[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

Epoxyethers. VI. A Triphenyl Substituted Epoxyether

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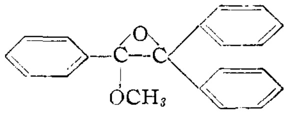
A new type of epoxyether I, fully substituted with aromatic groups, has been isolated in 80% yield from the corresponding α-chloroketone and sodium methoxide. I was characterized by hydrolysis and methanolysis. An acid-catalyzed rearrangement of the epoxyether to the α-methoxy ketone (III) was accomplished with dry hydrogen chloride or acetic acid as the catalyst.

This investigation resulted in the isolation and characterization of an epoxyether I fully substituted with aromatic groups. A representative member of this class of epoxyethers was needed in connection with the study of the chemistry of the epoxyethers being conducted in this Laboratory.[2]

The epoxyether I could not be prepared in the usual manner from the bromoketone II and sodium methoxide; the only product was the corresponding methoxyketone III. However, the chloroketone gave the epoxyether in excellent yield (80%). These reactions represent an interesting example in which a change in the nature of the halogen completely changes the course of the reaction of an α-haloketone with base. I proved to be less reactive to alcohol and organic acids than the epoxyethers previously isolated, but proved to be very labile to acid-catalyzed rearrangement to the α-methoxyketone.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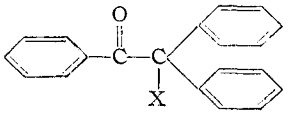

II, X = Br

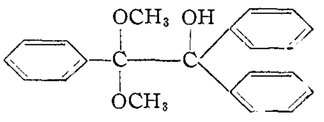
III, X = OCH_3

IV, X = Cl

V, X = OH

VII, X = $O\overset{O}{\overset{\|}{C}}—C_6H_5$

VIII, X = $O\overset{O}{\overset{\|}{C}}—CH_3$


VI

When the previously known α-bromo-α,α-diphenylacetophenone (II) was allowed to react with an alcoholic solution of sodium methoxide, the only product that could be isolated was the α-methoxy-α,α-diphenylacetophenone (III). The α-bromoketone II was readily solvolyzed by absolute methanol as shown by the fact that after an alcohol solution of the bromoketone II was heated to the reflux temperature for 1.5 minutes, a 60% yield of the α-methoxyketone III could be isolated. In the reaction of this bromoketone II with alcoholic sodium methoxide, solvolysis and/or displacement of the bromine atom by the reagent completely takes precedence over the attack by the base on the carbonyl group with subsequent formation of an epoxyether. None of the parent ketone, which would result from the displacement of the "positive"[3] halogen in II by hydrogen from the solvent, could be isolated in these experiments.

Although Gardeur[4] reported α-chloro-α,α-diphenylacetophenone (IV) as a heavy yellow oil from the direct chlorination of the parent ketone, no pure compound could be isolated by this chlorination procedure. The pure crystalline chloroketone IV would be prepared readily in 90% yield from the hydroxyketone V, thionyl chloride and pyridine. The α-hydroxy-α,α-diphenylacetophenone (V) was formed in 82% yield by hydrolysis of the α-bromoketone II in aqueous acetone solution. The structure of the chloroketone IV was confirmed by methanolysis to the α-methoxyketone in 95% yield and hydrolysis to the hydroxyketone in 94% yield.

The α-chloroketone was readily converted in alcohol solution containing one equivalent of sodium methoxide into the epoxyether I in 80% yield. The infrared spectrum of the epoxyether showed no absorption corresponding to a carbonyl or hydroxyl group and the compound was characterized by reaction with water, alcohol and organic acids.

The epoxyether I could be hydrolyzed in acid solution to the α-hydroxyketone V in 91% yield. In the presence of dry sodium methoxide or without a catalyst the epoxyether would not react with alcohol and could be recovered unchanged from alcohol after two days at the reflux temperature. In absolute methanol containing a drop of sulfuric acid, the epoxide ring of I was opened to give 40% of the α-hydroxyketal VI. The structure of VI was confirmed by hydrolysis of the ketal group to give the hydroxyketone V in 92% yield.

