

## Bis[4(1-methyl-1,2-epoxyethyl)] Derivatives of Phenyl Ether, 1,4-Diphenoxybenzene, and Bis(4-phenoxyphenyl) Ether

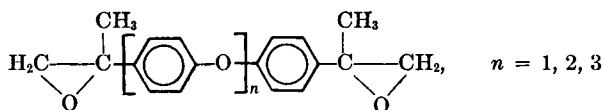
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### Synopsis

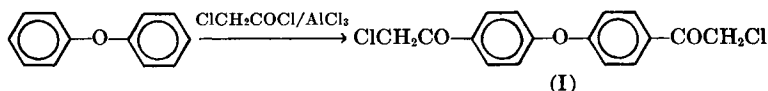
The syntheses of three new  $\alpha$ -methyl-substituted bis(epoxyethyl) derivatives of phenyl ether, 1,4-diphenoxybenzene, and bis(4-phenoxyphenyl) ether are reported. Improved procedures for preparing 1,4-diphenoxybenzene and bis(4-phenoxyphenyl) ether by the Ullmann method are described. Infrared spectral data for the bisepoxides and their precursors are given, as are some reactions of the bisepoxides.

No report has yet appeared on the synthesis of aliphatic epoxy derivatives of phenylene oxides. In connection with a study of epoxy monomers that can yield polymers possessing superior thermal and oxidative stability we have synthesized the first three members of a homologous series of bisepoxides, derived from phenyl ether and phenylene oxides, in which the aliphatic oxirane moiety has been reduced to its shortest length (i.e., epoxyethyl), and the reactive "benzylic" position has been blocked by methyl substitution.

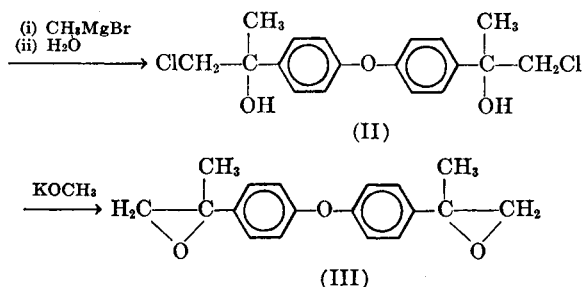
This article discusses the syntheses of three bisepoxides of the following structure:



Bis[4(1-methyl-1,2-epoxyethyl)phenyl] ether [compound (III), where  $n = 1$ ] was prepared as follows:



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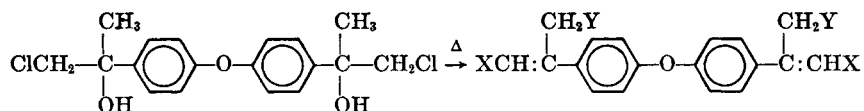


Kunckell<sup>1</sup> first prepared bis(4-chloroacetylphenyl) ether (I) as "greenish crystals," m.p. 111°C., and von Schickh<sup>2</sup> prepared this compound by adding phenyl ether and chloroacetyl chloride to sublimed aluminum chloride in the absence of solvent. The Friedel-Crafts reaction carried out in this manner gave only a 43% yield of (I), which melted at 102°C. We have greatly improved the synthesis by employing methylene chloride as the reaction medium, and in this solvent the Friedel-Crafts reaction proceeded *homogeneously* in yields exceeding 90%. After recrystallization pure (I) was obtained as colorless prisms, m.p. 114°C.

NOTE. Compound (I) was first prepared in the North American laboratory by Harold H. Chen, in 60–65% yield, with carbon disulfide as solvent. This procedure gave a mixture consisting of two immiscible liquid phases and was disadvantageous for large-scale preparations because of the hazard of explosion and fire.

The relative merits of carbon disulfide and methylene chloride as Friedel-Crafts solvents are discussed by Olah.<sup>3</sup>

The bischlorohydrin (II) was prepared in theoretical yield by treating (I) with methylmagnesium bromide in tetrahydrofuran below 0°C. After decomposition of the Grignard complex the tetrahydrofuran was removed *without* heating. If heat was applied to the bischlorohydrin, mixtures of vinyl derivatives resulted. The infrared spectra of these compounds showed strong absorption at 986 and 3080 cm.<sup>-1</sup>. No absorption for hydroxyl was detected, showing that (II) had entirely lost the elements of water. Since (II) is a ditertiary alcohol, it is probable that the elimination of two molecules of water gave a mixture of vinyl derivatives:



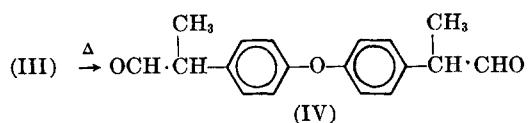
where X = H and Y = Cl, or X = Cl and Y = H. These vinyl compounds were not required in our synthesis program, and no effort was made to characterize them other than by infrared spectral analysis.

