product prepared as above melted at 202–202.7° after two recrystallizations from water.

Anal. Calcd. for $C_6H_{11}N_3O_4S$; N, 19.00; S, 14.50. Found: N, 19.10; S, 14.62.

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK

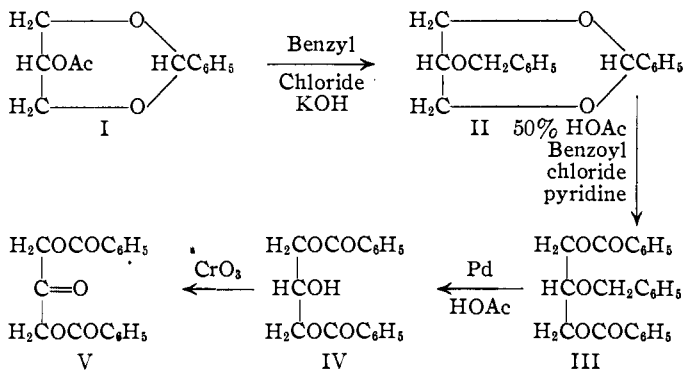
Some New Glycerol Derivatives

BY HOWARD L. WHITE[1]

RECEIVED FEBRUARY 18, 1952

As part of a projected synthesis of the interesting sugar streptose, which envisioned as one of the critical steps the oxidation of 2,4-dibenzoyl-5-desoxy-L-arabinose dimethyl acetal to the 3-ketone, it became desirable to study as a model the oxidation of 1,3-dibenzoylglycerol to the corresponding dihydroxyacetone derivative. The unduly cumbersome procedure employed in the synthesis of the required 1,3-dibenzoylglycerol was chosen to parallel in some of the essential steps the projected preparation of the above desoxyarabinose derivative from monoacetone-5-desoxy-L-arabinose.[2]

The reaction scheme employed, which is shown in formulas I–IV, follows essentially the procedure of Sowden and Fischer[3] for the preparation of 1,2-diacylglycerols from 1,2-monoacetoneglycerol. It consists first in the benzylation of 2-acetyl-1,3-benzylideneglycerol (I)[4] with benzyl chloride and powdered potassium hydroxide (a procedure used previously by Zemplén[5] for the benzylation of triacetyllevoglucosan). The benzylidene group was eliminated by hydrolysis with 50% acetic acid, and the dried residue benzoylated in pyridine solution. Finally, removal of the benzyl group was achieved by catalytic reduction with palladium-in-glacial acetic acid.



The desired oxidation of IV to the corresponding dihydroxyacetone derivative V previously prepared by Fischer[6] was readily effected with chromium trioxide in glacial acetic acid. An attempt to use the Oppenauer procedure for the oxidation, using cyclohexanone in boiling toluene as the hydrogen acceptor, failed to yield ketonic material.

(1) Armour and Company, Research Division, Chicago 9, Illinois.

(2) P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 189 (1936).

(3) J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, **63**, 3244 (1941).

(4) M. Bergmann and N. M. Carter, *Z. physiol. Chem.*, **191**, 211 (1930).

(5) G. Zemplén, Z. Csuros and S. Angyal, *Ber.*, **70**, 1848 (1937).

(6) H. O. L. Fischer, C. Taube and E. Baer, *ibid.*, **60**, 479 (1927).

Experimental

1,3-Benzylideneglycerol.—The procedure of Hibbert and Carter[7] as modified by Bergmann and Carter[4] was used. The best yield obtained after one recrystallization from ether was 15% of material, m.p. 82–83°.

2-Acetyl-1,3-benzylideneglycerol (I).[4]—A mixture of 2.5 g. of 1,3-benzylidene glycerol, 10 ml. of acetic anhydride and 10 ml. of pyridine was allowed to stand overnight at room temperature and was then poured into excess ice-water. The product was recrystallized once from ether; wt. 2.5 g., m.p. 100–102°.

2-Benzyl-1,3-benzylideneglycerol (II).—A mixture of 1.1 g. (5 millimoles) of 2-acetyl-1,3-benzylideneglycerol, 2.8 ml. (24 millimoles) of benzyl chloride and 25 ml. of xylene was stirred vigorously on the steam-bath for 4 hours with 13 g. (232 millimoles) of powdered potassium hydroxide. The mixture was cooled, ice was added and the xylene layer washed with water until neutral. It was then dried over calcium chloride and concentrated to dryness. The product was recrystallized once from ether; wt. 900 mg., m.p. 77–78°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.9, 76.1; H, 6.75, 6.70.

