The oil that initially precipitated completely crystallized after several hours. Stout rods of the colorless hydrochloride were obtained after one recrystallization from ethyl acetate, m.p. 216–219°.

*Anal.* Calcd. for $(C_{15}H_{13}N)_2 \cdot HCl$: C, 79.89; H, 6.04. Found: C, 80.27; H, 6.42.

When an ethanolic solution of this hydrochloride was treated with dilute ammonium hydroxide, a white solid precipitated, m.p. 163–166°. A mixed melting point with the original dimer was undepressed.

A monopicrate was prepared when a saturated solution of picric acid in ether was added to an ether–chloroform solution of the dimer. One crystallization from hexane–acetone gave a yellow solid, m.p. 237–238°.

*Anal.* Calcd. for $(C_{15}H_{13}N)_2 \cdot C_6H_3N_3O_7$: C, 67.18; H, 4.54; N, 10.88; mol. wt., 643.6. Found: C, 67.39; H, 4.66; N, 10.86; mol. wt., 630.[12]

**Action of Triethylamine on Crude N-Methyldiphenylacetimino Chloride.**—This crude imino chloride was prepared by heating under reflux a solution of 5.01 g. (0.0223 mole) of N-methyldiphenylacetamide and 4.63 g. (0.0222 mole) of phosphorus pentachloride in 35 ml. of dry benzene for 90 minutes. The reaction mixture was concentrated *in vacuo* and the residual oil co-distilled three times, *in vacuo*, with 20-ml. portions of dry benzene. The pale yellow imino chloride[13] was dissolved in 35 ml. of dry toluene and then 30 ml. of freshly distilled triethylamine was added. The reaction mixture, which soon precipitated triethylamine hydrochloride, was maintained at 100–110° in an atmosphere of dry nitrogen for six hours. The white precipitate was filtered, washed with dry ether and dried to a constant weight (2.68 g.). The filtrate was evaporated nearly to dryness and the residual mixture was treated with 30 ml. of dry ether and an additional 0.23 g. of white solid was filtered. The total weight of triethylamine hydrochloride was 2.91 g. (95%). The filtrate was again concentrated and the residual amber oil transferred to a 10-ml. distilling flask. Distillation afforded two distinct fractions: (1) 0.77 g. (17%), b.p. 120–140° (0.2 mm.); (2) 2.80 g. (61%), b.p. 215–225° (0.1 mm.). The first fraction was redistilled through a 30-cm. tubular column to give 0.11 g. (2.4%) of somewhat impure diphenylketene methylimine, b.p. 124–125° (0.15 mm.); $n^{25}_D$ 1.6141. The infrared spectrum showed the characteristic strong band at 4.98 $\mu$ in addition to weak absorption bands at 5.8 and 6.1 $\mu$, which are associated with the dimer impurity.

The second fraction readily crystallized. One recrystallization from hexane–acetone afforded a solid, m.p. 165–167°, which did not depress the melting point of the above-described dimer of diphenylketene methylimine obtained from the pyrolysis of N-methyldiphenylacetimino chloride.

**Hydrolysis of Ketenimines and Imino Chlorides.**—In each case hydrolysis was effected in aqueous acetone at room temperature. The addition of dilute hydrochloric acid greatly accelerated the hydrolysis of the ketenimines as indicated by the discharge of the yellow color. The properties and yields of the various hydrolysis products are listed in Table II.

**Acknowledgment.**—The authors wish to thank Miss Phylis Tocco and Mr. Robert French for the microanalyses.

DETROIT 1, MICHIGAN

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[12] We are indebted to Dr. J. M. Vandenbelt, Parke, Davis and Co., for the spectrophotometric molecular weight determination of this material as well as for the ultraviolet spectrum reported in this paper.