The epoxyether was singularly unreactive toward benzoic acid at ordinary temperature but after being heated to 225°, a 70% yield of the α-ketobenzoate VII could be isolated from the reaction mixture of I and benzoic acid. This ketobenzoate VII was identical with one made independently from the α-hydroxyketone and benzoyl chloride.

Previously, the Lewis-type acid, magnesium bromide, had been shown to cause the rearrangement of an epoxyether to an α-methoxyketone.[5] The epoxyether I, fully substituted by aromatic groups, was shown to undergo rearrangement to the methoxyketone very easily in the presence of a proton acid. From the epoxyether and a saturated

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(1) Abstracted in part from the M.S. thesis of Mr. J. J. DeYoung, Wayne University, 1951.

(2) The preceding paper in this series. C. L. Stevens and J. Tazuma. THIS JOURNAL, **76**, 715 (1954).

(3) For a discussion and investigation of the "positive" nature of the bromine atom in II see P. D. Bartlett and R. Altschul, *J. Org. Chem.*, **5**, 623 (1940).

(4) A. Gardeur, *Bull. classe. sci. Acad. roy. Belg.*, [3] **34**, 67 (1897); *Chem. Zentr.*, **68**, 661 (1897).

(5) C. L. Stevens, M. L. Weiner and R. C. Freeman, THIS JOURNAL, **75**, 3977 (1953).

solution of dry hydrogen chloride in methanol an 80% yield of α-methoxy-α,α-diphenylacetophenone (III) could be isolated.

When the epoxyether I was heated for eight hours with a mixture of acetic acid and acetic anhydride, a 70% yield of the α-ketoacetate VIII resulted. However, after the reaction mixture was heated for three hours, only 24% of the ketoacetate VIII was obtained. In addition, **α-methoxy-α,α-diphenylacetophenone** (III) was isolated in 50% yield. The only reasonable reaction course for the formation of the α-methoxyketone was by the rearrangement of the epoxyether I through the agency of the organic acid catalyst. The fact that the initial reaction gave 70% of α-ketoacetate and no methoxyketone III made necessary the conclusion that the methoxyketone was converted to the ketoacetate in the reaction mixture. This conclusion was confirmed by the fact that pure α-methoxyketone III, under the conditions of the reaction, was slowly solvolyzed and from this mixture 78% of the ketoacetate VIII could be isolated. The ketoacetate VIII was identical with an authentic sample prepared from the α-hydroxyketone V.

These reactions indicate that the formation of the ketoacetate from this epoxyether I and acetic acid proceeds largely by first rearrangement to the methoxyketone followed by solvolysis and is distinctly different from the previous facile reactions of organic acids with epoxyethers to form α-ketoesters.[6]

Experimental

α-Bromo-α,α-diphenylacetophenone (II).—α,α-Diphenylacetophenone, m.p. 137–138°, was prepared in 71% yield from a Friedel–Crafts reaction of desyl chloride with benzene in the presence of aluminum chloride.[7] A solution of 20 g. (0.07 mole) of α,α-diphenylacetophenone dissolved in 200 ml. of dry benzene was heated to the reflux temperature and 11.8 g. (0.07 mole) of bromine added over a period of one hour. After the reaction mixture was heated an additional half-hour, the excess benzene was distilled and the residue dissolved in heptane. After the heptane solution had cooled, 26 g. (97%) of α-bromo-α,α-diphenylacetophenone, m.p. 95–97°, was separated by filtration. An analytically pure sample of the bromoketone melted at 97–98°. Werner[8] reports the melting point to be 99°.

α-Methoxy-α,α-diphenylacetophenone (III).—α-Bromo-α,α-diphenylacetophenone (2.0 g.) was added to 35 ml. of absolute methanol which had been heated to the reflux temperature. After 1.5 minutes the solution was poured onto ice and the solid that formed was filtered, m.p. 89–90°. Recrystallization from a benzene–petroleum ether mixture gave 60% of α-methoxy-α,α-diphenylacetophenone, m.p. 91–93°. Werner[8] reports a melting point of 94°.