2-Benzyl-1,3-Dibenzoylglycerol (III).—A mixture of 9 g. of 2-benzyl-1,3-benzylideneglycerol and 100 ml. of 50% acetic acid was refluxed for 2 hours. Then 100 ml. of water was added and the solution concentrated *in vacuo*. The residue, dried by azeotropic distillation with alcohol followed by benzene, was dissolved in 80 ml. of dry pyridine and the solution cooled to 0°. To this was added a solution of 7.7 g. of benzoyl chloride (freshly distilled), in 80 ml. of dry pyridine. This mixture was allowed to stand at 4° for 40 hours. A few pieces of ice were added, the mixture allowed to stand a half hour, and then poured into a large excess of water. The ether extract of the resulting suspension was washed with ice-cold potassium bisulfate and sodium bicarbonate solution, dried over calcium chloride and concentrated to dryness. The residue after one recrystallization from ether weighed 3.3 g., m.p. 71.5–72.5°.

Anal. Calcd. for $C_{24}H_{22}O_5$: C, 73.84; H, 5.68. Found: C, 73.96; H, 5.65.

1,3-Dibenzoylglycerol (IV).—A solution of 3 g. (8 millimoles) of 2-benzyl-1,3-dibenzoylglycerol in 25 cc. of acetic acid was shaken with a previously reduced suspension of 250 mg. of palladium black (J. T. Baker) in 50 ml. of acetic acid under one atmosphere of hydrogen. After 10 millimoles of hydrogen was absorbed, the filtered solution was freeze dried. The oily residue (2.5 g., 8 millimoles) crystallized in the ice-box overnight and was used without further purification for the oxidation described below. For recrystallization the product was dissolved in ether and hexane was added to incipient turbidity. On cooling, preferably in a Dry Ice-bath, crystallization occurred, m.p. 51.5–54°.

Anal. Calcd. for $C_{17}H_{16}O_5$: C, 68.00; H, 5.37; $2C_6H_5CO$, 70.0. Found: C, 68.03; H, 5.34; C_6H_5CO,[8] 70.9.

Dibenzoyldihydroxyacetone (V).—A solution of 300 mg. (1 millimole) of 1,3-dibenzoylglycerol in 30 ml. of glacial acetic acid was mixed with a solution of 66 mg. (0.65 millimole, equivalent amount) of chromium trioxide in 30 ml. of glacial acetic acid. After one hour, a little ethanol was added and the mixture was concentrated to dryness *in vacuo*. The residue was dissolved in ether and the solution was washed with water, 10% sodium bicarbonate and again with water, dried over calcium chloride and concentrated to dryness *in vacuo*. The product crystallized from ether as long needles; wt. 96 mg., m.p. 118–119°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.65; H, 4.61.

Dibenzoyldihydroxyacetone was prepared by benzoylation of authentic dihydroxyacetone (purchased from Nutritional Biochemicals, Inc., Cleveland, Ohio) according to Fischer.[6] After two recrystallizations from ether, a 50%

(7) H. Hibbert and N. M. Carter, THIS JOURNAL, **51**, 1601 (1929).

(8) Pregl-Roth, "Die Quantitative organische Microanalyse," Julius Springer, Berlin, 1935, p. 235.

yield was obtained; m.p. 117°, mixed m.p. with compound from above synthesis 117.5–119°, m.p. Fischer 121°.

The dibenzoyldihydroxyacetone from both sources was converted into the phenylhydrazone[5]; a mixture of the two preparations showed no depression in melting point.

Oppenauer Oxidation of 1,3-Dibenzoylglycerol.—A mixture of 300 mg. of 1,3-dibenzoylglycerol (1 millimole), 7 cc. of cyclohexanone (67 millimoles), 520 mg. of aluminum *t*-butylate (2 millimoles) and 30 cc. of toluene was refluxed overnight. The aluminum was precipitated by the addition of the theoretical amount of water. The filtrate was concentrated to a sirup. This was dissolved in hexane and the solution chromatographed over alumina. The benzene–ether eluate was refluxed with thiosemicarbazide for 1 hour in methanol. The ultraviolet absorption spectrum[9] of the crude reaction mixture showed only insignificant absorption at 270 mμ indicating the presence of only a small amount of carbonyl compound in the chromatographed product.

Acknowledgment.—The author is indebted to Dr. Josef Fried for many helpful suggestions, to Mr. Joseph Feltzin for able technical assistance, and to Mr. Joseph F. Alicino and his associates for the microanalyses.

(9) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

SQUIBB INSTITUTE FOR MEDICAL RESEARCH
NEW BRUNSWICK, N. J.

