shown to be identical with IX, the structure proposed by Diels.

Anal. Calcd. for $C_4H_4N_4O_4$: C, 27.93; H, 2.32; N, 32.55; mol. W., 172. Found: C, 27.92, 27.96; H, 2.25, 2.26; N, 32.20, 32.30; Mol. W. (Rast), 195, 196.

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Stereochemical Control by Solvent in the Thermal Rearrangement of Aryl α-Phenethyl Ethers

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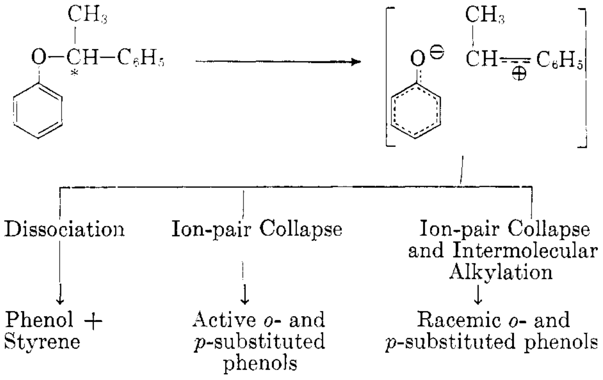
In the thermal rearrangement of alkyl aryl ethers to alkylphenols, it was shown[3] that an α-phenethyl group migrated (ortho or para) with retention of configuration. But when the reaction was necessarily intermolecular (as in the cross-alkylation of phenol with optically active α-phenethyl mesityl ether) optically inactive product was obtained. These stereochemical results were taken as evidence for an intramolecular thermal rearrangement, very likely proceeding *via* ionic intermediates.[3] This mechanism was made more explicit by Cram[4] who suggested the intermediacy of ion-pairs (Scheme 1).



Scheme 1. A Mechanism for Thermal Rearrangement of α-Phenethyl Aryl Ethers

Several alternatives may ensue following ionization. Dissociation could yield phenol and styrene, products always found in these reactions. Ion-pair collapse might give active or racemic alkylphenols, depending upon the degree to which the cationic part of the ion-pair maintains configuration. Alkylation by an intermolecular process would also give racemic alkylphenols.[5]

If an ion-pair mechanism of this type were operative, one would anticipate that retention of optical purity (and configuration) should be high in solvents of low ionizing power, but that in good ionizing solvents separation of the ion-pair partners into separately solvated ions should increase the chance for racemization of the cationic fragment, thus decreasing the overall stereospecificity of the rearrangement. Previous work[3] was done without a solvent; we wish here to report on the rearrangement of several α-phenethyl aryl ethers in 1*M* solutions in β-methylnaphthalene, phenyl ether, and diethylene glycol. The ethers had *p*-aryl substituents (CH_3, Cl, OCH_3) so that a single isomer (*o*-alkyl) would be formed on rearrangement.

Table I gives the yields and rotations of the several ethers and ortho-α-phenethylphenols prepared by the alkylation (O— and C—) of certain *p*-substituted phenols with optically active α-phenethyl chloride.[6] The ethers were rearranged thermally in several solvents, as shown in Table II. The per cent retention of optical purity was calculated as the ratio (×100) of rotations of *o*-α-phenethyl-*p*-X-phenol obtained by ether rearrangement to that obtained by direct synthesis (Table I). Suitable control experiments showed essentially no racemization of the products under rearrangement conditions.

The data in Tables I and II give additional[3] examples of thermal migration of an α-phenethyl

TABLE I

STEREOCHEMISTRY OF α-PHENETHYL ARYL ETHERS AND *o*-α-PHENETHYLPHENOLS PREPARED FROM CERTAIN *p*-X-PHENOLS

X	Rotation of RCl[a]	α-Phenethyl Aryl Ether % Yield	α-Phenethyl Aryl Ether Rotation	*o*-α-Phenethyl-*p*-X-phenol % Yield	*o*-α-Phenethyl-*p*-X-phenol Rotation
CH_3	+27.2	89.0	+2.52[b]	2.5	+6.25[c]
Cl	+42.5	57.3	+1.48[b]	4.6	+4.90[b]
OCH_3	+65.2	60.2[d]	+9.77[a]	6.8	+14.10[b]

[a] R = α-phenethyl, observed rotations at 25°, l = 1 dm., neat. [b] $[\alpha]_D^{25}$, c = 40, benzene. [c] $[\alpha]_D^{25}$, c = 20, benzene. [d] This ether is new; m.p. 21–21.5°, b.p. 138–141°/1 mm. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.11. Found: C, 78.68; H, 7.0.

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[1] Taken from a portion of the Ph.D. thesis of J. R. K. submitted to Michigan State University, 1957.

[2] Research Corporation Fellow 1956–57.

[3] H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 519 (1954).

[4] D. J. Cram in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, p. 298.

[5] Another alternative, collapse of the ion-pair to active or racemic ether, has not been tested experimentally.

