[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Epoxyethers. VII. Reaction of α-Haloaldehydes with Base

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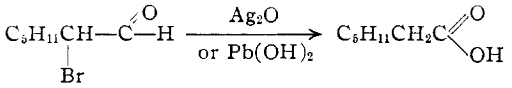
α-Chlorobutyraldehyde and α-chloroheptaldehyde, the structures of which were proved by oxidation to the acid, reacted with alcoholic sodium methoxide to give the corresponding α-hydroxyacetals. A derivative of the α-hydroxyacetal was oxidized to the corresponding acid as a proof of structure. Dry sodium methoxide reacted with the α-haloaldehydes to give epoxyethers, which were characterized by hydrolysis, methanolysis and reaction with organic acids.

This paper presents a continuation of the investigation in this Laboratory of the reactions of α-halocarbonyl compounds. In particular, this work resulted in the isolation and characterization of epoxyethers from α-haloaldehydes.

The preparation and reactions of α-haloaldehydes previously reported in the literature are few in number and the yields are generally poor. In 1944, Bedoukian[3] reviewed the available methods of preparation of α-bromoaldehydes and reported a new three-step synthesis of these aldehydes in 20–30% over-all yield. Recently Brown and Ash[4] reported a convenient synthesis of α-chlorobutyraldehyde using sulfuryl chloride as the chlorinating agent.

From an investigation of the reactions of α-bromoaldehydes, Kirrman[5] in 1927 suggested that these aldehydes behave as though they had the isomeric acyl bromide structure and that certain reagents dehydrohalogenate these α-bromoaldehydes with the formation of ketene intermediates. Thus, α-bromoheptaldehyde was reported to react with silver oxide or lead hydroxide to give heptanoic acid. Danilov[6] reported a similar reaction.



$$C_5H_{11}CH(Br)-C(=O)-H \xrightarrow[\text{or } Pb(OH)_2]{Ag_2O} C_5H_{11}CH_2C(=O)OH$$

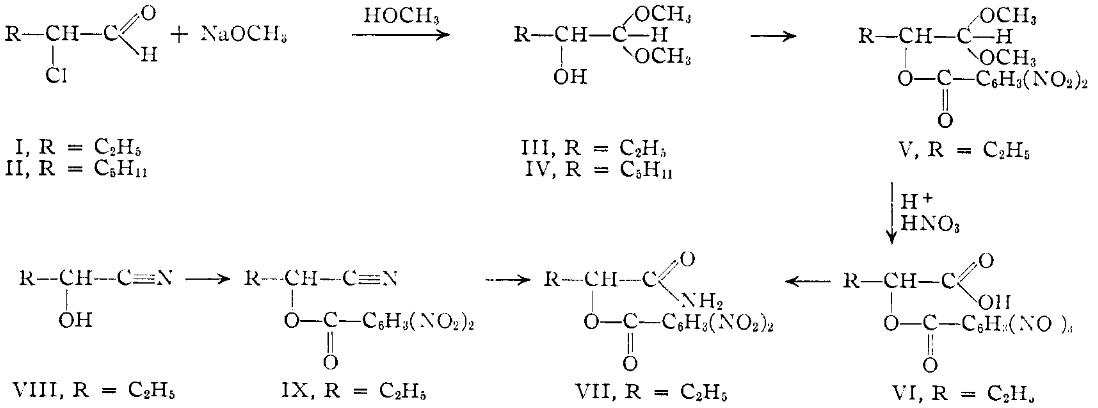
Recently Kirrman[7] has reinvestigated this abnormal hydrolysis of α-bromoaldehydes and discussed the formation of the acid in terms of a rearrangement of an epoxyalcohol intermediate.[8] Dworzak[9] as well as Kirrman[7] have isolated α-hydroxyaldehydes as dimers from the hydrolysis of α-bromoaldehydes.

In this work α-chlorobutyraldehyde (I) and α-chloroheptaldehyde (II) were prepared in 56 and 61% yields, respectively, by chlorination of the parent aldehyde using sulfuryl chloride.[4] The structures of both α-chloroaldehydes were proved by oxidation with nitric acid to the corresponding acid.

When α-chlorobutyraldehyde (I) was allowed to react at room temperature for one hour with an alcoholic solution of one equivalent of sodium methoxide, the product was 46% of α-hydroxybutyraldehyde dimethyl acetal (III). Under more vigorous conditions, α-chloroheptaldehyde gave 71% of α-hydroxyheptaldehyde dimethyl acetal (IV).

