shown to be present by the infrared spectrum of the gases. Recrystallization of the residue from isopropyl alcohol gave material having an infrared spectrum identical with that of dianilinium diphenylpyrophosphonate.[9]

*Phenylcarbamoyl hydrogen n-butylphosphonate,* m.p. 84–84.5° dec., neut. equiv., 257, 259 (calcd. 257.1), and *n-butylcarbamoyl hydrogen phenylphosphonate,* m.p. 52.5–55° dec., were prepared similarly.

Naval Research Laboratory,
Washington, D. C.

University of Maryland,
College Park, Md.

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[9] R. B. Fox and W. J. Bailey, in press.

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# Reactions of Vanillin and Its Derived Compounds. XXIX.[1] 3,3′,4,4′-Tetrahydroxybenzil and Its Reduction

Irwin A. Pearl, Horace B. Faber, Jr., and Waner C. Holman

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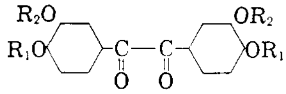
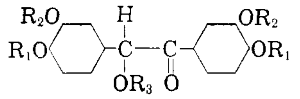
The need for 3,3′,4,4′-tetrahydroxybenzoin for testing in programs on the respiration and scab resistance of potatoes[2] led to a study of the preparation of this compound and other related products. Recent studies on vanillil and its reduction[3,4] indicated that the various monomolecular reduction products of vanillil could be prepared directly from vanillil by the use of various reducing systems. Accordingly, studies were made on the preparation of 3,3′,4,4′-tetrahydroxybenzil from vanillil and its use as a starting material for the preparation of its reduction products.

3,3′,4,4′-Tetrahydroxybenzil (I) was first prepared by Barger and Ewins[5] from piperil by treatment with phosphorus pentachloride followed by hydrolysis and more recently by Schales,[6] who treated 0.5 g. veratril (II) with 100 volumes of hydrobromic acid in acetic acid at 125–135°. The procedure of Schales was applied to vanillil (III) on a relatively large scale, but the melting points of the products obtained from several experiments varied somewhat and did not correspond with reported values for I. Vanillil was then demethylated with pyridine hydrochloride under conditions reported by Erdtman and Lindberg[7] and Hearon, Lackey, and Moyer[8] for the demethylation of conidendrin. Under these conditions the desired I was obtained in good yield. An attempt to demethylate vanillil with aluminum bromide under conditions employed for the production of protocatechualdehyde from vanillin[9] resulted in almost quantitative recovery of the starting material.

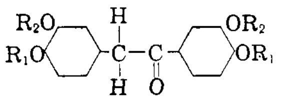
Reduction of I under conditions previously employed for the reduction of vanillil[4] and syringil[10] gave several of the monomolecular reduction products of I, but there appeared to be very little correlation between reduction of I and those of vanillil and syringil. The reduction products were characterized by means of their methyl ethers, acetates, and ultraviolet absorption spectra.



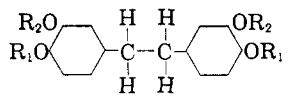
I. $R_1 = R_2 = H$
II. $R_1 = R_2 = CH_3$
III. $R_1 = H; R_2 = CH_3$
IV. $R_1 = R_2 = CH_3CO$



V. $R_1 = R_2 = R_3 = H$
VI. $R_1 = R_2 = CH_3; R_3 = H$
VII. $R_1 = R_2 = R_3 = CH_3CO$



VIII. $R_1 = R_2 = H$
IX. $R_1 = H; R_2 = CH_3$
X. $R_1 = R_2 = CH_3$
XI. $R_1 = CH_3CO; R_2 = CH_3$



XII. $R_1 = R_2 = H$
XIII. $R_1 = H; R_2 = CH_3$
XIV. $R_1 = R_2 = CH_3CO$

## EXPERIMENTAL[11]

*3,3′,4,4′-Tetrahydroxybenzil* (I). A mixture of 50 g. of III[3] and 50 g. of freshly precipitated, dry pyridine hydrochloride in a 500-ml. flask fitted with an air condenser was heated to 160° until complete solution resulted. The temperature was raised to 190–200°, and gentle refluxing was maintained for 2 hr. The clear melt was dissolved in 800 ml. of hot (70°) water, and the resulting solution was heated to boiling and filtered. The filtrate was acidified with 6*N* hydrochloric acid and allowed to stand at 20° overnight. The resulting dark-colored crystalline precipitate was filtered and washed with a little cold water to yield 40 g. (78%) of crude I dihydrate. The dark crystals were recrystallized from water in the presence of decolorizing carbon and air dried to yield light orange needles of I dihydrate melting first at 125–130° with gas evolution, solidifying, and melting again at 231–234°. Boiling the dihydrate with benzene under reflux and a water-separatory head gave dehydrated crystals melting at 234–236°. Barger and Ewins[5] dried their product in an oven at 110° and obtained the anhydrous product. These authors reported the analysis of the dihydrate from water, but did not report its melting point. The ultraviolet ab-

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[1] For paper XXVIII of this series, see *J. Org. Chem.* **22,** 1266 (1957).