Bis[4(1-methyl-1,2-epoxyethyl)phenyl] ether (III) was prepared in 80–85% yield by treating a methanolic solution of (II) with a stoichiometric amount of potassium methoxide. Preparations in which doubly

recrystallized (I), m.p. 114°C., was employed consistently gave (III) as a creamy-white microcrystalline aggregate. However, when impure (I) was used, the resulting (III) was contaminated with an orange-colored gummy by-product, which was very difficult to separate.

NOTE. Harold H. Chen was the first to prepare a 50 g. specimen of (III) in the North American laboratory. This tan-colored powder, m.p. 40–44°C., was shown in our investigation to be contaminated with residual potassium chloride, potassium hydroxide, methanol, and gummy by-products (possibly vinyl derivatives).

The facile rearrangement of styrene oxide to phenylacetaldehyde through the action of heat or Lewis acids<sup>4,5</sup> suggested that  $\alpha$ -methyl-substituted styrene oxide derivatives, such as (III) and its longer-chain homologues, would undergo a similar rearrangement:



The formation of bis[4(1-formylethyl)phenyl] ether (IV), or partially rearranged intermediates, was prevented by recrystallizing (III) from methanol at low temperature. This procedure yielded (III) as white crystals, which melted sharply at 51.5°C.

It is significant that the infrared spectrum of small specimens of (III) heated at 175°C. for 15 min. showed strong absorption for carbonyl at 1675 and 1720  $\text{cm}^{-1}$  and no absorption for the oxirane ring at 910  $\text{cm}^{-1}$ . Although no further characterization of the products of rearrangement was carried out, the spectral data strongly suggest that rearrangement of (III) to (IV) is very rapid at 175°C. The infrared spectrum of (III), which had been stored at 20°C for 6 months, showed strong absorption for carbonyl and no absorption for the oxirane group, indicating that even at ambient temperatures the rearrangement of (III) to (IV) occurs slowly. Infrared spectral data showed that specimens of (III) that had been stored at -20°C. for 6 months had undergone no rearrangement to compounds containing carbonyl groups.

The second homologue, 1,4-bis[4(1-methyl-1,2-epoxyethyl)phenoxy]-benzene [compound (VIII), where  $n = 2$ ], was prepared from 1,4-diphenoxybenzene (V). By suitably modifying previously published procedures,<sup>6,7</sup> (V) was prepared in 93% yield by the Ullmann method. The bischloro ketone (VI), and bischlorohydrin (VII) were synthesized by procedures and with precautions similar to those described for the preparation of (I) and (II).

Bis(4-phenoxyphenyl) ether (IX), the parent compound of the third bisepoxide [compound (XII), where  $n = 3$ ], was prepared in 95% yield with modifications of earlier Ullmann procedures.<sup>8-10</sup>

Lewis acid catalysts ( $\text{BF}_3$  etherate, *p*-toluenesulfonic acid, etc.) readily polymerized the three bisepoxides (III), (VIII), and (XII). Polymer-

ization studies, thermogravimetric analysis (TGA), differential thermal analysis (DTA), and chemical-resistance and oxidation data on the bis-epoxides will be published elsewhere.

## EXPERIMENTAL

### Reagents

All chemicals were of reagent grade, and chloroacetyl chloride was redistilled before use. Methylmagnesium bromide (2*M* in tetrahydrofuran and benzene) was supplied by Arapahoe Chemicals, Inc., Boulder, Colorado.

### Physical Measurements

Melting points were determined with a Fisher-Johns melting-point apparatus and are uncorrected. Infrared spectral data were determined with the use of potassium bromide pellets. A Beckman IR-4 spectrophotometer with sodium chloride optics was employed.