The structure of III was proved by preparation of the solid 3,5-dinitrobenzoate derivative V, hydrolysis of the acetal V and oxidation of the resulting aldehyde to the corresponding acid VI. The amide VII of this acid VI was identical with the amide prepared by the reactions VIII → IX → VII.

A previous attempt to prove the structure of III by conversion to α-chlorobutyraldehyde dimethyl acetal was unsuccessful. The sulfite ester of III failed to give the chloroaldehyde acetal with thionyl chloride or thionyl chloride and pyridine under a variety of conditions.



I, R = C_2H_5
II, R = C_5H_{11}
III, R = C_2H_5
IV, R = C_5H_{11}
V, R = C_2H_5
VIII, R = C_2H_5
IX, R = C_2H_5
VII, R = C_2H_5
VI, R = C_2H_5

α-Chlorobutyraldehyde (I), when allowed to re-

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(1) U. S. Public Health Service Predoctorate Fellow, 1951–1952. Abstracted in part from the Ph.D. thesis of E. Farkas, Wayne University, 1952.

(2) Ethyl Corporation Fellow, 1953–1954.

(3) P. Z. Bedoukian, THIS JOURNAL, **66**, 1325 (1944).

(4) A. B. Ash, Ph.D. thesis, Wayne University, 1948.

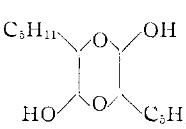
(5) A. Kirrman, *Compt. rend.*, **184**, 1463 (1927); **185**, 1482 (1927).

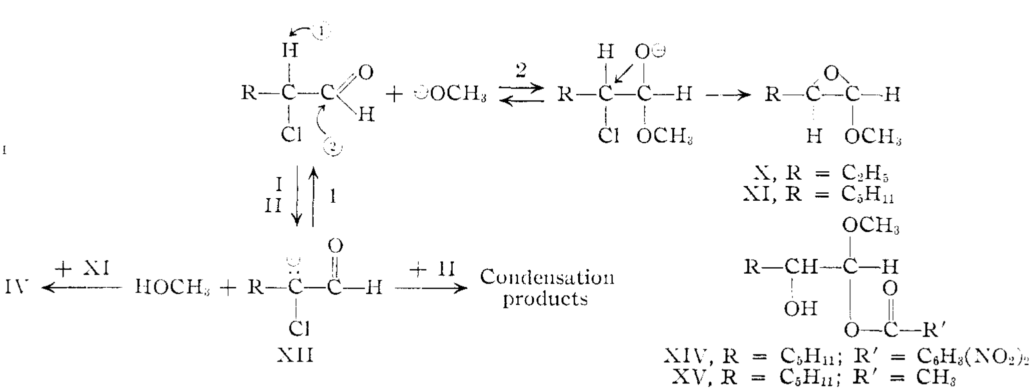
(6) S. Danilov and E. Venus-Danilova, *Ber.*, **62**, 2653 (1929).

(7) A. Kirrman, *Bull. soc. chim. France*, **707**, 711 (1950).

(8) Recently Cope (THIS JOURNAL, **73**, 4702 (1951)) proposed a mechanism for the rearrangement of α-haloketones to acids in the presence of silver nitrate in hydroxylic media. This mechanism involved initial hemiacetal formation or hydration of the carbonyl group followed by pinacol type rearrangement and appears to be a good alternate explanation for the formation of the heptanoic acid.

(9) R. Dworzak and P. Pfifferling, *Monatsh.*, **48**, 251 (1927).


XIII



act with dry sodium methoxide in ether, gave the epoxyether X in 14% yield. From the α-chloroheptaldehyde, the corresponding epoxyether XI could be obtained in 28% yield. The fact that from this latter reaction methyl alcohol and α-hydroxyacetal (IV) could be isolated indicated that the formation of the enolate ion XII was responsible for the low yield of epoxyether and the large amount of undistillable residue. The best yield of epoxyether from an α-haloaldehyde was 48% and was obtained from α-bromoheptaldehyde and dry sodium methoxide. The infrared spectra of these epoxyethers had no absorption bands corresponding to the bands of a hydroxyl or carbonyl group (*cf.* Fig. 1).