[13] To more definitely establish the nature of this material, in an identical experiment an aliquot of this oil was readily hydrolyzed in aqueous acetone solution to afford a 98% yield of crude N-methyldiphenylacetamide. One crystallization from aqueous acetone gave a 45% yield of pure N-methyldiphenylacetamide, m.p. 162–163°

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

# Epoxyethers. IX. Acid-catalyzed Rearrangements[1]

BY CALVIN L. STEVENS AND STANLEY J. DYKSTRA[2]

RECEIVED MARCH 24, 1954

A wide variety of epoxyethers were cleanly rearranged to give a good yield of the corresponding methoxy ketones using magnesium bromide as a catalyst (*cf.* Table I). The structures of the new epoxyethers were proved by degradation reactions and the methoxy ketones were prepared independently or the structures proved by a second order Beckmann degradation of the corresponding oxime.

The acid-catalyzed rearrangement of ethylene oxides to carbonyl compounds has been widely studied and has found much use.[3] The utility of the rearrangement is based upon the ability to predict the direction in which the oxide ring is opened as well as the choice of which of the two groups migrates during the rearrangement.

The oxide rearrangement has been recognized for some time as one of the group of pinacol-type rearrangements.[4] From the examples reported of the pinacol-type rearrangement, the course of the rearrangement of an individual compound must depend upon the nature of the group that is leaving,[4,5] the stability of the transition states,[5,6] the nature of the migrating group and the reaction media.

The ionization of the carbon–oxygen bond in oxides corresponds to the steps in which a group leaves in the pinacol rearrangement, and the relative ease of ionization of the two carbon–oxygen bonds in oxides generally determines the direction of ring opening in acid-catalyzed rearrangements.

In this work, examples of epoxyethers were chosen which demonstrate that the scope of the rearrangement is broad and that the reaction may be used for the preparation of methoxy ketones. In every example the direction of ring opening is predictable on the basis of the relative ease of ionization of the carbon–oxygen bonds since the methoxy ketone was the only product that could be isolated. Although the ability of one group to migrate in preference to another is dependent upon

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[2] Abstracted in part from the Ph.D. thesis of Mr. Stanley J. Dykstra, Wayne University, June, 1953.

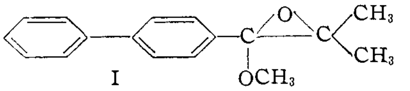
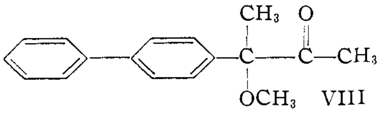
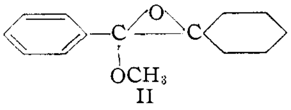
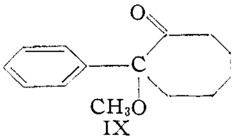
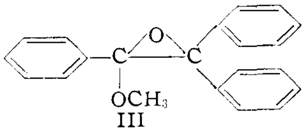
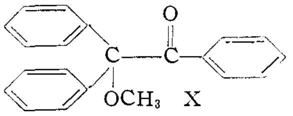
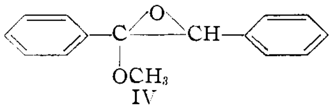
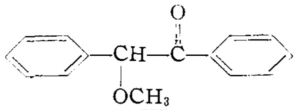
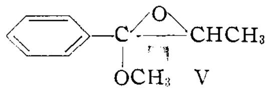
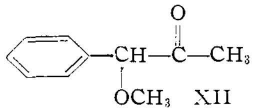
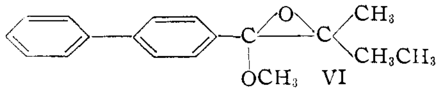
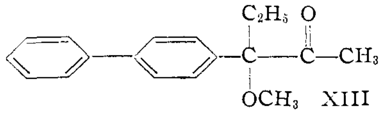
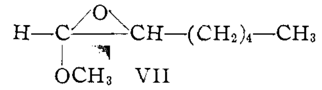
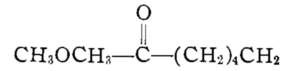
[3] A review of acid-catalyzed rearrangements of ethylene oxides has been written recently by S. Winstein and R. B. Henderson in R. C. Elderfield's "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. 1, 1950, p. 48.