### Bis(4-chloroacetylphenyl) Ether (I)

Finely powdered anhydrous aluminum chloride (579.6 g., 4.33 moles), anhydrous methylene chloride (500 ml.), and chloroacetyl chloride (434.0 g., 3.80 moles) were cooled to  $-10^{\circ}\text{C}$ . Phenyl ether (294.5 g., 1.73 moles) in methylene chloride (100 ml.) was added dropwise with stirring during 30 min., care being taken to maintain the temperature below  $10^{\circ}\text{C}$ . The mixture was stirred at  $10^{\circ}\text{C}$ . for 2.5 hr., during which HCl was copiously evolved, and then left unstirred at  $20^{\circ}\text{C}$ . overnight. The blood-red solution was poured onto crushed ice (ca. 2 kg.) and extracted with methylene chloride (500 ml.), and the extract washed to pH 7 with water, dried over anhydrous magnesium sulfate, and filtered. Solvent was removed on the steam bath, and the pale-tan crystalline product was evacuated at 10 mm. for 1 hr. The solid (550.0 g., 99.5%), m.p.  $105\text{--}107^{\circ}\text{C}$ ., was recrystallized twice from isopropanol with the use of decolorizing charcoal, and after drying *in vacuo* 508.0 g. (92.0%) of colorless prisms, m.p.  $114^{\circ}\text{C}$ ., were obtained. The infrared spectrum showed a strong absorption band at  $1700\text{ cm.}^{-1}$  ( $>\text{C}=\text{O}$ ) and a doublet at 763 and  $790\text{ cm.}^{-1}$  (C—Cl).

ANAL. Calcd. for  $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_3$ : C, 59.46%; H, 3.75%; Cl, 21.94%. Found: C, 59.52%; H, 3.74%; Cl, 21.80%.

### Bis[4(1-hydroxy-1-methyl-2-chloroethyl)phenyl] Ether (II)

Methylmagnesium bromide (2*M*, 1250 ml., 2.5 moles) and sodium-dried tetrahydrofuran (THF) were cooled to  $-5^{\circ}\text{C}$ ., then compound (I) (324.0 g., 1.0 mole) in THF (1200 ml.) was added dropwise with stirring during 45 min. at  $-5^{\circ}\text{C}$ . After being stirred an additional 45 min. at  $-5^{\circ}\text{C}$ . the solution was poured onto a mixture of crushed ice (ca. 1 kg.) and concentrated sulfuric acid (100 ml.). The THF layer was washed to pH 7

with water, dried over magnesium sulfate, and filtered. Solvent was removed with a rotary evaporator *without* heating to yield 355.7 g. (100%) of viscous pale-amber liquid. No elemental analysis data were obtained for (II). Its structure was inferred from its method of preparation and subsequent ring closure to the bisepoxide (III). The infrared spectrum of (II) showed strong absorption at 3480 ( $\text{—OH}$ ) and 760  $\text{cm.}^{-1}$  ( $\text{C—Cl}$ ).

### Bis[4(1-methyl-1,2-epoxyethyl)phenyl] Ether (III)

To a solution of (II) (355.7 g., 1.0 mole) in anhydrous methanol (1 liter) at  $-5^{\circ}\text{C.}$  was added 5*N* methanolic potassium hydroxide (396.0 ml., 2.0 moles) dropwise with stirring during 15 min. The mixture was stirred at  $0\text{--}10^{\circ}\text{C.}$  for 30 min. and filtered rapidly through a coarse-grade sintered-glass funnel, the solid [(III) and  $\text{KCl}$ ] was washed with fresh methanol (200 ml.), and the filtrate was refrigerated overnight at  $-20^{\circ}\text{C.}$  The crystalline bisepoxide was quickly filtered at  $-20^{\circ}\text{C.}$ , pressed, drained, and dried *in vacuo* to yield 228.7 g. (81.0%) of cream-colored crystals, m.p.  $44\text{--}45^{\circ}\text{C.}$  A further, less pure, crop of (III) (5–10%) was obtained by evaporating the mother liquor to half volume at  $10^{\circ}\text{C.}$

By dissolving (III) in the minimum volume of anhydrous acetone at  $20^{\circ}\text{C.}$ , filtering from a trace of microcrystalline potassium chloride, removing the acetone in a stream of air, redissolving the residue in the minimum volume of methanol at  $30^{\circ}\text{C.}$ , and cooling the solution to  $-30^{\circ}\text{C.}$ , white crystalline clusters of (III) were obtained. After drying *in vacuo* these crystals melted sharply at  $51.5^{\circ}\text{C.}$  The infrared spectrum showed strong bands at 3050 and 910  $\text{cm.}^{-1}$  (oxirane) and 2960  $\text{cm.}^{-1}$  ( $\text{C—CH}_3$ ).

ANAL. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.57%; H, 6.43%. Found: C, 76.30%; H, 6.24%.

