[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Stereochemistry of Aromatic Alkylations. I. Direct Nucleophilic Displacement in Phenols[1]

BY HAROLD HART AND HERBERT S. FLEUTERIO

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Displacement with stereochemical inversion and a high degree of retention of optical purity is shown to occur when phenols are nuclearly alkylated with α-phenylethyl chloride in alkaline solutions. The process does not proceed *via* the ether, but by direct C-alkylation. The configurations of 2-α-phenylethylphenol, 2-α-phenylethyl-*p*-cresol and 4-α-phenylethyl-2,6-xylenol have been related to α-phenylethyl chloride by oxidation to phenylmethylacetic acid, and thus also related to alanine and glyceraldehyde. Minimum values for the specific rotations of these alkylated phenols also have been set. A carbanion displacement mechanism resulting in direct aromatic alkylation is proposed as the major reaction path.

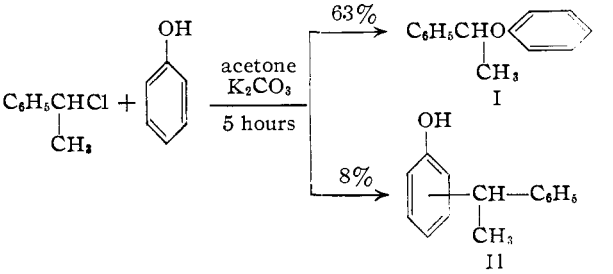
Introduction.—There have been only a few investigations of the direct alkylation of the aromatic nucleus with substances in which the carbon atom to become attached to the aromatic ring was asymmetric. Price and Lund[2] reported that the alkylation of benzene with optically active *s*-butyl alcohol, as catalyzed by boron trifluoride, resulted in nearly racemic *s*-butylbenzene, and this work was substantiated and extended by Burwell and Archer.[3] Price[4] suggested that the extensive racemization was the result of a planar carbonium ion intermediate. More recently, Burwell[5] showed that the alkylation of benzene by optically active *s*-butyl methyl ether with boron trifluoride yielded *s*-butylbenzene of inverted configuration and optical purity little greater than 1%. The drastic racemization was shown to accompany the alkylation step, and was not due to racemization of the ether before reaction, nor of the product subsequent to its formation (although with other alkylating agents, racemization may occur prior to alkylation[6]). It was suggested that the racemization may be connected with isomerization of an intermediate carbonium ion.

The stereochemistry of the rearrangement of alkyl aryl ethers to alkyl phenols by zinc chloride or sulfuric acid has been investigated by Wallis and co-workers[7] and this may be considered as an aromatic alkylation. But this type of reaction will be discussed in more detail in the following paper.

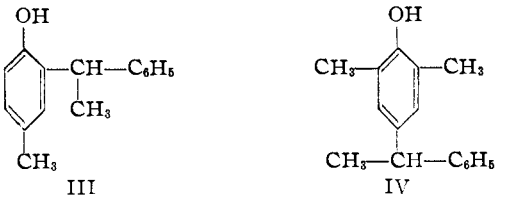
It will be noted that each of these studies involved alkylation under strongly acidic, and often heterogeneous conditions. It is the purpose of the present series of papers to examine the stereochemistry of aromatic alkylation under alkaline, neutral and acidic conditions. As our examples we have selected, respectively, (1) the C-alkylation which is known to accompany O-alkylation in the usual Claisen[8] preparation of alkyl phenyl ethers, (2) the rearrangement of alkyl aryl ethers to alkylphenols and (3) the direct alkylation of phenols with optically active halides of sufficient reactivity such that no added catalyst of the Friedel–Crafts type is necessary. Subsequent papers will deal with the alkylation of non-phenolic aromatics. The same series of compounds will be used in the first three papers, the α-phenylethyl group being the source of optically active substances. This paper deals with nuclear alkylation in an alkaline medium.

