tinued for three and a quarter hours longer during which time 40 ml. of fuming nitric acid, 10 ml. of fuming sulfuric acid and 13 ml. of concd. sulfuric acid were added in small portions keeping the ratio of the two acids constant. After pouring the mixture into 600 ml. of cold water, the precipitated crude product was purified by extraction first with ether in a Soxhlet apparatus, then with boiling glacial acetic acid in several portions, and finally with boiling chloroform in a continuous extractor. The residue at this point amounted to about 8 g., which after seven recrystallizations from nitrobenzene and glacial acetic acid was dried over concentrated sulfuric acid in a vacuum desiccator; m. p. 278–279° with decomposition. The compound is a pale yellowish powder which darkens on exposure to light and ignites with a flash when heated on a spatula in a flame. It gives no color with alcoholic potassium hydroxide but does give a black precipitate with sodium ethylate in pyridine. It is unaffected by bromine in carbon disulfide. *Anal.* Calcd. for $C_{37}H_{19}O_{18}N_9$: N, 14.39. Found: N, 14.31, 14.52, 14.40. The conditions described above for nitrating the triarylmethane are somewhat more severe than those used by Montagne[11] in nitrating triphenylmethane. They have been checked against the latter compound and found to give better yields of trinitrotriphenylmethane than were obtained by him.

Trimethyltrixenylchloromethane.—The procedure of Schlenk and Weickel[12] for preparing trixenylchloromethane was followed. After excess acetyl chloride was distilled from the reaction mixture the residue was shaken with anhydrous ether, filtered, and washed with more ether, m. p. 204–205°. *Anal.* Calcd. for $C_{40}H_{33}Cl$: Cl, 6.92. Found: Cl, 6.97, 7.00. Just as solid trixenylchloromethane turns pink on standing in a closed container, so does trimethyltrixenylchloromethane turn blue. Likewise if the anhydrous ether solution of either compound is heated in a test-tube under a steam jet, a red or blue band, as the case may be, appears on the side of the tube above the liquid. When the tube is held under the cold water tap, the color disappears. This phenomenon can be repeated as long as any anhydrous ether is left in the tube.

Summary

Trimethyltrixenylcarbinol has been prepared by the sodium condensation method for synthesis of tertiary carbinols.

Reduction to the methane, conversion of the latter to the perbromide, and hydrolysis to the original carbinol has been accomplished on both trixenyl- and trimethyltrixenylcarbinol.

Nitration of trixenylmethane produced a nonanitro compound.

The colors of compounds in the trixenylmethyl class are in general more intense than those of corresponding ones in the triphenylmethyl series.

CAMBRIDGE, MASS. RECEIVED JUNE 16, 1937

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[11] Montagne, *Rec. trav. chim.*, **24**, 125 (1905).

[12] Schlenk and Weickel, *Ann.*, **368**, 295 (1909).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation and Pyrolysis of Some Triphenylmethyl Ethers of Complex Function

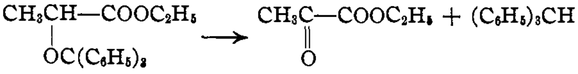
BY CHARLES D. HURD AND EDWARD M. FILACHIONE

The pyrolysis of several triphenylmethyl alkyl ethers into triphenylmethane and an aldehyde or ketone was established by Norris and Young[1]

$$Ph_3C—O—CH_2R \longrightarrow Ph_3CH + RCHO$$

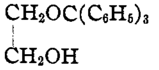
This interesting work made it seem reasonable to infer that more complex aldehydes or ketones might be synthesized similarly, such, for example, as ethyl pyruvate from ethyl lactate, glycolaldehyde from ethanediol (ethylene glycol), ethoxyacetaldehyde from ethanediol ethyl ether ("cellosolve"), or glyceraldehyde from glycerol.