### Rearrangement of (III) to (IV)

One-gram specimens of recrystallized (III) were heated in an air oven at  $175^{\circ}\text{C.}$  for 15 min. The infrared spectra of the products showed strong absorption for carbonyl at 1675 and 1720  $\text{cm.}^{-1}$ . No absorption for oxirane at 910  $\text{cm.}^{-1}$  was detected, indicating that rearrangement of (III) to (IV) was complete. The infrared spectrum of a 1 g. specimen of (III) which had been stored at  $20^{\circ}\text{C.}$  for 6 months showed strong absorption for carbonyl and no absorption for oxirane oxygen. Specimens of (III), and also of (VIII) and (XII), which had been stored at  $-20^{\circ}\text{C.}$  for 6 months, showed strong oxirane absorption at 910  $\text{cm.}^{-1}$  and no absorption for carbonyl.

### 1,4-Diphenoxybenzene (V)

In a 1-liter three-necked flask, fitted with a Dean-Stark trap, reflux condenser, motor-driven stirrer, and thermometer, were placed phenol (210.0 g., 2.1 moles) and powdered potassium hydroxide (112.0 g., 2.0 moles). Water and unreacted phenol were removed by vigorously stirring and heating the melt to  $180^{\circ}\text{C.}$  by means of a fused-metal bath. Freshly

precipitated, moist (i.e. "active") copper powder (10 g.) and 1,4-dibromobenzene (236.0 g., 1.0 mole) were added, and the temperature of the stirred mixture gradually was raised to 200°C. during 45 min. The melt was then heated at 240–260°C. for 3.5 hr., cooled to 115°C, xylene (500 ml.) was added, stirred 10 min., and filtered *hot* through a coarse-grade sintered-glass funnel. The solid residue was again extracted with hot (120°C.) xylene (500 ml.) and filtered. The xylene extract was washed with hot (90°C) 20% sodium hydroxide and then with water (90°C.) to pH 7. The xylene extract was dried with magnesium sulfate, and the solvent was removed with a heated rotary evaporator. The dried tan-colored crystalline product weighed 242.6 g. (92.7%). Recrystallization from isopropanol, with charcoal, yielded colorless prisms, m.p. 76.5°C. (lit., 77°C).<sup>11</sup>

ANAL. Calcd. for  $C_{18}H_{14}O_2$ : C, 82.42%; H, 5.38%. Found: C, 82.30%; H, 5.36%.

### 1,4-Bis(4-chloroacetylphenoxy)benzene (VI)

This compound was prepared by a procedure similar to that described for (I). The following amounts of reagents were employed: (V), 94.0 g., 0.36 mole, in  $CH_2Cl_2$ , 200 ml.;  $AlCl_3$ , 117 g., 0.88 mole;  $CH_2Cl_2$ , 180 ml.; and  $ClCH_2COCl$ , 90 g., 0.79 mole. After the initial reaction at  $-10^\circ C$  had subsided, the mixture was allowed to react at  $20^\circ C$ . for 3 days before working up. The yield of crude (VI), m.p.  $172^\circ C$ ., was 91.3%. Two recrystallizations from isopropanol, with charcoal, gave colorless needles that melted sharply at  $176^\circ C$ . The infrared spectrum showed strong absorption bands at 1710 ( $>CO$ ), 1210 and 1230 (Ar—O—Ar), and 778 and  $790\text{ cm.}^{-1}$  (C—Cl).

ANAL. Calcd. for  $C_{22}H_{16}Cl_2O_4$ : C, 63.63%; H, 3.88%; Cl, 17.08%. Found: C, 63.53%; H, 3.88%; Cl, 16.87%.

### 1,4-Bis[4(1-hydroxy-1-methyl-2-chloroethyl)phenoxy]benzene (VII)

To methylmagnesium bromide (2*M*, 125 ml., 0.25 mole) cooled to  $-5^\circ C$ . a solution of (VI) (41.5 g., 0.1 mole) in anhydrous THF (850 ml.) was added during 25 min. The mixture was worked up as described for the preparation of (II). Compound (VII) was obtained as a pale-amber viscous liquid in theoretical yield.

