hexane solution N-n-butyltritylamine hydrochloride was precipitated by bubbling in dry hydrochloric acid. After washing with boiling acetone the melting point was 165–166°, undepressed on admixture with an authentic sample.

Reaction of I with aniline. (a) *In cyclohexane.* In 5 ml. of cyclohexane containing 0.093 g. (1.0 mmole) of aniline, 0.150 g. (0.5 mmole) of I was dissolved, sealed in a vial and heated at 80° for 5 hr. After this time the solution showed a slight cloudiness which disappeared on extraction with water. The water layer titrated for thiocyanate ion accounted for 2.8% of the total sulfur. No thioureic sulfur was detected in the cyclohexane layer. This, evaporated to dryness, left a residue which, crystallized form acetonitrile, yielded I, m.p. 136–137°. Accounting for the solubility of I in acetonitrile, 93% recovery of unchanged I was obtained.

(b) *Without solvent.* In 1 ml. of aniline 0.301 g. (1.0 mmole) of I was dissolved under gentle heating. After a few hours at room temperature, the excess aniline was removed *in vacuo.* From the residue taken up in ethanol, N-phenyltritylamine (85%) was crystallized, m.p. 149–150° (lit.,[16] m.p. 149–150°).

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[16] M. Gomberg, *Ber.*, **35**, 1829 (1902).

Reaction of Salts of Organophosphorus Acids with Isocyanates[1]

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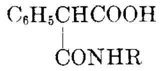
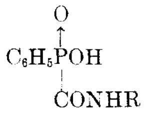
A general analogy in reactivity may be drawn between the α-hydrogen atom of a carboxylic acid and the P-hydrogen atom of a monobasic phosphinic acid, RP(O)H(OH). Reactions involving the carboxyl group and isocyanates are, of course, well known. In addition, Blicke and Zinnes[2] have shown that a carboxylic acid possessing an activated α-hydrogen, such as phenylacetic acid, forms an Ivanov reagent which can be condensed with phenyl isocyanate and the product hydrolyzed to yield N-phenyl phenylmalonamic acid (I). The base-catalyzed condensation involving the phosphorus-hydrogen group in dialkyl phosphonates with isocyanates to give dialkyl carbamoylphosphonates is also well established.[3]

We have found that the tertiary amine salts of phenylphosphinic acid and mandelic acid undergo condensation with isocyanates in the presence of excess amine. Reaction takes place at the P—H and α-O—H groups, respectively, to give salts of the corresponding carbamoyl derivatives (II and III). Tertiary amine half-salts of phosphonic acids condense at the weakly acidic O—H group with the formation of salts of the half-carbamoyl esters (IV), products analogous to those formed from mandelic acid.



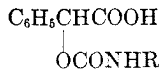
$$\begin{array}{l}\mathrm{C_6H_5CHCOOH}\\ \qquad|\\ \qquad\mathrm{CONHR}\end{array}$$

I



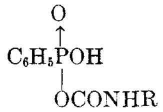
$$\begin{array}{l}\qquad\ \ \mathrm{O}\\ \qquad\ \ \uparrow\\ \mathrm{C_6H_5POH}\\ \qquad\ \ |\\ \qquad\ \ \mathrm{CONHR}\end{array}$$

II



$$\begin{array}{l}\mathrm{C_6H_5CHCOOH}\\ \qquad|\\ \qquad\mathrm{OCONHR}\end{array}$$

III



$$\begin{array}{l}\qquad\ \ \mathrm{O}\\ \qquad\ \ \uparrow\\ \mathrm{C_6H_5POH}\\ \qquad\ \ |\\ \qquad\ \ \mathrm{OCONHR}\end{array}$$

IV

The acids themselves are readily formed from the salts by treatment with excess mineral acid. These products are obtained in excellent yield, and salt formation therefore appears to be a suitable method for preventing an undesired reaction between an acidic group and an isocyanate. In a single experiment, treatment of phenylphosphinic acid with excess isopropylmagnesium bromide, followed by reaction with phenyl isocyanate, gave a low yield of II after hydrolysis of the bromomagnesium salt. No further investigation of this reaction was carried out, but it is possible that a phosphorus-Ivanov reagent was formed as an intermediate prior to the addition of the isocyanate.

