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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[1] Presented before the Division of Organic Chemistry, New York Section of the American Chemical Society Meeting-in-Miniature, New York City, March 14, 1958.

[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.

[3] J. U. Nef, *Ann.*, **318**, 40 (1901).

[4] F. W. Bushong, *Am. Chem. J.*, **30**, 212 (1903).

[5] J. B. Niederl, M. E. McGreal, and W. F. Hart, *J. Org. Chem.*, **14**, 579 (1949).

[6] L. Bert, *Bull. soc. chim.*, (4) **37**, 1258 (1925).

[7] S. S. Medivedew and E. N. Alexejewa, *Ber.*, **65**, 131 (1932).

[8] R. Levaillant and L. J. Simon, *Compt. rend.*, **169**, 854 (1919).

[9] R. Levaillant, *Compt. rend.*, **188**, 261 (1929).

[10] W. Nekrosow and J. F. Komissarow, *J. prakt. Chem.*, (2) **123**, 166 (1929).

[11] C. Barkenbus and J. J. Owen, *J. Am. Chem. Soc.*, **56**, 1204 (1924).

crude product are nearly quantitative but considerable losses were encountered in recrystallization and no attempt was made to rework the mother liquors.

The most satisfactory general method yet described for the preparation of di-*n*-alkyl sulfates is by the reaction of alkyl chlorosulfonates with dialkyl sulfites.[11,12] This method requires three equivalents of the alcohol, one equivalent being converted to the respective alkene or alkyl halide. Since our procedure requires but two equivalents of the alcohol, the percentage conversion is higher than the method employing the dialkyl sulfite, even though the percentage yields are not as high.

In the determination of the melting points of these compounds, particularly those of greatest chain length, there was some evidence of the mesomorphic state.[13] When examined under a polarizing microscope dioctadecyl sulfate exhibited the "stepped drops" and fanlike appearance (focal conics) characteristic of the smectic phase. The doubly refractive crystals are bladed and tend to form in parallel bunched or radially arranged aggregates.

Determination of the cooling curves revealed a marked transition point in the case of dioctadecyl sulfate, less distinct transition points for dihexadecyl and ditetradecyl sulfates and no transition point for didodecyl sulfate (Table I).

TABLE I

MESOMORPHIC DI-*n*-ALKYL SULFATES OF THE SMECTIC TYPE

Compound	Transition Point[a] (from Cooling Curve)	Freezing Point[a] (from Cooling Curve)	Melting Point[a] (by Fisher-Johns Apparatus)
Ditetradecyl sulfate	50.6–51.6	57.4–57.8	57.5–58.0
Dihexadecyl sulfate	60.1–61.1	66.0	66.5–67.0
Dioctadecyl sulfate	60.0–60.7	70.4–71.0	70.0–70.5

[a] Uncorrected.

EXPERIMENTAL

The alcohols used were obtained from Matheson, Coleman, and Bell and were the purest available. The dodecyl, tetradecyl, hexadecyl, and octadecyl alcohols used melted at 21–22°, 36–38°, 48–49°, and 56–58°, respectively. These were used without further purification.

Alkyl chlorosulfonates were prepared by the method of Barkenbus and Owen,[11] modified only in that the alcohols above octyl were added to the sulfuryl chloride as a suspension in dry benzene. Twenty-five ml. of benzene was used for 0.04 mole of the alcohol.

Alcoholates were prepared by adding the equivalent weight of sodium through a condenser to a refluxing solution of 0.04 mole of the alcohol in 25 ml. of anhydrous benzene. Refluxing was continued until the sodium had completely reacted.

Dialkyl sulfates by reaction of the alkyl chlorosulfonates and alcoholates (Procedure A, Table II) were prepared by adding slowly and with shaking 0.04 mole of the alkyl chlorosulfonate in 25 ml. of benzene to 0.04 mole of the sodium alcoholate in 25 ml. of benzene. The mixture was gently refluxed for $^1/_2$–1 hr. until the voluminous precipitate of sodium chloride was compact and settled. The reaction mixture was cooled, filtered and the solvent removed by evaporation. The dibutyl, dihexyl, and dioctyl sulfates were distilled from the crude reaction product at reduced pressure. The dioctyl sulfate distilled in this manner, without previous washing or purification, decomposed at 3-mm. pressure. The higher, solid esters were crystallized from the reaction mixture using decolorizing carbon and ethyl acetate as the solvent. Other solvents which may be used for crystallization are ether, ethyl alcohol, and acetone. Ligroin (b.p. 60–110°) was found to be useful as a solvent for final recrystallization to obtain maximum purity.