Although the alkylation of phenols with optically active halides under Claisen conditions has been observed to give some optically active nuclearly alkylated phenols,[9] the extent of retention of optical purity and the relative configurations of starting materials and products were not ascertained.

Alkylation Experiments.—When α-phenylethyl chloride was refluxed with phenol in acetone containing suspended potassium carbonate, α-phenylethyl phenyl ether (I) and a mixture of *o*- and *p*-α-phenylethylphenols (II) were formed.



II consisted predominantly (92%) of the ortho isomer, as determined spectrophotometrically.[10] In order to limit the C-alkylate to only one isomer, *p*-cresol and 2,6-xylenol were similarly treated, to give III and IV, respectively.



In each case, when optically active α-phenylethyl chloride was used, the products were also optically active. The stereochemical results for the C-alkylate are summarized in Table I. The stereochemis-

(1) Based upon the Ph.D. thesis of H.S.E., 1953. Presented in part at the Gordon Research Conference on Petroleum, June, 1952, and the Atlantic City A.C.S. Meeting, September, 1952.

(2) C. C. Price and M. Lund, THIS JOURNAL, **62**, 3105 (1940).

(3) R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942).

(4) C. C. Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 51.

(5) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, THIS JOURNAL, **74**, 4570 (1952).

(6) R. L. Burwell, Jr., *ibid.*, **64**, 1025 (1942).

(7) E. S. Wallis, *et al.*, *ibid.*, **56**, 1715 (1934); *J. Org. Chem.*, **5**, 184 (1940).

(8) L. Claisen, *et al.*, *Ann.*, **401**, 21 (1913); **442**, 237 (1925); *Z. angew. Chem.*, **36**, 478 (1923); *Ber.*, **59B**, 2344, 2351 (1926).

(9) See, for example, E. Alexander and R. Kluiber, THIS JOURNAL, **73**, 4304 (1951), who alkylated phenol and 2,6-xylenol with active 4-chloro-2-pentene. In both cases, some optically active C-alkylate was obtained.

(10) H. Hart, *Anal. Chem.*, **24**, 1500 (1952).

try of the ethers will be discussed in the following paper.

TABLE I

ROTATION DATA FOR C-ALKYLATION WITH α-PHENYLETHYL CHLORIDE

Phenol	$[\alpha]^{25}D$ of chloride Initial	Final	$\alpha^{25}D$ of C-alkylate	$[\alpha^{25}D]$ of phenylmethylacetic acid[d] in alcohol
Phenol[a]	30.4	26.6	−4.22	13.75 (*c* 27.7)
p-Cresol[a]	26.5	23.0	2.63	12.5 (*c* 6.15)
2,6-Xylenol[a]	27.1	20.9	0.44	4.13 (*c* 6.25)
Phenol[b]	15.5	7.08	−2.88	
Phenol[c]	7.02	2.50	−1.10	
p-Cresol[c]	22.9	10.0	1.77	9.65 (*c* 17.2)

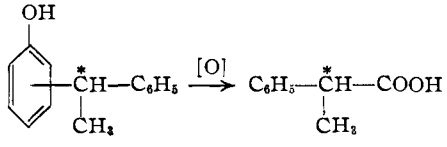
[a] Acetone–potassium carbonate procedure. [b] Sodium phenoxide in absolute alcohol procedure. [c] Sodium phenoxide or *p*-cresoxide in benzene procedure. [d] Obtained by permanganate oxidation of the C-alkylate.

It will be noted from Table I that the α-phenylethyl chloride racemizes somewhat during the reaction. This racemization is most extensive for the sodium phenoxide in ethanol conditions (> 50% in less than two hours) and least extensive for the acetone–potassium carbonate procedure (about 12% in five hours or 23% in 12 hours).

Before discussing the configurations of the C-alkylates, it is important to demonstrate that the process of C-alkylation is a direct one; *i.e.*, that the reaction does not proceed *via* ether formation, followed by rearrangement to the alkylated phenol. Claisen[8] had already demonstrated that this was the case for allylic halides, but it seemed desirable to verify this for α-phenylethyl chloride. Several experiments were performed toward this end.

