The amide (1 equivalent) was mixed, in a flask equipped with a reflux condenser, with anhydrous chloral (1.2–2.0 equivalents) and the mixture was heated under gentle reflux until a homogeneous mixture was obtained. Heating was continued until solid began to separate, the length of this heating period varying for the different amides. After cooling to room temperature, the solid mass was recrystallized from an appropriate solvent until the melting point remained constant (see Table I for the properties of the chloralamides).

Benzoylation of 1-(Furamido)-2,2,2-trichloroethanols (General Procedure B).—Solid 1-furamido-2,2,2-trichloroethanol (1 equivalent) was added to a solution of benzoyl chloride (2 equivalents) in excess pyridine. After 5–10 minutes, the mixture was poured into crushed ice and the aqueous mixture set aside for 24 hours. The crude solid was recrystallized from an appropriate solvent until the melting point was constant (see Table II).

Chlorination of 1-(Furamido)-2,2,2-trichloroethanols.—According to a modification of the method of Hirwe and Deshpandi,[17] the furamidotrichloroethanol was mixed, in a flask equipped with a reflux condenser, with an equimolar quantity of phosphorus pentachloride. The mixture was warmed very gently to initiate reaction and the source of heat was removed as soon as reaction began. When the vigorous initial reaction had subsided, the mixture was warmed very gently until a homogeneous liquid was obtained. The clear liquid was poured into three times its weight of crushed ice and the aqueous mixture was treated according to one of the following procedures.

Alkoxylation of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure C).—The supernatant liquid was decanted from the insoluble oily tetrachloroethane and the oil was washed thoroughly with cold water. The oil was immediately dissolved in an excess of the appropriate alcohol and the solution was heated under reflux for 5 hours. The hot mixture was poured into excess ice-water, the oil isolated and treated further as was appropriate (see Table II).

Ammoniation of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure D).—The aqueous mixture was extracted with four 50-ml. volumes of ether. The ether extracts were combined and added, without preliminary drying, to excess concentrated ammonium hydroxide or 33% aqueous methylamine. The mixture was shaken vigorously for 5 minutes. The layers were separated and the ethereal layer was concentrated by removal of the ether under reduced pressure. The residue was recrystallized from an appropriate solvent until the melting point was constant (see Table III).

Amination of 1-(Furamido)-1,2,2,2-tetrachloroethanes (General Procedure F).—The aqueous mixture was extracted with four 50-ml. volumes of ether, the ether extracts were combined and dried over magnesium sulfate. The magnesium sulfate was removed by filtration and the dry ether solution was chilled in an ice-bath. To the cold solution was added very slowly an excess (2.1 molecular equivalents) of the appropriate amine. The separated solid was removed by filtration and the filtrate was concentrated by distillation of the ether under reduced pressure. The residual solid was recrystallized from an appropriate solvent until the melting point was constant.

Ammoniation of 1-(2-Furamido)-1,2,2,2-tetrachloroethane; 1-(2-Furamido)-2,2,2-trichloroethylamine.—The aqueous mixture from chlorination of 20 g. (0.08 mole) of 1-(2-furamido)-2,2,2-trichloroethanol was extracted with four 100-ml. volumes of dry ether and the combined ether extracts were dried over magnesium sulfate.

In a 1-liter, 3-necked flask, fitted with a gas inlet tube and mechanical stirrer, and surrounded by an ice-bath, was placed 300 ml. of dry ether. Dry ammonia gas was passed into the ether for 15 minutes. While ammonia continued to pass through the well-stirred mixture, the previously prepared ether solution of the tetrachloro compound was added slowly, 1.5 hours being required to complete the addition.

The reaction mixture was subjected to filtration and the isolated solids were triturated with 100 ml. of dry ether. The combined filtrates were concentrated by distillation of the ether under reduced pressure. The residual solid, which weighed 12.5 g. (62%), melted at 77–80°. Four recrystallizations from a mixture of ethyl acetate and petroleum ether gave pale tan crystals which melted at 102.5–104°.

Anal. Calcd. for $C_7H_7O_2N_2Cl_3$: C, 32.64; H, 2.84; N, 10.88. Found: C, 32.79; H, 2.70; N, 10.63.

Treatment of an acidified ethanolic solution of this trichloroethylamine with an aqueous solution of sodium nitrite resulted in evolution of a gas and separation of the original trichloroethanol (identified by mixed melting point).

