Summary

The dielectric constants of dilute benzene solutions of hydrazine and several of its derivatives have been measured and their dipole moments calculated.

sponsible for the low electric moment of benzalazine. This possible explanation is, however, somewhat speculative since nothing is known about the effects of such systems.

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Synthetic Glycerides. IV. Esters of Aromatic and Aliphatic Acids

BY DONALD T. JACKSON AND C. G. KING

The general purpose of our investigation has been stated in previous communications.[1] The structural relationships found for fatty acid esters of glycerol have been in agreement with Fischer's[2] findings which showed that methods of preparation which were expected to yield β-monoglycerides gave α-monoglycerides, and that methods which were thought to yield α,β-diglycerides produced α,α'-diglycerides. However, Abderhalden and Eichwald[3] and Bergmann[4] apparently succeeded in preparing α,β-diglycerides of aromatic acids by an indirect and difficult method using propylamines.

Several investigators[5] have continued to use methods which give compounds of different structure than that assigned.[6]

Helferich and Sieber,[7] by the use of triphenylmethyl (trityl) ethers of glycerol, prepared the β-mono-(*p*-nitrobenzoate) and the β-monobenzoate (probably the first true β-esters of glycerol), and the α,β-dibenzoate.

Bergmann and Carter[8] prepared β-monopalmitin, the first fatty acid ester of this type, by the catalytic reduction of β-palmito-α,α'-benzylidene glycerol.

In the present investigation the β-mono-(*p*-nitrobenzoate) and the α,β-dibenzoate of glycerol were prepared by the method of Helferich and Sieber and their identity established by their ready conversion, when

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[1] Roche, Averill and King, THIS JOURNAL, **51**, 866 (1929); **52**, 365 (1930); Robinson, Roche and King, *ibid.*, **54**, 705 (1932).

[2] Fischer, *Ber.*, **53**, 1621 (1920).

[3] Abderhalden and Eichwald, *ibid.*, **49**, 2095 (1916).

[4] Bergmann, *Z. physiol. Chem.*, **137**, 27, 47 (1924).

[5] Heiduschka and Schuster, *J. prakt. Chem.*, **120**, 145 (1928); Thomson, *Trans. Roy. Soc. Canada*, **20**, 445 (1926); Whitby, *ibid.*, **13**, 255 (1919); *J. Chem. Soc.*, **129**, 1458 (1926); Delaby and Dubois, *Compt. rend.*, **187**, 767 (1928).

[6] Fairbourne, *J. Chem. Soc.*, 372 (1930).

[7] Helferich and Sieber, *Z. physiol. Chem.*, **175**, 311 (1928).

[8] Bergmann and Carter, *ibid.*, **191**, 211 (1930).

treated with acyl chlorides, into the β-mono-(*p*-nitrobenzoate)-α,α'-dibenzoate (melting point 87°) and the α-mono-(*p*-nitrobenzoate)-α',β-dibenzoate of glycerol (melting point 113°), respectively. These compounds, to our surprise, were identical with those prepared by Fischer's method (from acetone glycerol). Apparently there was no molecular rearrangement involving the migration of an acyl group in these glycerol esters of aromatic acids. However, when the same reactions were followed through for the preparation of β-monopalmitin, β-monostearin, α,β-dipalmitin and α,β-distearin, the only products which could be identified were the α-monoglycerides in the first case, and the symmetrical diglycerides in the second case. The symmetrical aromatic ester also melted lower than the unsymmetrical isomer, reversing the order for aliphatic esters. This peculiarity appears to be characteristic of the esters with one *p*-nitrobenzoate group.[9]

Experimental

The α,α'-ditrityl and α-monotrityl ethers of glycerol were prepared essentially as described by Helferich and co-workers, having melting points of 176° and 108–110°, respectively.

Preparation of α,α'-Ditrityl Ether of β-Monopalmitin.—To a solution of 5.7 g. of symmetrical ditrityl ether of glycerol dissolved in 20 cc. of dry benzene and 3 cc. of quinoline, there was added a mixture of 3 g. of palmityl chloride and 3 cc. of quinoline. This mixture was kept at 40° for eighty-four hours, by which time a heavy white precipitate of quinoline hydrochloride had settled out. The mixture was taken up in 50 cc. of benzene and 50 cc. of half-normal sulfuric acid, washed several times with half-normal sulfuric acid, then with 10% potassium bicarbonate solution and finally with water. After drying over sodium sulfate, the benzene was evaporated at room temperature. The sirup which remained was taken up in acetone and poured into anhydrous alcohol. A precipitate formed which, after several recrystallizations from acetone and alcohol, melted at 71.5°, yield 5.6 g.