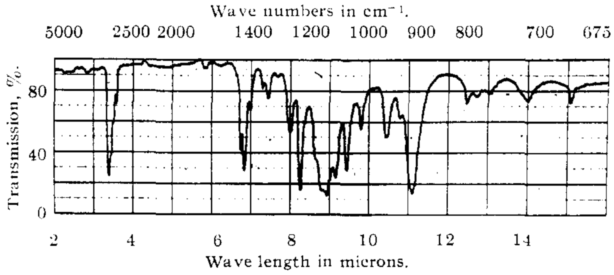


Fig. 1.—1-Methoxy-1,2-epoxybutane (X), infrared spectrum in carbon tetrachloride (compensated).

1-Methoxy-1,2-epoxybutane was stable at the reflux temperature for a short period of time. Alcoholysis of this epoxyether X gave a 49% yield of α-hydroxybutyraldehyde dimethyl acetal. XI gave an 84% yield of the corresponding α-hydroxyacetal IV.

Hydrolysis of XI gave 62% of the crystalline α-hydroxyheptaldehyde dimer.[9] The infrared spectra showed the presence of the hydroxyl group and the absence of a carbonyl group. These facts support a dioxane type stucture (XIII).[10]

Previously, epoxyethers have been known to react with organic acids to give esters of α-hydroxycarbonyl compounds and alcohol.[11] The mechanism of this reaction has been investigated in one example and a pseudoester (acylal) intermediate isolated.[12]

The epoxyether XI from α-bromoheptaldehyde reacted with 3,5-dinitrobenzoic acid and acetic acid to give relatively stable hemiacetal esters of α-hydroxyheptaldehyde (XIV and XV). XV was a liquid that could be distilled under reduced pressure without decomposition, while XIV was a solid stable below the melting point. Carbon and hydrogen analysis indicated that each of these pseudoesters was composed of the elements of the epoxyether plus the carboxylic acid. A methoxyl determination indicated the presence of a methoxy group and the infrared spectra indicated the presence of a hydroxyl and ester group. These data support the structural assignments of pseudoesters (acylals) as the only reasonable ones for XIV and XV.

Experimental

α-Chlorobutyraldehyde (I).—In a flask equipped with a stirrer and reflux condenser were placed 54 g. (0.75 mole) of freshly distilled butyraldehyde and 30 ml. of methylene chloride. After the solution was cooled to 10° in an ice-bath, a mixture of 101 g. (0.75 mole) of sulfuryl chloride and 10 ml. of methylene chloride slowly was added maintaining the temperature between 15–40°. An accumulation of unreacted sulfuryl chloride should be avoided at this point. After completion of the addition, the reaction was stirred for one-half hour and then heated for a similar period of time at the reflux temperature. All the volatile material was then distilled rapidly at reduced pressure and condensed in a cold trap. The condensate was fractionated through a 2 × 15 cm. total-reflux variable take-off column filled with helices to give 44 g. (56%) of the α-chlorobutyraldehyde,[4] b.p. 104–110°, d^{25}_4 1.1140, $n^{25}\text{D}$ 1.4231. The chlorine content of this material was 33.2% (calcd. 33.3).

The α-chlorobutyraldehyde was oxidized with fuming nitric acid to give a liquid acid which was then refluxed with thionyl chloride and poured into ammonium hydroxide to give an amide, m.p. 76–77°. A mixture melting point with an authentic sample of α-chlorobutyramide (m.p. 78–79°) was not depressed.

α-Chloroheptaldehyde (II).—Using the same procedure as for the preparation of α-chlorobutyraldehyde, the chloroheptaldehyde could be prepared in 61% yield. From 248 g. (2.17 moles) of heptaldehyde and 311 g. (2.3 moles) of sulfuryl chloride was obtained 196 g. of α-chloroheptaldehyde, b.p. 36–38 (2 mm.), $n^{25}\text{D}$ 1.4351, d^{25}_4 1.0221.

Anal. Calcd. for $C_7H_{13}ClO$: Cl, 23.85. Found: Cl, 23.67.

To an excess (200 ml.) of cold fuming nitric acid was added 28 g. of α-chloroheptaldehyde with rapid stirring. The reaction was allowed to warm slowly until nitrogen dioxide began to be evolved. After 10 hours, the reaction had separated into two layers. The organic layer was heated at the reflux temperature with excess thionyl chloride for 10 hours, after which time the α-chloroheptanoyl chloride was separated by distillation and amounted to 13.5 g. (39%), b.p. 90–91° (15 mm.), $n^{25}\text{D}$ 1.4491, d^{25}_4 1.1111.