Phenylamination of 1-(5-Nitro-2-furamido)-1,2,2,2-tetrachloroethane; 1-(5-Nitro-2-furamido)-1-phenylamino-2,2,2-trichloroethane.—Eight grams (0.03 mole) of 1-(5-nitro-2-furamido)-2,2,2-trichloroethanol was chlorinated as described above. The supernatant liquid was decanted from the solid tetrachloro compound. The solid was dissolved in 20 ml. of acetone and to the acetone solution was added carefully 15 g. (0.16 mole) of aniline. The hot mixture was poured into 150 ml. of cold water and the aqueous mixture was set aside for 24 hours. The solid was isolated to give 10.7 g. (100%) of orange solid which melted at 170–178° (dec.).

Recrystallization from glacial acetic acid gave bright yellow-orange crystals which melted at 195–196° (bath preheated to 185°).

Anal. Calcd. for $C_{13}H_{11}O_4N_3Cl_3$: C, 41.36; H, 2.67; N, 11.10. Found: C, 41.54; H, 2.86; N, 11.21.

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[17] N. W. Hirwe and J. S. Deshpandi, *Proc. Ind. Acad. Sci.*, **13A**, 277 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Ethylene Glycol Ethers of Pentaerythritol

BY STANLEY WAWZONEK AND COSTAS ISSIDORIDES[1]

RECEIVED NOVEMBER 17, 1952

The Tollens condensation of acetaldehyde and formaldehyde in 50% ethylene glycol yields pentaerythritol and the monoethylene glycol and the bis-(ethylene glycol) ethers of pentaerythritol. The structures of the last two compounds were demonstrated by synthesis from 3,3-bis-(hydroxymethyl)-oxacyclobutane and 2,6-dioxaspiro[3,3]heptane, respectively.

In a previous work[2] on the mechanism of the formation of dipentaerythritol in the preparation of pentaerythritol by the Tollens condensation, it was found that the methyl and dimethyl ethers of pentaerythritol could be made by running the condensation in 50% methanol.

The work has now been extended to a study of the condensation in 50% ethylene glycol to determine whether an ether I of the dipentaerythrityl type could be formed in this bifunctional solvent.

$$(HOCH_2)_3CCH_2OCH_2CH_2OCH_2C(CH_2OH)_3$$

I

When the Tollens condensation was carried out in the usual manner[2] and the products separated as the propionates, the main product after saponification was pentaerythritol. Other compounds

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[1] Abstracted in part from the Ph.D. thesis of Costas Issidorides, February, 1953.

[2] S. Wawzonek and D. A. Rees, THIS JOURNAL, **70**, 2433 (1948).

isolated and identified were the monoethylene glycol ether II and the bis-(ethylene glycol) ether III of pentaerythritol.

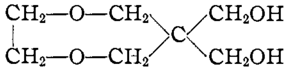
$$HOCH_2CH_2OCH_2C(CH_2OH)_3$$

II

$$(HOCH_2CH_2OCH_2)_2C(CH_2OH)_2$$

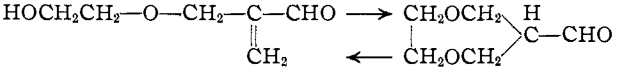
III

A fourth propionate fraction which was too small to purify or identify gave a saponification equivalent which suggested the presence of the cyclic ether IV.



IV

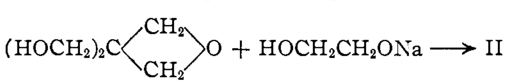
The formation of this compound could be consistent with the mechanism proposed[2] and would arise from the intermediate V which is the basis for the bis-(ethylene glycol) ether III.



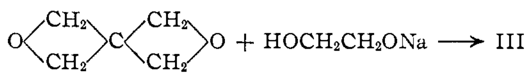
V

No evidence for the presence of the dipentaerythrityl type compound I could be obtained due to the extensive decomposition which took place in the distillation of the propionates above 215° at pressures below one millimeter. The possibility that the amount of this compound I formed is actually very small, is suggested by a comparison of the yields of the various compounds formed in ethylene glycol with those of the comparable compounds in methyl alcohol; the percentages differ very little from each other.

Since no mention is made of ethers of ethylene glycol and pentaerythritol in the literature with the exception of patents[3] which describe products from the reaction of ethylene oxide and pentaerythritol as viscous oils, the structures of the two ethers were demonstrated by independent syntheses. The monoethylene glycol ether II was prepared from 3,3-bis-(hydroxymethyl)-oxacyclobutane (VI) while the bis-(ethylene glycol) ether III was made from 2,6-dioxaspiro[3,3]heptane (VII).



