[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Preparation of Phosphonyl Chlorides by the Reaction of Hydrocarbons with Phosphorus Trichloride and Oxygen

BY W. L. JENSEN AND C. R. NOLLER

A previous publication[1] reported the preparation of organic phosphorus compounds by a new method in which a paraffin hydrocarbon reacts with phosphorus trichloride and oxygen to give alkanephosphonyl chlorides.

$$RH + PCl_3 + {}^1/_2O_2 \longrightarrow RPOCl_2 + HCl$$

Concurrently phosphorus trichloride is oxidized to phosphorus oxychloride.

$$PCl_3 + {}^1/_2O_2 \longrightarrow POCl_3$$

The investigation of this reaction has been continued to determine its ramifications and limitations.

In the reaction of cyclohexane, it was noted that hydrolysis of the residue remaining after removal of unreacted reagents and phosphorus oxychloride gave only 60–75% of the amount of cyclohexanephosphonic acid expected from the weight of the residue, assuming it to be cyclohexanephosphonyl chloride. From the mother liquors a second material has been isolated which was difficult to obtain in solid form and which potentiometric titration curves indicate is a diphosphonic acid. The product undoubtedly is a mixture of the three possible isomers. Because of decomposition, it was not possible to isolate by distillation at reduced pressure either the diphosphonyl chlorides or esters prepared from them.

It has been reported[1] that benzene does not enter into this reaction, but that toluene gives a phosphonyl chloride from which a crystalline phosphonic acid has been obtained. All of the monophosphonic acids of toluene are known, and the melting point of the phosphonic acid from toluene agreed with that of phenylmethanephosphonic acid.[2] Similarly the phosphonic acid isolated after hydrolysis of the reaction product from ethylbenzene had the properties of β-phenylethanephosphonic acid.[3] In this case identity was proven by direct comparison with a sample of β-phenylethanephosphonic acid prepared by the procedure of Kosolapoff.[4] Hydrolysis of the reaction products from *n*-propyl benzene and *s*-butylbenzene gave acids which could not be crystallized. Apparently as in the case of *n*-heptane, a mixture of isomers is obtained which does not crystallize.

A crystalline acid corresponding to diphenylmethanephosphoric acid was obtained by hydrolysis of the reaction products of diphenylmethane. Triphenylmethane, however, did not react. The yield of the monophosphonic acid from toluene was 13% and from diphenylmethane 2.3%. Apparently increasing the number of phenyl groups decreases the reactivity of the hydrogen on the carbon atom adjacent to the ring. The inhibiting action of the phenyl group is evident also from the fact that a 11% yield of β-phenylethanephosphonic acid was obtained from ethylbenzene and none of the α-isomer was isolated.

Neopentane is of interest since, as in the case of cyclohexane, only one monosubstitution product is possible, and the phosphonic acid should be obtained readily in pure form. In fact, pure neopentanephosphonic acid was isolated in 22% yield. An impure diphosphonic acid also was isolated.

It would be very desirable to be able to locate the position of the phosphonyl group by replacement by another functional group to give a compound of known constitution. Attempts in this direction have been unsuccessful. At present the only procedure available is direct comparison with phosphonic acids synthesized by other methods.

Experimental

Cyclohexanediphosphonic Acid.—Evaporation of the mother liquors from which cyclohexanephosphonic acid had been isolated gave a tacky residue which partially solidified on standing. The solid was separated, dried in a vacuum desiccator and extracted with hot acetone to remove cyclohexanephosphonic acid. The residue decomposed at 233° and was very soluble in cold water. Potentiometric titration indicated an equivalent weight of 63 assuming that the first inflection corresponded to two equivalents of alkali. The calculated value for a diphosphonic acid is 61.

Anal.[5] Calcd. for $C_6H_{14}O_6P_2$: P, 25.38. Found: P, 25.03, 24.92.

Phenylmethanephosphonic Acid.[2]—Oxygen was bubbled through a mixture of 32.3 g. (0.35 mole) of toluene and 192 g. (1.40 moles) of phosphorus trichloride at 40–50° until a drop in temperature indicated that the reaction was complete. The phosphorus oxychloride and most of the unchanged toluene were removed by distillation at reduced pressure, and the residue was hydrolyzed. The remaining toluene was separated and the water layer evaporated almost to dryness. The crystals which separated were removed and weighed 7.7 g. (12.8% yield based on toluene). Two crystallizations from water, including decolorization with Norite, gave a product, m. p. 167.4–169.0°. Letts and Blake[2] report 169–169.5° as the melting point for phenylmethanephosphonic acid. Potentiometric titration indicated that it was a dibasic acid with an equivalent weight of 88.8 compared with the calculated value of 86.

β-Phenylethanephosphonic Acid.—Applying the above procedure to ethylbenzene an 11% yield of β-phenylethanephosphonic acid was obtained which melted at 136–138°. The observed equivalent weight was 94 and the calculated

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[1] Clayton and Jensen, THIS JOURNAL, **70**, 3880 (1948).

[2] Litthauer, *Ber.*, **22**, 2144 (1889); Letts and Blake, *Trans. Roy. Soc. Edinburgh*, **35**, 612 (1890); Kosolapoff, THIS JOURNAL, **67**, 2259 (1945).

[3] Bergmann and Bondi, *Ber.*, **63**, 1158 (1930).

