If the assumption is made, in accordance with the stoichiometry of the reaction, that this mixture contains 0.19 g. of triphenylphosphine and 1.39 g. of triphenylphosphine oxide, then the residue, 1.05 g. contains 2.6% nitrogen. If it is then further assumed that this residue is a mixture of benzoic and benzoic *p*-nitrobenzoic anhydrides, then of this mixture 1.2 mole is benzoic anhydride and 1.0 mole is benzoic *p*-nitrobenzoic anhydride.

Benzoic Anhydride and Triphenylphosphine in the Presence of *p*-Nitrobenzoate.—To a mixture of 0.50 g. of triphenylphosphine and 1.13 g. (0.005 mole) of benzoic anhydride in 30 ml. of dry chloroform at a temperature of 50°, there was added 1.13 g. (0.005 mole) of trimethylammonium *p*-nitrobenzoate. The solution was allowed to stand for 5 min. and then poured into 20 ml. of 5% sodium bicarbonate solution. The chloroform was further extracted with 10 ml. of water and then dried over magnesium sulfate. The chloroform was evaporated to yield 1.60 g. of material which partially crystallized. Infrared analysis showed a small peak at 1531 cm.$^{-1}$.

Anal. Found: N, 0.19.

If we assume that of the 1.60 g. recovered 0.50 g. is triphenylphosphine then the remaining 1.10 g. contains 0.28% nitrogen, which using the reasoning applied above, indicates that the mixture contains 21 moles of benzoic anhydride to 1 mole of benzoic *p*-nitrobenzoic anhydride.

Benzoyl Peroxide and *p*-Nitrobenzoate Ion.—A solution of 1.21 g. (0.005 mole) of benzoyl peroxide and 1.13 g. (0.005 mole) of trimethylammonium *p*-nitrobenzoate in 30 ml. of chloroform was allowed to stand for two hours. The mixture was then extracted with two 10-ml. portions of 10% sodium bicarbonate solution followed by 10 ml. of water. The chloroform solution was dried over magnesium sulfate and the solvent was removed *in vacuo*. Infrared analysis of the resulting white solid showed the absence of the nitro group band at 1531 cm.$^{-1}$. The material was crystallized from chloroform–methanol to yield 0.95 g. (78%) of benzoyl peroxide, m.p. 103.5–104°.

NEW HAVEN, CONN.
NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

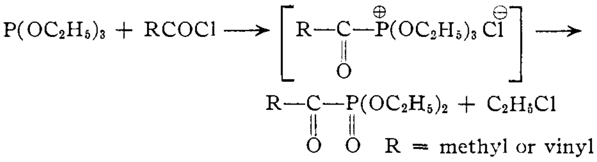
Preparation and Pyrolyses of Some Organophosphonates

BY LUTHER A. R. HALL AND C. WAYNE STEPHENS

RECEIVED JANUARY 12, 1956

Acyl phosphonates were prepared by the reaction of acyl halides and a trialkyl phosphite. Unexpected molecular weight observations on the products as well as an infrared study of by-products of the preparative reaction are discussed. The pyrolyses of diethyl 1-cyano-1-hydroxyethylphosphonate and 1,1-bis-(diethylphosphono)-ethyl acetate lead to excellent yields of acrylonitrile and acetic acid, respectively.

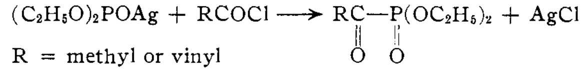
The reaction of acetyl chloride with triethyl phosphite in the Arbuzov reaction to yield diethyl acetylphosphonate has been reported along with the preparation of a cyanohydrin derivative.[1] It was desired to extend the Arbuzov reaction, which can be employed to prepare either alkyl- or acylphosphonates, to the preparation of unsaturated alkyl- or acylphosphonates.



$$\mathrm{P(OC_2H_5)_3 + RCOCl} \longrightarrow \left[\mathrm{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\overset{\oplus}{P}(OC_2H_5)_3\,\overset{\ominus}{Cl}}\right] \longrightarrow \mathrm{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{P}}(OC_2H_5)_2 + C_2H_5Cl}$$