To test this idea, the triphenylmethyl ethers of the above compounds were synthesized. One of the ethers, namely, ethyl α-triphenylmethoxypropionate (I), underwent pyrolysis in the anticipated manner. At 300°, ethyl pyruvate was formed in about 70% yield:



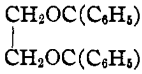
$$\underset{\text{I}}{CH_3CH(OC(C_6H_5)_3)—COOC_2H_5} \longrightarrow CH_3C(=O)—COOC_2H_5 + (C_6H_5)_3CH$$

This type of reaction, however, was not observed with the other ethers. Instead, ethanediol triphenylmethyl ether (II) underwent disproportionation at 140° into ethanediol and ethanediol triphenylmethyl diether (III).



$$CH_2OC(C_6H_5)_3—CH_2OH$$

II



$$CH_2OC(C_6H_5)_3—CH_2OC(C_6H_5)_3$$

III

This seemed to be an equilibrium reaction because the yield of III was made practically quantitative if the ethanediol was removed as formed by performing the reaction at 140° under diminished pressure. At atmospheric pressure the yield of III was only 33%. The reverse reaction was achieved by refluxing the diether (III) with ethanediol.

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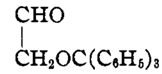
[1] Norris and Young, THIS JOURNAL, **46**, 2580 (1924); **52**, 753 (1930).

Pyrolysis of III occurred at 340–350°. Triphenylmethane was formed in about 65% yield but the corresponding aldehydes, glyoxal or triphenylmethoxyacetaldehyde (IV), were not isolated. The non-isolation of these aldehydes may be traceable, however, to their thermal instability since both carbon monoxide and formaldehyde (from glyoxal) were produced.

Benzophenone was also identified as a reaction product of III. It must have been formed by a breakdown of the triphenylmethoxy group.

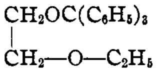
The striking contrast in the mode of decomposition of II from that of I or III makes it important to emphasize the fact that the decomposition temperatures of I and III were about 150–200° higher than the temperature required for the disproportionation of II. Temperatures of 300–350° are evidently required to break the C–O bond in such triphenylmethyl ethers.

To ascertain whether or not the absence of IV was due to its non-volatility and instability it was decided to study ethanediol ethyl triphenylmethyl diether (V). It seemed reasonable to expect that the C_2H_5–O group would be sufficiently more stable than the $(C_6H_5)_3C$–O group to resist rupture. If ethoxyacetaldehyde, $C_2H_5OCH_2CHO$, were isolable it would suggest that similar aldehyde derivatives might be anticipated from the higher polyhydric alcohols.



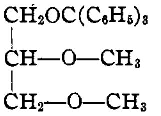
$$\begin{array}{l} CHO \\ | \\ CH_2OC(C_6H_5)_3 \end{array}$$

IV



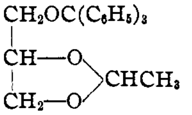
$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CH_2—O—C_2H_5 \end{array}$$

V



$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CH—O—CH_3 \\ | \\ CH_2—O—CH_3 \end{array}$$

VI



VII

Specifically, such compounds as these were in mind: the dimethyl ether of glyceraldehyde from (VI), the ethylidene derivative of glyceraldehyde from γ-triphenylmethoxypropylene acetal (VII) which was synthesized in this work, or the aldehyde form of pentamethylglucose from sorbitol pentamethyl triphenylmethyl hexaether, $CH_3OCH_2(CHOCH_3)_4CH_2OC(C_6H_5)_3$. However, ethoxyacetaldehyde could not be obtained from V; therefore, it seemed useless to attempt to extend the reaction in this direction.

The diether V behaved like III in its pyrolysis. It required a temperature of 330° and it gave rise to both triphenylmethane and benzophenone as reaction products.

Experimental Part

Preparation of the Ethers

Ethanediol Triphenylmethyl Ether (II).—The triphenylmethyl chloride (13.9 g., 0.05 mole) was dissolved in dry pyridine (35 cc.), and anhydrous ethanediol (ethylene glycol) (6.3 g., 0.1 mole) was added. The solution was left for three days at room temperature, then poured into an excess of dilute hydrochloric acid solution and extracted with ether. The extract was washed with water and sodium bicarbonate solution and then was dried over magnesium sulfate. The solid which remained after removal of the ether was recrystallized from petroleum ether. The yield was 13.4 g. (88%); m. p. 102–103°.

When Helferich's directions[2] were followed a smaller yield (38%) of less pure product (m. p. 95–98°; Helferich reported 98–100°) was obtained. The directions indicated above include two essential modifications. One was the use of a lower reaction temperature (room temperature, instead of 100°) to inhibit pyrolysis of II into III. The other was the use of petroleum ether instead of alcohol as a solvent for recrystallization. The small amount of III which was formed was insoluble in hot petroleum ether and, therefore, easily separated.