At room temperature the rate of the reaction between 4.0 g. (0.011 mole) of α-bromoketone II and 0.012 mole of sodium methoxide in 85 ml. of absolute methanol was followed by titration of an aliquot with standard acid. After five minutes 60% of the base was used; 70% was used after 15 minutes; and 92% was used after 30 minutes. Isolation of the product from this reaction or a similar reaction carried out at the reflux temperature gave only the α-methoxyketone III, m.p. 90–91°.

α-Chloro-α,α-diphenylacetophenone (IV).—A solution of 20 g. of α-bromo-α,α-diphenylacetophenone in 250 ml. of acetone and 100 ml. of water was heated to reflux for three hours and then poured onto ice. The oil that separated was extracted with ether and the ether solution dried. After the ether was evaporated, the residue was recrystallized from ligroin to give 13 g. (82%) of the α-hydroxyketone[8] V, m.p. 85–86°.

A mixture of 13 g. (0.045 mole) of α-hydroxy-α,α-diphenylacetophenone and 3.6 g. (0.045 mole) of dry pyridine was heated until solution resulted and then cooled in an ice-bath until solid. The solid was broken into small pieces and then 7.2 g. (0.06 mole) of thionyl chloride was added while the mixture was stirred vigorously and cooled in an ice-bath. After the addition of the thionyl chloride, the reaction was allowed to stand for one hour and then ice and water were added and the resulting solid mass broken. The organic material was extracted with ether, the ether solution was dried and the excess solvent distilled. The residue was dissolved in hot petroleum ether, from which 9.5 g. of product crystallized, m.p. 82–84°. Concentration of the mother liquor gave an additional 1.5 g., m.p. 82–84°. The total yield of α-chloro-α,α-diphenylacetophenone was 11 g. (90%) and an analytically pure sample had m.p. 84–85°.

Anal. Calcd. for $C_{20}H_{13}ClO$: C, 78.29; H, 4.93; Cl, 11.56. Found: C, 78.00; H, 5.07; Cl, 11.71.

Methanolysis of the chloroketone was accomplished by heating to reflux a solution of 2 g. of IV and 50 ml. of methanol for 12 hours, after which time the solution was cooled and 1.9 g. (95%) of the α-methoxyketone III crystallized, m.p. 91–93°. A mixture melting point with III obtained from the bromoketone was not depressed.

Hydrolysis of the chloroketone occurred when 1.5 g. of IV was dissolved in 20 ml. of acetone and 10 ml. of water and the resulting solution heated to reflux for eight hours. The mixture was cooled, water was added and the product was extracted with ether. After the ether solution was concentrated, recrystallization of the residue gave 1.8 g. (94%) of the α-hydroxyketone V, m.p. 81–83°. A mixture melting point with V obtained from II was not depressed.

1-Methoxy-1,2,2-triphenylethylene Oxide (I).—A mixture of 3.07 g. (0.01 mole) of α-chloro-α,α-diphenylacetophenone and a solution of 0.01 mole of sodium methoxide in 50 ml. of absolute methanol was stirred at room temperature for two hours. After one hour all the chloroketone had dissolved and after two hours a considerable amount of product had crystallized from the mixture. The reaction mixture was cooled in a Dry Ice and acetone bath and then filtered to give 1.2 g. of epoxy-ether, m.p. 109–111°. The filtrate was concentrated under reduced pressure and an additional 1.1 g. of product obtained. The total yield of 1-methoxy-1,2,2-triphenylethylene oxide was 2.3 g. (80%). Recrystallization from ligroin gave an analytically pure product, m.p. 114–115°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00; CH_3O, 10.26. Found: C, 83.40; H, 6.35; CH_3O, 10.24.

The epoxyether was hydrolyzed in 15 minutes when 0.5 g. of I, 10 ml. of water, one drop of sulfuric acid and enough acetone to make the mixture homogeneous were heated to the reflux temperature. After concentration of the solution and recrystallization of the precipitate, 0.4 g. (91%) of α-hydroxyketone V was obtained, m.p. 79–81°. Recrystallization from ligroin raised the melting point to 84–85° and the identity was established by mixture melting point determination.