VI



VII

These reactions are the first examples reported of the opening of trimethylene oxide rings by alkoxides and give better yields of the ethylene glycol ethers of pentaerythritol than those in the Tollens condensation.

The monoethylene glycol ether II offered no difficulty in the comparison of products from the two reactions since it is a solid. The bis-(ethylene glycol) ether, however, is an oil and was characterized as the tetratrityl ether.

Experimental[4]

Preparation of Pentaerythritol in 50% Ethylene Glycol.—The reaction was carried out under similar conditions to those reported previously[2] substituting ethylene glycol (750 ml.) for the methanol. The final solution was heated under reduced pressure (20 mm.) to remove the water and the main portion of the ethylene glycol.

Separation of the Products.—Propionylation of the products from the Tollens condensation was carried out as previously reported in the work with methanol[2] and gave a mixture of propionates (304 g.) which was separated by distillation through a Vigreux column at reduced pressure.

a. **Ethylene Glycol Dipropionate.**—This compound made up the greater part of the first fraction (15 g.) boiling at 75–78° (5 mm.). Its structure was demonstrated by its boiling point, 208–210° (748 mm.), its saponification equivalent and by transesterification to ethylene glycol, b.p. 190–197° (748 mm.).

b. **6,6-Dimethylol-1,4-dioxacycloheptane (IV).**—The second fraction (12 g.) boiling at 120–155° (3 mm.) upon further fractionation gave a product boiling over a temperature range of 130–155° (3 mm.). Six subfractions were obtained with the following saponification equivalents: 99, 103, 105, 124, 130, 125.

Anal. Calcd. for (IV) $C_{13}H_{22}O_6$: C, 56.92; H, 8.09; sapn. equiv., 137. Found: C, 52.91; H, 7.84; sapn. equiv., 130.

c. **Pentaerythrityl Tetrapropionate.**—The third fraction (177 g.) consisted mainly of pentaerythrityl tetrapropionate. Identification was accomplished by its boiling point, 173–175° (2 mm.), and transesterification with methanol to pentaerythritol, m.p. 257.5–259°.

d. **Pentaerythritol Tetrapropionate β-Hydroxyethyl Ether.**—This compound occurred as the fourth fraction (57 g.), b.p. 195–202° (3 mm.). The analytical sample had the following physical constants: b.p. 185–187° (2 mm.), $n^{24.5}D$ 1.4468, d^{24}_4 1.107.

Anal. Calcd. for $C_{19}H_{32}O_9$: C, 56.42; H, 7.97; sapn. equiv., 101. Found: C, 55.99; H, 8.36; sapn. equiv., 103.

Transesterification of the tetrapropionate (10.0 g.) by refluxing in methanol (150 ml.) with sodium methoxide (0.06 g. of sodium) for three hours gave a solution which was neutralized after part of the methanol (120 ml.) had been removed. Removal of the remaining liquid under reduced pressure gave pentaerythrityl β-hydroxyethyl ether as a pale yellow viscous oil (1.9 g.) boiling at 212° (1 mm.) which solidified upon cooling. Two recrystallizations from ethyl acetate gave a white solid melting at 76.5–77.5°.

Anal. Calcd. for $C_7H_{16}O_5$: C, 46.65; H, 8.95. Found: C, 46.58; H, 9.08.

e. **Pentaerythritol Tetrapropionate Di-β-hydroxyethyl Ether.**—This ester occurred as the fourth fraction (26 g.), b.p. 185–190° (1 mm.). The analytical sample had the following constants: b.p. 185–188° (1 mm.), $n^{25}D$ 1.4509.

Anal. Calcd. for $C_{21}H_{36}O_{10}$: C, 56.23; H, 8.09; sapn. equiv., 112. Found: C, 56.58; H, 7.96; sapn. equiv., 114.

Transesterification of the tetrapropionate of the diether (2.8 g.) in a manner similar to that used for the propionate of the monoethylene glycol ether, gave pentaerythrityl di-β-hydroxyethyl ether as an oil that could not be crystallized or distilled under reduced pressure.

Tritylation of the product (dried at 120° under reduced pressure for six hours) was accomplished by treating in dry pyridine (10 ml.) with trityl chloride (6.9 g.) for 1.3 hours at 100°. Addition of water (10 ml.) to a cooled mixture gave a gum which was removed and triturated with cold water. The solid obtained was washed with water and ethanol and then extracted with a mixture of hot absolute ethanol (24 ml.) and acetone (6 ml.), absolute ethanol (30 ml.) and 95% ethanol (30 ml.). The resulting solid when recrystallized three times from acetone melted at 146.5–148°, yield 2.4 g.