[6] The procedure, using potassium carbonate suspended in acetone, was that of H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 516 (1954). It is assumed in the present work (but was proved previously) that the ether and ortho-alkylphenols have identical configurations, opposite to that of the α-phenethyl chloride used. It is further assumed that they also have equal optical purity.

TABLE II

STEREOCHEMISTRY OF THERMAL REARRANGEMENT OF CERTAIN α-PHENETHYL p-X-PHENYL ETHERS IN SEVERAL SOLVENTS

X	Solvent[a]	Rotation of Ether[b]	o-α-Phenethyl-p-X-phenol % Yield[c]	o-α-Phenethyl-p-X-phenol Rotation[d]	% Retention of Optical Purity
CH_3	N	+2.52	10.4	+5.65	90.4
CH_3	PE	+2.52	12.3	+5.45	87.2
CH_3	DG	+2.52	17.0	+1.02	16.3
OCH_3	PE	+9.77	14.9	+6.90	48.9
OCH_3	DG	+9.77	18.4	+1.95	13.8
Cl	PE	+1.48	16.2	+2.65	54.0

[a] N = β-methylnaphthalene, PE = phenyl ether, DG = diethylene glycol. [b] These values have the same significance as in Column 4, Table I. [c] This is the yield of distilled o-alkylphenol isolated after 5 hr. reflux of a $1M$ solution of the particular ether in the indicated solvent. [d] $[\alpha]_D^{24-26}$, c = 20, benzene.

group from oxygen to the ring with retention of configuration. They demonstrate further that the extent to which optical purity is retained depends indeed upon the solvent in a fashion predictable from the ion-pair mechanism. Racemization was nearly complete in the highly polar diethyleneglycol, whereas the non-polar β-methylnaphthalene allowed a high degree of retention of optical purity.

The series of para substituents was too limited to draw any definite conclusions, though one would expect that substituents which stabilize the phenolate anion might decrease the stereospecificity of the reaction. In the same solvent (phenyl ether) methyl (87% retention) seemed superior to methoxyl or chlorine (49 and 54% respectively).

In summary, these experiments lend considerable support to the suggestion[4] that alkyl aryl ethers which cannot isomerize by a cyclic path[7] rearrange to phenols by an ion-pair mechanism.

EXPERIMENTAL

Preparation of the ethers. The procedure of Hart and Eleuterio[6] was used. Yields and optical rotations are given in Table I.

Solvents. Commercially available solvents were purified by vacuum distillation; β-methylnaphthalene, b.p. 88–91°/5 mm., phenyl ether, b.p. 103–105°/4 mm., diethylene glycol 92–95°/4 mm.

Rearrangement procedure. A solution of 0.05 mole of the ether in 50 g. of solvent was refluxed for 5 hr. at atmospheric pressure, nitrogen atmosphere. Reflux temperatures ranged from 240–260°. After cooling to room temperature 100 ml. of benzene was added and the mixture extracted with four 50-ml. portions of Claisen's alkali (350 g. of potassium hydroxide in 250 g. of water, diluted to one liter with methanol). When the solvent was diethylene glycol, 100 ml. of water was added to the cool reaction mixture which was then extracted with two 100-ml. portions of benzene. The latter was then extracted with Claisen's alkali as above.

The combined alkaline extracts were acidified with 1:2 sulfuric acid, extracted with benzene, dried over anhydrous sodium sulfate, and fractionated. The *ortho*-α-phenethylphenols were identified and checked for purity by comparison of their infrared spectra with those of authentic samples. Yields and optical rotations are summarized in Table II.

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[7] See J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, 1956, p. 455, for a recent review of the Claisen and similar rearrangements.

Preparation of Higher Di-n-alkyl Sulfates[1,2]

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There are numerous references in the chemical literature to the fact that only low to moderate yields of dialkyl sulfates are obtained by the reaction of alkyl chlorosulfonates with alcoholates[3–5] and by the reaction of sulfuryl chloride with alcoholates[4,6,7] and alcohols.[4,8–10] All cases studied involved the preparation of symmetrically and unsymmetrically substituted[4,5] dialkyl sulfates from the lower alcohols. Our experiments with butyl, hexyl, and octyl alcohols confirm these data. However, we have found that from fair to good yields of di-n-alkyl sulfates in which the alkyl groups contain an even number of carbon atoms may be obtained from decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl alcohols by reaction of the alkyl chlorosulfonates with the alcoholates or alcohols.

$$ROSO_2Cl + RONa \longrightarrow (RO)_2SO_2 + NaCl$$
$$ROSO_2Cl + ROH \longrightarrow (RO)_2SO_2 + HCl$$

The best yields are obtained by use of the alcohols at moderate temperature, the yields increasing with increasing chain length. All of these compounds have been previously described.[11] The yields reported are minimal. The yields of the

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(2) Portions of this paper have been abstracted from the thesis of Robert J. Kiesel presented to the Graduate School of St. John's University in partial fulfillment of the requirements for the degree of Master of Science, June 1958.

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