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.

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Concerning the Spectrum of Chlorophyll in Piperidine[1]

BY JOHN W. WEIGL AND ROBERT LIVINGSTON

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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]

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(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.

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Mercuric Nitrate Addition Compounds of Various Pyridine Bases

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

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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-

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

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

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