[4] *Cf.* G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 494–519.

[5] E. R. Alexander and D. C. Dittmer, THIS JOURNAL, **73**, 1665 (1951).

[6] D. Curtin, *et al.*, *ibid.*, **72**, 961 (1950); **73**, 992, 3453 (1951).

TABLE I

| Epoxyether | Methoxy ketone | Yield, % | Procedure |
|---|---|---|---|
|  I |  VIII | 86 | A |
|  II |  IX | 72 | A |
|  III |  X | 68 | A |
|  IV |  XI | 52 | B |
|  V |  XII | 80 | B |
|  VI |  XIII | 84 | A |
|  VII |  $CH_3OCH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_4CH_2$ XIV | 49 | B |

the factors listed above, in practice a rearrangement which involved migration of a phenyl group required the mildest reaction conditions[7] while one which involved migration of an alkyl group required the most strenuous conditions. Among those examples in which both carbon atoms of the epoxyether were asymmetric, a rearrangement was found in which hydrogen migrated in preference to a phenyl group and another in which an ethyl group migrated in preference to a methyl group.

The rearrangement of the epoxyether I[8] was first attempted with magnesium bromide in refluxing ether, reaction conditions which had previously been known to cause the rearrangement of IV.[9] Under these conditions the epoxyether was recovered unchanged. However, when a solution of I and magnesium bromide in dibutyl ether was heated to the reflux temperature, the epoxyether was smoothly converted to the methoxy ketone VIII with rearrangement of a methyl group. The structure of the resulting methoxy ketone VIII was proved by a Beckmann degradation of the corresponding oxime.

The fact that epoxyethers only rearranged with ring opening in the direction that formed the methoxy ketone was applied in the synthesis of the cycloheptanone derivative IX. Using the same conditions described above, the readily available epoxyether II[10] was converted with ring enlargement to IX. The structure of the methoxy ketone was again proved by Beckmann degradation of the oxime.

Since the dialkyl epoxyethers I, II and VI did not rearrange in the presence of magnesium bromide in diethyl ether solution at the reflux temperature, these epoxyethers should behave normally in reactions with the Grignard reagent.[11]

The epoxyether III is the most labile to rearrangement of any epoxyether isolated thus far. Magnesium bromide in refluxing dibutyl ether or diethyl ether, dry hydrogen chloride in ether,[7] or a carboxylic acid[7] will convert III to X in good yield.

The epoxyethers IV, V, VI and VII are characterized by the fact that both carbon atoms of the epoxide group are asymmetric. The sharp melting points of IV, V and VI indicate that they are pure racemates and not mixtures of diastereoisomers.

The rearrangement of IV to XI took place smoothly in refluxing diethyl ether in the presence of magnesium bromide. The interesting feature of this reaction is that hydrogen migrated in preference to the phenyl group. The low yield (52%) of the methoxy ketone XI was attributed to technical difficulties in the isolation and purification. A determined effort to find evidence for the presence of a significant amount of an aldehyde (resulting from migration of phenyl) in the reaction mixture was

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[7] *Cf.* C. L. Stevens and J. J. DeYoung, THIS JOURNAL, **76**, 718 (1954).

[8] C. L. Stevens and S. J. Dykstra, *ibid.*, **75**, 5975 (1953).

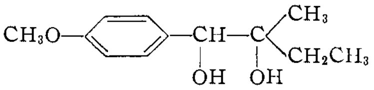
[9] C. L. Stevens, M. Weiner and R. C. Freeman, *ibid.*, **75**, 3977 (1953).

[10] C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

[11] For the reactions of IV and V with Grignard reagents, see C. L. Stevens, M. L. Weiner and C. T. Lenk, *ibid.*, **76**, 2698 (1954).

fruitless. Rearrangement of V under the same conditions proceeded cleanly to give 80% of XII in which the hydrogen had migrated in preference to a methyl group.

