needle-like solid was obtained, m.p. 101–102°. This gave no melting point depression when mixed with an authentic sample of bis-(*p*-tolylmercapto)-ethyne.[12] Based on the amount of XIII formed and *p*-toluenethiol recovered, the conversion in the addition reaction was 75% and the yield 90%.

A sample of the oil obtained in a repetition of the addition reaction could be caused to crystallize from methanol to give a crystalline solid, m.p. 46–47°. This compound also contained both chlorine and sulfur. A fraction of the solid (0.68 g.) was dissolved in a solution of 20 ml. of glacial acetic acid and 5 ml. of 30% hydrogen peroxide and heated on the steam-bath for 1 hour. The hot oxidation mixture was poured on ice, and the resulting sulfone filtered and recrystallized to give 0.74 g. of a crystalline solid, m.p. 157–158° (90% yield). This sulfone did not depress the melting point of an authentic sample of 1-chloro-1,2-di-(*p*-tolylsulfonyl)-ethene (XIIa). On this basis, the product was assigned the structure 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene (XII).

Reaction of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene with *p*-Toluenethiol in the Presence of a Catalytic Amount of Sodium *p*-Toluenethiolate.—A solution prepared from 0.85 g. (0.0069 mole) of *p*-toluenethiol, 2.0 g. (0.0059 mole) of 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene, 10 ml. of a sodium ethoxide solution (0.2 g./100 ml., 0.02 g., 0.0008 mole) and 75 ml. of absolute ethanol was refluxed for 18 hours under a nitrogen atmosphere. No sodium chloride was isolated. On concentrating the ethanol solution, 1.70 g. of a solid was obtained, m.p. 157–158°. This did not depress the melting point of an authentic sample of XII. This represents 85% recovery of starting material.

Reaction of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene with Sodium *p*-Toluenethiolate in the Presence of Sodium Ethoxide.—The following mixture was heated to reflux under a nitrogen atmosphere for 2 hours: 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene (2.43 g., 0.0071 mole), *p*-toluenethiol (1.06 g., 0.009 mole) and sodium (0.23 g., 0.10 mole) in 75 ml. of absolute ethanol. Sodium chloride was filtered from the hot solution, which on concentration and cooling gave 2.70 g. of solid (XIV), m.p. 56–57° (97% yield). No depression was observed in the melting point of an authentic sample of 1,1,2-tris-(*p*-tolylmercapto)-ethene.

Dehydrohalogenation of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene (XII) with Alcoholic Potassium Hydroxide.—A solution prepared from 2.0 g. (0.0065 mole) of 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene, 2.0 g. (0.035 mole) of potassium hydroxide and 50 ml. of ethanol was refluxed for 15 minutes. On cooling the ethanolic solution, 1.65 g. (94% yield) of solid was crystallized, m.p. 101–102°. This did not depress the melting point of an authentic sample of bis-(*p*-tolylmercapto)-ethyne (XIII).[12]

Reaction of Bis-(*p*-tolylmercapto)-ethyne (XIII) with *p*-Toluenethiol.—Sodium (0.10 g., 0.004 mole) was dissolved in absolute ethanol followed by *p*-toluenethiol (2.4 g., 0.0195 mole) so that the total volume was 100 ml. This was added rapidly to a refluxing solution of XIII (5.0 g., 0.020 mole) in 50 ml. of absolute ethanol and allowed to reflux for an additional hour under a nitrogen atmosphere. After concentration to approx. 100 ml., the solution on cooling gave 6.5 g. (90% yield) of solid, m.p. 56–57°. No depression was observed in the mixed melting point of the above product and an authentic sample of 1,1,2-tris-(*p*-tolylmercapto)-ethene.

Reaction of 1,1,2-Tris-(*p*-tolylmercapto)-ethene (XIV) with *n*-Butyllithium.—A solution of *n*-butyllithium in ether (100 ml.) was prepared from lithium wire (1 g., 0.14 mole) and *n*-butyl bromide (7.6 g., 0.055 mole) by the method of Gilman.[14] A solution of XIV (10.0 g., 0.025 mole) in 50 ml. of anhydrous ether was added to the *n*-butyllithium solution with stirring, and maintained at 0° for 2 hours under a nitrogen atmosphere. The solution was allowed to warm up to room temperature and stirred for an additional 2 hours and then quenched with 50 ml. of water. The ether layer was separated and dried over magnesium sulfate while the aqueous layer was acidified with concd. hydrochloric acid, and extracted with petroleum ether (35–37°) which was dried over magnesium sulfate. On evaporation of petroleum ether, 3.55 g. (0.028 mole) of *p*-toluenethiol, m.p. 40–42°, was obtained. Evaporation of the ether solution gave a material, which was recrystallized from ethanol to give 1.84 g. of solid, m.p. 101–102°. This did not depress the melting point of an authentic sample of bis-(*p*-tolylmercapto)-ethyne. The yield of XIV was 37%.