TABLE II

YIELDS, %, OF THE DI-*n*-ALKYL SULFATES $(RO)_2SO_2$

R	Procedure A	Procedure B	Procedure C
Butyl	5.0	5.0	
Hexyl	10.2	10.0	
Decyl	19.5	27.1	21.5
Dodecyl	26.6	65.8	30.3
Tetradecyl	39.5	66.2	35.7
Hexadecyl	51.0	67.6	44.6
Octadecyl	56.5	74.0	48.3

Dialkyl sulfates by reaction of alkyl chlorosulfonates with alcohols (Procedure B, Table II). An equivalent amount of the alcohol was added to 0.04 mole of the alkyl chlorosulfonate in 25 ml. of benzene and the mixture gently refluxed while a slow stream of air was bubbled through the reaction mixture. In a short time there were an evolution of gases and a gradual darkening of the reaction mixture. Refluxing with bubbling of air through the reaction mixture was continued for 10 hr. The solvent was then removed by evaporation on a steam bath and the crude product was worked up as described above. This procedure in general gives better yields than by the use of the alcoholate.

Dialkyl sulfates by reaction of alkyl chlorosulfonates with alcohols at elevated temperature (Procedure C, Table II). A modification of Procedure B was used in which the alkyl chlorosulfonate was prepared without the use of benzene, the aeration to remove hydrogen chloride being conducted on a steam bath at a high enough temperature to prevent the alkyl chlorosulfonate from solidifying. The alkyl chlorosulfonate was then added in portions with shaking to the equivalent amount of alcohol preheated to 120–125° in an oil bath. There was a gradual darkening of the reaction mixture. The temperature was maintained at 120–125° for 2 hr. After cooling the reaction product was worked up as previously described. In general, the yields by this procedure are somewhat lower than by either of the above described methods.

It has been postulated[4,7] that the hydrogen chloride produced in this reaction lowers the yield by causing decomposition of the dialkyl sulfate formed. Attempts to prevent the evolution of the hydrogen chloride by the addition of bases or active metals were not successful. Addition of an equivalent amount of pyridine gave a sulfur-containing salt of pyridine and not the hydrochloride; anhydrous borax used in the reaction of butyl alcohol with butyl chlorosulfonate produced butyl borate. Magnesium metal did not entirely suppress hydrogen chloride evolution, as this gas was evolved together with hydrogen.

The mesomorphic state of the members of this series of dialkyl sulfates having the greatest chain length was studied by means of heating and cooling curves. A sufficient amount of the compound to cover, when molten, the bulb of an

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(12) R. Levaillant, *Compt. rend.*, **197**, 648 (1933).

(13) S. Glasstone, *Textbook of Physical Chemistry*, 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, p. 514.

TABLE III

Physical Properties of the Di-*n*-alkyl Sulfates $(RO)_2SO_2$

R	Formula	B.P.[a]	M.P.[a]	Analysis					
				C		H		S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Butyl	$C_8H_{18}O_4S$	96–98/3 mm.							
Hexyl	$C_{12}H_{26}O_4S$	123–126/3 mm.							
Decyl	$C_{20}H_{42}O_4S$		37.5–38.0	63.44	63.45	11.19	10.91	8.47	8.37
Dodecyl	$C_{24}H_{50}O_4S$		47.8–48.5	66.30	66.42	11.59	11.49	7.37	7.28
Tetradecyl	$C_{28}H_{58}O_4S$		57.5–58.0	68.51	68.80	11.91	11.84	6.53	6.46
Hexadecyl	$C_{32}H_{66}O_4S$		66.5–67.0	70.27	70.15	12.16	12.31	5.86	5.31
Octadecyl	$C_{36}H_{74}O_4S$		70.0–70.5	71.70	71.88	12.37	12.17	5.32	5.24

[a] Boiling points and melting points are uncorrected.