### 1,4-Bis[4(1-methyl-1,2-epoxyethyl)phenoxy]benzene (VIII)

Compound (VII) was dissolved in anhydrous methanol, cooled to  $10^\circ C$ ., and then treated with 5*N* methanolic potassium hydroxide (39.6 ml., 0.2 mole) with the use of the same procedure as for (III). Compound (VIII) (36.8 g., 98.4%) was obtained as a white microcrystalline solid, m.p.  $100\text{--}101^\circ C$ . Recrystallization from the minimum volume of acetone at  $30^\circ C$ . and cooling to  $-30^\circ C$ . yielded (VIII), which melted sharply at  $103.5^\circ C$ . The infrared spectrum showed strong bands at  $2970\text{ cm.}^{-1}$  (C— $CH_3$ ) and  $910\text{ cm.}^{-1}$  (oxirane).

ANAL. Calcd. for  $C_{24}H_{22}O_4$ : C, 76.99%; H, 5.92%. Found: C, 76.41%; H, 5.84%.

### Bis(4-phenoxyphenyl) Ether (IX)

This compound was prepared in 95% yield from potassium phenoxide (261.6 g., 1.98 moles), "active" copper powder (10 g.), and bis-(4-bromophenyl) ether (196.8 g., 0.60 mole) with the use of the procedure described for the preparation of (V). The pale-tan crystalline product was recrystallized from isopropanol, with charcoal, and (IX) was obtained as scintillating white prisms, m.p. 110°C. (lit., 110.3°C.).<sup>10</sup>

### Bis[4(4-chloroacetylphenoxy)phenyl] Ether (X)

By allowing aluminum chloride (0.88 mole), chloroacetyl chloride (0.79 mole) and (IX) (0.36 mole) to react in methylene chloride (900 ml.) at 25°C. for 5 days a 69% yield of (X) was obtained as pale-tan crystals. Recrystallization from a 1:2 mixture of benzene and acetone, with charcoal, yielded colorless platelets with a nacreous reflex, m.p. 161°C. The infrared spectrum showed bands at 1680  $cm^{-1}$  ( $>CO$ ) and 788 and 796  $cm^{-1}$  (C—Cl).

ANAL. Calcd. for  $C_{23}H_{20}Cl_2O_5$ : C, 66.28%; H, 3.97%; Cl, 13.98%. Found: C, 66.57%; H, 3.95%; Cl, 13.63%.

### Bis{4[4(1-hydroxy-1-methyl-2-chloroethyl)phenoxy]phenyl} Ether (XI)

A solution of (X) (50.7 g., 0.1 mole) in THF (1 liter) and benzene (300 ml.) was added during 45 min. to stirred 2M methylmagnesium bromide (125 ml., 0.25 mole) at -5°C. The mixture was then worked up, as in the preparation of (II), to give a theoretical yield of viscous pale-amber liquid.

### Bis{4[4(1-methyl-1,2-epoxyethyl)phenoxy]phenyl} Ether (XII)

Compound (XI) was dissolved in anhydrous methanol (700 ml.) and cooled to 5°C, and 5N methanolic potassium hydroxide (39.6 ml., 0.2 mole) was added, with stirring, during 10 min. The mixture was worked up, as for (VIII), to yield 51% of a white, microcrystalline solid, which was recrystallized by dissolving in the minimum volume of anhydrous THF at 30°C., filtering from residual potassium chloride, and cooling to -30°C. The white crystalline bisepoxide melted sharply at 119°C. The infrared spectrum of (XII) showed strong absorption at 910  $cm^{-1}$  (oxirane) and no absorption due to —OH or —Cl.

ANAL. Calcd. for  $C_{30}H_{26}O_5$ : C, 77.24%; H, 5.62%. Found: C, 77.63%; H, 5.43%.

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### Résumé

Les synthèses de trois dérivés bis(époxyéthyl) de l'éther phénylique, du 1,4-diphénoxybenzène et de l'éther bis(4-phénoxyphényle) substitués par le groupe alpha méthyle sont rapportées. Des procédés améliorés de préparation du 1,4-diphénoxybenzène et de l'éther bis(4-phénoxyphényl) par la méthode de Ullmann sont décrits. Les résultats d'analyses spectrales infrarouges de ces deux époxydes et de leurs précurseurs sont donnés, de même que certaines réactions des bis-époxydes.

### Zusammenfassung

Über die Synthese dreier neuer methylsubstituierter Derivate von Phenyläther, 1,4-Diphenoxybenzol und Bis-(4-phenoxyphenyl)-äther wird berichtet. Verbesserte Verfahren zur Darstellung von 1,4-Diphenoxybenzol und Bis-(4-phenoxyphenyl)-äther nach der Methode von Ullmann werden beschrieben. Infrarotspektroskopische Daten für die Bis-epoxyde und ihre Vorstufen sowie einige Reaktionen der Bis-epoxyde werden angegeben.

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