was possible that the xanthene 3 opened to form 2-benzyl-6-methylphenol (2) as shown in eq 4. This is not the case, for the product from compound 5 was 2-(3,5-dimethyl-4-methoxybenzyl)-6-methylphenol (11) and the product from compound 8 was 2-(2-methylbenzyl)phenol (9), show-

ing that the benzyl methylene group occupied the aryl position originally attached to oxygen (eq 5 and 6).
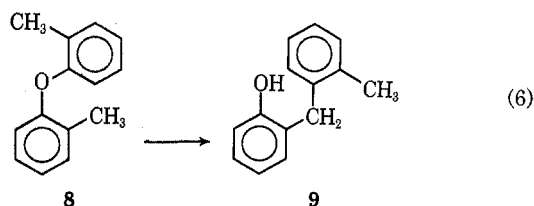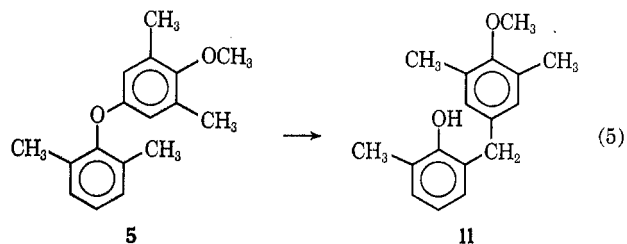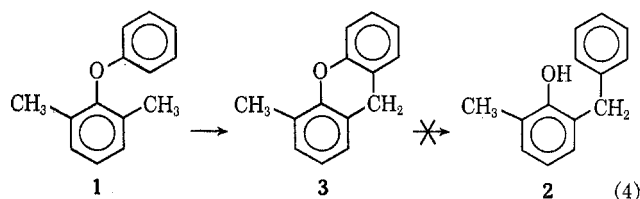
Compounds 4 and 8 showed that, even with an open *ortho* position, the phenyl group migrated to the methyl carbon, establishing that this reaction was not a simple variant of the well-known rearrangement of phenyl ether to o-phenylphenol[10] (eq 6 and 7).

Compound 6 was prepared and rearranged to determine if the phenyl group would migrate exclusively to an aliphatic carbon or if an aryl group *ortho* to the ether linkage would compete. The only phenolic product obtained was 2-benzyl-6-phenylphenol (13) (eq 8). Compound 7 established that a phenyl-substituted o-methyl group was considerably more reactive than an unsubstituted o-methyl group, for the product

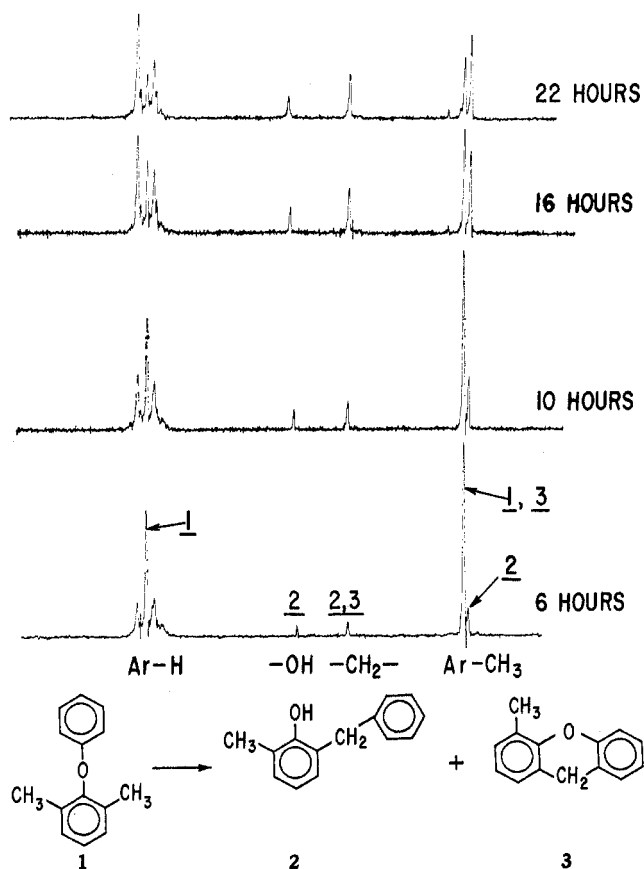(10) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

Figure 2.—The rate of rearrangement of 2,6-dimethylphenyl phenyl ether, Ⓐ; original sample, Ⓑ; further recrystallization, Ⓒ, ~2% sulfur.

