Experimental

Methods.—The spectra reported were determined with a Beckman spectrophotometer, Model DU. Measurements were made at 1 mμ intervals throughout the critical ranges. The appropriate amounts of purines and triazolopyrimidines were dissolved in 100 cc. of water and diluted 1 to 10 with 0.1 *M* phosphate buffer. In the case of the pyrimidines the spectral determinations at *p*H 6 were made in the following manner: solutions were first prepared at *p*H 2 and then diluted 1 to 10 with phosphate buffer of *p*H 6.53 and the spectrum determined immediately.

Materials.—The purity of each compound (Tables I and II) was determined by the counter-current distribution method and each was shown to be homogeneous within experimental error (0.5 to 2.0%). All compounds were synthesized in this Laboratory with the exception of hypoxanthine which was a commercial sample and which was shown to contain about 3–4% adenine.

5,7-Diamino-1-*v*-triazolo[*d*]pyrimidine sulfate.—2,4,5,6-Tetraminopyrimidine sulfate (9 g.) was dissolved in 1500 cc. of boiling water. The solution was decolorized, filtered and cooled to about 15°. Sodium nitrite (2.8 g.) in 5 cc. of water was added. After fifteen minutes the product was collected by filtration. It was recrystallized from hot 2 *N* sulfuric acid. The resulting triazolopyrimidine sulfate was taken up in dilute ammonia, decolorized and filtered. To the clear solution was added 12 cc. of 18 *N* sulfuric acid and the sulfate precipitated. The mixture was heated until all the solid had gone into solution and the solution was again decolorized, filtered and cooled, yielding 2.2 g. of product. Another recrystallization from 2 *N* sulfuric acid gave a sample which was homogeneous when investigated by counter-current distribution.[5]

Anal. Calcd. for $(C_4H_5N_7)_2H_2SO_4$: S, 7.99. Found: S, 7.87.

5-Amino-7-hydroxy-1-*v*-triazolo[*d*]pyrimidine Hydrochloride.[15]—Ten grams of 2,4,5-triamino-6-hydroxypyrimidine sulfate was dissolved in 150 cc. of 18 *N* sulfuric acid. To the solution at 0° was added slowly 3 g. of sodium nitrite in 15 cc. of water. After two hours the solution was filtered and the residue discarded. The filtrate was brought to *p*H 5 with sodium hydroxide and the free triazolopyrimidine separated. The product was collected by filtration and dissolved in dilute aqueous ammonia. Acidification with glacial acetic acid produced a white precipitate (2.3 g.) which was recrystallized three times from 6 *N* hydrochloric acid.

Anal. Calcd. for $C_4H_4ON_6 \cdot HCl$: Cl, 18.80. Found: Cl, 18.75.

7-Amino-5-hydroxy-1-*v*-triazolo[*d*]pyrimidine Hydrochloride.—Ten grams of 4,5,6-triamino-2-hydroxypyrimidine sulfate was dissolved in 1500 cc. of boiling water, decolorized and filtered. The solution was cooled to room temperature and 3.4 g. of sodium nitrite in 10 cc. of water was added in several portions. The product was collected by filtration and reprecipitated from dilute aqueous ammonia by the addition of glacial acetic acid; yield 2 g. The base was recrystallized twice from 6 *N* hydrochloric acid.

Anal. Calcd. for $C_4H_4ON_6 \cdot HCl$: Cl, 18.80. Found: Cl, 18.95.

5,7-Dihydroxy-1-*v*-triazolo[*d*]pyrimidine.[16]—4,5-Diamino-2,6-dihydroxypyrimidine sulfate (1.7 g.) was dissolved in 375 cc. of boiling water and the solution decolorized. The solution was cooled to room temperature and 0.8 g. of sodium nitrite in 10 cc. of water was added. The mixture was allowed to stand overnight at room temperature and then evaporated to dryness under diminished pressure. The yellow residue was taken up in dilute ammonia, decolorized, reprecipitated with acetic acid, and recrystallized twice from water.

Anal. Calcd. for $C_4H_3O_2N_5$: N, 45.72. Found: N, 45.40.

The authors wish to thank Thelma Kaplan for assistance and Roscoe C. Funk, Jr., and Alice Angelos for analyses.

Summary

The ultraviolet absorption at various *p*H values of several pyrimidines, purines and triazolopyrimidines of known purity are presented. The variations of the spectra with certain substituents and the similarities of the spectra of the pyrimidines and the related purines and triazolopyrimidines are discussed. It is concluded that the ultraviolet absorption spectra of purines are due principally to the pyrimidine moiety and that the major chromophore in the pyrimidine ring is the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=N-$ system.