α-Hydroxy-α,α-diphenylacetophenone Dimethylketal.—A solution of 0.5 g. of the epoxyether I in 20 ml. of absolute methanol was heated to the reflux temperature for 15 minutes after the addition of one drop of concentrated sulfuric acid. After this time the solution was neutralized with solid sodium carbonate and cooled to −20°. The precipitated solid was filtered and amounted to 0.16 g. (40%), m.p. 131–132°. Recrystallization raised the melting point to 134–135°.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63; OCH_3, 18.56. Found: C, 79.04; H, 6.93; OCH_3, 18.61.

From the mother liquor, 0.15 g. (33%) of starting epoxyether I could be recovered, m.p. 109–111°, the identity of which was shown by mixture melting point determination.

The α-hydroxyketal VI was hydrolyzed to confirm the structure. A solution of 0.5 g. of VI, 10 ml. of acetone, 5 ml. of water and a drop of sulfuric acid was heated to the reflux temperature for 15 minutes. The solution was cooled, water was added and the organic material was extracted with ligroin. From the ligroin solution 0.35 g. (92%) of α-hydroxy-α,α-diphenylacetophenone (V) could be isolated, m.p. 84–85°.

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(6) 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 and S. Dykstra, *ibid.*, **76**, 5975 (1954).

(7) R. Anschütz and P. Forster, *Ann.*, **368**, 91 (1909).

(8) A. Werner, *Ber.*, **39**, 1278 (1906).

Reaction of the Epoxyether with Benzoic Acid.—In a 6-in. test-tube was placed 0.6 g. of I and 0.6 g. of benzoic acid. The solids were pulverized and mixed and then heated over a Bunsen burner to 225°. The melt was cooled and then extracted with ethyl ether, after which the ether solution was washed with sodium carbonate solution. The ether was evaporated and the residue recrystallized from ligroin to give 0.52 g. (70%) of α-hydroxy-α,α-diphenylacetophenone benzoate (VII), m.p. 151–152°.

Anal. Calcd. for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found: C, 82.82; H, 5.23.

The ketobenzoate VII was prepared independently from 2 g. of α-hydroxyketone (V), 12 g. of benzoyl chloride and 30 ml. of dry pyridine. After the reaction mixture had refluxed for four days, the excess benzoyl chloride was decomposed by the addition of ice and water to the cooled solution. Dilute hydrochloric acid was added and the organic material extracted with ether. The ethereal solution was washed with sodium carbonate solution, dried and the ether evaporated. Recrystallization of the residue from a benzene-ligroin mixture gave 0.6 g. (23%) of the ketobenzoate VII, m.p. 150–151°. A mixture melting point with VII from the epoxyether was not depressed.

Rearrangement of the Epoxyether (I).—Dry hydrogen chloride was bubbled into 25 ml. of cold methanol until the alcohol was saturated and then 0.55 g. of epoxyether was added and the solution heated to reflux for five hours. The reaction was acidic to litmus after this time. The solution was cooled in an ice-bath and the resulting solid separated by filtration. The solid proved to be α-methoxy-α,α-diphenylacetophenone (III) and amounted to 0.4 g. (80%), m.p. 90–91°. A mixture melting point with authentic III was not depressed.

Reaction of the Epoxyether with Acetic Acid.—A solution of 0.45 g. of epoxyether I in 15 ml. of acetic acid and 10 ml. of acetic anhydride was heated to the reflux temperature for eight hours. After the solution had cooled, aqueous sodium carbonate was added and the organic material was extracted with ether. The ether solution was concentrated and the residue dissolved in ligroin from which 0.45 g. (70%) of α-hydroxy-α,α-diphenylacetophenone acetate (VIII), m.p. 145–146°, could be isolated.

An authentic sample of ketoacetate VIII was prepared by acetylation of the hydroxyketone V. A solution of 4 g. of V and 75 ml. of acetic anhydride was heated at the reflux temperature for 14 hours, after which time the mixture was poured onto ice. The solid that formed was filtered and recrystallized from ligroin to give 2.3 g. (66%) of the ketoacetate,[9] m.p. 143–144°. A mixture melting point with VIII from the epoxyether was not depressed.