[2] L. A. Schaal and G. Johnson, *Phytopathology* **45,** 626 (1955).

[3] I. A. Pearl, *J. Am. Chem. Soc.* **74,** 4260 (1952).

[4] I. A. Pearl, *J. Am. Chem. Soc.* **74,** 4593 (1952).

[5] G. Barger and A. J. Ewins, *J. Chem. Soc.* **93,** 737 (1907).

[6] O. Schales, *Arch. Biochem. Biophys.* **34,** 56 (1951).

[7] H. Erdtman and B. Lindberg, *Acta Chem. Scand.* **3,** 982 (1949).

[8] W. M. Hearon, H. B. Lackey, and W. W. Moyer, *J. Am. Chem. Soc.* **73,** 4005 (1951).

[9] I. A. Pearl and D. L. Beyer, *J. Am. Chem. Soc.* **75,** 2630 (1953).

[10] I. A. Pearl, *J. Org. Chem.* **22,** 1229 (1957).

[11] All melting points are uncorrected. Ultraviolet spectral data are for solutions in 95% ethanol and were obtained by Mr. Lowell Sell. Analyses were performed by the Analytical Department of The Institute of Paper Chemistry and by Huffman Microanalytical Laboratories, Wheatridge, Colorado.

sorption spectrum was essentially identical with that reported earlier for III[12] and indicated the following maxima: $\lambda_{max}$ 232 m$\mu$, $\epsilon$ 21550; $\lambda_{max}$ 289 m$\mu$, $\epsilon$ 16300; $\lambda_{max}$ 325 m$\mu$, $\epsilon$ 18300.

A solution of 50 g. of III in 500 ml. of boiling glacial acetic acid was treated with 100 ml. of 48% hydrobromic acid, and the mixture was boiled under reflux for 3 hr. and allowed to cool. The reaction mixture was concentrated to one-half volume under reduced pressure, and the residue was diluted with 3 l. of water and allowed to stand overnight. The heavy precipitate was filtered, washed, and air dried to yield 44 g. of product as light yellow crystals. Recrystallization from water gave bright yellow crystals melting at 113° with gas evolution, solidifying, and remelting at 233–235°. Analysis indicated the monohydrate of I. The ultraviolet absorption spectrum was identical with that of the dihydrate.

*Anal.* Calcd. for $C_{14}H_{12}O_7$: C, 57.54; H, 4.14. Found: C, 57.25; H, 4.57.

Acetylation of either the monohydrate, the dihydrate, or the parent anhydrous I with acetic anhydride in pyridine, and recrystallization from ethanol gave yellow needles of 3,3',4,4'-tetraacetoxybenzil (IV) melting at 133–134°: $\lambda_{max}$ 268 m$\mu$, $\epsilon$ 21000.

*Anal.* Calcd. for $C_{22}H_{18}O_{10}$: C, 59.73; H, 4.10. Found: C, 59.73; H, 4.15.

Methylation of any of the three forms of I with dimethyl sulfate and alkali and recrystallization of the product from glacial acetic acid yielded yellow crystals melting at 220–221° and not depressing a mixed melting point with authentic II.[4]

*3,3',4,4'-Tetrahydroxybenzoin* (V). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 25 ml. of glacial acetic acid and 5 g. of granulated tin. The mixture was heated on the steam bath for 1.5 hr. and filtered. The precipitate was washed with hot water, and the combined filtrate and washings were concentrated under reduced pressure. After standing at room temperature, the solution deposited 1.2 g. of tan crystals which were recrystallized from water in the presence of decolorizing carbon to yield light tan needles of V hemihydrate melting at 186–188°. The ultraviolet absorption spectrum was identical with that of authentic veratroin (VI) and indicated the following maxima: $\lambda_{max}$ 232 m$\mu$, $\epsilon$ 19750; $\lambda_{max}$ 281 m$\mu$, $\epsilon$ 14780; $\lambda_{max}$ 325 m$\mu$, $\epsilon$ 17250.

*Anal.* Calcd. for $C_{14}H_{13}O_{6.5}$: C, 58.90; H, 4.46. Found: C, 58.92; H, 4.59.