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[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

Reaction of Paraffin Hydrocarbons with Phosphorus Trichloride and Oxygen to Produce Alkanephosphonyl Chlorides

BY J. O. CLAYTON AND W. L. JENSEN[1]

In an investigation of organic phosphorus compounds a new synthetic method was discovered for producing phosphonyl chlorides from aliphatic hydrocarbons. On mixing open chain or cyclic aliphatic hydrocarbons with phosphorus trichloride and bubbling the mixtures with oxygen alkane or cycloalkanephosphonyl chlorides were produced.

Petroleum white oil, consisting of hydrocarbons containing branched paraffin chains and saturated, alicyclic rings offered the advantage of providing a mixture of types so that reaction could be more readily detected should the reaction rates be low for certain hydrocarbon types. A mixture of white oil and phosphorus trichloride was bubbled with oxygen until the initial temperature rise subsided. The resulting material was hydrolyzed with water and washed several times with water. This reaction product was found to be acidic and to contain phosphorus.

Pure hydrocarbons were also investigated in order to determine the type of reaction product, the nature of the reactants and the yields. Liquid open chain aliphatic hydrocarbons, cyclohexane, toluene and higher benzene homologs reacted to give phosphorus containing products but benzene did not react. Olefins reacted readily but, in the case of the lower molecule weight straight chain

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olefins, the products of reaction contained chlorine which would not hydrolyze with water indicating, probably, an addition of phosphorus trichloride across the double bond as described by Kharasch, Jensen and Urry.[2] The dichlorophosphine formed in these cases probably oxidized to the phosphonyl chloride. A polymer of *n*-butene having a molecular weight of 466 behaved like a paraffin yielding a reaction product which contained no chlorine after hydrolysis with water at room temperature.

An extension of the reaction method to propane gave a small yield of product when the hydrocarbon gas was mixed with oxygen and bubbled through phosphorus trichloride using a porous glass diffusion disc.

The resulting products appear to be alkanephosphonyl chlorides. Analytical results support this conclusion and the pure compounds react readily with water to yield dibasic acids having the properties of phosphonic acids. In work by one of the authors, to be reported in detail later, the reaction product derived from toluene was isolated and the melting point of the hydrolyzed product was found to agree with that published for phenylmethanephosphonic acid.[3]

The reaction of phosphorus trichloride in the absence of oxygen with aromatic hydrocarbons has been described by Michaelis and co-workers[4] and by Kosolapoff and Huber.[5] This reaction is slow in the absence of a catalyst and in the case of benzene good yields of phenyldichlorophosphine can only be obtained at very high temperatures. With benzene and toluene dichlorophosphines are formed by long-continued refluxing of the reactants in the presence of aluminum chloride. On the other hand, the present reaction is very rapid and does not involve reaction of the hydrocarbon with phosphorus trichloride followed by oxidation of the resulting dichlorophosphine to a phosphonyl chloride since under the conditions used the hydrocarbon will not react with phosphorus trichloride nor will it react with phosphorus oxychloride. Generally the yields of phosphonyl chlorides have been about 25% based on the phosphorus trichloride charged, while most of the phosphorus trichloride is converted to phosphorus oxychloride.

The effect of light on the reaction was investigated and found to have no appreciable influence on the yield. Thus, using petroleum white oil as the hydrocarbon the yield in the dark was found to be 23% (based on phosphorus trichloride), illuminated with a tungsten filament lamp 21, and illuminated with a mercury vapor, quartz lamp 21. The initial temperature in these experiments was about 25°, and the maximum temperature attained, due to heat liberation, was about 65°.

Sulfuric acid and iodine both prevented the formation of organic phosphonyl chlorides from petroleum white oil; aluminum chloride decreased the yield while acetyl peroxide and pyridine had no effect.

The substitution of phosphorus tribromide for phosphorus trichloride resulted in a total lack of reaction. No temperature increase was noted in passing oxygen through either a mixture of phosphorus tribromide and cyclohexane or through phosphorus tribromide alone. Distillation of the mixture using cyclohexane failed to reveal the presence of any reaction products.

Experimental

Reaction with Petroleum White Oil.—In eight experiments oxygen was bubbled through a mixture of petroleum white oil and phosphorus trichloride and the product hydrolyzed with water. The molecular weight of the hydrocarbon averaged about 500 and the aromatic content was essentially zero. In six of these experiments using equimolar weights of reactants the yields remained practically constant between 21 and 25% based on phosphorus trichloride in spite of variations in temperature, light intensity and total quantity of reactants. With molar ratios of phosphorus trichloride to hydrocarbon of 2.0 and 5.0 the yields were 18% and 15%, respectively.

