The ethyl pyruvate was quite pure since, on redistillation, 7 g. (a 71% yield) was collected at 146–149°; n^{20}_D 1.4100. Its semicarbazone melted at 207–208°.

Ethanediol Ethyl Triphenylmethyl Diether, V.—Fourteen out of twenty grams of this ether was recovered after maintaining it for ninety minutes at 295–310°, but fairly complete decomposition was realized in three hours at 325–330° (bath temp.). In the latter case, 45.8 g. of the diether was heated in a 100-cc. Claisen flask and a stream of nitrogen was bubbled through the liquid to assist in the volatilization of the reaction products. During the three hours there was collected 11.8 g. of a volatile fraction (A). The residue was distilled at 35 mm. There was obtained a 10.2-g. fraction (B) at 160–190°, a 14.7-g. fraction (C) at 190–220°, and 5.7 g. of tarry residue.

Fraction A contained acetaldehyde, ethanediol ethyl ether and ethanediol ethyl diether. Redistillation gave these fractions (°C., g.): to 27, 1.8; 70–125, 2.2; 125–135, 5.1.

The first fraction was acetaldehyde. The 2,4-dinitrophenylhydrazone prepared from it melted at 155°. The 125–135° fraction, d^{20}_{20} 0.91, was a mixture of "cellosolve" (b. p. 135°, d^{15} 0.935) and its ethyl ether (b. p. 123.5°, d^{20} 0.848). It was insoluble in water, but reacted readily with sodium. It gave no test with Schiff's reagent. It was hydrolyzed to ethanediol by heating 0.5 cc. of it with 2 cc. of 48% hydriodic acid on the steam-bath for fifteen minutes. The solution was diluted, the iodine destroyed by sodium thiosulfate and the mixture extracted with ether. The aqueous layer was made basic with 30% sodium hydroxide and shaken with benzoyl chloride. The solid which separated, after recrystallization from alcohol-water, melted at 71–72°. A mixed melting point with an authentic specimen of ethylene benzoate was 72°.

About 3 g. of triphenylmethane separated from fraction B on standing. The oily filtrate was then seeded with a crystal of benzophenone, whereupon a considerable quantity of crude benzophenone separated. It melted at 41–43° (mixture m. p. with benzophenone, m. p. 49°, was 45–47°). It yielded the oxime of m. p. 142–144° readily. This fraction appeared to consist of 7 g. of triphenylmethane and 3.2 g. of benzophenone.

Fraction (C) was practically pure triphenylmethane. The total triphenylmethane (21.7 g.) is 65% of the theoretical.

Summary

Improved directions are given for the synthesis of ethanediol triphenylmethyl ether from ethanediol. This compound was synthesized also by refluxing the ethanediol with ethanediol triphenylmethyl diether. Ethyl α-triphenylmethoxypropionate was prepared from ethyl lactate; ethanediol ethyl triphenylmethyl diether from ethanediol ethyl ether; and γ-triphenylmethoxypropylene acetal from γ-hydroxypropylene acetal.

Pyrolysis of ethanediol triphenylmethyl ether occurred at 140°. The reaction, which was a disproportionation into ethanediol and ethanediol triphenylmethyl diether, occurred almost quantitatively if performed under diminished pressure.

Temperatures of 330–300° were required for the pyrolysis of ethanediol triphenylmethyl diether or of ethanediol ethyl triphenylmethyl diether. Both compounds yielded triphenylmethane and benzophenone as reaction products. The reaction was not suitable for the synthesis of aldehydes. A good yield of ethyl pyruvate was obtained by pyrolysis of ethyl α-triphenylmethoxypropionate.

EVANSTON, ILLINOIS RECEIVED JULY 1, 1937

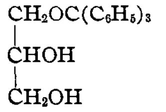
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Triphenylmethyl Ethers of Glycerol and Glycerol Derivatives

BY CHARLES D. HURD, CLINTON O. MACK, E. M. FILACHIONE AND JOHN C. SOWDEN

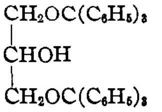
In the work with ethylene glycol[1] it was established that entirely different reactions were encountered in the pyrolyses of the triphenylmethyl monoether and diether. The monoether changed at a comparatively low temperature into the diether and ethylene glycol. The diether required a temperature of 330–350° for decomposition and the products included triphenylmethane, benzophenone, carbon monoxide and formaldehyde, but no glyoxal.