Anal. Calcd. for $C_7H_{12}ClO_2$: Cl, 38.6. Found: Cl, 38.8.

The α-chloroacid chloride (7 g.) was added slowly to cold

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(10) *Cf.* J. C. Sheehan, R. C. O'Neill and M. A. White, THIS JOURNAL, **72**, 3376 (1950).

(11) C. L. Stevens, W. Malik and R. Pratt, *ibid.*, **72**, 4758 (1950); C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952); C. L. Stevens, M. L. Weiner and R. Freeman, *ibid.*, **75**, 3977 (1953).

(12) C. L. Stevens and S. Dykstra, *ibid.*, **75**, 5979 (1953)

ammonium hydroxide. The amide that formed was filtered and dried and amounted to 5 g. (80%). Recrystallization from a ligroin–acetone mixture gave pure α-chloroheptanamide, m.p. 64–65°.

Anal. Calcd. for $C_7H_{14}ClNO$: C, 51.37; H, 8.62. Found: C, 51.52; H, 8.61.

This amide did not depress the melting point of an authentic sample made by chlorination of heptanoyl chloride with sulfuryl chloride followed by treatment of the acid chloride with ammonia.

α-Hydroxybutyraldehyde Dimethyl Acetal.—To 180 ml. of dry methanol was added slowly 14.7 g. (0.64 g. atom) of sodium metal. After reaction of the sodium, the temperature was maintained below 20° and 70 g. (0.65 mole) of freshly distilled α-chlorobutyraldehyde was added. The ice-bath was removed and the reaction mixture was stirred for one hour. Titration of an aliquot with acid indicated 83% of the base was used. The salts were separated by centrifugation and distillation gave 39.2 g. (46%) of α-hydroxybutyraldehyde dimethyl acetal, b.p. 39–42° (1 mm.), $n^{25}D$ 1.4150.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.51; OCH_3, 46.25. Found: C, 53.38; H, 10.33; OCH_3, 46.0.

α-Hydroxyheptaldehyde Dimethyl Acetal.—The preparation was the same as in the butyraldehyde series except that the reaction mixture was heated to reflux for two hours. From 18 g. of α-chloroheptaldehyde was obtained 16.2 g. (71%) of the dimethyl acetal of α-hydroxyheptaldehyde, b.p. 82–84° (3 mm.), $n^{25}D$ 1.4262.

Anal. Calcd. for $C_9H_{20}O_3$: C, 61.33; H, 11.44. Found: C, 60.87; H, 11.35.

α-Hydroxybutyraldehyde Dimethyl Acetal Sulfite Ester.—To 60 g. of dry pyridine was added 15 g. (0.111 mole) of α-hydroxybutyraldehyde dimethyl acetal in 50 ml. of anhydrous ether. The solution was cooled to 10° in an ice-bath and 40 g. (0.33 mole) of thionyl chloride added slowly with stirring. After all of the thionyl chloride was added the reaction was poured onto cracked ice. The ether layer was separated, washed with bicarbonate solution; dried over sodium sulfite and distilled to give 12.2 g. (70%) of the sulfite ester, b.p. 119–121° (0.8 mm.), $n^{25}D$ 1.4431.

Anal. Calcd. for $C_{12}H_{26}O_7S$: OCH_3, 39.4; S, 10.21. Found: OCH_3, 39.3; S, 10.7.

α-Chlorobutyraldehyde Dimethyl Acetal (III).—To 22 ml. of anhydrous methanol was added 10 g. of α-chlorobutyraldehyde. A little dry hydrogen chloride gas was bubbled into the solution and then the reaction mixture was allowed to stand at room temperature for 24 hours. Distillation gave 12.3 g. (84%) of the α-chlorobutyraldehyde dimethyl acetal, b.p. 67–70° (16 mm.), $n^{25}D$ 1.4231.

Anal. Calcd. for $C_6H_{13}O_2Cl$: Cl, 23.27. Found: Cl, 23.00.

