[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

Orientation in Aromatic Compounds of Phosphorus. II. Nitration of Diethyl Benzenephosphonate

BY GENNADY M. KOSOLAPOFF

Although the results of nitration of benzenephosphonic acid have been reported,[1,2] the esters of this acid have not been subjected to this reaction. A study of the aromatic reactions of such esters is of importance because of the ready availability of these derivatives by the modified Friedel–Crafts reaction.[3] In addition, the observations on the possible effect of the ester grouping, in comparison with the free acid, may be expected to be of interest.

Nitration of benzenephosphonic acid with fuming nitric acid has been reported to yield the *m*-nitro isomer.[2] The early work of Michaelis and his co-workers,[1] in which the product was separated from the unreacted material by a tedious crystallization of its barium salt, indicated the formation of a product, which melted at 140°, described as the para-derivative, without further proof of structure. Nijk,[2] in making a more thorough investigation, showed that the compound reported by Michaelis was the *m*-isomer; it should be noted that the yield of the purified product was only 50–60%.[2]

Preliminary experiments indicated that diethyl benzenephosphonate nitrates much more sluggishly than dibutyl benzylphosphonate[4] in the cold with either fuming nitric acid or with mixed acid. Satisfactory nitration was performed, however, with fuming nitric acid at somewhat above room temperature. Separation of the nitrated product from the original material was readily accomplished by fractional distillation. The boiling point spread of more than thirty degrees permitted a much more rapid and convenient method for the separation of unreacted material than the previously reported procedures.[1,2] The product of nitration showed a boiling range of several degrees, which indicated the presence of isomeric nitro derivatives; this range was much too narrow, however, for a practical separation of the isomers by distillation. The nitrated product, therefore, was either hydrolyzed to the free acid (mixture) and the latter reduced to the amino derivative, or first reduced to the amino acid ester (mixture) and then hydrolyzed. The results were identical in either case: 3-aminobenzenephosphonic acid was isolated in pure state along with the 2-amino isomer, which could not be obtained completely free from the 3-isomer. The over-all yield of the amino acid mixture from the nitro ester averaged 86%. Although the *p*-amino isomer was not detected, the formation of the *p*-nitro compound in the nitration mixture is not excluded, because of the possibility of decomposition of the phosphanilic acid. Unfortunately, no data on such decomposition are available at this time; however, it has been noted that the yields of phosphanilic acid are severely reduced if the ammonolysis, used in its synthesis, is unduly prolonged. It is of interest to note that the mixture of the nitrobenzenephosphonic acids melts at the same temperature as the *m*-nitro isomer, as reported by Nijk,[2] and several attempts to separate this mixture by crystallization (from water or from organic solvents), were fruitless. This fact calls for a re-examination of the nitration products of the free acid, particularly in view of the fact that the total yield of positively identified products from such nitrations has been far below the theoretical.

Experimental Part

Nitration of Diethyl Benzenephosphonate.—Nitration of the ester under previously reported conditions[4] gave but 15–20% conversions. However, addition of 42.8 g. (0.2 mole) of diethyl benzenephosphonate to 130 ml. of fuming nitric acid (d. 1.5) over one hour at 30–35° and stirring at this temperature for one hour, followed by quenching with ice-water, washing with water and dilute sodium carbonate solution (after dilution with 300 ml. of benzene), and distillation *in vacuo*, resulted in isolation of the nitration products in the form of a pale yellow liquid, which boiled at 135–145° at 0.5 mm.; the original ester boils at 99–100° at 0.5 mm. In several experiments the average yield of the product was 35 g. (67.5%), with recovery of 7 g. of unreacted ester.

Identification of the Products.—Reduction of the nitrated product (15 g.) by addition to a mixture of 38 g. of iron filings and 45 ml. of 8% acetic acid with vigorous stirring at 60–70°, followed by stirring at 80° for forty-five minutes, resulted in isolation, after neutralization with sodium carbonate, extraction with benzene and washing with water, of the isomer mixture of diethyl aminobenzenephosphonates in the form of an oil, which could not be distilled or crystallized. Hydrolysis of this mixture by boiling concentrated hydrochloric acid (150 ml.) for four hours, followed by the removal of the bulk of hydrochloric acid *in vacuo* and careful neutralization of the residue to a weak congo red end-point by means of sodium carbonate, gave 8.6 g. (86%) of the mixed 2- and 3-aminobenzenephosphonic acids, in the form of a colorless, very sparingly soluble, crystalline powder. The decomposition range, 290–296°, of this material indicates the absence of appreciable amounts of the para isomer, which develops a characteristic blue decomposition color at lower temperatures. In addition, its characteristic acetyl derivative could not be detected following Bauer's method of preparation.[5]

Treatment of this mixture (1.73 g.), in water containing just enough hydrochloric acid to give a clear solution, with bromine resulted in isolation of 0.9 g. of 2,4,6-tribromoaniline (27%), m. p. 118°, and 2.5 g. of 2,4,6-tribromo-3-aminobenzenephosphonic acid (61%), which decomposed at 222–223° (Nijk[2] reports 222°). The former substance forms as a result of dephosphonation of

(1) Michaelis, *Ber.*, **8**, 493 (1875); Michaelis and Benzinger, *Ann.*, **188**, 278 (1877).

(2) Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

(3) Kosolapoff and Huber, THIS JOURNAL, **69**, 2020 (1947).

(4) Kosolapoff, THIS JOURNAL, **71**, 1876 (1949).

(5) Bauer, THIS JOURNAL, **63**, 2137 (1941).

