

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

The Phosphonation of Aromatic Compounds with Phosphoric Anhydride¹

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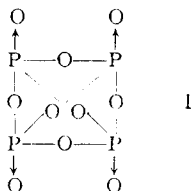
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Benzene, chlorobenzene, *o*-xylene and naphthalene are phosphonated by hexagonal phosphoric anhydride in a temperature range of about 275–325°. A primary reaction product is formed by addition of one molecule of the aromatic compound to one molecule of P_4O_{10} with opening of a covalent P–O bond. In the cases of chlorobenzene, *o*-xylene and naphthalene there are also formed secondary reaction products which are phosphonic anhydrides of the type $(ArPO_2)_x$. The primary reaction products are insoluble in the aromatic compound while the secondary ones are soluble. Both the primary and the secondary products give the phosphonic acid when hydrolyzed and the phosphonic dichloride when chlorinated with phosphorus pentachloride.

While the sulfonation and nitration of aromatic compounds belong to the most widely used and best investigated organic reactions, a corresponding phosphonation of the aromatic nucleus by the aid of phosphoric acid or one of its anhydrides has never been accomplished so far.² Using specific conditions we have succeeded in phosphonating aromatic compounds with hexagonal phosphoric anhydride.

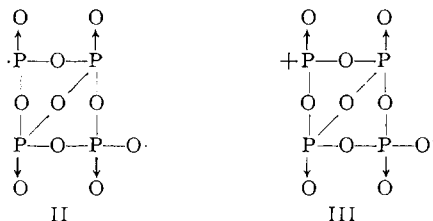
According to Hill, Faust and Hendricks,³ phosphoric anhydride exists in three crystalline modifications. The commercial "phosphorus pentoxide" consists predominantly of a metastable crystal form belonging to the rhombohedral division of the hexagonal system. There is another metastable orthorhombic form and a stable tetragonal form. The conversion of the hexagonal metastable form into the other two forms is immeasurably slow at room temperature. At 180° the conversion into the orthorhombic form takes about 60 days, but it takes only about 60 minutes at 378°. By interpolation one may conclude that the conversion of the hexagonal form into the orthorhombic form would progress at a reasonable rate in a temperature range between 250 and 325°. It is also within this temperature range that the vapor pressure of hexagonal phosphoric anhydride becomes noticeable, being, e.g., at 216.2° only 0.5 cm., but at 253° 2.2 cm., at 278.4° 5.5 cm., at 300.9° 12.3 cm., and at 324.8° 27.2 cm.⁴

The structure of hexagonal phosphoric anhydride, P_4O_{10} , has been determined by electron diffraction studies⁵ as



On the other hand, the orthorhombic and tetragonal forms represent macromolecules as has been

shown by de Decker⁶ and by MacGillavry, de Decker and Nijland.⁷ It is therefore clear that the conversion of the hexagonal form into the orthorhombic form must start with the breaking of one of the covalent P–O bonds, which might result either in a biradical II or, more probably, in a hybrid ion III.



Either one should react with aromatic compounds and the reaction of the latter should result in an electrophilic substitution corresponding to that caused by the nitronium ion $+NO_2$.

We have investigated the reaction of pure commercial phosphoric anhydride with some aromatic compounds⁸ at various temperatures and have found that at temperatures below 250° the substitution reactions take place only to a minor extent, but that generally in a temperature range of 250 to 325° these reactions do take place and organophosphorus compounds are formed.

The optimum conditions for the reaction of benzene with phosphoric anhydride are a temperature of about 275° and a reaction time of about 24 hours, the reaction being carried out in an autoclave with shaking or stirring. The contents of the cooled autoclave consist of a dark, brittle pitch and unchanged benzene. The weight of the pitch corresponds approximately to the sum of the phosphoric anhydride used plus one molecular equivalent of benzene for each molecular equivalent of P_4O_{10} . Its solution in ice-water does not contain the hydrolysis product of phosphoric anhydride, i.e., tetrametaphosphoric acid, nor does it contain orthophosphoric acid. However, when the aqueous solution is boiled for a short time, complete hydrolysis takes place and afterwards the solution does contain orthophosphoric acid.

It is very probable that this primary reaction product, which is the main constituent of the above mentioned pitch, has the formula V

(1) Presented at the 124th National ACS Meeting in Chicago, September 7, 1953.

(2) According to F. Jostes and J. Cronjé, *Ber.*, **71B**, 2335 (1938), the brick-red products obtained by H. Giran, *Compt. rend.*, **126**, 592 (1898), and **129**, 964 (1899), from commercial benzene and phosphoric anhydride are due to the former's thiophene content.

(3) W. L. Hill, G. T. Faust and S. B. Hendricks, *THIS JOURNAL*, **65**, 794 (1943).

(4) J. C. Southard and R. A. Nelson, *ibid.*, **59**, 911 (1937).

(5) G. C. Hampson and A. J. Stosick, *ibid.*, **60**, 1814 (1938). X-Ray diffraction pattern and crystal structure, cf. H. C. J. de Decker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941).

(6) H. C. J. de Decker, *ibid.*, **60**, 413 (1941).

(7) C. H. MacGillavry, H. C. J. de Decker and L. M. Nijland, *Nature*, **164**, 448 (1949).

(8) The aromatic compounds must be free of substituents (such as OH, NH_2 , COOH, etc.) which *per se* would react with P_4O_{10} .