The conclusion that an ethyl group would migrate in preference to a methyl group in the pinacol-type reaction resulted from a detailed investigation by Tiffeneau[12] and his co-workers. To test this conclusion for the rearrangement of epoxyethers, an example was chosen in which both the starting oxide and the final product were well defined crystalline solids. The epoxyether VI was prepared by the usual method from the bromoketone and characterized by hydrolysis, alcoholysis and reaction with 3,5-dinitrobenzoic acid. Rearrangement of this epoxyether VI using the same conditions as for I and II involve migration of the ethyl group and gave the solid methoxy ketone XIII in 84% yield. No isomeric methoxy ketone could be detected. The structure of XIII was proved by conversion to *p*-phenylpropiophenone *via* a Beckmann degradation of the oxime. Although only one diastereoisomer of VI was subjected to rearrangement in this study, Tiffeneau and Weill[13] claimed that the pinacol rearrangement of both diastereoisomers of XV, a compound with many similar features to VI, proceeded with preferential migration of the ethyl group.



XV

Finally the epoxyether VII, derived from α-haloheptaldehyde, was converted to the methoxy ketone XIV using magnesium bromide dissolved in refluxing ether. The methoxymethyl ketone was prepared independently and proved to be identical in all respects with XIV.

## Experimental

**Rearrangement of 1,2-Epoxy-2-methyl-1-methoxy-1-(*p*-biphenyl)-propane (I). Rearrangement Procedure A.**—Anhydrous magnesium bromide was prepared from the reaction of ethylene dibromide and magnesium in anhydrous ether. The anhydrous magnesium bromide (5.7 g., 0.03 mole) was dissolved in 120 ml. of dibutyl ether. The solution was heated to the reflux temperature and stirred, after which 7.2 g. (0.03 mole) of the epoxyether[8] (I) dissolved in 60 ml. of dibutyl ether was added dropwise. The mixture was stirred at the reflux temperature for seven hours after which the reaction was cooled to *ca.* 100° and 8 ml. of dioxane was added to precipitate the magnesium bromide. The mixture was stirred an additional 12 hours at 100° and then the dioxane complex was separated by centrifugation. The supernatant layer was evaporated and the residue dissolved in methanol and treated with charcoal. The 3-methoxy-3-(*p*-biphenyl)-butanone-2 (VIII) crystallized from the methanol and amounted to 6.2 g. (86%), m.p. 43–44°.

*Anal.* Calcd. for C$_{17}$H$_{18}$O$_2$(OCH$_3$): C, 80.28; H, 7.13; OCH$_3$, 12.20. Found: C, 80.22; H, 7.18; OCH$_3$, 11.80.

**Proof of Structure of the α-Methoxy Ketone (VIII).**—The oxime was prepared from 0.25 g. (1 millimole) of VIII and 0.12 g. (1.7 millimoles) of hydroxylamine hydrochloride dissolved in 15 ml. of methanol and 0.2 ml. of 1.5 *N* potassium hydroxide. The 3-methoxy-3-(*p*-biphenyl)-butanone-2 oxime was recrystallized from methylcyclohexane and amounted to 0.25 g. (95%), m.p. 154–155°.

*Anal.* Calcd. for C$_{17}$H$_{19}$NO$_2$: C, 75.81; H, 7.11. Found: C, 75.47; H, 7.24.

Following the general procedure of Buck and Ide,[14] 0.10 g. (0.4 millimole) of the oxime of VIII was subjected to the second order Beckmann reaction to give 0.04 g. (55%) of *p*-phenylacetophenone, m.p. 119–120°. When mixed with an authentic sample (m.p. 120–121°) the mixture melted at 120–121°.

