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).

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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]

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-

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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.

[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).

TABLE I

MERCURIC NITRATE–PYRIDINE BASE ADDITION COMPOUNDS

(a) Desiccator dried; (b) vacuum dried; (c) nitric acid decomposition, reference 5; (d) hydrogen peroxide decomposition, reference 4

Pyridine base	M.p., °C.		Analyses (% Hg)				Calcd. for 2 base/1Hg$(NO_3)_2$
			(a)		(b)		
	(a)	(b)	(c)	(d)	(c)	(d)	
Pyridine	234–236[e]	233–235	41.6	42.2	40.7	41.7	42.4
Quinoline	178 dec.[f]	179–181 dec.	34.8	35.1	35.0	35.2	34.6
β-Picoline	131–133 dec.	174–175 dec.	37.6	37.2	38.4	38.0	39.3
Lepidine	148 dec.	137 dec.	35.2	34.5	31.8	32.1	32.8
2,3-Lutidine	104–106 dec.	145	44.5	46.6	38.1	38.0	37.2[g]
α-Picoline	122–125 dec.	109–115 dec.	51.0	48.7	..	..	50.4[h]

[e] Pyridine nitrate, m.p. 118, sublimes during determination. Reported to decompose without melting; reference 2. [f] Reported, m.p. 183°; reference 3. [g] 1/1 Ratio; Hg, calcd. 46.5%. [h] Value calcd. for $^1/_2$ ratio.

curic nitrate except for the 2,3-lutidine complex and the α-picoline complex for which the analyses agreed with a one to one ratio and a one to two ratio, respectively. After vacuum drying the analyses were in at least fair agreement with the values prior to vacuum drying except again for the 2,3-lutidine complex which analyzed for a two to one base to salt ratio. This change in ratio, involving a loss of mercury, can be explained as a loss of the volatile nitrate from the less stable one to one complex. The change in melting point on vacuum drying observed with this compound is consistent with the possibility of such a change. The α-picoline complex, which sublimed on vacuum drying, was not analyzed as a vacuum-dried sample. These analytical data do not require that these complexes contain water of crystallization.

Experimental

The mercuric nitrate reagent was prepared by suspending 216.6 g. (1 mole) of yellow mercuric oxide in 91.4 g. of concd. nitric acid and stirring until solution was complete. The addition compounds were precipitated by adding 0.1 mole of the base to 26.3 g. (0.1 mole) of the reagent with stirring and cooling over a five-minute period. The precipitated solid was collected on a filter and recrystallized from water (pyridine, β-picoline, quinoline, lepidine) or from ethanol (α-picoline, 2,3-lutidine). The solids were dried in a desiccator over anhydrous calcium chloride and potassium hydroxide or in drying pistol over phosphorus pentoxide at 2–6 mm. Melting points are uncorrected. Mercury analysis were made by procedures previously described.[4,5] Data are recorded in the Table.

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NEW COMPOUNDS

Tetraallylethylenediamine and Hexaallylethylenediammonium Dibromide

In the course of polymerization studies in this Laboratory,[1] tetraallylethylenediamine was prepared as an intermediate for the preparation of hexaallylethylenediammonium dibromide. The physical constants of these compounds have not been previously reported. Since polymerization studies of the quaternary ammonium salt as well as the properties of the polymer have been reported in a later paper,[2] it seems important that the preparation and properties of these compounds be recorded.

Tetraallylethylenediamine.—To a suspension of 67.2 g. of $NaHCO_3$ in 65 cc. of water was added 69 g. (0.71 mole) of diallylamine. With stirring, 66 g. (0.35 mole) of ethylene bromide was added dropwise. After the addition was complete, the mixture was heated under reflux for nine hr. After cooling, the sodium bromide was removed by filtration, and the filtrate saturated with NaOH. The amine layer was separated, dried over solid NaOH, and distilled; yield 32 g. (41%), b.p. 92° (3 mm.), d^{25}_{25} 0.8517, n^{25}_D 1.4702.

Anal. Calcd. for $C_{14}H_{24}N_2$: N, 12.71. Found: N, 12.62.

Hexaallylethylenediammonium Dibromide.—To 58 g. (0.26 mole) of tetraallylethylenediamine dissolved in 50 cc. of dry acetophenone, was added dropwise, with stirring, 63 g. (0.52 mole) of allyl bromide. The solution became warm on addition of the allyl bromide. Stirring was continued for four hr. after which time the salt began to precipitate. After an additional two hr., the salt was removed by filtration, washed several times with dry ether and dried; yield 108 g. (90%), m.p. 140°. After recrystallization from ethanol, the product had a melting point of 142°.

Anal. Calcd. for $C_{20}H_{34}N_2Br_2$: Br, 34.57. Found: Br, 34.28.

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ROBERT L. BUNCH

RECEIVED FEBRUARY 29, 1952

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[1] G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

[2] G. B. Butler, R. L. Bunch and F. L. Ingley, *ibid.*, **74**, 2543 (1952).

Some Sulfonium and Selenonium Salts[1]

Continuing the search for additional compounds which cause damage to tumor cells *in vivo*,[2] salts have been prepared by reaction of methyl sulfide, methyl ethyl sulfide, ethyl sulfide, bis-(2-hydroxyethyl) sulfide, and ethyl selenide with *p*-fluorophenacyl chloride, *p*-phenylphenacyl bromide and β-naphthacyl bromide. In some cases the reaction was carried out in refluxing alcohol solution according to the method of Bost and Schultzer,[3] but in other cases best results were obtained by mixing the reactants and allowing them to stand at room temperature. Attempts to prepare sulfonium salts from bis-(2-cyanoethyl) sulfide were unsuccessful. The methods used are illustrated below and the properties of the products are listed in Table I. The salts were white or light buff solids which decomposed slowly on standing at room temperature and melted with decomposition on heating. The β-naphthacyl and *p*-phenylphenacyl salts were very slightly soluble in water (about 1 to 4 mg./ml.), while all the *p*-fluorophenacyl salts, except that of ethyl selenide, were more soluble.

Method I.—A solution of 7.25 g. of *p*-fluorophenacyl chloride in a slight excess of methyl sulfide was kept at room temperature for 1 day, then 6.8 g. (65%) of *p*-fluorophenacyl dimethyl sulfonium chloride was recovered by suction filtration and recrystallized from warm methanol by gradual

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[1] This research was supported in part by a grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service, and in part by a grant from the Damon Runyon Memorial Fund for Cancer Research.

[2] C. T. Bahner, *Texas Reports on Biology and Medicine*, **8**, 448 (1950); Henry A. Rutter, Jr., THIS JOURNAL, **73**, 5905 (1951).

[3] R. W. Bost and H. C. Schultzer, *ibid.*, **64**, 1165 (1942).