This paper reports a similar study, dealing with glycerol and certain of its derivatives. Two of the compounds (I–II) possessed available hydroxyl groups in the molecule. The remaining four compounds (III–VI) did not. From the results with the glycol derivatives, it would be expected that the first two compounds should behave differently from the others and such was found to be the case. Glycerol triphenylmethyl ether (I) changed at 180–190° into glycerol α,



$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

I



$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CHOH \\ | \\ CH_2OC(C_6H_5)_3 \end{array}$$

II

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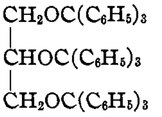
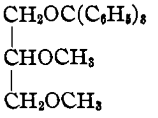
(1) Hurd and Filachione, THIS JOURNAL, 59, 1949 (1937).

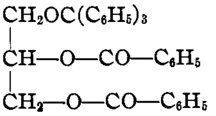
γ-bis-triphenylmethyl diether (II). The latter, in turn, changed at 260° into glycerol triphenylmethyl triether (III). It was found also that if a mixture of glycerol and II was heated at 210°, there was reaction to form I. This reversible pyrolysis of I is strictly analogous to the behavior observed in the glycol series.


$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CHOC(C_6H_5)_3 \\ | \\ CH_2OC(C_6H_5)_3 \end{array}$$

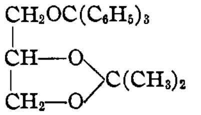
III


$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CHOCH_3 \\ | \\ CH_2OCH_3 \end{array}$$

IV


$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CH{-}O{-}CO{-}C_6H_5 \\ | \\ CH_2{-}O{-}CO{-}C_6H_5 \end{array}$$

V



VI

2,2-Dimethyl-4-(triphenylmethoxymethyl)-dioxolane (VI) decomposed at 320° in the complex manner observed with the glycol diethers. The products identified were triphenylmethane, benzophenone and acetone. Pyrolysis of β,γ-dibenzoxypropyl triphenylmethyl ether (V) produced triphenylmethane also. Since V is not only an ether but also a benzoic ester, it was reasonable to expect benzoic acid among the products. It was found, but in a quantity corresponding to about one quarter of the total benzoyl content. No evidence for aldehydes could be obtained in the reaction products.

The triethers III and IV were synthesized but not pyrolyzed since it seemed evident from the preceding work that it would be impossible to control the reaction to stop at a glyceraldehyde stage.

Experimental Part

Glycerol α-triphenylmethyl ether (I) and glycerol α,γ-bis-triphenylmethyl diether (II) were prepared by Helferich's[2] method. In some runs the m. p. of I was 93–94°, the same as that reported by Helferich; in others, the value was 108–110°, for which also there is precedent.[3] The lower melting variety was used in the synthesis of II and V whereas the other was used for IV. It is interesting to note that Norris and Cresswell[4] reported two melting points (82.5 or 95.5°) for methyl triphenylmethyl ether.

β,γ-Dibenzoxypropyl triphenylmethyl ether (V), m. p. 92°, was prepared from I at 0° by reaction with benzoyl chloride and pyridine.[5] The 2,2-dimethyl-4-(hydroxymethyl)-dioxolane ("acetone-glycerol"), b. p. 80–82° (12 mm.), was obtained in 80% yield by Fischer's method.[6]

Glycerol Triphenylmethyl Triether (III).—To 12.6 g. (0.039 mole) of triphenylmethyl bromide was added 25 cc. of anhydrous pyridine which contained 1.2 g. (0.013 mole) of dry glycerol. The mixture was heated at 100° for five hours and then left overnight before being poured into water. The solid was taken up in chloroform and the solution washed with dilute hydrochloric acid, water and sodium bicarbonate solution. After being dried, the solvent was evaporated and the residue was dissolved in the minimum amount of hot benzene. About half as much hot alcohol was added. The crystals which separated on cooling were recrystallized in the same way. After drying in an oven at 85° the melting point was found to be 196–197°; yield, 19%. The triether was quite soluble in chloroform and hot benzene but much less soluble in alcohol and ether.