The rearrangement was shown to be intramolecular by heating a mixture of o-tolyl ether (8) and 2,6-dimethylphenyl phenyl ether (1) for 18 hr at 370°. Although the rearrangement rates are similar, no cross products were observed (eq 10).

Figure 1.—A time study of the rearrangement of 2,6-dimethylphenyl phenyl ether at 370°. The peaks are labeled as being due to **1**, **2**, or **3** respectively. It was not possible to include a standard; so peak positions are not given.

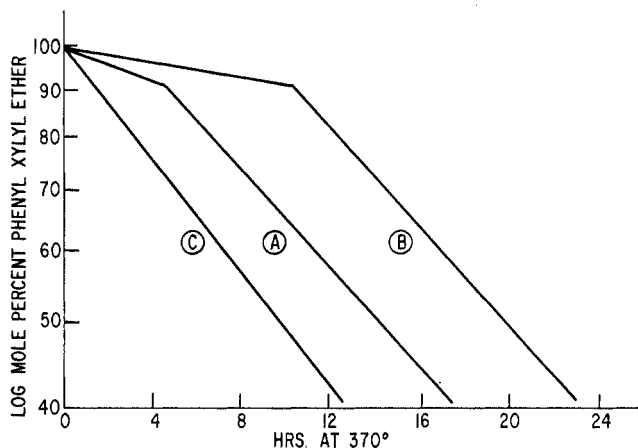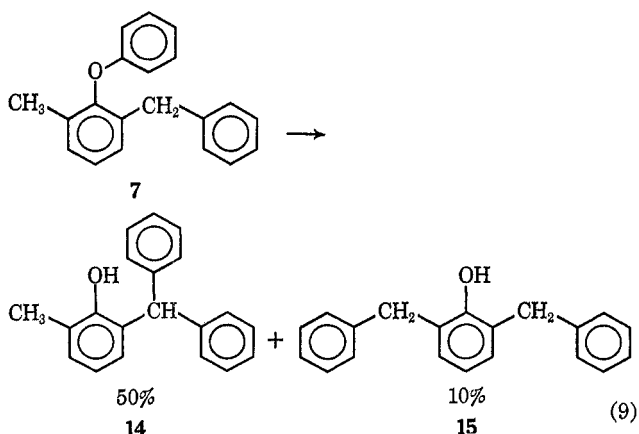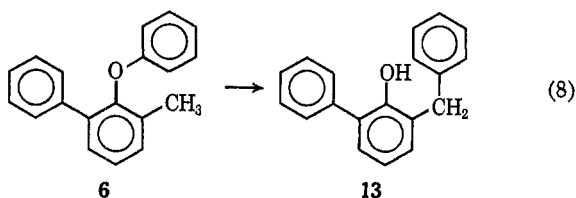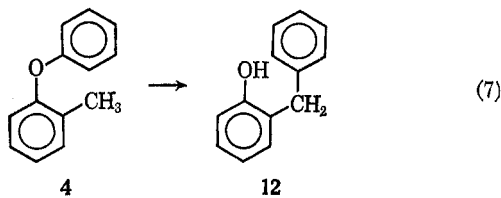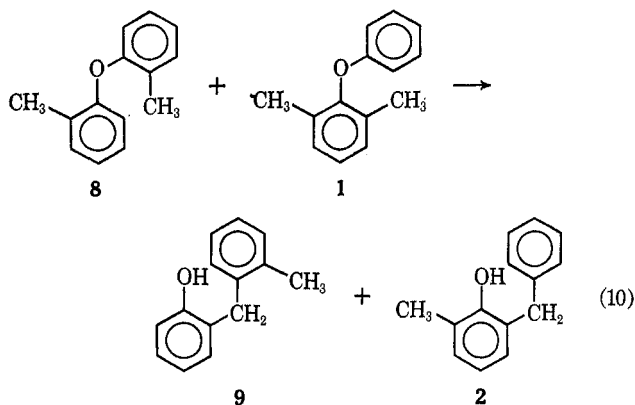was largely 2-diphenylmethyl-6-methylphenol (14) (eq 9).[11]