**α-Methoxy-α-phenylcycloheptanone (IX).**—2-Methoxy-2-phenyl-1-oxaspiro[3,5]octane[10] (II) was rearranged using procedure A. From 24.2 g. (0.11 mole) of epoxyether was obtained 17.5 g. (72%) of the 2-methoxy-2-phenylcycloheptanone (IX), b.p. 119–121° (0.9 mm.), $n^{25}$D 1.5408. The ketone solidified when cooled and was recrystallized from pentane, m.p. 33–34°.

*Anal.* Calcd. for C$_{14}$H$_{18}$O$_2$: C, 77.02; H, 8.33. Found: C, 76.76; H, 8.22.

The oxime of IX was prepared by the procedure described above. From 2.18 g. of IX was obtained 2.0 g. (86%) of α-methoxy-α-phenylcycloheptanone oxime, m.p. 94–95°. Three recrystallizations from petroleum ether raised the melting point to 99–100°.

*Anal.* Calcd. for C$_{14}$H$_{18}$NO$_2$: C, 72.07; H, 8.21. Found: C, 72.20; H, 8.46.

This oxime of IX was subjected to the Beckmann degradation conditions of Buck and Ide[14] and the resulting nitrile was hydrolyzed without purification with 3 ml. of concentrated hydrochloric acid. From 1 g. of the oxime was obtained 0.51 g. (54%) of ε-benzoylcaproic acid, m.p. 82–83°. The semicarbazone derivative melted at 176–177°. A mixture melting point determination with an authentic sample of the acid[15] (m.p. 84–85°) or the semicarbazone gave no depression.

**Rearrangement of 1,2,2-Triphenyl-1-methoxyepoxyethane (III).**—Procedure A was used for the rearrangement and from 2 g. of the epoxyether III,[7] m.p. 114–115°, was obtained 1.33 g. (68%) of α,α-diphenyl-α-methoxyacetophenone (X), m.p. 90–92°. When mixed with an authentic sample,[7] m.p. 91–93°, the melting point of the mixture was 91–93°.

**Preparation and Characterization of 1,2-Epoxy-2-methyl-1-methoxy-1-(*p*-biphenyl)-butane (VI).**—α-Methyl-*p*-phenylbutyrophenone was prepared by the procedure of Long and Henze.[16] In carbon disulfide solvent and aluminum chloride catalyst, 154 g. (1.0 mole) of diphenyl was condensed with 132.5 g. (1.1 moles) of α-methylbutyryl chloride to give 206 g. (86%) of the ketone, b.p. 150–160° (0.8 mm.), $n^{25}$D 1.5979.

*Anal.* Calcd. for C$_{17}$H$_{18}$O: C, 85.67; H, 7.61. Found: C, 85.39; H, 7.27.

The oxime, m.p. 109–110°, was prepared in 60% yield.

*Anal.* Calcd. for C$_{17}$H$_{19}$NO: C, 80.59; H, 7.56. Found: C, 80.62; H, 7.96.

Bromination of the ketone in glacial acetic acid gave a 93% yield of α-methyl-α-bromobutyrophenone, m.p. 68–69°.

*Anal.* Calcd. for C$_{17}$H$_{17}$BrO: C, 64.34; H, 5.40. Found: C, 64.45; H, 5.52.

A solution of 26.2 g. (0.08 mole) of the bromoketone in 200 ml. of absolute methanol was heated at the reflux temperature with 25 ml. of a 3.3 *N* sodium methoxide solution for two minutes, after which the reaction mixture was poured on ice and extracted with methylcyclohexane. Distillation gave 17.8 g. (83%) of the epoxyether VI, b.p. 136–137° (0.6 mm.). The distillate solidified and was recrystallized from pentane, m.p. 43–44°.

*Anal.* Calcd. for C$_{18}$H$_{20}$O$_2$: C, 80.56; H, 7.51. Found: C, 80.41; H, 7.80.