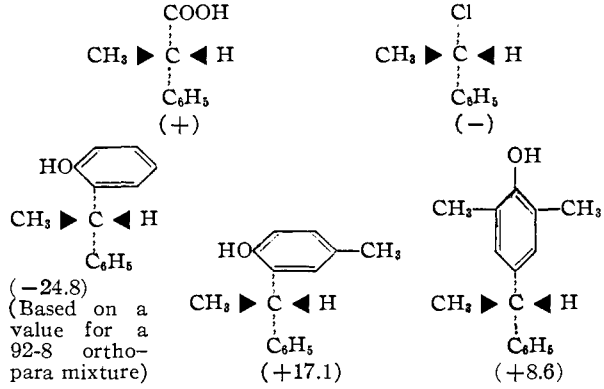
I was found to be stable under alkylation conditions; it was recovered unchanged after refluxing for five hours with sodium *p*-cresoxide in benzene. In another experiment, α-phenylethyl mesityl ether was prepared in the acetone–potassium carbonate manner, in the presence of I. The mesitol is of course incapable of giving C-alkylate (no available ortho or para positions), but I might rearrange. No C-alkylate was found, however, and since these conditions (24 hours of reflux) were more strenuous than those under which I itself was prepared, it seems safe to conclude that I will not rearrange to II under the conditions of their preparation.

Configurations of α-Phenylethylphenols.—It seemed particularly desirable to establish the configurations of the α-phenylethylphenols relative to α-phenylethyl chloride, and also, if possible, to determine the extent of retention of optical purity. Both objectives could be accomplished by a rather simple procedure involving oxidation of the phenolic ring to a carboxyl group. Neutral permanganate



in aqueous acetone at room temperature gave 25–35% yields of phenylmethylacetic acid, either when the phenolic ring was otherwise unsubstituted as in II, or when it contained methyl groups, as with III and IV. Since this reaction does not involve the asymmetric carbon atom, the configurations of the phenylmethylacetic acid and the alkylated phenols should be identical. Bernstein and Whitmore[11] have related (+)phenylmethylacetic acid to (−)α-phenylethylamine which, in turn,[12] has been related to (−)α-phenylethyl chloride. These configurations have been reviewed recently by Mislow,[13] and it is also possible to relate all of these substances to the configurational standard D(+)-glyceraldehyde.

As may be seen from Table I, (+)α-phenylethyl chloride gave C-alkylate which, in every case, gave (+)phenylmethylacetic acid. Since these have opposite configurations, one concludes that *C-alkylation of phenols in alkaline solution is accompanied by inversion of configuration.* The configurations of some of the pertinent compounds are given in the formulas.



If one knows the value for the specific rotation of optically pure phenylmethylacetic acid, it then becomes possible to set minimum values for the rotations of the optically pure α-phenylethylphenols. Values calculated in this way for homogeneous liquid in a 1-dm. tube are indicated below each of the above formulas.[14]

Retention of Optical Purity.—In order to determine the extent of retention of optical purity in the C-alkylation it is necessary to know the rotation of

(11) H. I. Bernstein and F. C. Whitmore, THIS JOURNAL, **61**, 1324 (1939).

(12) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, L. Masterman and A. D. Scott, *J. Chem. Soc.* 1252 (1937).

(13) K. Mislow and M. Heffler, THIS JOURNAL, **74**, 3668 (1952).