α-Hydroxybutyraldehyde Dimethyl Acetal 3,5-Dinitrobenzoate (V).—A mixture of 4 g. (0.03 mole) of the hydroxyacetal and 10 ml. of dry pyridine was cooled in an ice-bath and 6.92 g. (0.03 mole) of 3,5-dinitrobenzoyl chloride added. The reaction was permitted to stand overnight and then poured onto 50 g. of cracked ice. The precipitate was filtered and recrystallized from ligroin to give 6.25 g. (64%) of the hydroxyacetal 3,5-dinitrobenzoate, m.p. 105–106°.

Anal. Calcd. for $C_{13}H_{16}O_8N_2$: C, 47.56; H, 4.91. Found: C, 47.62; H, 5.05.

3,5-Dinitrobenzoate of α-Hydroxybutyramide (VII).—The 3,5-dinitrobenzoate acetal (2.0 g.) was added to 15 ml. of fuming nitric acid and the mixture warmed on a steam-bath for two hours and then poured onto cracked ice. The precipitate was filtered and recrystallized from a water–ethanol mixture to give 1.84 g. (75%) of the 3,5-dinitrobenzoate of α-hydroxybutyric acid (VI), m.p. 153–154°.

Anal. Calcd. for $C_{11}H_{10}O_8N_2$: C, 44.30; H, 3.38. Found: C, 44.50; H, 3.67.

The acid (VI, 0.5 g.) and 5 ml. of thionyl chloride were heated to reflux for one hour. The excess thionyl chloride was evaporated with a warm aspirator and the remaining liquid was added slowly to cold ammonium hydroxide with stirring. After recrystallization from a water–alcohol mixture, the amide VII 0.31 g. (62%), melted at 133–134°.

Anal. Calcd. for $C_{11}H_{11}N_3O_7$: C, 44.44; H, 3.73. Found: C, 44.75; H, 3.85.

Independent Synthesis of the 3,5-Dinitrobenzoate of α-Hydroxybutyramide (VII).—The cyanohydrin of propionaldehyde was prepared from 80 g. (1.4 moles) of freshly distilled aldehyde, 74 g. (1.5 moles) of sodium cyanide and 92 ml. (1.7 moles) of concentrated sulfuric acid. Distillation gave 57 g. (49%) of the cyanohydrin, b.p. 103–105° (20 mm.).

A mixture of 10 g. (0.12 mole) of cyanohydrin and 10 ml. of pyridine was cooled in an ice-bath and 27 g. (0.12 mole) of 3,5-dinitrobenzoyl chloride added. The resulting purple solution was allowed to stand overnight and then poured onto cracked ice. After filtration, recrystallization from ethanol gave 20.5 g. (59%) of the 3,5-dinitrobenzoate of propionaldehyde cyanohydrin (IX), m.p. 83–84°.

Anal. Calcd. for $C_{11}H_9O_6N_3$: C, 47.32; H, 3.25. Found: C, 47.22; H, 3.21.

The nitrile (2 g.) was dissolved in 10 ml. of concentrated sulfuric acid and the solution placed on a steam-bath until a brown color appeared. The material was then poured onto cracked ice and stirred until crystallization resulted. The product was washed with ether and recrystallized from ethanol–water to give 0.82 g. (37%) of the amide VII, m.p. 133–134°. The mixed melting point with material from the oxidation of the hydroxyl aldehyde derivative was not depressed.

1-Methoxy-1,2-epoxybutane (X).—Anhydrous sodium methoxide was prepared by dissolving 4.6 g. (0.2 g. atom) of sodium in 70 ml. of absolute methanol. After the sodium had reacted, the excess methanol was removed and the sodium methoxide stirred until finely powdered and heated under reduced pressure until the last of the methanol was removed. After 100 ml. of anhydrous ether was added and the suspension cooled in an ice-bath, 20 g. (0.2 mole) of α-chlorobutyraldehyde dissolved in 30 ml. of ether was added in four minutes. After the addition, all the salts dissolved and a clear pale yellow solution resulted. After about five minutes, sodium chloride slowly precipitated and after the reaction was stirred one hour at the temperature of the ice-bath and two hours at room temperature, the salts were separated by centrifugation and the ether evaporated under vacuum. The crude epoxyether was distilled rapidly from the reaction residue at 1 mm. and condensed in a Dry-Ice trap.