When 0.3 g. (1.1 millimoles) of the epoxyether VI was allowed to react in an anhydrous ether solution with 0.4 g. (2.0 millimoles) of 3,5-dinitrobenzoic acid, 0.35 g. (70%) of the 3,5-dinitrobenzoate of α-hydroxy-α-methyl-*p*-phenylbutyrophenone, m.p. 146–147°, was obtained.

*Anal.* Calcd. for C$_{24}$H$_{20}$N$_2$O$_7$: C, 64.28; H, 4.50. Found: C, 64.17; H, 4.64.

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(12) Described in a series of twenty-one papers: M. Tiffeneau, *et al.*, *Bull. soc. chim.*, **49**, 1595 (1931).

(13) P. Weill, *ibid.*, 1795 (1931).

(14) J. Buck and J. Ide, THIS JOURNAL, **53**, 1912 (1931).

(15) The authentic sample was kindly supplied by Prof. C. Hauser, *cf.* THIS JOURNAL, **70**, 4023 (1948).

(16) L. Long and H. Henze, *ibid.*, **63**, 1939 (1941).

Hydrolysis of the epoxyether was accomplished by allowing 0.6 g. of the epoxyether to dissolve in an acetone–water mixture and remain at room temperature for one week. After extraction with ether, the solvent was removed and the residue was recrystallized from petroleum ether to give 0.16 g. (30%) of $\alpha$-hydroxy-$\alpha$-methyl-*p*-phenylbutyrophenone, m.p. 47–48°.

*Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.78; H, 7.39.

Methanolysis of 3.0 g. (0.011 mole) of the epoxyether proceeded in the presence of a catalytic amount of sulfuric acid with the liberation of heat. After the initial reaction had subsided, the reaction mixture was refluxed for one-half hour. After removal of the excess methanol, the residue was recrystallized from petroleum ether (b.p. 30–60°). Two crops of the crystalline $\alpha$-hydroxy-$\alpha$-methyl-*p*-phenylbutyrophenone dimethyl ketal, m.p. 73–75°, were obtained and amounted to 3.21 g. (95%). Further recrystallization from pentane raised the melting point to 75–76°.

*Anal.* Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.42; H, 8.41.

Hydrolysis of 0.44 g. of the hydroxy ketal in aqueous methanol solution to which a drop of concentrated sulfuric acid has been added gave 0.28 g. (75%) of $\alpha$-hydroxy ketone, m.p. 47–48°. The melting point was not depressed when mixed with the hydroxy ketone obtained from the hydrolysis of the epoxyether.

**3-Methoxy-3-(*p*-biphenyl)-pentanone-2** (XIII).—Procedure A was followed for the rearrangement of 1,2-epoxy-2-methyl-1-methoxy-1-(*p*-biphenyl)-butane (VI). From 17.8 g. of this epoxyether, 17 g. (96%) of crude solid methoxy ketone could be isolated. One recrystallization gave 15.1 g. (84%) of methoxy ketone melting above 87°. Neither repeated recrystallization of this material and the residues or examination of the various fractions by means of the infrared spectra gave any evidence of an isomeric methoxy ketone. Recrystallization of a small portion from petroleum ether gave an analytically pure sample, m.p. 95.5–96.5°.

*Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.31; H, 7.53.

The oxime of XIII was prepared by the method of Bachmann and Barton.[17] One gram of the ketone gave 0.9 g. (82%) of 3-methoxy-3-(*p*-biphenyl)-pentanone-2 oxime, m.p. 166–167°.

*Anal.* Calcd. for $C_{18}H_{21}NO_2$: C, 76.24; H, 7.46. Found: C, 76.27; H, 7.45.

Degradation of 0.25 g. of the oxime of XIII under the Beckmann conditions previously described gave 0.12 g. (69%) of *p*-phenylpropiophenone, m.p. 96–97°. A mixture melting point determination with an authentic sample of *p*-phenylpropiophenone gave no depression of the melting point.