Ethanediol triphenylmethyl diether (III) was prepared according to the directions of Helferich, Spiedel and Toeldte.[2]

Ethyl α-Triphenylmethoxypropionate.—An unsuccessful attempt was made to prepare the ether by refluxing an acetone solution of triphenylmethyl chloride and ethyl lactate in the presence of potassium carbonate. Instead there was obtained an 80% conversion of the chloride to triphenylcarbinol.

The following procedure gave rise to a 60% yield of the ether. To a solution of 9.5 g. of triphenylmethyl chloride in 25 cc. of pyridine was added 4.8 g. (a 20% excess) of freshly distilled ethyl lactate (b. p. 148–150°) and the solution was heated on the steam-bath for five hours. The solution was then poured into 150 cc. of water and the oil extracted with ether. The ether solution was washed with dilute hydrochloric acid till free of pyridine, then washed with water, followed by a sodium bicarbonate wash. The ether solution was dried with calcium chloride and the ether evaporated. The oily residue was recrystallized from alcohol. It was noticed that this substance shows a remarkable tendency to supersaturate, especially when impure. However, by allowing the hot alcohol solution to cool slowly to room temperature and letting the solution remain undisturbed, beautiful crystals were deposited. The yield was 7.3 g.; m. p. 74–76°. After several recrystallizations from alcohol, the melting point was raised to 79–80°.

Anal. (by M. A. Pollack). Calcd. for $C_{24}H_{24}O_3$: C, 79.96; H, 6.72. Found: C, 80.10; H, 6.79.

Ethanediol Ethyl Triphenylmethyl Diether (V). (The Triphenylmethyl Ether of "Cellosolve").—In a 200-cc. round-bottomed flask was placed 39 g. of triphenylchloromethane, 60 cc. of anhydrous pyridine and 25 g. (a 100% excess) of anhydrous ethanediol ethyl ether ("cellosolve"). The solution was heated on the steam-bath for five hours. On pouring the cooled solution into cold water a solid

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[2] Helferich, Spiedel and Toeldte, *Ber.*, **56**, 766 (1923).

separated which was collected on a filter, dissolved in ether, and the ether solution washed with dilute hydrochloric acid, water, and sodium bicarbonate solution. After drying and removing the solvent, the solid was crystallized from alcohol. The yield was 43 g., or 92%. The melting point was 77–78°.

In other experiments in which equal molecular quantities of the chloride and cellosolve were used, the yields varied from 61 to 83%.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.09; H, 7.28. Found: C, 83.04; H, 7.19.

γ-Triphenylmethoxypropylene Acetal (or **2-Methyl-4-triphenylmethoxymethyldioxolane**) (**VII**).—γ-Hydroxypropylene acetal,[3] b. p. 184–185°, n^{23}D, 1.4407, was prepared by the directions of Hill and Hibbert.[4] Twenty grams (a 20% excess) of the acetal was added to a solution of 38 g. of triphenylchloromethane in 85 cc. of dry pyridine. The solution was heated on the steam-bath for five hours, and allowed to stand overnight, then heated for another hour. After cooling, the solution was poured into 400 cc. of cold water. The oil that came down was extracted with ether, but about 400 cc. of ether was necessary to complete the extraction. The ether solution was washed with dilute hydrochloric acid, water, sodium bicarbonate, dried over potassium carbonate, and the ether removed by distillation. To the residue was added the minimum amount of boiling ethyl ether that would bring all of it into solution. On cooling in the refrigerator, crystals were deposited which were collected on a filter. The filtrate was concentrated. On cooling, a second crop of crystals was obtained. When a third concentration of the filtrate was tried, an oil separated along with some of the crystalline compound. The yield of the pure triphenylmethyl ether, m. p. 105–106°, was 29.2 g., or 59% of the theoretical value.

Anal. Calcd. for $C_{24}H_{24}O_3$: C, 79.96; H, 6.72. Found: C, 79.67; H, 6.47.

Pyrolysis of the Ethers

Ethanediol Triphenylmethyl Ether: (1) at Atmospheric Pressure.—Eight grams of II, m. p. 103°, was heated at 140–145° for forty-five minutes. Droplets which formed on the side of the flask were removed and identified as ethanediol by reaction with benzoyl chloride and sodium hydroxide. The ethylene benzoate melted at 69–70°.