R = methyl or vinyl

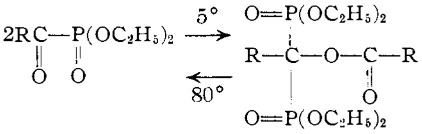
The acylphosphonates possess an active carbonyl group which can undergo many of the normal carbonyl reactions including formation of hydrazones with materials such as 2,4-dinitrophenylhydrazine.[1c] The phosphonates above can also be prepared by the procedure



$$\mathrm{(C_2H_5O)_2POAg + RCOCl \longrightarrow R\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{P}}(OC_2H_5)_2 + AgCl}$$

R = methyl or vinyl

The α-ketophosphonates prepared exhibited molecular weight properties which indicated that they could exist in an equilibrium between a monomeric and a postulated dimeric form. Other materials such as acetyl cyanide (pyruvonitrile) are known to form dimers easily. In the case of α-ketophosphonates the equilibrium is apparently reversible.

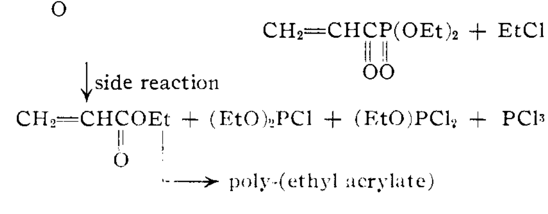


$$\mathrm{2R\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{P}}(OC_2H_5)_2 \underset{80^\circ}{\overset{5^\circ}{\rightleftharpoons}} R{-}\overset{\displaystyle O{=}P(OC_2H_5)_2}{\overset{|}{\underset{\displaystyle O{=}P(OC_2H_5)_2}{\underset{|}{C}}}}{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R}$$

monomer
R = methyl or vinyl dimer

The molecular weight of these compounds taken by a cryoscopic method in benzene at 5° showed them both to be essentially dimers, while ebullioscopic molecular weights in benzene at 80° indicated them to be all or largely monomeric. It is presumed that at room temperature they exist as some mixture of the two forms. Attempts to dimerize diethyl acetylphosphonate deliberately using alkaline catalyst were unsuccessful, however.

While the preparation of diethyl acetylphosphonate was relatively straightforward, the same method applied to the formation of diethyl acrylylphosphonate led to a rather large variety of products including the desired one. A possible side reaction that could occur in the reaction of acrylyl chloride and triethyl phosphite is



$$\mathrm{CH_2{=}CH\underset{\displaystyle O}{\underset{\|}{C}}Cl + P(OEt)_3 \xrightarrow[\text{desired}]{} CH_2{=}CH\underset{\displaystyle O}{\underset{\|}{C}}\underset{\displaystyle O}{\underset{\|}{P}}(OEt)_2 + EtCl}$$

$$\Big\downarrow \text{side reaction}$$

$$\mathrm{CH_2{=}CH\underset{\displaystyle O}{\underset{\|}{C}}OEt + (EtO)_2PCl + (EtO)PCl_2 + PCl_3}$$

$$\longrightarrow \text{poly-(ethyl acrylate)}$$

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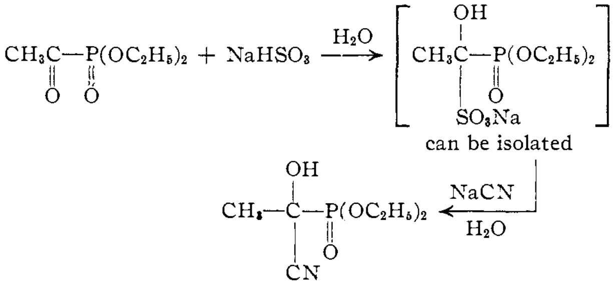
(1) (a) M. I. Kabachnik and P. A. Rossiiskaya, *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 364 (1945); *C. A.*, **40**, 4688 (1946); (b) M. I. Kabachnik, P. A. Rossiiskaya and E. S. Shepeleva, *ibid.*, 163 (1947); *C. A.*, **42**, 4133 (1948); (c) A. E. Arbuzov and M. M. Azanovskaya, *Doklady Akad. Nauk. S.S.S.R.*, **58**, 1961 (1947); *C. A.*, **46**, 8606 (1952).