**Rearrangement of 1,2-Diphenyl-1-methoxyethylene Oxide** (IV). **Rearrangement Procedure** B.—In 100 ml. of anhydrous ethyl ether 4.25 g. (0.023 mole) of anhydrous magnesium bromide was stirred vigorously in a creased flask at the reflux temperature. To the solution was added 4.4 g. (0.021 mole) of the epoxide IV in 50 ml. of anhydrous ether. A white precipitate formed immediately and the mixture was stirred at the reflux temperature for ten hours. Ten milliliters of dioxane was added to precipitate the magnesium bromide and the reaction was stirred for five hours. The solid magnesium bromide dioxane complex was removed by centrifugation and the solvent removed under vacuum from the supernatant liquid. Distillation of the residue gave only one fraction of 2.91 g. (66%) of benzoin methyl ether, b.p. 115–117° (0.25 mm.). The infrared spectrum of this fraction was identical with one taken of an authentic sample of benzoin methyl ether. Crystallization of this fraction from methanol gave 2.30 g. (52%) of benzoin methyl ether, m.p. 47–48°. The melting point was not depressed when mixed with an authentic sample of benzoin methyl ether.

In a similar experiment, portions of the crude rearrangement product were examined for the presence of an aldehyde fraction. A 0.4-g. portion was treated with Tollens reagent; on heating, a silver mirror formed. The reaction mixture was extracted with 10 ml. of 10% sodium hydroxide solution and filtered. The filtrate was acidified with nitric acid and extracted with ether. On evaporation of the ether 0.50 g. of benzoic acid, m.p. 121–122°, was obtained. No trace of $\alpha$-methoxydiphenylacetic acid reported to melt at 99–100°,[18] was observed. The original reagent presumably oxidized a derivative of benzoin.

A 1-g. portion was treated with saturated sodium bisulfite solution, a small amount of precipitate formed which was removed by filtration. Acidification with dilute sulfuric acid gave only a trace of organic material.

**Rearrangement of 1,2-Epoxy-1-methoxyheptane** (VII).—Procedure B was used in the rearrangement of 1.64 g. (0.0115 mole) of the epoxyether VII with 2.3 g. (0.0125 mole) of magnesium bromide. To prevent the contamination of the rearrangement product with dioxane, the complex was decomposed with 5 ml. of a saturated solution of ammonium chloride. The ether layer was decanted and dried over sodium sulfate. The ether was removed under vacuum and the residue distilled through a 6-inch Vigreux column to give 0.79 g. (49%) of 1-methoxy-2-heptanone[19] (XIV), b.p. 58–59° (4.3 mm.), $n^{25}_{D}$ 1.4192.

*Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.67; H, 11.19. Found: C, 66.81; H, 11.5.

The infrared spectrum was identical with that of an authentic sample.[20]

The semicarbazone of XIV was prepared in 79% crude yield. Analytically pure material, m.p. 69–70°, was isolated in 43% yield and when mixed with an authentic sample did not depress the melting point.

*Anal.* Calcd. for $C_9H_{19}N_3O_2$: C, 53.71; H, 9.52. Found: C, 53.37; H, 9.33.

The 2,4-dinitrophenylhydrazone derivative, m.p. 79–80°, was prepared and proved to be identical with an authentic sample by mixture melting point determination.

*Anal.* Calcd. for $C_{14}H_{20}N_4O_5$: C, 51.84; H, 6.21. Found: C, 51.78; H, 6.38.

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[17] W. E. Bachmann and M. X. Barton, *J. Org. Chem.*, **3**, 300 (1938).

[18] Y. S. Zal'kind and P. S. Bataev, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1858 (1947); *C. A.*, **42**, 4161 (1948).

[19] H. Henze and N. Rigler, THIS JOURNAL, **56**, 1350 (1934), reported this methoxyketone, b.p. 191–191.5°, $n^{20}_{D}$ 1.4220, from the reaction of the Grignard reagent with methoxyacetonitrile.

[20] Prepared in this Laboratory from the corresponding diazoketone by T. H. Coffield and will be reported later.