Reaction with *n*-Heptane.—Forty-one grams (0.41 mole) of *n*-heptane (99% pure) was mixed with an excess (224 g., 1.64 moles) of phosphorus trichloride and bubbled, by means of a sintered glass plate, with oxygen at a slow rate for five hours. The maximum temperature was kept below 60° by means of a water-bath. The light yellow liquid was distilled at 10 mm. of mercury pressure discarding the phosphorus oxychloride boiling below 90° and collecting 28.1 g. between 106 and 108° and approximately 16 g. of residue. The narrow boiling fraction which could not be made to crystallize, was analyzed for phosphorus and chlorine.

Anal. Calcd. for $C_7H_{15}POCl_2$: P, 14.29; Cl, 32.67. Found: P, 14.54; Cl, 32.88.

Preparation of Phosphonic Acid from *n*-Heptane.—A second experiment was carried out in a similar manner except that equimolar amounts of *n*-heptane and phosphorus trichloride were used and the resulting acid chloride was hydrolyzed by pouring onto ice. The phosphonic acid was taken up in petroleum ether, dried with sodium sulfate and the ether removed by distillation. The liquid product was analyzed.

Anal. Calcd. for $C_7H_{17}PO_3$: P, 17.22; equivalent weight, 90.08. Found: P, 16.6; equivalent weight, 94.

A titration curve showed the acid to be dibasic with a dissociation constant for the first hydrogen of approximately $K_A = 10^{-4}$.

Reaction with 3-Methylpentane.—Because of the symmetry of 3-methylpentane it would be expected that a single isomer might result in this reaction if the rates of reactions for different types of hydrogens are markedly different. The failure of the reaction product of *n*-heptane to crystallize may have been due to a mixture of isomers, and for this reason the reaction product of 3-methylpentane was investigated. While the resulting phosphonyl chloride did not crystallize, the acid formed on hydrolysis did.

A mixture of 33.8 g. (0.39 mole) of technical 3-methylpentane and 269 g. (1.96 mole) of phosphorus trichloride was bubbled with oxygen until no further reaction was evident, distilled and a fraction weighing 29.0 g. boiling between 110 and 120° at a pressure of 16–18 mm. of mercury collected. This yellow, viscous oil was analyzed for phosphorus and chlorine.

Anal. Calcd. for $C_6H_{13}POCl_2$: P, 15.28; Cl, 34.93. Found: P, 15.15; Cl, 36.8.

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[2] Kharasch, Jensen and Urry, THIS JOURNAL, **67**, 1864 (1945).

[3] (a) Litthauer, *Ber.*, **22**, 2144 (1886); (b) Kosolapoff, THIS JOURNAL, **67**, 2259 (1945).

[4] Michaelis, *Ann.*, **181**, 280 (1876); Michaelis, *Ber.*, **12**, 1009 (1879); Michaelis and Paneck, *Ann.*, **212**, 206 (1882).

[5] Kosolapoff and Huber, THIS JOURNAL, **69**, 2020 (1947).

Preparation of 3-Methylpentanephosphonic Acid.—Sixteen grams of the acid chloride was hydrolyzed by adding to water and the resulting oil slowly crystallized. After recrystallization from water and drying under vacuum, it was a colorless, semi-solid material and further purification was not attempted.

Anal. Calcd. for $C_6H_{15}PO_3$: P, 18.67; equivalent weight, 83.07. Found: P, 18.60; equivalent weight, 83.09.

The acid was dibasic with a dissociation constant for the first hydrogen of approximately $K_A = 10^{-4}$.

Reaction with Cyclohexane.—Forty-two grams (0.5 mole) of cyclohexane (95% pure) was mixed with 274 g. (2.0 moles) of phosphorus trichloride and bubbled with oxygen until the exothermic reaction was over. The mixture was distilled at 10–15 mm. of mercury pressure and a fraction weighing 49 g. was taken boiling between 115 and 130°. This was redistilled at 15 to 16 mm. of mercury pressure and yielded 36 g. of a colorless liquid boiling between 127.5 and 128.2° which after a short time crystallized to needles with the following properties: d^{20} (supercooled liquid) 1.2955 g./cc., n^{20}_D (supercooled liquid) 1.5059, freezing point (cooling curve) 37.0–37.5°.

Anal. Calcd. for $C_6H_{11}POCl_2$: C, 35.80; H, 5.47; P, 15.43; Cl, 35.28. Found: C, 35.58; H, 5.65; P, 15.35; Cl, 34.95.