(14) We have used the value of H. S. Raper (*J. Chem. Soc.*, **123**, 2557 (1923)) of $[\alpha]^{20}D$ 81.1° for phenylmethylacetic acid in alcohol as the solvent. The value reported by P. A. Levene, L. A. Mikeska and K. Passoth (*J. Biol. Chem.*, **88**, 27 (1930)) of $[\alpha]^{25}D$ 54.2° is probably quite low. In fact, one can obtain a check on Raper's value in the following manner. G. L. Arcus and J. Kenyon (*J. Chem. Soc.*, 916 (1939)), prepared optically pure phenylmethylacetic acid and obtained $[\alpha]D$ +92.5° in benzene. This is 1.218 times Levene's best value (P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **100**, 685 (1933)) for this solvent. This factor can be applied to Levene's value for the pure acid (same sample, no solvent) giving 90.2. The sample on which Levene obtained a rotation in ethanol had a rotation $[\alpha]^{25}D$ 59.1 when homogeneous. Applying a correction factor of 90.2/59.1 = 1.526 we get 82.5 from Levene's data for an alcohol solution, a value in close agreement with that observed by Raper. As a further check, we note that the Arcus and Kenyon value in chloroform of $[\alpha]D$ +74.8° is close to that reported by Raper in the same solvent ($[\alpha]^{20}D$ +76.2°). Finally, it is not clear how pure the phenylmethylacetic acid of Bernstein and Whitmore[11] was, since they do not indicate whether the rotation they measured was for the homogeneous acid or a solution of it. We use Raper's value in alcohol, because it is a reasonably reliable experimental one (although he did not obtain the acid in crystalline form whereas Arcus and Kenyon did).

optically pure α-phenylethyl chloride. Gerrard[15] has reported a specific rotation of $[\alpha]^{16}D$ 93.5°, but this value is probably low.[16] We shall use the experimental value of 103.7° for the specific rotation of α-phenylethyl chloride in our subsequent calculations. Since this is an experimental value, it is a minimum one, and will therefore give a maximum figure for the extent of racemization accompanying C-alkylation. Using the data for *p*-cresol, initial chloride $\alpha^{25}D$ +26.5° ($[\alpha]D$ 24.9°) gave ultimately phenylmethylacetic acid $[\alpha]^{23}D$ +12.5°. The *maximum* racemization in the over-all process then is about 36%.[17] A roughly comparable value is obtained from the phenol experiments, although it is necessary to neglect the fact that two isomeric C-alkylates are obtained. With 2,6-xylenol, the extent of racemization appears to be somewhat larger.

Mechanism.—In the medium in which phenols have been nuclearly alkylated as described in this paper, there is undoubtedly an appreciable concentration of phenoxide ions. The stereochemistry of C-alkylation was the same when phenoxide ions were specifically prepared, as when the acetone–potassium carbonate procedure was employed (see Table I). In view of the observed inversion of configuration and high (at least 64%) retention of optical purity, it is suggested that the major reaction path in Claisen C-alkylation is a nucleophilic displacement of halogen by phenoxide ion.

An analogous nucleophilic displacement also has been suggested for the Reimer–Tiemann reaction.[18]

One has the problem of explaining the predominance of *o*-alkylation, when ortho and para positions are available. Thus with phenol, over 90% ortho alkylation was observed, whereas 67% would be the statistical value. This can be explained in the following manner. The primary mode of attack will be by the oxygen end of the phenoxide ion, since this is the region of greatest concentration of negative charge. Clearly this is so, since the major product is the ether. It follows that since the phenoxide ion will approach the positive end of the carbon–chlorine dipole most frequently at the oxygen end of the ion, collisions involving the ortho carbons will be more frequent than those involving the para carbon, giving rise primarily to *o*-C-alkylate. When, of course, ortho positions are unavailable, *p*-C-alkylate will be obtained.

It is believed that these experiments demonstrate the first direct aromatic alkylation with a high retention of optical purity and predominant inversion of configuration.