2-aminobenzenephosphonic acid. Repeated fractional crystallization of the amino acid mixture from water resulted in isolation of the 3-isomer, in the form of colorless needles, which decomposed at 290–292° (heated block); this product gave no detectable amounts of tribromoaniline on treatment with bromine water. The 2-isomer could not be freed of the 3-isomer completely and the material always gave small amounts of the above-mentioned tribromoaminobenzenephosphonic acid with bromine water, in addition to the normally expected tribromoaniline; this imperfect material showed a decomposition range of 294–296° (heated block).

Hydrolysis of the mixed diethyl nitrobenzenephosphonates (20 g., 0.0775 mole) by boiling with concentrated hydrochloric acid (175 ml.) for five hours resulted in isolation of 11–12.5 g. (78.5–89.5%) of the free acid mixture, which after crystallization from benzene–ether–ligroin mixture melted at 138–139°. This mixture, in the form of fine, almost colorless needles, could not be resolved into its components by crystallization. Reduction with alkaline sulfide, according to the previously described procedure,[6] gave the amino acid mixture similar to the one described above.

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Summary

Nitration of diethyl benzenephosphonate results in the formation of appreciable amounts of the *o*-nitro isomer, along with the *m*-nitro isomer.

(6) Kosolapoff, THIS JOURNAL, **69**, 2112 (1947).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Some Steric Effects of the Cyclohexyl Group in Organosilicon Compounds

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In earlier studies[3,4] the writers found that chlorotricyclohexylgermane, $(C_6H_{11})_3GeCl$, was the sole product of the action of a large excess of cyclohexyllithium upon germanium tetrachloride, no tetracyclohexylgermane apparently being formed. However, the halogen atom of this substituted germane was found to be replaceable by normal alkyl, benzyl and phenyl groups. Attempts to substitute the chlorine atom by the sterically hindered isopropyl, cyclohexyl and *o*-tolyl groups were unsuccessful.

Efforts to prepare tricyclohexylphenylsilane, $(C_6H_{11})_3SiC_6H_5$, by the action of a large excess of cyclohexylmagnesium bromide on phenyltrichlorosilane were reported as unsuccessful by Cusa and Kipping.[5] Instead of the expected tricyclohexyl derivative, they obtained dicyclohexylphenylsilane, $(C_6H_{11})_2SiH\cdot C_6H_5$. This compound was brominated and then alkylated, using ethylmagnesium bromide at 160–180° to form dicyclohexylphenylethylsilane. The failure to obtain tricyclohexylphenylsilane was attributed to the steric effect associated with the cyclohexyl group.

These results led the authors to investigate the extent of substitution of the cyclohexyl group in the silane molecule by the use of cyclohexyllithium upon silicon tetrachloride. Under conventional experimental conditions three cyclohexyl groups are substituted for chlorine atoms in the reaction of cyclohexyllithium in large excess with silicon tetrachloride.

$$3C_6H_{11}Li + SiCl_4 \longrightarrow (C_6H_{11})_3SiCl + 3LiCl$$

The reaction of the tricyclohexylsilicon compound, however, differed from its germanium analog in that efforts to replace the chlorine atom by methyl, ethyl and phenyl groups were unsuccessful.

$$(C_6H_{11})_3SiCl + RLi \longrightarrow \text{No reaction}$$

Both Grignard and organolithium compounds were employed as alkylating agents and the ether was replaced by higher boiling solvents in an endeavor to force the reaction. In addition, since the Si–Br bond is reported[6] as weaker than the Si–Cl bond, bromotricyclohexylsilane was prepared and its alkylation attempted but still no evidence of further substitution was observed.

Chlorotricyclohexylsilane failed to respond to sodium condensation in boiling toluene, whereas bromotricyclohexylgermane condensed to form hexacyclohexylgermane,[3] $(C_6H_{11})_3Ge–Ge(C_6H_{11})_3$, under similar conditions.

Chlorotricyclohexylsilane was reduced to tricyclohexylsilane, $(C_6H_{11})_3SiH$, by lithium aluminum hydride in ether solution. This silane was brominated and iodinated to form the corresponding halides. Hydrolysis of the chloride yielded tricyclohexylsilanol, $(C_6H_{11})_3SiOH$, which was esterified by boiling with acetic anhydride to form acetoxytricyclohexylsilane.

Experimental

Synthesis of Chlorotricyclohexylsilane Using Cyclohexyllithium.—Cyclohexyllithium was prepared by adding, over a period of four hours, 95 g. (0.8 mole) of chlorocyclohexane to 500 ml. of low-boiling petroleum ether containing an excess of lithium metal shot in a one-liter, three-necked flask fitted with a mercury-sealed, air-driven stirrer, a reflux condenser protected by a calcium chloride tube, and a dropping funnel containing the chlorocyclohexane. The reaction mixture was stirred and heated on a warm water-bath to initiate the reaction, after which

(1) Part II from a thesis submitted by W. H. Nebergall to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. See THIS JOURNAL, **71**, 1720 (1949), for Part I.

(2) Present address: Indiana University.

(3) Johnson and Nebergall, THIS JOURNAL, **70**, 1706 (1948).

(4) Johnson and Nebergall, *ibid.*, **71**, 1720 (1949).

(5) Cusa and Kipping, *J. Chem. Soc.*, 1040 (1933).

(6) Linus Pauling, "The Nature of the Chemical Bond," 2d ed., Cornell University Press, Ithaca, New York, 1940, p. 53.