Acknowledgment.—The authors gratefully acknowledge support of this work by the Office of Ordnance Research, Department of the Army, under contract No. DA 33-008-ORD 983.

[14] H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 285.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Epoxyethers. XII.[1] Reduction with Lithium Aluminum Hydride

BY CALVIN L. STEVENS AND THOMAS H. COFFIELD[2,3]

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Five epoxyethers were subjected to reduction with lithium aluminum hydride reagent. Each of the epoxyethers I–IV was reduced in *ca.* 80% yield by attack of hydride ion upon the carbon containing the ether group. No evidence was found for partial attack upon the other carbon of the oxide. The triphenyl substituted epoxyether V was not reduced. The structures of the methoxy alcohols VI, VII and IX were proven by independent synthesis. A new and convenient method for the preparation of solid ester derivatives of tertiary alcohols was found which involved reaction with sodium dispersion to form the alcohol salt and then reaction with *p*-nitrobenzoyl chloride.

From the various acid-catalyzed openings of epoxyethers that have been investigated, previously the epoxyethers have been shown to open significantly faster than ordinary oxides and the opening reaction has been shown to proceed by attack of the nucleophilic agent on the epoxide carbon that contained the ether group.[4] The ease and direction of opening are predictable from the known ability of the ether group to facilitate the development of a positive charge on an adjacent carbon (in this example, the ketal carbon of the epoxyether). This property of the ether group has also been used to explain the ease and direction of the acid-catalyzed rearrangement of epoxyethers.[5]

The chemical reduction of epoxyethers with lithium aluminum hydride is here shown to follow the course of the previous acid-catalyzed ring opening reactions. In the reactions, hydride ion attacked the ketal carbon to give methoxy alcohols. The

[1] Paper XI is the THIS JOURNAL, **79**, 3448 (1957).

[2] Abstracted from the dissertation submitted by T. H. Coffield in partial fulfillment of the requirement for the degree of Doctor of Philosophy, Wayne University, 1955.

[3] Ethyl Corporation Fellow.

[4] C. L. Stevens, M. L. Weiner and C. T. Lenk, THIS JOURNAL, **76**, 2698 (1954), and preceding papers in the epoxyether series.

[5] C. L. Stevens and S. J. Dykstra, *ibid.*, **76**, 4402 (1954).

epoxyethers I-IV gave the corresponding methoxy alcohols VI–IX in *ca.* 80% yield.

In the example of epoxyether I, attack of the hydride ion upon the other carbon atom of the oxide would be expected to produce a stable metal salt of the alcoholate of isobutyrophenone or the fully reduced phenylisopropylcarbinol. After hydrolysis of the reaction mixture, neither isobutyrophenone nor the carbinol could be detected, indicating that the attack was cleanly on the ketal carbon.

The structures of the methoxy alcohols VI and VII were proved by independent synthesis starting from methyl α-methoxyphenylacetate (X), which was treated with excess methylmagnesium bromide to yield VI in 86% yield. Ethylmagnesium bromide and X gave VII in 82% yield. The two samples prepared by independent synthesis had the same physical properties, analysis and infrared spectra as the corresponding products from reduction of the epoxyethers. The identity of the products was further confirmed by preparation of solid ester derivatives of the tertiary alcohol group.

Ordinary methods for the preparation of derivatives of the tertiary alcohols VI and VII failed. However, the *p*-nitrobenzoate esters of VI and VII could be made rapidly and conveniently by treatment of a toluene solution of the alcohol with one equivalent of sodium dispersion (6 μ particle size), followed by addition of *p*-nitrobenzoyl chloride.

The structure of the methoxy alcohol IX was proved by reduction of the corresponding methoxy ketone with lithium aluminum hydride in 75% yield.

The structure VIII was assigned on the basis of the physical properties, infrared spectra, analysis and a positive iodoform test. The amount of diastereoisomers present in this reduction product was not determined.[6]

The triphenyl-substituted epoxyether V was not reduced by lithium aluminum hydride under the conditions used.

The epoxyether I was prepared from α-bromoisobutyrophenone and dry sodium methoxide in ether in 74% yield.[7] Previously an identical reaction had been reported[8] in which the product was assigned the structure of α-methoxyisobutyrophenone. The epoxyether had the same physical properties as the previously reported α-methoxy ketone, but had no carbonyl absorption band in the infrared spectrum and reacted exothermically with methanol containing acid catalyst to give α-hydroxyisobutyrophenone dimethyl ketal in 96% yield. The product reacted with dinitrobenzoic acid to give the α-hydroxyisobutyrophenone 3,5-dinitrobenzoate in 76% yield. These data leave no doubt that the compound is the epoxyether I.