Redistillation of the crude epoxyether gave 2.7 g. (14%) of 1-methoxy-1,2-epoxybutane, b.p. 87–89° (150 mm.), $n^{25}D$ 1.3948, d^{25}_4 0.9210.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.79; H, 9.87; OCH_3, 30.3. Found: C, 58.91; H, 9.85; OCH_3, 30.0.

This epoxyether was recovered unchanged after being heated for 15 minutes at the reflux temperature at atmospheric pressure. After the epoxyether (1.4 g.) was dissolved in 7 ml. of methanol, addition of one drop of sulfuric acid caused the epoxyether to react with the liberation of heat. After 12 hours the reaction was neutralized with solid sodium carbonate and the excess methanol was evaporated under reduced pressure. Distillation gave 0.9 g. (49%) of the dimethyl acetal of α-hydroxybutyraldehyde, b.p. 44–47° (2 mm.), $n^{25}D$ 1.4157.

The 3,5-dinitrobenzoate derivative could be prepared in 45% yield, m.p. 105–106°, a mixture m.p. with the sample from above, 105–106°.

1-Methoxy-1,2-epoxyheptane (XI).—This epoxyether was prepared in the same manner as in the butane series. From 24 g. (0.16 mole) of α-chloroheptaldehyde was obtained 6.4 g. (28%) of 1-methoxy-1,2-epoxyheptane, b.p. 54–55° (6 mm.), $n^{25}D$ 1.4164, d^{25}_4 0.8939.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.19. Found: C, 66.73; H, 11.37.

The epoxyether could be prepared in better yield from the α-bromoaldehyde. α-Bromoheptaldehyde was prepared according to the directions of Bedoukian, b.p. 84–86° (15 mm.), $n^{25}D$ 1.4585.

From 25 g. (0.13 mole) of the α-bromoheptaldehyde was obtained 8.9 g. (48%) of the epoxyether, b.p. 66–69° (8 mm.), $n^{25}D$ 1.4154.

Alcoholysis of the epoxyether gave the hydroxy acetal IV. From 3 g. of epoxyether and 12 ml. of anhydrous methanol, 3 g. (84%) of the dimethylacetal of α-hydroxyheptaldehyde was isolated by distillation, b.p. 93–95° (5 mm.), $n^{25}D$ 1.4262.

Hydrolysis of the epoxyether gave the α-hydroxyaldehyde dimer XIII. The epoxyether (1 g.) was heated to the reflux temperature in a solution of 10 ml. of acetone, two drops of hydrochloric acid and enough water to make the solution turbid. Evaporation of the solvents left the product as white crystals. Recrystallization from an ether–petroleum ether mixture gave 0.55 g. (62%) of α-hydroxyheptaldehyde dimer, m.p. 120–122°.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.57; H, 10.84. Found: C, 64.09; H, 10.81.

Reaction of the Epoxyether XI with Organic Acids.—A solution of 4 g. (0.03 mole) of the epoxyether XI in 20 ml. of anhydrous ether was cooled in an ice-bath and 6 g. (0.03 mole) of 3,5-dinitrobenzoic acid added slowly. The reaction was allowed to stand overnight at room temperature. The ether solution was then quickly washed with 10% cold aqueous bicarbonate solution, dried with sodium sulfate and the ether removed with a water aspirator. The resulting solid was recrystallized from an ether–petroleum mixture to give 7.85 g. (79%) of white crystalline acylal, 1-methoxy-2-hydroxyheptyl 3,5-dinitrobenzoate (XIV), m.p. 86–87°.

Anal. Calcd. for $C_{15}H_{20}O_8N_2$: C, 50.56; H, 5.66. Found: C, 50.16; H, 5.60.

This pseudoester decomposed when heated above the melting point.

From 4 g. (0.03 mole) of epoxyether and 1.7 g. (0.03 mole) of acetic acid by a similar procedure was obtained 4.1 g. (73%) of the corresponding acylal, 1-methoxy-2-hydroxyheptyl acetate (XV), b.p. 73–77° (2 mm.), $n^{25}D$ 1.4282.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 58.79; H, 9.87; OCH_3, 15.2. Found: C, 58.23; H, 9.62; OCH_3, 14.8.

Acknowledgment.—The authors wish to thank Miss Phylis Tocco and Mr. Michael Papo for the microanalyses.