The formation of many by-products was indicated by the numerous fractions obtained on distillation. This was also shown by the formation of resin in the still-pot and the study of the infrared spectra of all the products.

The infrared spectra of the various fractions from the preparative reaction for diethyl acrylylphosphonate were very complex and difficult to interpret. From the multiplicity of carbonyl and unsaturation bands, it was clear that a large number of by-products were being formed along with the desired diethyl acrylylphosphonate. It was impossible to assign a definite portion of this spectrum to diethyl acrylylphosphonate although a certain number of bands seemed to be associated most probably with the diethyl acrylylphosphonate molecule. There were, for example, five different types of carbonyl bands and four different unsaturation bands in the spectra of the fraction believed to be the diethyl acrylylphosphonate product. This fraction possessed the proper phosphorus analysis and molecular weight. Two of these carbonyl bands were strong. One corresponded to the normal acrylate ester band wave length. The other band was shifted to shorter wave lengths. It was assumed that the latter band was due to carbonyl adjacent to P=O. The normal ester band could have resulted from the dimeric form of diethyl acrylylphosphonate, the polymeric form thereof or from polyacrylates prepared by a polymerization of ethyl acrylate by-product. Unsaturation bands also varied with the different fractions. There was a relationship between the appearance and disappearance of carbonyl and unsaturation bands; however, due to the lack of pure authentic samples, no definite assignments could be given. There was no hydroxyl band present in the diethyl acrylylphosphonate spectra and only a small trace of P–H impurities.

Diethyl acrylylphosphonate prepared from silver diethyl phosphite had a similar spectrum to that from triethyl phosphite and acrylyl chloride, but more impurities were present. This caused more extraneous bands to appear which made difficult point-by-point comparison of the two diethyl acrylylphosphonate spectra. A similarity between the two was enough to conclude that diethyl acrylylphosphonate was formed by both reaction routes.

The carbonyl adjacent to the phosphonate can also undergo normal bisulfite addition followed by reaction with cyanide to form a normal cyanohydrin.[1b]



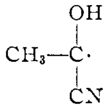
$$\underset{O}{\overset{}{CH_3C}}-\underset{O}{P}(OC_2H_5)_2 + NaHSO_3 \xrightarrow{H_2O} \left[CH_3\overset{OH}{\underset{SO_3Na}{C}}-\underset{O}{P}(OC_2H_5)_2\right] \xrightarrow[H_2O]{NaCN} CH_3-\overset{OH}{\underset{CN}{C}}-\underset{O}{P}(OC_2H_5)_2$$

can be isolated

The infrared spectrum of this material was rather anomalous in light of subsequent reactions of the product. The infrared spectrum of diethyl 1-cyano-1-hydroxyethylphosphonate showed no absorption in the hydroxyl region indicating no hydrogen bonded hydroxyl and the general unavailability of hydroxyl groups. This was confirmed by failure of the material to undergo acetylation upon refluxing with acetic anhydride for a prolonged period. The above spectrum also showed no absorption in the nitrile region. However, this evidence was contradicted by the production of acrylonitrile upon pyrolysis and the fact that cyanohydrins often show very weak or no infrared absorption in the nitrile region.[2]

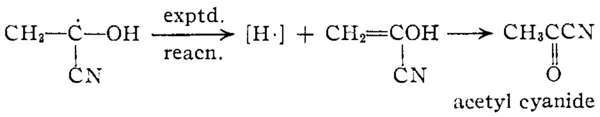
The successful dehydration or deacetylation of selected phosphonates would lead to vinyl monomers containing phosphorus. The relative weakness of the C–P bond (the slightly smaller energy needed to rupture this bond compared to that for C–H, C–C, C–O, etc., bonds) negates any hope of securing most vinyl monomers containing phosphorus by straight thermal or pyrolytic means.[3] It was found that the pyrolyses of diethyl 1-cyano-1-hydroxyethylphosphonate and 1,1-bis-(diethylphosphono)-ethyl acetate lead to acrylonitrile and acetic acid which are relatively thermally stable.