The reaction does not appear to proceed by prior cleavage of the ether bond, since neither 3-methylphenyl phenyl ether (16) nor 4-methylphenyl phenyl ether (17) rearranged.
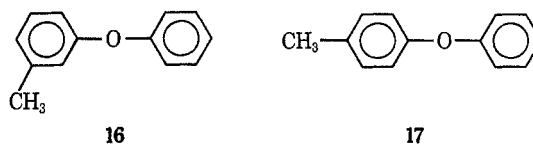
The rate of reaction of compound 1 was followed by simultaneously heating several samples and periodically analyzing a sample by vapor phase chromatography; or, more simply, by running the reaction in an evacuated, heavy-walled nmr tube and analyzing by nmr spectroscopy. Figure 1 shows the changes that occur in the nmr spectrum of a sample of 2,6-dimethylphenyl phenyl ether (1). New peaks appear due to products 2 and 3 at the expense of 1. The data obtained from the nmr spectra were integrated, and after solving the simultaneous equations, plotted as shown in curve A of Figure 2. Purification of compound 1 by recrystallization approximately doubled the inhibition period, as

(11) The ratio of **14:15** varied with reaction temperature; *e.g.*, at 370° the ratio was 5:1 while at 350° it was 10:1.

Figure 3.—Esr spectrum of 2-Benzyl-6-methylphenyl phenyl ether (7) after 30 hr at 300°.

shown in curve B. In both cases the ultimate rate was the same.[12]
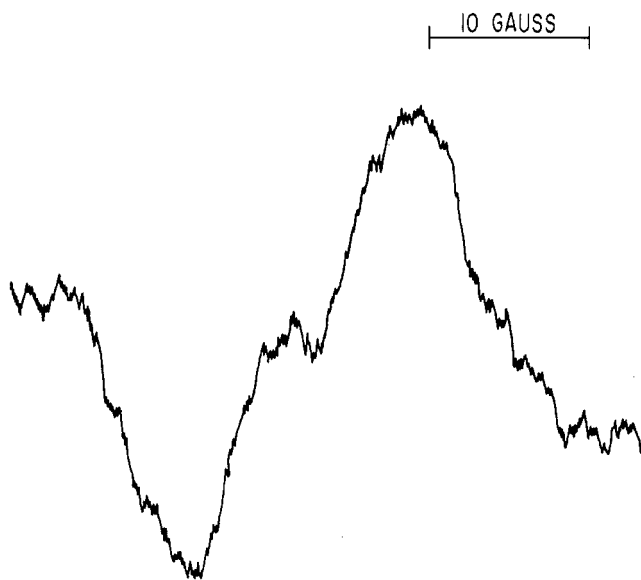
Since the reaction showed an inhibition period which increased on further purification, an attempt was made to determine the nature of the rate-accelerating impurities. A number of acids, bases, reducing agents, and oxidizing agents were examined.

The formation of xanthene and the rearrangement reaction were found to be generally unaffected by reducing agents, metals, bases, organic acids, or glass wool. However, oxidizing agents such as selenium dioxide, sulfuric acid, oxygen, and sulfur had a pronounced effect on the reaction. Curve C (Figure 2) shows the effect of 2% sulfur on the pyrolysis of 2,6-dimethylphenyl phenyl ether (1).

Table II shows the results of a study of the effect of sulfur on the yield of products and their distribution in the rearrangement of 2,6-dimethylphenyl phenyl ether (1) at 370° for 1.5 hr. The addition of even a small amount of sulfur increases the yields of both 2 and 3. With the addition of increasing amounts of sulfur, xanthene (3), a minor product in the uncatalyzed reaction (eq 1), becomes the major reaction product. This increase in xanthene formation is accompanied by unknown side reactions, as indicated by the drop in the total yield of identified products.

The increased yield of xanthene was not due to oxidation of phenol 2 by sulfur, in analogy to eq 3, for heating compound 2 with sulfur for 4 hr at 370° gave only a trace amount of 4-methylxanthene (3).

The inhibition period and its disappearance on adding oxidizing agents may be attributed to an autocatalytic process. However, the abrupt slope change which characterizes the inhibition is unlike the "S"-shape curve expected for an autocatalytic process but more like the inhibition period often found in free-radical chain reactions.