The new epoxyether II was prepared from the corresponding α-bromoketone in 57% yield.

The reduction of epoxides with hydride ion has been investigated recently by VanderWerf[9] and the *p*-methoxystyrene oxide used in that study can be considered a vinylog of an epoxyether. The present example fully confirms such a consideration since the opening is exclusively in the direction predicted by the previous work.

Experimental

Epoxyethers.—The epoxyether I was prepared in 74% yield from α-bromoisobutyrophenone by the procedure previously published[7] for the ethoxy analog. The 1,2-epoxy-3-methyl-1-methoxy-1-phenylpropane had b.p. 68–70° (3 mm.), $n^{25}\mathrm{D}$ 1.4905.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.21; H, 7.93. Found: C, 74.55; H, 8.15.

3,5-Dinitrobenzoic acid reacted rapidly with I to give 76% of α-hydroxyisobutyrophenone 3,5-dinitrobenzoate, m.p. 151–152°. A mixture melting point with an authentic sample[7] was not depressed.

The epoxyether reacted rapidly with methyl alcohol catalyzed by acid to give 96% of α-hydroxyisobutyrophenone dimethyl ketal, m.p. 58–59°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.53; H, 8.65. Found: C, 68.44; H, 8.62.

The epoxyether II was made from α-bromo-α-ethyl butyrophenone, which had b.p. 130–131° (5 mm.), $n^{23}\mathrm{D}$ 1.5476.

Anal. Calcd. for $C_{12}H_{15}BrO$: C, 56.47; H, 5.93. Found: C, 56.95; H, 5.93.

1,2-Epoxy-2-ethyl-1-methoxy-1-phenylbutane (II) was isolated in 57% yield from the bromoketone and had b.p. 81–82° (2.7 mm.), $n^{22}\mathrm{D}$ 1.4892.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.65; H, 8.79. Found: C, 75.73; H, 9.06.

The epoxyethers III,[10] IV[11] and V[12] have been prepared previously.

Formation of the Methoxy Alcohols by Reduction of Epoxyethers with Lithium Aluminum Hydride.—The epoxyethers were reduced by the following procedure and the yields and properties are given in Table I.

In a 500-ml. 3-necked flask equipped with a stirrer, reflux condenser and dropping funnel were placed 100 ml. of anhydrous ether and 5 g. (0.132 mole) of lithium aluminum hydride. This mixture was cooled to 0° and 0.056 mole of the epoxyether dissolved in 50 ml. of anhydrous ether was added dropwise. After the addition was complete, the mixture was heated to the reflux temperature for 2 hours and then cooled and hydrolyzed with excess saturated ammonium chloride solution. The ether layer was separated, dried, evaporated and the residual liquid distilled through a Vigreux column.

Independent Synthesis of VI and VII.—The methoxy alcohols VI and VII were prepared independently from methyl α-methoxyphenylacetate. This ester was made in 74% yield by esterification of the corresponding acid[13] with methanol in the presence of sulfuric acid, b.p. 74–75° (0.4 mm.), $n^{24}\mathrm{D}$ 1.5020.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.73. Found: C, 66.39; H, 6.86.

Treatment of the α-methoxyester with excess methylmagnesium bromide gave 86% yield of 1-phenyl-1-methoxy-2-methylpropanol-2 (VI), the physical properties and infrared spectrum of which were identical with the product from reduction of the epoxyether.

Similar treatment of the ester with ethylmagnesium bromide gave 82% of 1-phenyl-1-methoxy-2-ethylbutanol-2 (VII) which was identical in all respects with the material from reduction.

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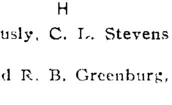
[6] On the basis that the liquid epoxyether is mostly *trans* (phenyl and methyl groups) and that hydride reduction is with inversion, the product is predicted to be mainly *erythro*.



[7] The directions have been published previously, C. L. Stevens and J. Tazuma, THIS JOURNAL, **76**, 715 (1954)

[8] J. G. Aston, J. T. Clark, K. A. Burgess and R. B. Greenburg, *ibid.*, **64**, 300 (1942).

[9] A. Feldstein and C. A. VanderWerf, *ibid.*, **76**, 1626 (1954).