Acetylation with acetic anhydride in pyridine yielded 3,3',4,4'-tetrahydroxybenzoin pentaacetate (VII) as colorless needles from ethanol melting at 182–183°.

*Anal.* Calcd. for $C_{24}H_{22}O_{11}$: C, 59.26; H, 4.56. Found: C, 59.68; H, 4.32.

*3,3',4,4'-Tetrahydroxydeoxybenzoin* (VIII). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 10 g. of granulated tin and then slowly with 10 ml. of concd. hydrochloric acid. The mixture was heated on the steam bath 1.5 hr. and filtered. The precipitate was washed with hot water, and the combined filtrate and washings were concentrated under reduced pressure. After standing several days at room temperature the solution deposited 2.2 g. of dark crystals which were recrystallized from water in the presence of decolorizing carbon to yield light tan crystals of VIII monohydrate melting at 196–198° and having the following maxima in its ultraviolet absorption spectrum: $\lambda_{max}$ 231 m$\mu$, $\epsilon$ 18800; $\lambda_{max}$ 281 m$\mu$, $\epsilon$ 11950; $\lambda_{max}$ 310 m$\mu$, $\epsilon$ 8720. The ultraviolet absorption spectrum was identical with that of deoxyvanilloin (IX).

*Anal.* Calcd. for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.59; H, 5.19.

Acetylation with acetic anhydride in pyridine yielded 3,3',4,4'-tetraacetoxydeoxybenzoin (X) as light yellow needles from ethanol melting at 127–128° and having the following maximum in its ultraviolet absorption spectrum: $\lambda_{max}$ 293 m$\mu$, $\epsilon$ 26950. The spectrum was essentially identical with that of deoxyvanilloin diacetate (XI).

*Anal.* Calcd. for $C_{22}H_{20}O_9$: C, 61.68; H, 4.71. Found: C, 61.55; H, 4.74.

VIII was also prepared by reduction of I dihydrate with tin amalgam and hydrochloric acid[13] in either aqueous or dilute ethanolic solution.

*3,3',4,4'-Tetrahydroxybibenzyl* (XII). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 10 g. of zinc dust and heated to boiling. The mixture was removed from the source of heat and treated portionwise with 40 ml. of concd. hydrochloric acid. The solution decolorized after the first addition. The mixture was allowed to stand 5 min. after the last addition and filtered hot. The zinc residue was washed with water, and the combined filtrate and washings were concentrated by distillation under reduced pressure. The concentrated solution deposited crystals upon standing at room temperature. The crystals were filtered and recrystallized from water to give 4.0 g. of XII as tan crystals melting at 151–152°. The ultraviolet absorption spectrum had a maximum at 283 m$\mu$ ($\epsilon$ 6750) and was essentially identical with that of bivanillyl (XIII) except for a slight maximum in the latter at 230 m$\mu$.

*Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.31; H, 6.15.

Acetylation and recrystallization from ethanol yielded 3,3',4,4'-tetraacetoxybivanillyl (XIV) melting at 148–149° and having the following maxima in its ultraviolet absorption spectrum: $\lambda_{max}$ 266 m$\mu$, $\epsilon$ 1680; $\lambda_{max}$ 272 m$\mu$, 1660.

*Anal.* Calcd. for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.70; H, 5.33.

*Unsuccessful reductions of I.* Attempted reductions of I with zinc and ammonium chloride, aluminum and hydrochloric acid, aluminum amalgam and ammonium hydroxide, tin amalgam and hydrochloric acid, sodium borohydride, sodium trimethoxyborohydride in alkaline solution, sodium hydrosulfite in alkaline solution, zinc and sodium hydroxide, and Raney nickel alloy in sodium hydroxide solution under conditions reported previously[4,10,13] resulted in either the recovery of starting material or in the production of highly colored tarry materials from which no crystalline products could be isolated.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WIS.

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[12] I. A. Pearl and E. E. Dickey, *J. Am. Chem. Soc.* **74**, 614 (1952).

[13] I. A. Pearl and W. M. Dehn, *J. Am. Chem. Soc.* **60**, 57 (1938).

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## Decomposition of Acyl Nitrates. Reaction of Trifluoroacetic Anhydride with Nitric Acid

ROBERT BOSCHAN

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A low yield of fluoropicrin (III) has been obtained from the reaction of trifluoroacetic anhydride (I) with nitric acid at 100°. The formation of this material very likely proceeds *via* the intermediate trifluoroacetyl nitrate (II), which decomposes as shown in a manner similar to that previously postulated in the conversion of alkyl chloroformates to nitrate esters[1] and of dialkyl carbamyl

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[1] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).