Anal. Calcd. for $C_{85}H_{76}O_6$: C, 85.53; H, 6.42. Found: C, 84.97; H, 6.47.

Pentaerythritol Tetraacetate β-Hydroxyethyl Ether.—To a refluxing solution of sodium (3.2 g.) in ethylene glycol (200 ml.) 3,3-bis-(hydroxymethyl)-oxacyclobutane[5] (17 g.)

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[3] I. G. Farbenind. A. G., French Patent 650,973 (1938); P. I. Bowman, R. H. Barth and H. Burrell, U. S. Patent 2,401,743 (1946); H. Sokol, U. S. Patent, 2,527,970 (1950).

[4] Melting points and boiling points are not corrected.

[5] F. Govaert and M. Beyaert, *Proc. Acad. Sci. Amsterdam*, **42**, 790 (1939).

in ethylene glycol (160 ml.) was added in the course of 10 minutes and the resulting solution refluxed for 24 hours. After cooling, the solution was neutralized with diluted hydrochloric acid and the excess ethylene glycol removed under reduced pressure.

Acetylation of the oil was accomplished by stirring at 0° with acetic anhydride (200 ml.) and concentrated sulfuric acid (4 ml.) for two hours, then overnight at room temperature and finally at 100° for 2.5 hours. Removal of the excess acetic anhydride under reduced pressure was followed by the addition of ice and neutralization with sodium bicarbonate. Extraction with ether gave an oil which was fractionated through a 15-cm. vacuum-jacketed Vigreux column; b.p. 184–187° (2 mm.), yield 27 g. (76%), $n^{28.5}_{D}$ 1.4454, $d^{28.5}_{4}$ 1.165.

Anal. Calcd. for $C_{15}H_{24}O_9$: C, 51.72; H, 6.94; sapn. equiv., 87. Found: C, 51.51; H, 6.89; sapn. equiv., 87.

Pentaerythritol β-Hydroxyethyl Ether.—Pentaerythritol tetraacetate β-hydroxyethyl ether (28 g.) was saponified by heating with sodium ethoxide (0.2 g. of sodium) in absolute ethanol (500 ml.) for one hour. Partial removal of the solvent (540 ml.) was followed by neutralization with dilute hydrochloric acid and evaporation to dryness under reduced pressure. The oil upon distillation and then recrystallization twice from acetone melted at 77.5–78.5°, yield 6.5 g. (45%). A mixture with a sample prepared from the Tollens condensation melted at the same point.

Pentaerythrityl Dichloride.—To a well-stirred solution of monobenzalpentaerythritol[6] (156.8 g.) in dry pyridine (110.7 g.) at 0° was added slowly pure thionyl chloride (176 g.) in chloroform (175 ml.). The resulting mixture was stirred for 12 hours at room temperature and then refluxed for 4 hours. Removal of the chloroform under reduced pressure followed by the addition of water and extraction with ether gave a solid melting at 74–76°. The solid was not purified but refluxed with 0.5 *N* hydrochloric acid (1200 ml.) and dioxane (600 ml.) for four hours. Removal of the benzaldehyde by steam distillation was followed by concentration of the solution to 200 ml. and extraction with seven 150-ml. portions of ether. The solid obtained in this manner was recrystallized from a mixture of chloroform and carbon tetrachloride; m.p. 79–80°, yield 93 g. (77%). Two further recrystallizations from carbon tetrachloride gave a white solid melting at 80.5–81.5°.

Anal. Calcd. for $C_5H_{10}O_2Cl_2$: C, 34.70; H, 5.82. Found: C, 35.05; H, 5.94.

The following melting points have been recorded in the literature for pentaerythrityl dichloride: 65°,[7] 70–80°,[8] 83°[9] and 95°.[10]

Monobenzalpentaerythrityl Dichloride.—A mixture of pentaerythrityl dichloride (8.6 g.), benzaldehyde (5.3 g.) and concentrated hydrochloric acid (1 ml.) in water (100 ml.) was shaken mechanically at room temperature for 60 hours. The solid formed when recrystallized from an ethanol–water mixture melted at 77.5–78.5°, yield 7.7 g. (75%).