Experimental

Materials.—α-Phenylethyl alcohol was resolved according to the procedure of Downer and Kenyon[19] and converted to the chloride *via* the procedure of McKenzie and Clough[20] and also the procedures of Gerrard[15] and Burwell.[16]

Alkylation of Phenol. (a) Acetone–Potassium Carbonate Procedure.—A stirred mixture of 108.4 g. (1.15 moles) of phenol, 38 g. (1 mole) of potassium carbonate, 178 g. (1.26 moles) of α-phenylethyl chloride and 200 ml. acetone was refluxed for five hours. After cooling and addition of one liter of water, the mixture was extracted with petroleum ether (40–60°). The organic layer was extracted four times with 10% sodium hydroxide, twice with water, and dried over anhydrous sodium sulfate. Removal of the solvent and distillation of the residue gave three main fractions; recovered α-phenylethyl chloride, 83.9 g., b.p. 71° (10 mm.), $n^{21}D$ 1.5232; α-phenylethyl phenyl ether,[21] 81.4 g., b.p. 143–145° (10 mm.) and an unidentified material, 2.0 g., b.p. 180–220° (10 mm.).

Acidification of the alkaline extracts gave an oil which was extracted with benzene and dried over anhydrous sodium sulfate. Removal of the solvent and distillation of the residue gave phenol, 20.2 g., b.p. 180°, tribromo derivative, m.p. 95° and a mixture of α-phenylethyl phenols, 10.0 g., b.p. 160–170° (5 mm.). Spectrophotometric analysis[10] showed the mixture to contain 92% of the ortho isomer.

On a smaller scale, α-phenylethyl chloride ($\alpha^{25}D$ +30.4°) gave α-phenylethyl phenyl ether ($\alpha^{25}D$ +11.34°), recovered α-phenylethyl chloride ($\alpha^{25}D$ +26.6°) and α-phenylethylated phenols ($\alpha^{25}D$ −4.22°) all l = 1 dm., homogeneous.

(b) **Sodium Phenoxide–Alcohol Procedure.**—Phenol (9.4 g., 0.1 mole) was added to a solution of 2.3 g. (0.1 mole) of sodium in 30 ml. of absolute alcohol. To this was added 23.0 g. (0.16 mole) of α-phenylethyl chloride (αD +15.5°), and the solution refluxed until no longer alkaline (1.5 hours). After cooling, water was added, the mixture acidified and extracted with petroleum ether. The organic layer was extracted several times with 10% sodium hydroxide, water, and dried (sodium sulfate). Distillation gave 12.4 g. of α-phenylethyl chloride (αD +7.08°) and 5.0 g. of α-phenylethyl phenyl ether (αD +5.0°).

The alkaline extract was acidified, and the resulting oil taken up in benzene, dried (sodium sulfate) and distilled, yielding 1.0 g. of phenol and 2.0 g. of α-phenylethylphenols (αD −2.88°), shown spectrophotometrically to be 88% the ortho isomer.

(c) **Sodium Phenoxide–Benzene Procedure.**—A benzene solution (100 ml.) of 7.5 g. (0.08 mole) of phenol was refluxed with 1.83 g. (0.08 mole) of sodium sand until the latter had all reacted. To this was added 12.4 g. (0.088 mole) of α-phenylethyl chloride (αD +7.02°), and the mixture refluxed for five hours. Working up in the usual manner gave 2.0 g. of α-phenylethyl chloride (αD +2.5°), 1.5 g. of α-phenylethyl phenyl ether (αD +2.3°), 1.0 g. of phenol and 2.0 g. of α-phenylethylphenols (αD −1.1°).

Alkylation of *p*-Cresol.—Using the acetone–potassium carbonate procedure, a 58% yield of α-phenylethyl *p*-tolyl ether and 4.8% of *o*-α-phenylethyl-*p*-cresol was obtained. Using the sodium *p*-cresoxide–benzene procedure, a 21% yield of the ether and 12% yield of the C-alkylate was obtained. Pertinent stereochemical data are given in Table I.

Alkylation of 2,6-Xylenol.—The acetone–potassium carbonate procedure with 12 hours of reflux gave a 41% yield of α-phenylethyl 2,6-xylyl ether and 6.5% of 4-α-phenylethyl-2,6-xylenol. Stereochemical data are given in Table I.