Preparation of Cyclohexanephosphonic Acid.—Twenty-six grams of cyclohexanephosphonyl chloride was poured into water, stirred and gently heated. The water was then evaporated until crystallization occurred on cooling. The solid was filtered off, dried in vacuum and the melting point determined (160–163°). It was recrystallized five more times from water using Norite to remove color. The following properties were determined: m. p. 166–167°, K_A(1st H) 4 × 10^{-5}, K_A(2nd H) 2 × 10^{-10}.

Anal. Calcd. for $C_6H_{13}PO_3$: C, 43.87; H, 7.99; P, 18.90. Found: C, 42.27; H, 7.98; P, 18.91. (Low carbon values were obtained on several repetitions of carbon–hydrogen analysis. It was noted that this compound on burning left a black colored glaze on porcelain ware and the low carbon determinations are believed to be due to colloidally dispersed carbon contained in the glaze.)

Reaction with Propane.—A mixture of oxygen and propane was bubbled through phosphorus trichloride until the heat effect had subsided. Distillation yielded phosphorus oxychloride and a small amount of higher boiling material which hydrolyzed to a dibasic acid with an equivalent weight of 64. The calculated equivalent weight of propanephosphonic acid is 62.0.

Summary

A new synthesis for alkane- and cycloalkanephosphonyl chlorides is described. The method involves the reaction of a hydrocarbon with phosphorus trichloride and oxygen, and has been used in the synthesis of several new alkane- and cycloalkanephosphonyl chlorides and phosphonic acids, properties of which are presented.

Richmond, California Received April 14, 1948

[Contribution from the Research Laboratory, Victor Chemical Works]

The Preparation of Tetraethyl Pyrophosphate and Other Tetraalkyl Pyrophosphates

By A. D. F. Toy

Introduction

The chemistry of the inorganic polyphosphates is quite well established, but very little is known concerning the organic polyphosphates. The discovery by German chemists that the so-called "hexaethyl tetraphosphate"[1,2,3] is of value as an economic poison has shown the necessity for more extended research on the organic polyphosphates. Earlier investigation of the organic polyphosphates in this Laboratory had already led to the development of a superior process[4,5] for the synthesis of hexaethyl tetraphosphate. This process involves the interaction of phosphoric anhydride with triethyl phosphate and yields a product having properties identical with that made by the Schrader[1] process. Subsequent research had shown that hexaethyl tetraphosphate is not a pure compound but consists of a mixture of several ethyl polyphosphates. This conclusion was also verified by Hall and Jacobson.[6]

Our investigations were therefore extended to the ethyl esters of other phosphoric acids, including pyro- and triphosphoric acids. During the course of these studies we found that tetraethyl pyrophosphate is a much more toxic substance than the so-called "hexaethyl tetraphosphate." This same fact was reported independently by Ludvik and Decker.[7]

The preparation of pure vacuum distillable tetraethyl pyrophosphate has been described by several investigators. Arbuzov and Arbuzov[8] claimed to have obtained it in very small yield when they fractionally distilled a complex mixture resulting from the action of bromine or chlorine on diethyl sodium phosphite. Hall and Jacobson found that the method described by Cavalier[9] and Clermont[10] which involves the action of silver pyrophosphate on ethyl iodide also produces distillable tetraethyl pyrophosphate in low yield. Distillable tetraethyl pyrophosphate may also be obtained in 20–30% yield by extraction with chloroform or benzene of the partially hydrolyzed non-distillable ethyl polyphosphates produced by the modified Schrader or Woodstock processes.[6] The acidic components of these mixtures are removed in the aqueous layer; the tetraethyl pyrophosphate is recovered by the fractional distillation of the organic extract.

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(1) Schrader, German Patent 720,577 (1942); U. S. Patent 2,336,302 (1943).

(2) Hall, P. B. Rept. 252 (1945).

(3) Kilgore, *Soap and Sanit. Chemicals*, [12] **21**, 138 (1945).

(4) Woodstock, U. S. Patent 2,402,703 (1946).

(5) Adler and Woodstock, *Chem. Ind.*, **51**, 516 (1942).

(6) Hall and Jacobson, *Ind. Eng. Chem.*, **40**, 694 (1948).

(7) Ludvik and Decker, *J. Econ. Entomol.*, **40**, 97 (1947).

(8) Arbuzov and Arbuzov, *J. prakt. Chem.*, **130**, 103 (1931); *Ber.*, **65**, 195 (1932).

(9) Cavalier, *Compt. rend.*, **142**, 885 (1906).

(10) Clermont, *Ann. chim.*, **44**, 330 (1855).