In a similar experiment in which triphenylmethyl chloride was used instead of the bromide, a 12% yield was realized. Generally, the chloride is more convenient to use than the bromide since it is much more soluble in pyridine

Anal. Calcd. for $C_{60}H_{50}O_3$: C, 87.98; H, 6.16. Found C, 87.59; H, 6.14.

Glycerol α-Triphenylmethyl β,γ-Dimethyl Triether (IV).—Ten grams of I was dissolved in a mixture of 75 cc. of benzene and 34 g. of methyl iodide. Mechanical stirring was started and the mixture was treated, during three and one-half hours, with 28 g. of silver oxide. A bath temperature of 35–50° was maintained around the reaction vessel. The reaction was continued, with stirring, for an additional five and one-half hours at 45–50°. Then, the mixture was cooled, filtered and distilled. There was collected 6.8 g. (a 63% yield) of the desired triether at 210–212° (3 mm.). It was a viscous colorless sirup which resisted solidification, but after standing for several months at room temperature it crystallized spontaneously. This material melted at 45–50°. It was very soluble in most solvents but it crystallized from low-boiling petroleum ether at 0°.

Anal. (by Mr. S. Cristol). Calcd. for $C_{24}H_{26}O_3$: C, 79.5; H, 7.24. Found: C, 79.5; H, 7.21.

2,2-Dimethyl-4-(triphenylmethoxymethyl)-dioxolane (VI).—Twenty grams of 2,2-dimethyl-4-(hydroxymethyl)-dioxolane was dissolved in 100 cc. of pyridine and the mixture was treated with 42 g. of triphenylchloromethane. After twenty-four hours at room temperature the mixture was filtered to remove the pyridine hydrochloride. The filtrate was poured into 800 cc. of water and the oily layer was separated by three extractions with ether. The extract was washed with dilute hydrochloric acid, water, and finally with potassium carbonate solution. Then it was dried and the solvent distilled off. The residual sirup was dissolved in 50 cc. of warm benzene and 100 cc. of petroleum ether was added. On cooling, 1.7 g. of triphenylcarbinol separated. The solvents were removed at reduced pressure and the residue was crystallized from 50 cc. of absolute alcohol. A recrystallization from 90% alcohol yielded 41 g. of crystals which melted at 71–73°. The yield was 73%.

Anal. (by Mr. Cristol). Calcd. for $C_{25}H_{26}O_3$: C, 80.1; H, 7.00. Found: C, 79.3; H, 7.01.

Pyrolysis of the Ethers

Glycerol Triphenylmethyl Ether (I).—About 0.2 g. of I was heated in a test-tube at 180–190° for ninety minutes.

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(2) Helferich, *Ber.*, **56**, 766 (1923).

(3) Jackson and King, THIS JOURNAL, **55**, 678 (1933); Verkade, Lee and Meerburg, *Rec. trav. chim.*, **54**, 716 (1935).

(4) Norris and Cresswell, THIS JOURNAL, **55**, 4948 (1933).

(5) Helferich and Sieber, *Z. physiol. Chem.*, **170**, 31 (1927).

(6) Fischer and Pfähler, *Ber.*, **53**, 1606 (1920).

Then the reaction product was dissolved in 4 cc. of hot acetone and 2 cc. of water was added dropwise until incipient cloudiness. About 0.05 g. of large crystalline flakes separated on cooling; m. p. 168–169°. Addition of more water brought about the precipitation of an additional 0.1 g. It was glycerol triphenylmethyl diether. When mixed with an authentic specimen, the mixture melted at 168–169°.

Glycerol α,γ-Bis-triphenylmethyl Diether (II).—Half a gram of II was placed in a test-tube which was heated gradually during thirty-seven minutes to 260°. No decomposition was evident at 180°. The melt, which solidified on cooling, was dissolved in 5 cc. of hot acetone. White crystals of glycerol triphenylmethyl triether (III) separated readily as the solution was brought to room temperature. With no further purification, the crystals melted at 188–190° and did not depress the melting point of synthetic glycerol triphenylmethyl triether.