Evidence for Direct C-Alkylation.—A suspension of 0.2 mole of sodium *p*-cresoxide in 50 ml. of benzene was treated with 0.1 mole of phenyl α-phenylethyl ether and refluxed for five hours. The unchanged reactants were recovered (>90%).

Mesitol and α-phenylethyl chloride were allowed to reflux according to the acetone–potassium carbonate procedure for 24 hours in the presence of 0.1 mole of α-phenylethyl phenyl ether. No alkali-soluble product, except recovered excess mesitol, was obtained.

General Procedure for Oxidation of α-Phenylethylphenols to Phenylmethylacetic Acid.—To a solution of 0.0125 mole of the alkylated phenol in 250 ml. of acetone maintained at no greater than 30°, there was added 15.1 g. (0.1 mole) of potassium permanganate in 750 ml. of water. The mixture was stirred for 45 minutes, acidified with 6 *N* sulfuric acid, and the precipitated manganese dioxide destroyed with so-

(15) W. Gerrard, *J. Chem. Soc.*, 741 (1946).

(16) R. L. Burwell, Jr., private communication. A ratio as high as 2.50 for observed homogeneous rotations of chloride to alcohol was obtained. Using the densities of chloride and alcohol as 1.063 and 1.013, respectively, and a specific rotation for the alcohol $[\alpha]D$ 43.6° (E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939)) one obtains $[\alpha]D$ 103.7° for the chloride. For a more detailed discussion, see R. L. Burwell, Jr., A. D. Shields and H. Hart, THIS JOURNAL, paper in press.

(17) (1 − (103.7/24.9) × (12.5/81.1)) × 100.

(18) E. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 202.

(19) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).

(20) A. McKenzie and G. W. Clough, *ibid.*, **103**, 687 (1913).

(21) The identity of the ethers will be established in the following paper.

dium bisulfite. The mixture was extracted with five 50-ml. portions of benzene, and the water layer discarded. The benzene solution was extracted with 10% sodium bicarbonate, and the extracts acidified and extracted with benzene. The benzene solution was dried (sodium sulfate) and after removal of the solvent, distilled in a semi-micro column. There was no appreciable fore-run, and about 0.4–0.5 g. of phenylmethylacetic acid was obtained, b.p. 145–148° (15 mm.), $n^{20}D$ 1.5210, neut. equiv. 151.2 (calcd. 150.0). With S-benzylthiouronium chloride a flaky white salt, m.p. 151–152°, was obtained (mixed m.p. with an authentic sample, 151–152°). The yield of phenylmethylacetic acid was from 25–35% for the different alkylated phenols. Pertinent stereochemical data are given in Table I.

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The Stereochemistry of Aromatic Alkylations. II. The Thermal Rearrangement of Alkyl Aryl Ethers[1]

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The reaction of phenoxide ion with α-phenylethyl chloride is shown to be second order, and, since the α-phenylethyl phenyl ether formed from optically active halide had a high rotation, it is assumed that the reaction proceeded primarily with inversion (S_N2). The α-phenylethyl ethers of phenol, *p*-cresol, 2,6-xylenol and mesitol were prepared and their configurations thus assigned. α-Phenylethyl phenyl ether rearranged at 200° in five hours to give a 33% yield of α-phenylethylphenols (85% ortho). Similar results were obtained with the ethers of *p*-cresol and 2,6-xylenol, the latter giving 4-α-phenylethyl-2,6-dimethylphenol (23%). With optically active ethers, appreciable optical activity was retained, and the α-phenylethyl group migrated with retention of configuration, *even on para migration*. When optically active α-phenylethyl mesityl ether was treated with an excess of phenol at 200° for seven hours, a 44% yield of completely racemic α-phenylethylphenols was obtained. Thus, the reaction can apparently proceed in at least two manners: intramolecularly, with retention of configuration, and intermolecularly, *via* a symmetrical intermediate (radical or ion).