Evidence for the presence of free radicals was found in the rearrangement of ether 7. An esr signal was detected when 7 was heated at 300° to 60% conversion in the cavity of an esr spectrometer. The spectrum, shown in Figure 3, was quite weak. The g value was approximately 2.0; more accurate measurement was not possible because of the high temperature employed. Other ethers did not show a signal. However, as indicated in Table I, only ether 7 is reactive at 300°, the maximum temperature attainable in the apparatus.

Additional support for the intermediacy of radicals was given by mass spectrometric detection of trace amounts of hydrogen and methane in the reaction of compound 1. For example, 0.3% hydrogen and 0.06% methane were detected after ether 1 was heated at 370° for 8 hr.

Discussion

To our knowledge, this is the first example of migration of an aromatic group from oxygen to an aliphatic carbon. Although the reaction bears some resemblance to the rearrangement of alkyl-substituted aryl sulfones studied by Truce[13] (eq 11), an attempted reaction of 1

$$\text{(11)}$$
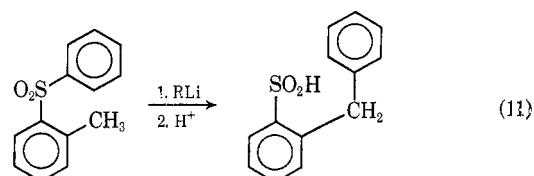
under the conditions used by Truce failed to give any rearrangement.

In view of the above evidence, the mechanism appears to be a radical process initiated by abstraction of a hydrogen atom from a methyl group by an impurity. The benzyl radical generated rearranges to a phenoxy radical, which abstracts hydrogen from another molecule of starting ether to continue the chain reaction.

TABLE II

EFFECT OF SULFUR ON THE REACTION OF 2,6-DIMETHYLPHENYL PHENYL ETHER (1) AT 370° FOR 1.5 HR UNDER VACUUM

Sulfur, wt %	2,6-Dimethylphenyl phenyl ether (1)	2-Methyl-6-benzyl-phenol (2)	4-Methyl-xanthene (3)	Total
0	98	2		100
2	68	16	9	93
8	38	15	22	75
16	25	13	36	74
32	12	7	19	38

ᵃ Analysis made by vapor phase chromatography.

(12) In a determination of the temperature effect, the final reaction rate at 370° was found to be six times faster than at 350°, corresponding to an E_a of ca. 75 kcal/mol.

(13) W. E. Truce, W. J. Ray, O. L. Norman, and D. B. Eickemeyer, *J. Amer. Chem. Soc.*, 80, 3625 (1958); W. E. Truce and W. J. Ray, *ibid.*, 81, 481, 484 (1959).

Oxidation of the benzyl radical to a carbonium ion followed by ring closure produces the xanthene. In the presence of an oxidant, such as sulfur, the oxidation of the benzyl radical is more extensive and larger amounts of xanthene result. Dewar has recently proposed oxidation of a benzyl radical to a carbonium ion by manganic acetate.[14]

Long-range migrations of a phenyl group under free-radical conditions have been postulated in the past, such as 1,5-phenyl migration in the homolysis of di-o-phenoxybenzoyl peroxide[15] and 1,4-phenyl rearrangement in the decarbonylation of 5-methyl-5-phenyl-hexanal.[16]

The electrolysis of 3,3,3-triphenylpropionic acid[17] in methanol to form the phenyl ester of 3,3-diphenyl-3-methoxypropionic acid involves a 1,4-phenyl migration.

In all of these rearrangement reactions, the driving force appears to be the formation of a more stable radical.

Experimental Section

Analyses were obtained by the Analytical Section of the General Electric Research and Development Center. Infrared spectra were determined on a Perkin-Elmer Model 421 spectrometer in carbon tetrachloride. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride or neat in the case of rate studies. Gas chromatograms were determined on an F & M gas chromatograph, Model 700, using either a 2-ft SE 30 silicone gum rubber column or a 6-ft Apiezon L column. Gas analyses were made with a Consolidated Electrodynamics Model 21-620 mass spectrometer. All melting points are uncorrected, but were taken with standardized thermometers. Electron spin resonance spectra were measured with a Varian spectrometer with 100-kcps field modulation operating at a frequency of 9.15 GHz and equipped with a Vairan 4500-41-A high–low bridge system.