Reaction of the Diether (II) with Glycerol.—A mixture of 6.1 g. of II and 50 g. of glycerol was heated with stirring for three hours at 205–215°. Then it was cooled and poured into 250 cc. of water. The mixture was twice extracted with a total of 500 cc. of ether, the extract dried over potassium carbonate and the ether distilled off. After several recrystallizations of the residue from alcohol–water mixtures, 2.4 g. (33% yield) of glycerol triphenylmethyl monoether, m. p. and mixed m. p. 105–107°, was obtained.

β,γ-Dibenzoxypropyl Triphenylmethyl Ether (V).—Fifteen grams of V was heated for sixteen hours at 260–300° (bath temperature) and 5–8 mm. The reaction flask was an all-glass Claisen flask, connected in series to two receivers, one at 100° and the next at −80°. There were separated from the first receiver 1.5 g. of benzoic acid (m. p. 122°; converted to benzo-*p*-toluidide, m. p. 157°) and 3.1 g. of triphenylmethane (m. p. 93–94°). The cold receiver contained about 1 cc. of an unidentified, lachrymatory liquid. It was unsaturated for it decolorized bromine (in carbon tetrachloride), but apparently it was not an aldehyde for it gave negative tests with Schiff's or Tollens' reagent.

2,2 - Dimethyl - 4 - (triphenylmethoxymethyl)-dioxolane (VI).—The 50-cc. reaction flask used in this experiment was sealed directly to a receiver at −80° which, in turn, was connected to a 2.5-liter gas-collecting bottle filled with a concd. solution of potassium hydroxide. The gaseous reaction products were collected by sweeping the system out with a current of carbon dioxide, a slow stream of which was maintained throughout the experiment.

Twenty grams of VI was heated for three and three-quarters hours at 310–328° (bath temp.). The gas evolution was small for only about 300 cc. was obtained. In the cold receiver there was 5.2 g. of a liquid which contained much acetone; *e. g.*, its 2,4-dinitrophenylhydrazone (orange, long needle crystals from alcohol) melted at 123–124.5°. An authentic specimen of acetone 2,4-dinitrophenylhydrazone, m. p. 125–126°, differed physically for it was light yellow and almost flocculent. However, the mixed melting point was 124–125°.

The derivative with benzaldehyde also melted low for dibenzalacetone. In contrast to the m. p. of 111–112° it melted at 104–107° after several crystallizations, but the mixed melting point was 106–107°. No aldehydes were detected by means of dimethyldihydroresorcinol,[7] although the method was shown to be capable of detecting formaldehyde readily in a mixture made up of one drop of formalin in 1 cc. of acetone and 5 cc. of water.

Distillation of the residue in the flask at 15 mm. yielded 1.4 g. of benzophenone between 80–189°, 8.5 g. of triphenylmethane at 190–205°, and 3–4 g. of residue. The fractions of distillate solidified. The ketone melted at 45–47° and the hydrocarbon, after crystallization from alcohol, at 90–91.5°. The phenylhydrazone, prepared from the ketone, melted at 136–137°.

Summary

These new derivatives of glycerol were prepared: glycerol triphenylmethyl triether, glycerol α-triphenylmethyl β,γ-dimethyl triether, and 2,2-dimethyl-4-(triphenylmethoxymethyl)-dioxolane.

Disproportionation reactions were encountered during pyrolysis of glycerol triphenylmethyl mono- or diethers. The monoether yielded the diether at 185°, and at 260° the diether produced the triether. The reverse of the first of these reactions was achieved by heating the diether with glycerol at 210°.

Pyrolysis of β,γ-dibenzoxypropyl triphenylmethyl ether yielded benzoic acid and triphenylmethane but no aldehyde. The products formed from 2,2-dimethyl-4-(triphenylmethoxymethyl)-dioxolane at 320° were acetone, benzophenone and triphenylmethane.

EVANSTON, ILLINOIS RECEIVED JULY 26, 1937

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[7] Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).