Anal. Calcd. for $C_{12}H_{14}O_2Cl_2$: C, 55.19; H, 5.40. Found: C, 55.37; H, 5.39.

This solid when mixed with the sample isolated in the reaction of monobenzalpentaerythritol and thionyl chloride melted at the same point.

2,6-Dioxaspiro[3,3]heptane (VII).—This compound was prepared according to the method of Backer and Keuning[11] using pentaerythrityl dichloride in place of the pentaerythrityl bromide. Pentaerythrityl dichloride (40 g.) gave 2,6-dioxaspiro[3,3]heptane (4 g.) (17%) melting at 89–90° (b.p. 168–173° (750 mm.)).

Pentaerythritol Tetraacetate Di-β-hydroxyethyl Ether.—To a solution of sodium (1.84 g.) in ethylene glycol (120 ml.) at 140–150° was added in the course of 10 minutes 2,6-dioxaspiro[3,3]heptane (4 g.) in ethylene glycol (80 ml.). The resulting solution was heated at 145–155° for 11 hours, at 160° for 11 hours and finally at reflux for 1.5 hours. Neutralization with hydrochloric acid was followed by removal of the ethylene glycol under reduced pressure and acetylation with acetic anhydride (80 ml.) and sulfuric acid (1.2 ml.) in a manner similar to that used for the monoethylene glycol ether of pentaerythritol. Distillation of the residual oil gave di-β-hydroxyethylpentaerythrityl ether tetraacetate (8.7 g.) (55%) boiling at 195–197° (2 mm.), n^{25}_{D} 1.4487.

Anal. Calcd. for $C_{17}H_{28}O_{10}$: C, 52.03; H, 7.19; sapn. equiv., 98. Found: C, 51.56; H, 7.20; sapn. equiv., 102.

A sample of the tetraacetate (4.0 g.) after transesterification and tritylation in a manner similar to that used with the sample from the tetrapropionate gave the tetratrityl ether (4.1 g.) melting at 148–150°. A mixture with the trityl ether prepared from the tetrapropionate melted at the same point.

Acknowledgment.—The authors are indebted to the Research Corporation for financial support.

IOWA CITY, IOWA

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[6] E. Bograchov, THIS JOURNAL, **72**, 2268 (1950).

[7] J. Bougault, *Compt. rend.*, **123**, 187 (1896).

[8] H. Rapoport, THIS JOURNAL, **68**, 341 (1946).

[9] A. Mooradian and J. B. Cloke, *ibid.*, **67**, 942 (1945).

[10] H. Fecht, *Ber.*, **40**, 3883 (1907).

[11] H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, **53**, 812 (1934).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Aryl Amines. XV. Stereoisomeric Diglutarimidomesitylenes

BY ROGER ADAMS AND DALE C. BLOMSTROM[1]

RECEIVED DECEMBER 29, 1952

Bis-(α,α-dimethylglutarimido)-mesitylene (IV) has been prepared and separated into two forms which are shown to be *cis–trans* isomers by infrared spectra and by nitration to give an analogous pair of stereoisomeric nitro compounds. The previously reported explanation of the absence of isomerism in homologous five-membered ring compounds is thus confirmed.

Previous papers in this series[2] have reported the separation of numerous N,N′-dialkyl-N,N′-diarylsulfonyldiaminomesitylenes into *cis* and *trans* isomers. The stereoisomerism is caused by restricted rotation about two carbon–nitrogen bonds. *cis* and *trans* forms were also isolated in analogous derivatives of diaminodurene[3] and triaminomesitylene.[4]

Adams and Campbell[5] prepared several compounds such as I and II, in which the nitrogen atoms of diaminomesitylene were incorporated into five-membered rings, but were able to find only one product in each case. However in compound III, which is closely related to II, *cis* and *trans* forms were isolated. This difference in behavior between II and III was attributed to a decrease

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[1] An abstract of a thesis submitted by Dale C. Blomstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Cincinnati Chemical Company Fellow, 1950–1951; Standard Oil Company of Indiana Fellow, 1951–1952; University of Illinois Fellow, 1952–1953.

[2] R. Adams and J. J. Tjepkema, THIS JOURNAL, **70**, 4204 (1948); R. Adams and M. Rothstein, *ibid.*, **71**, 1620 (1949).

[3] R. Adams and N. K. Nelson, *ibid.*, **72**, 132 (1950).

[4] R. Adams and B. Englund, *ibid.*, **72**, 135 (1950).

[5] R. Adams and J. B. Campbell, *ibid.*, **72**, 128 (1950).