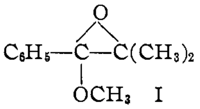
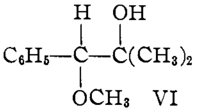
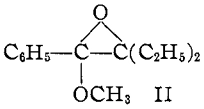
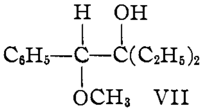
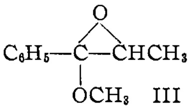
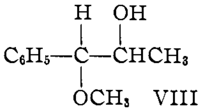
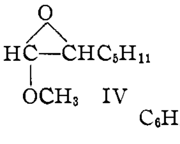
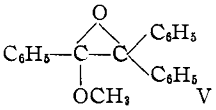
[10] C. L. Stevens, W. Malik and R. Pratt, *ibid.*, **72**, 4758 (1950).

[11] C. L. Stevens, E. Farkas and B. Gillis, *ibid.*, **76**, 2695 (1954).

[12] C. L. Stevens and J. J. DeYoung, *ibid.*, **76**, 718 (1954).

[13] W. Reeve and I. Christoffel, *ibid.*, **72**, 1480 (1950).

TABLE I

Epoxyether	Product	Yield, %	Properties of product B.p. °C.	Mm.	$n^{25}D$	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
 I	 $C_6H_5-\underset{OCH_3}{\overset{H}{C}}-\overset{OH}{C}(CH_3)_2$ VI	82	70	1.0	1.5038	73.30	73.49	8.95	9.26
 II	 $C_6H_5-\underset{OCH_3}{\overset{H}{C}}-\overset{OH}{C}(C_2H_5)_2$ VII	82	81	0.6	1.5027	74.96	75.36	9.68	9.73
 III	 $C_6H_5-\underset{OCH_3}{\overset{H}{C}}-\overset{OH}{C}HCH_3$ VIII	83	68	1	1.5111	72.26	72.56	8.49	8.38
 IV	$CH_3OCH_2\underset{OH}{C}HC_5H_{11}$ IX	80	64	4	1.4235	66.61	66.27	11.80	12.13
 V									

p-**Nitrobenzoate Derivatives of VI and VII.**—The identity of these preparations was further confirmed by the preparation of solid *p*-nitrobenzoate derivatives of the tertiary alcohols by the following procedure.

To 0.01 mole of the alcohol in 15 ml. of toluene was added 1 g. (0.022 g. atom) of 50% sodium dispersion in toluene[14] and the mixture refluxed 5 minutes. A solution of 5 g. (0.027 mole) of *p*-nitrobenzoyl chloride in 20 ml. of toluene then was added rapidly during which time a vigorous reaction occurred. The mixture was stirred for an additional hour at 50° and then the precipitated salts were filtered. The toluene was evaporated and the resulting solid was dissolved in a 10% solution of sodium hydroxide in water-acetone (50–50). After stirring for two minutes to hydrolyze the excess acid chloride 200 ml. of water was added followed by ether extraction of the reaction mixture to remove the ester. The ether was evaporated and the resulting oil crystallized from petroleum ether to give the derivative in *ca.* 50% yield. The *p*-nitrobenzoate derivative of VII was isolated in 50% yield, m.p. 83–84°. The reduction product and the product from independent synthesis gave the same derivative as indicated by mixture melting point determinations.

Anal. Calcd. for $C_{20}H_{23}O_5N$: C, 67.21; H, 6.91. Found: C, 67.24; H, 6.98.

The *p*-nitrobenzoate derivative of VI was isolated in 40% yield, m.p. 84–85°. A mixture melting point of the derivative of VI made from reduction and from independent synthesis was not depressed.

Anal. Calcd. for $C_{18}H_{19}O_5N$: C, 65.65; H, 5.82. Found: C, 65.73; H, 6.00.

Independent Synthesis of 1-Methoxyheptanol-2.—The corresponding methoxymethyl ketone was prepared from the diazoketone according to the procedure of Newman.[15] From 18.8 g. (0.14 mole) of caproyl chloride was obtained 10.25 g. (50%) of 1-methoxy-2-heptanone,[5] b.p. 62–63° (5 mm.), $n^{25}D$ 1.4188. The heptanone was reduced with lithium aluminum hydride to give the alcohol IX in 75% yield.

The physical properties and infrared spectrum of the product from independent synthesis were identical with those listed for IX in Table I. Each preparation was converted to a 3,5-dinitrobenzoate derivative in 75% yield and the melting points of these derivatives were not depressed on admixture, m.p. 38–40°.

Anal. Calcd. for $C_{15}H_{20}O_7N_2$: C, 52.93; H, 5.92. Found: C, 53.27; H, 5.87.

DETROIT 2, MICHIGAN

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[14] We are indebted to the Ethyl Corporation for the 50% sodium dispersion in toluene, average particle size 6 μ.

[15] M. S. Newman and P. F. Beal III, THIS JOURNAL, **72**, 5161 (1950).