The α,α'-ditrityl ethers of β-monostearin, m. p. 78.5–79.5°, β-mono-(*p*-nitrobenzoate), m. p. 187.5° and β-monolaurin, m. p. 47°, were prepared in a similar manner.

Preparation of Monotrityl Derivatives.—The α-monotrityl ethers of α,β-dipalmitin, melting point 40.5–41.5°, of α,β-distearin, melting point 46–48°, and of α,β-dibenzoate of glycerol, melting point 92–94°, were prepared according to the method which is described for the preparation of the α-monotrityl ether of α,β-dipalmitin. A mixture of 11.2 g. of palmityl chloride and 5 cc. of quinoline was added to a solution of 6.7 g. of glycerol monotrityl ether dissolved in 20 cc. of benzene and 5 cc. of quinoline. The reaction mixture, after standing at 35–40° for twenty-four hours, was taken up in benzene, washed with cold half-normal sulfuric acid, then with 10% potassium bicarbonate solution and dried over sodium sulfate. The product was crystallized by evaporation of the benzene and recrystallized from acetone–alcohol mixture; melting point 40.5–41.5°; yield 40%.

Removal of Trityl Groups.—The following procedure for the removal of the trityl groups from α,α'-ditrityl ether of β-monopalmitin was used for all compounds of this type. A solution of 5 g. of the ditrityl ether of β-monopalmitin was shaken for one hour at 0° with 15 cc. of a chloroform solution saturated at 0° with hydrogen bromide. Any triphenylmethyl bromide which separated was filtered off. The filtrate was washed with

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[9] *Ber.*, **53**, 1596 (1920); *ibid.*, **54**, 936 (1921).

potassium bicarbonate solution and with water, dried over sodium sulfate, and the solvent evaporated. The residue was taken up in acetone, petroleum ether was added and the solution allowed to stand. Crystals of triphenylcarbinol (from the hydrolysis of triphenylmethyl bromide) soon appeared and were filtered off. The α-monopalmitin crystallized out after evaporating part of the solvent and cooling.

Molecular weights were determined for all of the new compounds and most of the intermediates used in their preparation, using the method of Menzies and Wright,[10] with ethyl acetate as the solvent.

Summary

The β-mono-(*p*-nitrobenzoate) and the α,β-dibenzoate of glycerol have been prepared from glycerol trityl ethers and found to correspond to the compounds previously prepared by Helferich and Sieber. These compounds, when thus prepared, apparently do not undergo a rearrangement involving the migration of the aromatic acyl group. The same procedures when used for the preparation of β-monopalmitin, β-monostearin, α,β-dipalmitin and α,β-distearin resulted in the migration of the aliphatic acyl groups and the production of the isomeric α-monoglycerides and α,α′-diglycerides.

The synthesis and identification of the following compounds has been described: the α,α′-ditrityl ether of β-monostearin, the α,α′-ditrityl ether of β-monolaurin, the α-monotrityl ether of α,β-dipalmitin, the α-monotrityl ether of α,β-distearin, and the α-monotrityl ether of acetoneglycerol.

[10] Menzies and Wright, THIS JOURNAL, **43**, 2314 (1921).

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The Number of Structurally Isomeric Hydrocarbons of the Ethylene Series[1]

BY HENRY R. HENZE AND CHARLES M. BLAIR

The method for calculating the number of structural isomers by establishing a unique relationship between the number of structurally isomeric hydrocarbons of the methane series and of the acetylene series and the alkyl groups of which these may be considered to be composed may also be utilized successfully in calculating the number of structurally isomeric hydrocarbons of the ethylene series.

The homologs of ethylene are divided into four groups: A, consisting of those hydrocarbons which may be formed, theoretically, by replacing one hydrogen atom of ethylene by an alkyl radical; B, in which two hydrogen atoms are replaced by alkyl groups; C, in which three hydrogen atoms are replaced by alkyls; and D, in which all four hydrogen atoms are replaced.

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[1] This paper was presented before the Central Texas Section of the American Chemical Society at its annual meeting in Waco, Texas, on April 23, 1932. Previous contributions in this series are Henze and Blair, THIS JOURNAL, **53**, 3042–3046, 3077–3085 (1931); **54**, 1098–1106, 1538–1545 (1932); Coffman, Blair with Henze, *ibid.*, **55**, 252–253 (1933).