Materials.—The following diphenyl ethers were prepared by a modification of the Ullmann diphenyl ether synthesis.[18]

2,6-Dimethylphenyl phenyl ether (1) was prepared from 2,6-dimethylphenol and bromobenzene in 25% yield: mp 55–56.5° from hexane.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.78; J, 7.34.

4-Methylxanthene (3) was prepared from 2-hydroxy-3-methyl-2'-chlorodiphenylmethane in 38% yield: mp 37–38° from methyl alcohol (lit.[19] mp 40°).

Anal. Calcd for $C_{14}H_{12}O$: mol wt, 196. Found: mol wt, 208 (vapor phase osmometry).

2-Methylphenyl phenyl ether (4) was prepared from o-cresol and bromobenzene in 14% yield: bp 90° (0.03 mm); n^{25}D 1.5684 [lit.[20] bp 123–124° (9 mm); n^{25}D 1.5710].

4-(2,6-Dimethylphenoxy)-2,6-dimethylanisole (5) was provided by Dr. D. A. Bolon of this laboratory.[18]

2-Methyl-6-phenylphenyl phenyl ether (6) was prepared from 2-methyl-6-phenylphenol and bromobenzene in 30% yield: mp 61–62.5°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19; mol wt, 260. Found: C, 87.7; H, 6.29; mol wt, 255 (vapor phase osmometry).

2-Benzyl-6-methylphenyl phenyl ether (7) was prepared from 2-benzyl-6-methylphenol and bromobenzene in 20% yield: bp 143° (0.1 mm).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61; mol wt, 274. Found: C, 87.7; H, 6.29; mol wt, 267 (vapor phase osmometry).

Di-o-tolyl ether (8) was prepared from o-cresol and 2-methylbromobenzene in 50% yield: bp 88° (0.5 mm). Redistillation gave bp 74–76° (0.35 mm); n^{30}D 1.5644.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.81, 84.86; H, 7.11, 7.03.

3-Methylphenyl phenyl ether (16) was prepared from m-cresol and bromobenzene in 35% yield: bp 95° (0.05 mm); n^{25}D 1.5700 [lit.[20] bp 154–155° (25 mm); n^{25}D 1.5711].

4-Methylphenyl phenyl ether (17) was prepared from p-cresol and bromobenzene in 41% yield: bp 94° (0.05 mm); n^{25}D 1.5685 [lit.[20] bp 125–126° (9 mm); n^{25}D 1.5701].

Preparation of Phenols. 2-Benzyl-6-methylphenol (2) was prepared by dissolving o-cresol (108 g, 1.0 mol) in 200 ml of toluene. Sodium hydroxide (40 g, 1.0 mol) was added and the mixture was heated to reflux. The water that formed was removed azeotropically, benzyl chloride (126 g, 1.0 mol) was added, and the heating was continued for 5 hr. The reaction was terminated by cooling and the phenol was isolated by extraction with Claisen's alkali. The basic solution was washed with ether and poured onto ice. After acidification with HCl, the mixture was extracted with ether and the ether was evaporated to give the crude product. Vacuum distillation followed by recrystallization of the distillate from hexane gave 61 g (30.8%) of 2: mp 50–51° (lit.[21] mp 51–52°).

2-(2-Methylbenzyl)phenol (9) was prepared from the lithium salt of phenol and o-methylbenzyl chloride in the same manner as for 2. The crude product was recrystallized from hexane to give 9 in 50% yield: mp 50.5–52.5°; nmr (CCl₄) δ 2.13 (s, 3, CH₃), 3.80 (s, 2, CH₂), 5.00 (s, 1, OH), and 6.40–7.05 (m, 9, Ar).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.8; H, 7.1.