Triethylamine appears to be the most useful salt-forming reagent in this reaction from the standpoint of ease of handling of the products; N-ethylmorpholine and diethylcyclohexylamine gave hygroscopic salts and no reaction involving the phosphorus compound was observed in the presence of pyridine or under Schotten-Baumann conditions. Anilinium and n-butylammonium salts gave only the urea derivatives. Benzene or other hydrocarbons in which the starting salts, prepared *in situ* by mixing equimolar amounts of acid and amine, are somewhat soluble are suitable solvents; an attempted reaction in acetone with phenylphosphinic acid was unsuccessful. Attempts to prepare the triethylamine salt of phenylphosphinic acid in carbon tetrachloride led to a vigorous reaction from which triethylamine hydrochloride precipitated. It is possible that the trichloromethyl derivative has been formed as appears to be the case with dialkyl phosphonates.[4]

EXPERIMENTAL[5]

Triethylammonium phenyl(phenylcarbamoyl)phosphinate. To a stirred two-phased mixture of 14.2 g. (0.1 mole) of

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[1] Based on a portion of the doctoral thesis submitted to the University of Maryland in June 1959 by Robert B. Fox; presented in part at the 130th meeting of the American Chemical Society at Atlantic City, N. J., September 1956, Abstracts p. 50–O.

[2] F. F. Blicke and H. Zinnes, *J. Am. Chem. Soc.*, **77**, 4849 (1955).

[3] (a) R. B. Fox and D. L. Venezky, *J. Am. Chem. Soc.*, **78**, 1661 (1956). (b) A. N. Pudovik and A. V. Kuznetsova, *Zhur. Obshcheĭ Khim.* **25**, 1369 (1955). (c) A. N. Pudovik, I. V. Konovalova, and R. E. Krivonosova, *Zhur. Obshcheĭ Khim.*, **26**, 3110 (1956). (d) E. C. Ladd and M. O. Harvey, Canadian Patent **509,034** (1955).

[4] F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 674 (1947).

[5] All melting points were taken in sealed capillary tubes and are corrected; those accompanied by decomposition gave a gas, but sintering did not take place.

phenylphosphinic acid, 50 ml. of triethylamine, and 50 ml. of benzene was added 13.1 g. (0.11 mole) of phenyl isocyanate over a period of 20 min. During the addition, the temperature of the mixture rose to 55° since no external cooling was used. After being stirred for an additional 45 min., the slurry was filtered and the precipitate washed with ether and petroleum ether to yield 34 g. (96%) of crude salt. Recrystallization from hot 2:1 acetone-chloroform solution gave purified material, m.p. 165–167° dec.

Anal. Calcd. for $C_{19}H_{27}N_2O_3P$: C, 62.96; H, 7.51; P, 8.54. Found: C, 63.31; H, 7.75; P, 8.36.

Triethylammonium phenyl(p-chlorophenylcarbamoyl)phosphinate, m.p. 170–170.5° dec. (from ethanol) was prepared similarly in a 78% yield.

Anal. Calcd. for $C_{19}H_{26}ClN_2O_3P$: C, 57.45; H, 6.60; P, 7.80. Found: C, 57.50; H, 7.13; P, 7.76.

A similar reaction carried out in acetone with phenyl isocyanate gave no precipitate even after being heated under reflux for 2 hr. Concentration of the solution gave an oil which on treatment with water deposited a nearly theoretical yield of diphenylurea. The same result was obtained with pyridine as the base in benzene or by shaking phenyl isocyanate with sodium phenylphosphinate in 10% aqueous sodium hydroxide. The aniline and *n*-butylamine salts without excess amine gave only diphenylurea and *N-n*-butyl-*N'*-phenylurea, respectively.

Phenyl(phenylcarbamoyl)phosphinic acid (II. R = C_6H_5). A filtered solution of 34.7 g. of the crude triethylamine salt of phenyl(phenylcarbamoyl)phosphinic acid in 75 ml. of water was treated with 10.3 ml. of concd. hydrochloric acid. The resulting oil solidified to give 22.4 g. (90%) of the acid; two recrystallizations from hot water afforded colorless needles, m.p. 153.0–153.5° dec.