DETROIT 1, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Epoxyethers. VIII. The Reaction of Epoxyethers with Grignard Reagents

BY CALVIN L. STEVENS, MILTON L. WEINER[1] AND CARL T. LENK[2]

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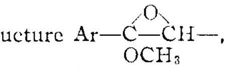
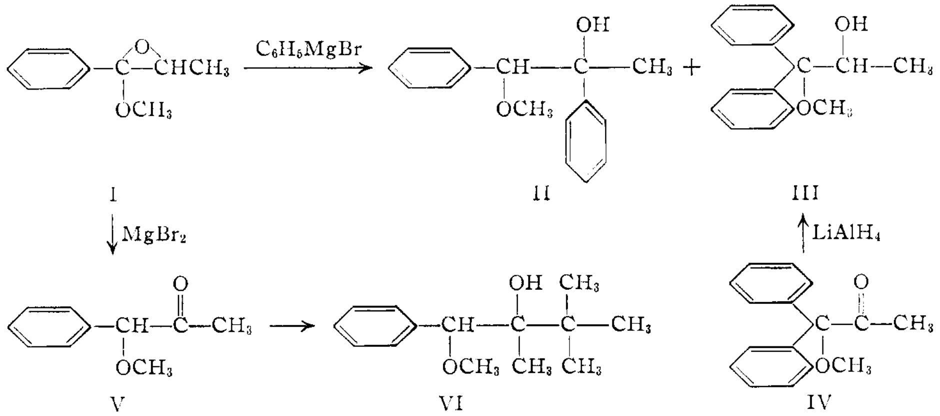
The reaction of a Grignard reagent with certain epoxyethers, which have the characteristic structure  $Ar\text{—}\overset{\diagup O \diagdown}{\underset{OCH_3}{C}\text{—}CH}\text{—}$, has been shown to proceed to give two types of products. One product was a monomethyl ether of a substituted ethylene glycol that resulted from the attachment of the organic radical of the Grignard reagent to the carbon of the epoxide that contained the methoxyl group. The other product was an isomeric monomethyl ether of an ethylene glycol that resulted first from rearrangement of the epoxyether to the methoxyketone, Ar–$CHOCH_3$–CO–, followed by addition of the Grignard reagent to the carboxyl group of this ketone.

Ordinary 1,2-epoxides are known to undergo ring-opening reactions with Grignard reagents. These ethylene oxides react less readily than carbonyl compounds with the Grignard reagent, and in many instances the reaction must be heated above the reflux temperature of ether. The most important complication in this reaction is the rearrangement of the ethylene oxide prior to addition of the Grignard reagent.[3]

Epoxyethers have been shown in this investigation to react readily with Grignard reagents at the reflux temperature of ether or below, but in the examples studied the reactions are complicated by rearrangement of the epoxyether.



The epoxyether, 1-phenyl-1-methoxy-1,2-epoxypropane (I) reacted readily with phenylmagnesium bromide at room temperature to give 86% of a mixture of isomers from which a 24% yield of crystalline 1,2-diphenyl-1-methoxy-2-propanol (II) and a 42% yield of 1,1-diphenyl-1-methoxy-2-propanol (III) could be separated. The structure of III was proved by independent synthesis from 1,1-diphenyl-1-methoxy-2-propanone[4] (IV) by reduction with lithium aluminum hydride in 78% yield. The formation of III from the epoxyether and the Grignard reagent is comparable to the normal ring-opening reactions with ethylene oxides. In this instance the carbon of the epoxide that contains the methoxy group is most susceptible to attack by the nucleophilic reagent.

The structure of II was proved by synthesis from 1-methoxy-1-phenyl-2-propanone (V). V could be prepared by the alcoholysis of the corresponding

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[1] Atomic Energy Predoctoral Fellow, 1950–1952. Abstracted in part from the Doctoral thesis of M. L. Weiner, Wayne University, 1952.

[2] Parke, Davis and Company Fellow, 1951–1952.

[3] Recently the literature concerned with the reaction of Grignard reagents with the oxirane ring has been exhaustively reviewed by N. G. Gaylord and E. I. Becker, *Chem. Revs.*, **49**, 413 (1951).

[4] The structure of IV has recently been proved in this Laboratory by synthesis from α-methoxydiphenylacetonitrile and methylmagnesium iodide and by alcoholysis of the corresponding bromoketone: C. L. Stevens and C. T. Lenk, *J. Org. Chem.*, in press.