The rearrangement of an alkyl aryl ether to an alkylphenol can be thought of as an aromatic alkylation, and may take place as a true intramolecular rearrangement (as, for example, in the Claisen rearrangement of allyl phenyl ethers)[6] or intermolecularly *via* a variety of paths (involving ionic, radical, or molecular intermediates). We exclude from discussion here (but will consider in a later paper) rearrangements brought about by acidic catalysts such as zinc chloride or sulfuric acid,[2,3] and consider now only thermal transformations.

Alexander and Kluiber[4] have recently studied the thermal rearrangement of (−)α,γ-dimethylallyl phenyl ether and (−)α,β-dimethylallyl-2,6-xylyl ether, and found that both ortho and para rearrangement must have involved partial formation of the new carbon–carbon bond simultaneous with cleavage of the carbon–oxygen bond, because optical activity was retained. These results are compatible with the usual cyclic transition state considered to be operative in rearrangements of allyl phenyl ethers.[5,6] It should be noted, however, that the asymmetric center in the alkylated phenol is not the same as the one in the ether, but rather there is destruction of one asymmetric center and creation of another. We sought a case in which the asymmetric center in the ether and alkylated phenol would be the same (as in the secondary butyl phenyl ethers and phenols[2,3]).

Because the benzyl group is often similar in its behavior to the allyl group, there have been several attempts to carry out reactions analogous to the Claisen rearrangement with benzyl aryl ethers. Powell and Adams[7] were unable to isolate benzyl phenols from refluxed benzyl phenyl ether, but did obtain some toluene, possibly derived from benzyl radicals. Behagel and Freiensehner,[8] however, did isolate very low yields of benzyl- and dibenzylphenols, and also demonstrated cross-benzylation, as in the *p*-benzylation of methyl α-naphthyl ether by benzyl phenyl ether. When the reaction was carried out in quinoline[9] as the solvent, benzylquinolines and toluene were obtained in addition to benzylphenols, and Hickinbottom suggests cleavage into benzyl radicals.

We have prepared the optically active α-phenylethyl ethers of phenol, *p*-cresol, 2,6-xylenol and mesitol, and studied their thermal behavior. In order to establish the steric course of the reactions which occurred, it was necessary first to determine the stereochemical configurations of the ethers.

Kinetics and Stereochemistry of the Reaction of α-Phenylethyl Chloride with Phenoxide Ion.—The reaction of α-phenylethyl chloride with methoxide and ethoxide ions has been shown[10] to proceed primarily as a bimolecular nucleophilic displacement with inversion of configuration. Although it was felt that reaction with phenoxide ion would proceed in an analogous manner, kinetics were run to establish that this was in fact the case. The data for a typical run are given in Table I, and a

(1) See footnote 1 of the preceding paper.

(2) See papers by M. M. Sprung and E. S. Wallis, THIS JOURNAL, **56**, 1715 (1934); W. I. Gilbert and E. S. Wallis, *J. Org. Chem.*, **5**, 184 (1940), on the stereochemistry of the catalyzed rearrangements.

(3) We are indebted to Dr. Patrick A. Diassi for an abstract of a paper by J. F. Lane and Diassi on the stereochemistry of the catalyzed rearrangement of *s*-butyl phenyl ether presented by them at a North Jersey Section Meeting-in-miniature early in 1952.

(4) E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

(5) D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

(6) J. P. Ryan and P. R. O'Connor, THIS JOURNAL, **74**, 5866 (1952); H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953).

(7) S. G. Powell and R. Adams, *ibid.*, **42**, 646 (1920).

(8) O. Behagel and H. Freiensehner, *Ber.*, **67B**, 1368 (1934).

(9) W. J. Hickinbottom, *Nature*, **143**, 520 (1939).

(10) E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).