In another experiment 1.0 g. of the epoxyether, 15 ml. of acetic acid and 10 ml. of acetic anhydride were heated to the reflux temperature for only three hours. The reaction was then poured onto a mixture of ice and potassium carbonate solution, after which the organic material was extracted with ether. The ether solution was concentrated and the residue dissolved in hot ligroin. After the ligroin solution had cooled, 0.25 g. (24%) of α-hydroxy-α,α-diphenylacetophenoneacetate, m.p. 141–142°, was obtained. Recrystallization from ligroin raised the melting point to 146–147° and the identity of the compound was proved by a mixture melting point determination with an authentic sample.

The initial ligroin mother liquor was concentrated to give 0.5 g. (50%) of α-methoxy-α,α-diphenylacetophenone (III), m.p. 86–90°. The compound caused no depression of melting point when mixed with authentic III.

Solvolysis of α-Methoxy-α,α-diphenylacetophenone.—Pure α-methoxyketone III, m.p. 90–92° (1.5 g.) was dissolved in 15 ml. of acetic acid and 10 ml. of acetic anhydride and heated to reflux for a total of 16 hours. The product was isolated by the same procedure as given above and proved to be the ketoacetate VIII, 1.1 g. (78%), m.p. 146–148°.

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[9] M. M. Delacre, *Bull. soc. chim. France*, [3] **13**, 857 (1895), reported a melting point of 144–145°.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Sulfostyrenes.[1] Preparation and Polymerization of Potassium *p*-Vinylbenzenesulfonate[2]

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p-Vinylbenzenesulfonic acid (sulfostyrene) has been prepared by dehydrohalogenation of β-bromoethylbenzenesulfonyl chloride, isolated as its toluidine and potassium salts, and characterized. The potassium salt has been polymerized to high viscosity polymers. The reduced viscosities (η_{sp}/c) for these polymers are non-linear functions of concentration (c) and show a marked increase as the concentration decreases (Fig. 1). A previously developed relation (equation 2) involving reciprocal reduced viscosity and concentration, but not square root of the concentration (Fig. 2), gives a linear plot (Fig. 3), as does also a log–log plot of reduced viscosity and concentration (Fig. 4). Both of these linear plots have finite intercepts roughly proportional to the specific viscosities of the polymers. The intercepts of the log–log plots are multiples of the D factors of equation 2 for these polysulfostyrenes and are, to the extent that the D factors are also, related to the intrinsic viscosity of the polymer.

Polysulfostyrenes are useful cation exchange resins but, prior to the studies reported herein, they have been available only by the sulfonation of polystyrene. This method of preparation limits the capacity of the polymer to that degree of sulfonation obtainable without excessive decomposition of the polymer or sulfone formation[4,5] and raises a question as to the homogeneous distribution of the sulfo groups amongst the phenyl radicals. Preparation of polysulfostyrenes by polymerization of suitable monomers offers a means of avoiding both of these problems. In this paper we wish to describe the first preparation of monomeric salts of *p*-vinylbenzenesulfonic acid and some characteristics of the polymers obtained on polymerization of the potassium salt.

In our previous work we have described the results obtained in studying various synthetic routes to a sulfostyrene or derivatives thereof. Syntheses starting with *p*-ethylbenzenesulfonyl chloride, a readily available intermediate, involving bromination at the α-position of the ethyl group and subsequent dehydrohalogenation have been

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[1] Previous papers in this series: (a) R. H. Wiley and C. C. Ketterer, THIS JOURNAL, **75**, 4519 (1953); (b) R. H. Wiley, R. P. Davis and N. R. Smith, *J. Org. Chem.*, **18**, 1372 (1953); (c) R. H. Wiley and R. P. Davis, THIS JOURNAL, **74**, 6142 (1952).

[2] This research was supported under Contract AT-(40-1)-229 between the Atomic Energy Commission and the University of Louisville.

[3] Predoctoral research assistant.

[4] R. Signer and A. Demagistri, *J. chim. phys.*, **47**, 704 (1950).

[5] W. C. Baumann and J. Eichhorn, THIS JOURNAL, **69**, 2830 (1947).