The pyrolysis of diethyl 1-cyano-1-hydroxyethylphosphonate produced an unexpectedly high yield of acrylonitrile (83%). It is thought that the C–P bond was the first to rupture during even mild pyrolysis, and the first species formed in the hot tube was probably



$$CH_3-\overset{OH}{\underset{CN}{C}}\cdot$$

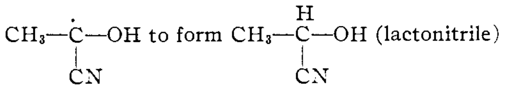
which could undergo several different reaction routes to give some stable product(s). (The phosphonate parts of the pyrolysis products were not identified.) Then



$$CH_3-\overset{\cdot}{\underset{CN}{C}}-OH \xrightarrow[\text{reacn.}]{\text{exptd.}} [H\cdot] + CH_2{=}\underset{CN}{C}OH \longrightarrow CH_3\underset{O}{C}CN$$

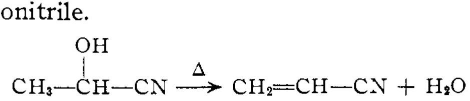
acetyl cyanide

While this reaction could lead to acetyl cyanide, the H· formed could combine with



$CH_3-\overset{\cdot}{\underset{CN}{C}}-OH$ to form $CH_3-\overset{H}{\underset{CN}{C}}-OH$ (lactonitrile)

which would undergo dehydration to the observed acrylonitrile.



$$CH_3-\overset{OH}{CH}-CN \xrightarrow{\Delta} CH_2{=}CH-CN + H_2O$$

This mechanism would assume the equal molar formation of acetyl cyanide and acrylonitrile. This was not apparently the case unless the acetyl cyanide so formed was essentially quantitatively reduced to lactonitrile which was then dehydrated to acrylonitrile. The presence of reducing materials (phosphorus containing) in the system as seen from subjective identification of phosphine type mate-

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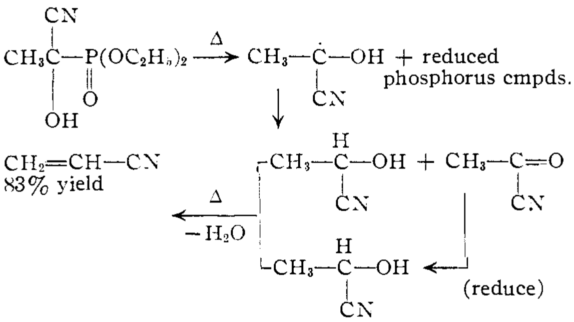
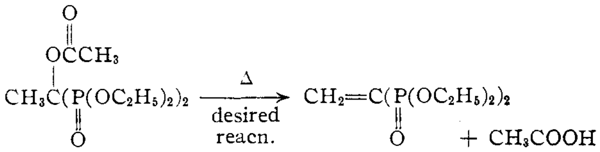
(2) R. E. Kitson and H. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

(3) L. C. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939; M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953).

rials, arising from the other half of the original molecule, makes the preparation of lactonitrile from pyruvonitrile feasible. The observed over-all reaction would thus be



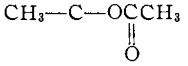
The pyrolysis of 1,1-bis-(diethylphosphono)-ethyl acetate gave an excellent yield of acetic acid (79%). The acetic acid could arise from two possible mechanisms. The desired reaction would give acetic acid as one product along with vinylidene di-(diethyl)-phosphonate. The relative weakness of



$$CH_3C(OCOCH_3)(P(O)(OC_2H_5)_2)_2 \xrightarrow[\text{desired reacn.}]{\Delta} CH_2{=}C(P(O)(OC_2H_5)_2)_2 + CH_3COOH$$

the C–P bond makes this reaction unlikely.

Acetic acid could also arise from the pyrolysis of vinyl acetate[4] which could be formed from the



$$CH_3{-}\ddot{C}{-}OC(O)CH_3$$

obtained by splitting of the C–P bonds in the pyrolyzed starting material.