2-(3,5-Dimethyl-4-methoxybenzyl)-6-methylphenol (11) was prepared by adding a solution of 3-methyl-2-hydroxybenzyl alcohol (10.0 g, 0.072 mol) in carbon tetrachloride to a solution of methyl 2,6-dimethylphenyl ether (40.0 g, 0.3 mol) in carbon tetrachloride containing SnCl₄. The addition was carried out over 3 hr in order to maintain the reaction solution at 15°. At the end of the addition, vpc indicated that no benzyl alcohol remained. The carbon tetrachloride was removed under vacuum (20 mm) and the oily residue was taken up in ether. The ether solution was extracted with Claisen's alkali and the basic extracts were acidified with HCl. The acid solution was extracted with ether and the phenolic products were isolated by removing the ether. Vpc of this material indicated that it was a mixture containing four products. The two major products had retention times of ca. 21 min and constituted 65% of the mixture. Two minor products appeared at ca. 30–31 min. Both the major peaks were trapped from the vpc and both gave m/e 256 for the molecular ions. The major one of the two, ca. 45% yield by vpc, was isolated by preparative vpc. Short path distillation gave 11: bp 150° (bath temperature, 0.15 mm); nmr (CCl₄) δ 2.16, 2.20 (s, 9, CH₃), 3.65 (s, 3, OCH₃), 3.78 (s, 2, CH₂), and 6.6–7.0 (m, 5, Ar); mass spectrum m/e 256.

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.89. Found: C, 79.7; H, 7.9.

2-Benzylphenol (12) was obtained from K & K Laboratories.

2-Benzyl-6-phenylphenol (13) was prepared from o-phenylphenol (34 g, 0.2 mol), benzylchloride (23 ml, 0.2 mol), and magnesium methoxide (from 6 g of Mg) in 150 ml of toluene at reflux for 3 days. The reaction solution was cooled and poured onto HCl solution containing ice. The mixture was diluted with ether, and the organic layer was separated, washed with water, and dried. The crude product was obtained by removing the solvent. Distillation at 160° (10 μ) gave 18 g (34.6%) of a mixture of the o-benzyl compound, 13, and the p-benzyl compound. A 5-g quantity of this mixture was placed on a silica gel column, and elution with benzene gave a cut containing 0.5 g of pure 13. Distillation in a bulb-to-bulb apparatus gave a colorless oil: bp 160–165° (bath temperature, 0.15 mm); nmr (CCl₄) δ 4.0 (s, 2, CH₂), 5.15 (s, 1, OH), and 6.4–7.8 (m, 13, Ar); ir (neat) 3520 cm⁻¹; mass spectrum m/e 260, 182, and 91.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.7; H, 6.37.

2,6-Dibenzylphenol (15) was provided by Dr. A. Hay of this laboratory and had been prepared by the method of Horning.[22]

(14) P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966).

(15) D. F. DeTar and A. Hlynsky, *ibid.*, **77**, 4411 (1955).

(16) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(17) H. Breederveld and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **76**, 297 (1957).

(18) D. A. Bolon, *J. Org. Chem.*, **32**, 1584 (1967).

(19) R. J. McConnel, V. Petrow, and B. Sturgeon, *J. Chem. Soc.*, 812 (1956).

(20) C. M. Suter and F. O. Green, *J. Amer. Chem. Soc.*, **59**, 2579 (1937).

(21) P. Schorigin, *Chem. Ber.*, **58**, 2028 (1925).

(22) E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

2-Diphenylmethyl-6-methylphenol (14) was prepared from the sodium salt of cresol and benzhydryl chloride in the same manner as for 2. The crude product was recrystallized from methyl alcohol–water: mp 76–77.5° (lit.[23] mp 76–78°).

The Rearrangement of 2,6-Dimethylphenyl Phenyl Ether (1).— 2,6-Dimethylphenyl phenyl ether (1, 1.0 g, 0.005 mol) was placed in a heavy-wall Pyrex tube and the tube was sealed under vacuum. The tube was heated in a furnace at 370° for 3.5 hr, cooled, and opened. Vpc indicated the presence of unreacted starting material and a more polar product in a 2:1 ratio. One half of the crude product was taken up in hexane and extracted with 25% aqueous potassium hydroxide solution. The basic extracts were combined and acidified with hydrochloric acid. The acidified solution was extracted with ether and the ether was stripped to give 125 mg of material. All of this was placed on two preparative tlc silica gel plates and developed in benzene. The major uv absorbing zone was cut out and the product was recovered by elution with acetone. 2-Benzyl-6-methylphenol (2), yield 110 mg (22%), was obtained. This product had the same nmr and ir spectra as authentic material.

When this reaction was run for a longer time, the yield increased and 4-methylxanthene (3) was detected as a minor product.

The Rearrangement of Compounds 4, 5, 6, 7, and 8.—These reactions were carried out in a similar manner as for 1 at the temperatures listed in Table I. The products were isolated either by chemical means, as for 1, or by trapping from vpc. They were identified by comparison with authentic compounds.