Anschutz thermometer suspended in a 10 × 70 mm. test tube was placed in the tube. The test tube was suspended in a 20 × 50 mm. vial by means of a notched cork ring, the vial serving as an air bath. The vial was immersed in a 400-ml. beaker filled with water which was heated and stirred by a magnetic stirrer hot plate.

The temperature of the water bath was slowly raised (about 2 degrees per minute) and readings were made every 30 sec. The thermometer readings were then plotted against time. The cooling curve was obtained by removing the water bath after the temperature had been raised well above the melting point and thermometer readings were made at thirty second intervals.

Another procedure employed was to suspend a second Anschutz thermometer in the water bath and take readings of the thermometer in the tube at intervals of one degree change of the water bath temperature. In some respects this procedure is superior as the rate of heating or cooling has less effect on the curve obtained.

The transition point (conversion from crystalline solid or clear isotropic liquid to the turbid mesomorphic stage) was marked by a break in the heating and cooling curves. As would be expected the melting point or freezing point (conversion of turbid mesomorphic stage to clear isotropic liquid or crystalline solid) did not involve as marked a temperature change and consequently not as distinct a break in the curves obtained. In general, there was good agreement in the results obtained from the heating and cooling curves, but the cooling curves gave better results at the freezing point.

Melting points were checked using a Fisher-Johns apparatus. The results agreed within the range of accuracy obtainable by this method, and are in substantial agreement with the melting points previously published.

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A New Synthesis of *cis*-9,10-Epoxyoctadecane

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Boeseken and Belinfante[2] in a four step synthesis prepared *cis*-9,10-epoxyoctadecane by epoxidation of *cis*-9,10-octadecene which they obtained by the reduction of oleyl iodide with a copper-zinc couple in acetic acid.

We have prepared *cis*-9,10-epoxyoctadecane by a new three step synthesis. Oleyl alcohol was converted to oleyl tosylate, and the latter was cleaved with $LiAlH_4$ to *cis*-9,10-octadecene which was then epoxidized with peracetic acid to give the desired compound in 47% over-all yield.

The geometrical structure of the *cis*-9,10-epoxyoctadecane was verified by the appearance in its infrared absorption spectrum of a peak at 825 cm.$^{-1}$ which Shreve *et al.*[3] reported to be characteristic of *cis* epoxides, and by the absence of a peak at 893 cm.$^{-1}$ which they reported to be characteristic of *trans* epoxides. A peak was also observed at 905 cm.$^{-1}$ which was shown to be present in *cis*-9,10-epoxyoctadecanol and absent in *trans*-9,10-epoxyoctadecanol. This new peak was obscured in previous work with the isomeric epoxystearic acids and esters[3] by the COO vibrations in this region.

Table I lists the physical properties of *cis*-9,10-epoxyoctadecane and its intermediates.

EXPERIMENTAL

Oleyl alcohol. Commercial oleyl alcohol, Cachalot 0-8 grade, obtained from M. Michel and Co.[4] was purified by the method of Swern, *et al.*[5] The cuts boiling between 184–187° at 4.5 mm., n_D^{25} 1.4590, iodine value 93.5 (purity 98.6%) were used to make the tosylate. Infrared analysis showed this material to contain about 2% elaidyl alcohol.[3]

Synthesis of oleyl tosylate. The procedure of Shirley[6] was followed essentially, except that the *p*-toluenesulfonyl chloride was added as a pyridine solution. After the reaction mixture had been stirred at 10 ± 2° for 6 hr., it was poured into cold water and transferred to a separatory funnel. The upper oil layer was washed with two successive portions of cold methanol. The lower (tosylate) layer from these extractions was drained into a round-bottom flask, and the pyridine and methanol were removed *in vacuo* under a

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(1) Fellow of National Renderers Association.

(2) J. Boeseken and A. H. Belinfante, *Rec. trav. chim.*, **45**, 914 (1926).

(3) O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

(4) Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

(5) D. Swern, H. B. Knight, and T. W. Findley, *Oil & Soap*, Vol. **XXI**, 133 (1944).

(6) D. A. Shirley and W. H. Reedy, *J. Am. Chem. Soc.*, **73**, 458 (1951).