Experimental

Diethyl Acetylphosphonate.—The general method of Kabachnik and Rossiiskaya[1] was followed using distilled triethyl phosphite (commercial triethyl phosphite contained undesirable ethyl alcohol, diethyl chlorophosphine and diethyl phosphonate impurities) and acetyl chloride to prepare colorless diethyl acetylphosphonate isolated by distillation at 90–111° (3.5 mm.) in a yield of 135.9 g. (76%), $n^{25}D$ 1.4240 (reported[1c], $n^{20}D$ 1.4207 and for the dimer $n^{20}D$ 1.4317).

Anal. Calcd. for $C_6H_{13}O_4P$: mol. wt., 180. Found: mol. wt., 205 (ebullioscopic in benzene); mol. wt., 352 (cryoscopic in benzene). Apparently this material exists as a dimer at 5°, while at 80° about 85% as a monomer.

The 2,4-dinitrophenylhydrazone had a m.p. 116–132° (reported[1c] m.p. 133.5–134°).

Anal. Calcd. for $C_{12}H_{17}N_4O_7P$: C, 40.00; H, 4.75; N, 15.55. Found: C, 39.97; H, 4.49; N, 15.81.

The residues from the distillation of diethyl acetylphosphonate were distilled to give a slightly yellowish oil, b.p. 175–176° (2 mm.) believed to be **1,1-bis-(diethylphosphono)-ethyl acetate**. Arbuzov and Azanovskaya[1c] found a product b.p. 158–162° (2–3 mm.) that they assumed to be the above dimer.

Attempts to dimerize diethyl acetylphosphonate deliberately using pyridine as a basic catalyst failed to give the desired product. Unchanged monomer and a black resin were isolated. Diethyl acetylphosphonate was also made by the reaction of acetyl chloride with silver diethyl phosphite.

The silver diethyl phosphite was prepared by the procedure of Milobendski and Szwejkowska[5] in a yield of 66% from diethyl phosphite and ammoniacal silver nitrate followed by careful neutralization with dilute nitric acid.

Diethyl acetylphosphonate was made by the reaction of a slurry in benzene of 15 g. (0.06 mole) of silver diethyl phosphite with a large excess (11.9 g.) of acetyl chloride. The silver chloride formed was removed by filtration and the benzene and excess acetyl chloride distilled *in vacuo* to yield 11 g. of a pale yellow oil containing no chlorine.

Comparison of the infrared absorption spectrum of this oil with that of a sample prepared from triethyl phosphite and acetyl chloride showed them to be essentially the same. There was about 10% acetic anhydride impurity in the product prepared by this silver salt method.

Diethyl Acrylylphosphonate.—This was prepared by a modification of the method used for diethyl acetylphosphonate and poly-(diethyl methacrylylphosphonate).[6] To 166 g. (1 mole) of distilled triethyl phosphite in a bath at −80° was added dropwise over a 30-minute period 90.5 g. (1 mole) of acrylyl chloride. Initially a colorless gelatinous precipitate formed which became a viscous yellow solution on warming. This suddenly altered to a very fluid and fuming system at a temperature still below 30° becoming progressively darker to a final brown-orange color. During this period the effluent gases were trapped and found to be essentially a quantitative amount of ethyl chloride containing small amounts of acrylyl chloride. This was proved conclusively using infrared spectra. The material was allowed to stand overnight and was then fractioned by vacuum distillation at low pressure. The fraction boiling in the range of 200–207° (5–10 mm.) was believed to be the desired product, $n^{25}D$ 1.4519. The subsequent infrared spectra of this and the other fractions make it clear that there were many by-products. As was seen with diethyl acetylphosphonate, this material also apparently exists as an equilibrium between all dimer at 5° and all monomer at 80° with both forms presumably present at room temperature.

Anal. Calcd. for $C_7H_{13}O_4P$: P, 16.2; mol. wt., 192. Found: P, 16.4; mol. wt. (ebullioscopic in benzene), 179; mol. wt. (cryoscopic in benzene), 384.