[4] Kosolapoff, THIS JOURNAL, **67**, 1180 (1945).

[5] Microanalyses by C. W. Koch, Albany, Calif.

value 93. A sample prepared by the method of Kosolapoff[4] melted at 136.5–138° and did not depress the melting point of the compound prepared from ethylbenzene.

Diphenylmethanephosphonic Acid.—An approximately 2% yield of this acid was obtained by the usual procedure from diphenylmethane. It melted at 234–237° and titration indicated an equivalent weight of 123 compared with the calculated value of 124.

Anal. Calcd. for $C_{13}H_{13}O_3P$: P, 12.48. Found: P, 12.2, 12.55.

When triphenylmethane was treated in the same way, it was recovered unchanged and no phosphonic acid could be isolated.

Neopentanephosphonic Acid and Neopentanediphosphonic Acid.—The reaction of neopentane[6] was carried out at 0° and gave rise to a 22% yield of the monophosphonic acid. After crystallization from carbon tetrachloride it melted at 140–141.5°. Titration gave an equivalent weight of 79 compared with the calculated value of 76.

Anal. Calcd. for $C_5H_{13}O_3P$: P, 20.37. Found: P, 20.27, 20.46.

The aqueous filtrate remaining after removal of the monophosphonic acid was evaporated to dryness. The residue was an oil which slowly solidified. No suitable solvent was found for crystallization, but successive extractions at the boiling point of the solvent with ether, benzene, and acetone, followed by solution in dioxane and precipitation with ether gave a white product that melted at 160–167°. It behaved like cyclohexanediphosphonic acid on potentiometric titration, and the observed equivalent weight was 61. The calculated value is 58.

Anal. Calcd. for $C_5H_{14}O_6P_2$: P, 26.69. Found: P, 26.92, 26.86.

Summary

In the reaction of cyclohexane and neopentane with phosphorus trichloride and oxygen, diphosphonyl chlorides are formed in addition to the monosubstitution products. When mixed aromatic aliphatic hydrocarbons react, substitution in the aliphatic side chain takes place. The ease of substitution on the methane carbon atom as determined by the yield of monophosphonic acid decreases with increasing number of aryl groups. In the case of ethylbenzene substitution takes place on the β-carbon atom of the side-chain. With larger alkyl side chains mixtures appear to be formed.

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[6] A sample of neopentane of 99% purity was supplied by the California Research Corporation.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

A New Method for the Preparation of Disodium Dihydrogen Hypophosphate

BY ELMER LEININGER AND THOMAS CHULSKI[1]

Hypophosphates offer the possibility of a number of analytical applications particularly to the separation and determination of some of the quadrivalent elements including thorium, since their hypophosphates are very insoluble in acid solution.

These applications would be greatly facilitated if good methods for the preparation and determination of hypophosphates were available. While investigating these possibilities it was noted that red phosphorus reacts vigorously with a solution of sodium chlorite. The only reference to this reaction found in the literature was the statement that a solution of chlorous acid instantly dissolves red phosphorus.[2] However, the products formed were not mentioned. Therefore the solution resulting from the reaction of red phosphorus with a sodium chlorite solution was tested and found to contain hypophosphorous, phosphorous, hypophosphoric and orthophosphoric acids. A relatively high yield of hypophosphoric acid was apparent upon neutralization with sodium hydroxide by the precipitation of crystalline disodium dihydrogen hypophosphate hexahydrate. On the basis of this reaction, a new method for the preparation of this salt has been developed. Volumetric methods for the determination of hypophosphate will be presented in another paper.

Most of the methods found in the literature for the formation of hypophosphates depend upon the oxidation of yellow or red phosphorus. In these reactions some of the phosphorus is oxidized to each of the higher oxidation states and the yield of hypophosphate is low.

Yellow phosphorus may be oxidized by air[3] or by cupric nitrate.[4,5] The air oxidation is slow and the cupric nitrate method involves the evolution of large quantities of phosphine.

Red phosphorus may be oxidized by hypochlorites,[6,7] alkaline permanganate,[8] hydrogen peroxide[8] or iodine.[9] The use of red phosphorus is more desirable; however none of these reactions has been adapted to the preparation of hypophosphate in quantity.

The phosphorus trihalides, upon hydrolysis and treatment with iodine, yield some hypophosphate.[9] A method involving the electrolytic oxidation of a metallic phosphide to hypophosphate has been reported.[5]

Experimental

Apparatus and Materials.—Since the reaction between red phosphorus and sodium chlorite may become very

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[1] Present address: Lindsay Light and Chemical Company, West Chicago, Ill.

[2] Schiel, *Ann.*, **109**, 317 (1859).

[3] Van Name and Huff, *Am. J. Sci.*, **46**, 587 (1918).

[4] Jung, *Asoc. quim. Argentina*, **30**, 99 (1942).

[5] Rosenheim and Pinsker, *Z. anorg. Chem.*, **64**, 327 (1909).

[6] Probst, *Z. anorg. u. allgem. Chem.*, **179**, 155 (1929).

[7] Speter, *Rec. trav. chim.*, **46**, 588 (1927).

[8] Vogel, *Z. angew. Chem.*, **42**, 263 (1929).

[9] Kolitowska, *Roczniki Chem.*, **16**, 313 (1936); **17**, 616 (1937); *Z. anorg. u. allgem. Chem.*, **230**, 310 (1937).