Concerning the Spectrum of Chlorophyll in Piperidine[1]

BY JOHN W. WEIGL AND ROBERT LIVINGSTON

RECEIVED JANUARY 24, 1952

A number of years ago, Katz and Wassink[2] measured the absorption spectrum of a mixture of chlorophylls a and b in a variety of solvents. They were able to demonstrate a fair correlation between the wave length of the red peak and the polarizability of the solvent. One point only for the solvent piperidine was very far out of line (6420 Å.). Since this has been mentioned occasionally in the literature as a real exception[3] we felt it worth while to re-check this datum.

An ether solution of purified chlorophyll a, whose spectrum had been checked, was evaporated to dryness under a stream of purified helium gas and immediately redissolved in an equal volume of piperidine (Eastman Kodak Co., "Practical" grade). The color of the solution changed from bluish to yellowish green. The spectral shifts observed resembled closely those described by Katz and Wassink: the major red peak shifted to about 6425 Å. and decreased in intensity by about 35% while the major blue peak was intensified by 63% and shifted to about 4300 Å. The first minor red peak remained at about 6120 Å. but became some 25% weaker; other minor peaks were hardly noticeable. Forty-five minutes standing in the dark at room temperature with limited access to air produced no further changes.

The piperidine was now evaporated under helium and replaced by redistilled ether. The color and spectrum of chlorophyll a failed to return; instead, a very slight *blue* shift of the "piperidine spectrum" was observed. Clearly, the piperidine had caused an irreversible change in the chlorophyll. The similarity of these spectra to that of Katz and Wassink suggests that they were observing the results of an irreversible reaction of chlorophyll in piperidine.

The same explanation probably applies to the similar marked shift in spectrum which occurs when chlorophyll a is dissolved in pure benzylamine.[4]

(1) This work was made possible by the support of the Office of Naval Research (NR059,028, Contract N6ori-212, T.O. I).

(2) E. Katz and E. C. Wassink, *Enzymologia*, **7**, 97 (1939).

(3) For instance, E. I. Rabinowitch, "Photosynthesis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, pp. 638, 642.

(4) R. Livingston, W. Watson and J. McArdle, THIS JOURNAL, **71**, 1542 (1949). It should be noted that Figs. 5 and 6 were inadvertently interchanged in this paper.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

Mercuric Nitrate Addition Compounds of Various Pyridine Bases

BY RICHARD H. WILEY, JOHN L. HARTMAN AND EDWIN L. DEYOUNG[1]

RECEIVED FEBRUARY 27, 1952

Although a great variety of metal salt–pyridine base addition compounds are known, only pyridine[2] and quinoline[3] mercuric nitrate complexes have been described, and these but incompletely, in the literature. This note will serve to record the preparation and properties of a variety of such compounds.

Eleven variously substituted pyridines listed in the Table were selected for examination. Each of these was added to a mercuric nitrate solution prepared by dissolving mercuric oxide in concd. nitric acid. Of the eleven compounds, only 2,4-lutidine failed to form a precipitate of the addition compound under these conditions. Four of the bases—isoquinoline, quinaldine, acridine and 2-methyl-5-ethyl-pyridine—precipitated as solid addition compounds which could not be recrystallized from any solvent tested. The remaining bases—pyridine, α-picoline, β-picoline, 2,3-dimethylpyridine, quinoline and lepidine—gave recrystallizable solids.

The melting points of the recrystallized addition compounds, given in the table, were, with the exception of that from pyridine itself, fairly sharp but with decomposition. The product obtained by vacuum drying the recrystallized 2,3-lutidine complex was the only sample which melted without decomposition.

Mercury analyses, recorded in the table, were made by two procedures using a hydrogen peroxide–sulfuric acid[4] and a nitric acid–sulfuric acid[5] decomposition on recrystallized samples dried in a desiccator over anhydrous calcium chloride–potassium hydroxide and dried in vacuum over phosphorus pentoxide. The desiccator dried samples gave analytical values by both procedures corresponding to two to one mole ratio of base to mer-

(1) Most of this information was submitted as a thesis in partial fulfilment of the requirements for Honors by E. L. DeYoung.

(2) L. Pesci, *Gazz. chim. ital.*, **25, II**, 430 (1895); **28, II**, 471 (1898); D. Stroholm, *Z. anorg. Chem.*, **57**, 103 (1908).

(3) H. Schiff, *Ann.*, **131**, 113 (1864).

(4) D. L. Tabern and E. F. Shelberg, *Anal. Chem.*, **4**, 401 (1932).

(5) E. E. Aristoff, *et al.*, *Ind. Eng. Chem.*, **40**, 1281 (1948).