Diethyl acrylylphosphonate was also prepared by the reaction of silver diethyl phosphite and acrylyl chloride.

Diethyl 1-Cyano-1-hydroxyethylphosphonate.—This was made by the method of Kabachnik, Rossiiskaya and Shepeleva[1b] using diethyl acetylphosphonate and sodium bisulfite in distilled water. This mixture was treated with an aqueous sodium cyanide solution to yield an oily product. The oil was extracted with ether, dried, and distilled to give 56.3 g. (53%) of colorless product, b.p. 132° (3.3 mm.), $n^{25}D$ 1.4130.

Anal. Calcd. for $C_7H_{14}NO_4P$: C, 40.58; H, 6.81; N, 6.76. Found: C, 40.75; H, 6.72; N, 6.52.

Pyrolyses: Diethyl 1-Cyano-1-hydroxyethylphosphonate.—This material was pyrolyzed through a quartz tube over pieces of quartz tubing to 820° at 3–4 mm. pressure at a rate of 25 g./hour to give acrylonitrile in 83% yield. Decomposition began at 520°. The identity of the obtained acrylonitrile was established beyond doubt by comparison of its infrared spectrum with those of authentic samples of acetyl cyanide and acrylonitrile. Polyphosphorus compounds were also formed, but not identified.

1,1-Bis-(diethylphosphono)-ethyl Acetate.—Pyrolysis of this material using the same method as above at 770° at 2–6 mm. pressure at a rate of 15 g./hour did not yield as an isolable product the desired vinylidene di-(diethyl)-phosphonate. Acetic acid arising from the above reaction, or from the further pyrolysis of the expected product vinyl acetate,[4] was obtained in a 79% yield. It was identified by comparison of its infrared spectrum with that of an authentic sample. This product showed none of the dimer bands found in the spectrum of glacial acetic acid.

The other unidentified products of the pyrolysis were various phosphorus compounds including the phosphine type which flashed mildly when brought in contact with air.

Acknowledgments.—The authors wish to acknowledge the assistance given by Drs. N. A.

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[4] W. P. Ratchford, C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1864 (1944); W. P. Ratchford and C. H. Fisher, *Ind. Eng. Chem.*, **37**, 382 (1945).

[5] T. Milobendski and M. Szwejkowska, *Chem. Polsk.*, **15**, 56 (1917); *Chem. Zentr.*, **89**, I, 914 (1918).

[6] M. L. Ernsberger, U. S. Patent 2,491,920; *C. A.*, **44**, 2547 (1950).

Higgins and Ralph G. Beaman on direction of this research, by Dr. C. R. Bohn on the infrared analyses and their interpretations and by members of the analytical divisions of the Pioneering Research Laboratory.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENTS OF BIOCHEMISTRY AND UROLOGY, COLLEGE OF MEDICINE, STATE UNIVERSITY OF IOWA]

Phosphoramides Labeled with P^{32} which also Contain Phosphoric Acid Monoester Groupings

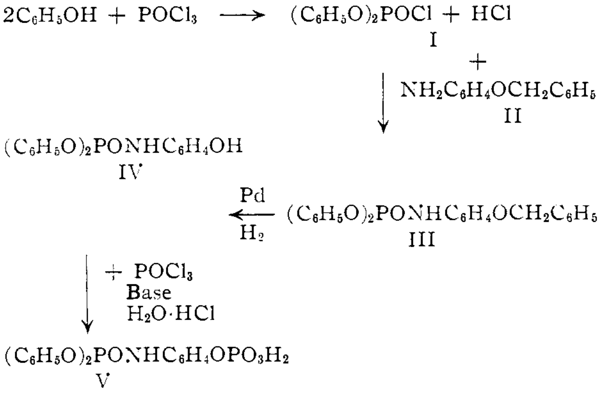
BY STANTON A. HARRIS[1] AND JOHN P. HUMMEL

RECEIVED DECEMBER 21, 1955

4-(O,O-Diphenylphosphoramido)-phenylphosphoric acid (D4P) in which the phosphoramido group has been labeled with P^{32} has been prepared for the purpose of testing its potential concentration in prostatic tissue.