When the contents of the flask were extracted with two 20-cc. portions of boiling acetone there remained undissolved 2.4 g. (33%) of the diether (III), m. p. 180–183°. From the acetone solution there was obtained 4.3 g. of the starting material, II, by evaporation and crystallization from petroleum ether.

(2) Under Diminished Pressure.—Eight grams of II was placed in a small distilling flask set up for vacuum distillation. The flask was heated at 140–145° and 6 mm. In a short time there was frothing in the flask and ethanediol, later characterized as ethylene benzoate, m. p. 72°, distilled.

The contents of the flask became solid after twenty-five minutes of heating but were kept at 140° for forty-five minutes longer. The solid in the flask was the diether (III) in practically pure condition since it melted at 184–185°. The yield was about quantitative.

Pyrolysis of Ethanediol Triphenylmethyl Diether, III.—Preliminary experiments revealed that when this ether was heated for an hour at 280° (bath temperature) seven-tenths of it was recoverable. Half of it was recoverable after heating at 310–320°, but extensive decomposition occurred at 340–350°.

A 70-cc. Claisen flask was provided with an inlet for the delivery of a stream of carbon dioxide. The outlet of the flask was attached to a water condenser and receiver. In turn, the receiver was connected to a gas-washing bottle partly filled with water (to scrub out any formaldehyde) and then to a gas-collecting bottle filled with 20% potassium hydroxide solution.

Twenty grams (0.037 mole) of III was placed in the flask and the air in the system was swept out by a current of carbon dioxide. Then the reaction flask was heated for three hours by a salt bath at 330–350°. A slow stream of carbon dioxide was maintained throughout.

The solution in the bubbler was shown to contain formaldehyde by making the methone derivative, which melted at 182–185°. About 440 cc. (S.T.P.) of carbon monoxide was collected in the gas receiver. There was no ethylene.

The residue in the flask was distilled at 8 mm. A fraction was collected at 188–195°, leaving 3.4 g. of residue. The distillate, on recrystallization from methanol, yielded 11 g. (61% yield) of triphenylmethane, m. p. 93°. Evaporation of the methanol solution revealed 1.6 g. of an oil which was identified as benzophenone. Its 2,4-dinitrophenylhydrazone melted at 239–240° (mixed m. p. also 239–240°).

Preparation of II by Reaction of Ethanediol with III.—In a 100-cc. flask, 8 g. of the diether (III) was stirred mechanically with 400 cc. of anhydrous ethanediol and heated to gentle refluxing. Two layers were present at the start but after an hour the solution became homogeneous. The viscid oil obtained on cooling was poured into water and extracted with ether. About 0.8 g. of III remained undissolved. The ether extract was dried and evaporated. The residue was crystallized from petroleum ether; yield 7.2 g. Recrystallization gave rise to 6.2 g. (77% yield, based on unrecovered III) of pure ethanediol triphenylmethyl ether, m. p. and mixed m. p. 103°. From the petroleum ether filtrates there was isolated a gram of triphenylmethane (m. p. 85–87°, mixture m. p. 89–91°).

Very little reaction occurred between ethanediol and III (vigorously stirred) in one hundred minutes at 140–150°. Therefore, the higher refluxing temperature is essential.

Ethyl α-Triphenylmethoxypropionate (I).—For this pyrolysis, 30.5 g. of the substance was placed in a 100-cc. Claisen flask fitted with a small water condenser. A slow stream of nitrogen was bubbled through the liquid while the flask was heated by a bath at 300°. In three hours, 7.3 g. of distillate (ethyl pyruvate) had collected. The residue in the flask, on vacuum distillation, yielded 17 g. of crude triphenylmethane, b. p. 200–212° at 20 mm. There was 4 g. of a tarry residue. Recrystallization from alcohol yielded 15.2 g. of pure triphenylmethane (74% yield).

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(3) The name ethylideneglycerol is avoided because such a name implies the presence of three hydroxyls.

(4) Hill and Hibbert, THIS JOURNAL, **50**, 2242 (1928).

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

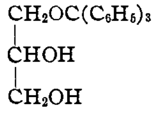
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Triphenylmethyl Ethers of Glycerol and Glycerol Derivatives

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

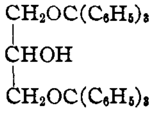
In the work with ethylene glycol[1] it was established that entirely different reactions were encountered in the pyrolyses of the triphenylmethyl monoether and diether. The monoether changed at a comparatively low temperature into the diether and ethylene glycol. The diether required a temperature of 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).