Rate Measurements.—A thick-wall nmr tube containing 2,6-dimethylphenyl phenyl ether (1, 100 mg) was degassed and sealed under vacuum. An nmr spectrum of the molten sample was measured after heating the tube to ca. 70°. The tube was placed in an electric furnace at 370 ± 2° and removed at intervals of 2–4 hr. The sample was cooled, the nmr spectrum was measured, and the composition of the sample was determined from the areas of the methyl and methylene peaks in compounds 1, 2, and 3. Percentage composition with time results are recorded in Table III.

In another determination, an internal standard, 1,1-diphenylpropane, which was stable at 370°, was also present in the nmr tube (30 mg with 100 mg of 1). Similar conversions into 2 and 3 were found.

(23) H. A. Iddles, D. H. Chadwick, J. W. Clapp, and R. T. Hart, *J. Amer. Chem. Soc.*, **64**, 2154 (1942).

TABLE III

Time at 370° hr	Mol %		
	1	2	3
2	98	2	
4	95	5	
6	93	7	
8	93	7	
10.5	89	11	
13	81	19	
15.5	74	25	1
17.5	70	29	1
21	59	38	3
24	38	59	3
41	18	75	8

At the end of the heating period, the tubes were opened and the mixture was analyzed quantitatively by vpc. The yields were in agreement with the nmr values.

Rearrangements were also carried out on small samples of 1 in evacuated ampoules which were heated at 370° for varying intervals, then opened and analyzed quantitatively by vpc. Naphthalene (50 mg per 100 mg of 1) was included as an internal standard in some cases.

When samples were analyzed on a 2-ft silicone rubber column, it was found convenient to convert the phenolic product, 2, into the trimethylsilylether derivative, which no longer overlapped the methylxanthene peak. Quantitative silylation was accomplished in several minutes by adding 2 drops of bistrimethylsilylacetamide to 1 drop of the reaction mixture.

Rearrangements were also run in an identical manner on samples of 1 which contained sulfur (2 mg per 100 mg of 1) and on a sample of 1 which had been recrystallized two additional times. The rate curves are given in Figure 2.

Registry No.—1, 22040-02-4; 6, 22040-03-5; 7, 22040-04-6; 8, 4731-34-4; 9, 22040-06-8; 11, 22040-07-9; 13, 22040-08-0.

Arylation by Aromatic Nitro Compounds at High Temperatures. VI. Reactions of Nitrobenzene and Nitrobenzene-d5 with Pyridine

ELLIS K. FIELDS

Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana 46394

SEYMOUR MEYERSON

Research and Development Department, American Oil Company, Whiting, Indiana 46394

Nitrobenzene reacts with pyridine at 600° to give phenylpyridines and bipyridines as major products. Isomer distribution of phenylpyridines is about the same as from phenyl radical sources in the liquid phase; however, product distribution from pyridine differs sharply between nitrobenzene at 600° and benzenediazonium chloride at 100°. Product yields increase considerably with increasing mole ratios of pyridine to nitrobenzene. Deuterated reagents give higher ratios of "normal" to "intramolecularly scrambled" arylation products than in the reactions of nitrobenzene with benzene or toluene. Evidently, the heteroatom in pyridine constitutes an appreciable barrier to intramolecular movement of protium and deuterium.

Earlier papers in this series have described the reactions at high temperatures of nitrobenzene, alone and with benzene and benzene-d_6;[1a] with aromatic fluorine derivatives;[1b] and with toluene and toluene-α-d_3.[1c] This paper concerns the reactions of nitro-benzene and nitrobenzene-d_5 with pyridine; a few details were mentioned in a preliminary communication.[1d]

Experimental Section

Equipment and procedures are fully described in ref 1c.
Materials.—With the exception of labeled compounds and analytical standards, all chemicals were reagent grade.
Nitrobenzene-d_5 was prepared in 50 mol % yield by nitrating benzene-d_6 with nitrogen pentoxide in carbon tetrachloride ac-

(1) (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967); (b) *J. Org. Chem.*, **32**, 3114 (1967); (c) *ibid.*, **33**, 2315 (1968); (d) *J. Amer. Chem. Soc.*, **89**, 724 (1967).