In order to test the proposition that compounds having an orthophosphoric acid monoester grouping may be hydrolyzed by the acid phosphatase of the human prostate *in vivo*, it was desirable to synthesize phosphorylatable compounds insoluble in biological fluids and labeled with a radioactive element. If the phosphoric acid ester of such a compound were hydrolyzed by prostatic enzyme, the alcohol residue should be preferentially deposited in prostatic tissue. P^{32} was chosen because of its desirable radiation characteristics, chemical properties and ease of analysis. For this purpose it was necessary that the labeled phosphorus be bound in a manner that would make it relatively stable to the enzyme present in the body. Mixed ester amides of orthophosphoric acid were selected as the most readily obtainable compounds which possessed these characteristics. Finally it was necessary for these compounds to possess one or more hydroxyl groups which could be phosphorylated to form an ortho ester capable of being split by acid phosphatase.

The following syntheses have been carried out to produce these compounds



$$2C_6H_5OH + POCl_3 \longrightarrow \underset{\text{I}}{(C_6H_5O)_2POCl} + HCl$$

$$\text{I} + \underset{\text{II}}{NH_2C_6H_4OCH_2C_6H_5} \longrightarrow \underset{\text{III}}{(C_6H_5O)_2PONHC_6H_4OCH_2C_6H_5}$$

$$\text{III} \xrightarrow[H_2]{Pd} \underset{\text{IV}}{(C_6H_5O)_2PONHC_6H_4OH}$$

$$\text{IV} \xrightarrow{+\,POCl_3,\ \text{Base},\ H_2O{\cdot}HCl} \underset{\text{V}}{(C_6H_5O)_2PONHC_6H_4OPO_3H_2}$$

Compound V was first synthesized from unlabeled phosphorus oxychloride and its toxicity was determined. The synthesis was then repeated with P^{32}-labeled phosphorus oxychloride which was prepared from radioactive phosphoric acid by treating it with phosphorus pentachloride as described by Kalinsky and Weinstein.[2] This phosphoric acid ester, V, was insoluble in water and soluble in ethanol. After acidification with strong hydrochloric acid, the gummy acid was washed with water and dissolved in ethanol from which the cyclohexylamine salt was obtained readily. This salt apparently was a mixture of the mono- and diamine salts; therefore it was converted to the barium salt by shaking with barium acetate solution. The barium salt gave good analytical figures which proved the composition of compound V. The soluble sodium salt was easily obtained from the insoluble barium salt by shaking with a slight excess of sodium sulfate solution. The resulting colorless solution, after sterilization by filtration, proved to be satisfactory for intravenous or subcutaneous injections.

The results of the pharmacological and clinical testing of this compound will be described elsewhere. 4-(O,O-Diphenylphosphoramido)-phenylphosphoric acid (D4P) as its sodium salt was given intramuscularly to dogs and also to elderly men just previous to scheduled partial prostatectomies. A transient concentration of this compound was observed in prostatic tissue which was less than that found in liver, kidney, jejunum and lung, but higher than the concentrations which were found in most of the other tissues.

Acknowledgments.—The authors wish to acknowledge the use of the facilities of the Radiation Research Laboratory of the College of Medicine of the State University of Iowa and to thank Professor Titus C. Evans, Head of that laboratory, for his help and advice during the synthesis of the radioactive compounds.

The authors wish to thank Professor Rubin H. Flocks, M.D., Head of the Department of Urology, for his encouragement and sponsorship of this project.

Experimental

P^{32}-Labeled Diphenyl Phosphorochloridate[3] **(I)**.—Radioactive phosphorus oxychloride (5.49 g.) prepared by the method of Kalinsky and Weinstein[2] was heated with 6.75 g. of phenol in 15 ml. of xylene solution for 36 hours in an oil-bath at 160–170°. The product was transferred by suction

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[1] Visiting Professor at State University of Iowa for the school year of 1954–1955 while on leave-of-absence from Merck & Co., Inc., Rahway, New Jersey.

[2] J. L. Kalinsky and A. Weinstein, THIS JOURNAL, **76**, 5882 (1954).

[3] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 244.