Anal. Calcd. for $C_{13}H_{12}NO_3P$: C, 59.76; H, 4.64; P, 11.9; neut. equiv., 261.2. Found: C, 60.11; H, 5.42; P, 12.4; neut. equiv., 260.5.

Phenyl(p-chlorophenylcarbamoyl)phosphinic acid, m.p. 161.5–162° dec. (from water, acetone, or methanol) was also prepared in this way in 98% yield.

Anal. Calcd. for $C_{13}H_{11}ClNO_3P$: C, 52.81; H, 3.75; P, 10.5; neut. equiv., 295.7. Found: C, 52.99; H, 4.29; P, 10.4; neut. equiv., 297.4.

Phenyl(2,5-dichlorophenylcarbamoyl)phosphinic acid was prepared without isolation of the intermediate salt. 2,5-Dichlorophenyl isocyanate (9.4 g., 0.05 mole) was added rapidly to a stirred mixture of 7.1 g. (0.05 mole) of phenylphosphinic acid and 5.05 g. (0.05 mole) of triethylamine cooled in an ice bath. After 5 min. the cold reaction mass was taken up in 50 ml. of methanol and the resulting mixture was filtered; the filtrate was diluted with an equal volume of water and the aqueous solution was treated with an excess of concd. hydrochloric acid to precipitate 10.2 g. (62%) of the crude acid, m.p. 141–143°. Two recrystallizations from hot benzene gave analytically pure material, m.p. 153°.

Anal. Calcd. for $C_{13}H_{10}NO_3P$: neut. equiv., 330.1. Found: neut. equiv., 330.2, 329.0.

A filtered aqueous solution of the hygroscopic reaction mass formed from equimolar amounts of phenylphosphinic acid, triethylamine, and *n*-butyl isocyanate was treated with a large excess of hydrochloric acid to precipitate a 71% yield of crude *phenyl(n-butylcarbamoyl)phosphinic acid.* Several recrystallizations from acetone and, finally, one from water afforded a product melting at 95° followed by resolidification and remelting at 116°, which appeared to be the monohydrate of this acid.

Anal. Calcd. for $C_{11}H_{18}NO_4P$: C, 50.95; H, 6.23; neut. equiv., 259.3. Found: C, 50.84; H, 7.01; neut. equiv., 259.

Phenyl(phenylcarbamoyloxy)acetic acid (III. R = C_6H_5). A mixture of 4.56 g. (0.03 mole) of mandelic acid and 3.03 g. (0.03 mole) of triethylamine in 30 ml. of benzene at 30° was treated with 3.57 g. (0.03 mole) of phenyl isocyanate over a 5-min. period. After being heated under reflux for 2 hr., the clear solution was concentrated to give 7.5 g. (67%) of crude salt. This represented only the first crop of material deposited; no attempt at complete recovery was made since subsequent crops came down as oils. Repeated recrystallization of the salt afforded material melting at 122.5–123.5°. Treatment of a filtered hot aqueous solution of the crude salt with excess concd. hydrochloric acid precipitated the urethan of mandelic acid, m.p. 149.5–150.0° dec. (from benzene) (reported m.p. 147–149° dec.[6] and 150–152°[7]).

Anal. Calcd. for $C_{15}H_{13}NO_4$: neut. equiv., 271.2. Found: neut. equiv., 270.5.

Authentic mandelanilide, m.p. 149–150° (from diisopropyl ether), prepared directly from mandelic acid and phenyl isocyanate in the absence of base[6,8] greatly depresses the melting point of the above urethan.

Modified Ivanov reaction. To a solution of isopropylmagnesium bromide heated under reflux (prepared from 0.22 mole of magnesium and 0.26 mole of isopropyl bromide in 150 ml. of diethyl ether) was added 14.2 g. (0.10 mole) of phenylphosphinic acid in 150 ml. of benzene over a 55-min. period. The evolution of a gas was apparent, and near the end of the addition, a black semisolid mass began to form. After being stirred for 1 hr. at 59° the mixture was cooled and 11.9 g. (0.1 mole) of phenyl isocyanate was added rapidly; no gas formation or heat generation was observed during this addition. After the mixture was heated under reflux for 2 hr. and was allowed to stand overnight, the resulting gray solid was broken up and the mixture added to 300 ml. of 10% aqueous ammonium chloride. No products other than diphenylurea were isolated from the organic layer, but treatment of the aqueous phase with concd. hydrochloric acid precipitated 3.5 g. (13.5%) of an acid, m.p. 147–149° dec., which did not depress the melting point of the phenyl(phenylcarbamoyl)phosphinic acid described above.

Triethylammonium phenylcarbamoyl phenylphosphonate. At 25° (water bath) 6.55 g. (0.055 mole) of phenyl isocyanate was added in 15 min. to a slurry prepared from 5.05 g. (0.05 mole) of triethylamine and 7.9 g. (0.05 mole) of phenylphosphonic acid in 150 ml. of dry acetone. After the mixture had been stirred for 1 hr. at room temperature, the precipitate was removed by filtration and washed with ether to give 18.3 g. (97%) of the salt, m.p. 128.5–129.5° dec., without further purification.

Anal. Calcd. for $C_{19}H_{27}N_2O_4P$: C, 60.30; H, 7.18; N, 7.39; P, 8.19. Found: C, 60.29; H, 7.08; N, 7.36; P, 8.18.

When this reaction was carried out at 55°, gases absorbable by Ascarite were formed in an amount approaching the theoretical for carbon dioxide. The fact that sealed tubes containing the pure salt at room temperature developed pressure over a period of weeks indicated considerable instability.

By the above method were prepared samples of very hygroscopic and thermally unstable crude *triethylammonium n-butylcarbamoyl phenylphosphonate,* m.p. 87.5–89° dec. (from benzene) in 69% yield and *triethylammonium phenylcarbamoyl n-butylphosphonate,* m.p. 93–94° dec. in 61% yield.

Phenylcarbamoyl hydrogen phenylphosphonate (IV. R = C_6H_5). A solution of the triethylamine salt of phenylcarbamoyl hydrogen phenylphosphonate in dilute hydrochloric acid (neutral or alkaline solutions of this salt decompose fairly rapidly with the formation of insoluble material) was treated with concd. hydrochloric acid to precipitate a solid which after being washed with diethyl ether gave 13.1 g. of the crude acid, m.p. 71–72° dec. Recrystallization from cold aqueous acetone gave analytically pure material, m.p. 67.5° dec.; upon melting, this substance evolved a gas, resolidified, and then melted at 176–182°.

Anal. Calcd. for $C_{13}H_{12}NO_4P$: neut. equiv., 277.2. Found: neut. equiv., 276, 278 in 50% aqueous acetone.

A sample of this acid was heated at 150° and the evolved gases passed through Drierite. Only carbon dioxide was

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[6] E. Fischer and H. O. L. Fischer, *Ber.*, **47**, 779 (1914).

[7] H. Aspelund, *Acta Acad. Aboensis, Math. et Phys.* **12**, No. 5, 1 (1940).

[8] A. Haller, *Compt. rend.*, **121**, 191 (1895).

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.

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(9) R. B. Fox and W. J. Bailey, in press.

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

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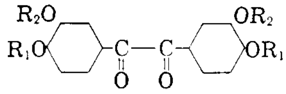
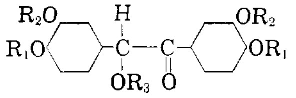
The need for 3,3′,4,4′-tetrahydroxybenzoin for testing in programs on the respiration and scab resistance of potatoes[2] led to a study of the preparation of this compound and other related products. Recent studies on vanillil and its reduction[3,4] indicated that the various monomolecular reduction 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.

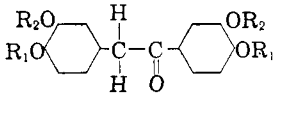
Reduction of I under conditions previously employed for the reduction of vanillil[4] and syringil[10] gave several of the monomolecular reduction products of I, but there appeared to be very little correlation between reduction of I and those of vanillil and syringil. The reduction products were characterized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



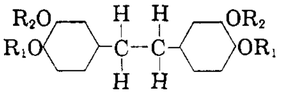
I. $R_1 = R_2 = H$
II. $R_1 = R_2 = CH_3$
III. $R_1 = H; R_2 = CH_3$
IV. $R_1 = R_2 = CH_3CO$



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.