[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PA.]

Nitrile Formation by Reaction of Triphosphonitrilic Chloride with Carboxylic Acid Salts[1]

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The phosphonitrilic chlorides easily undergo nucleophilic substitution reactions. However, an effort to prepare triphosphonitrilic benzoate by a solid phase reaction of $(NPCl_2)_3$ with sodium benzoate resulted surprisingly in benzonitrile, benzoic anhydride and a phosphorus compound believed to be a precursor of trisodium metaphosphate. Although benzoic acid did not give the nitrile, benzoic acid in the presence of pyridine did. Reaction with the sodium salts of acetic, *p*-methoxybenzoic, lauric and *p*-chlorobenzoic acids gave the corresponding nitriles. A mechanism has been developed for these reactions and is based on the substitution of oxygen for nitrogen in the phosphonitrile ring.

I. Introduction

The chlorine atoms on cyclic tri- and tetraphosphonitrilic chloride can be replaced through nucleophilic reactions and various investigators have combined alcohols,[2–4] alcoholates,[5] phenols and phenolates[6] and amines[7–10] with them to form substitution products. We have been studying substitution reactions of the phosphonitriles and, as part of this work, treated trimeric phosphonitrilic chloride with anhydrous sodium benzoate in the absence of solvent hoping to obtain $[NP(C_6H_5COO)_2]_3$. On heating the reaction mixture, however, a vigorous reaction took place with formation of a colorless liquid which, on isolation, was found to be benzonitrile. Other reaction products were found to be NaCl, benzoic anhydride and a phosphorus-containing compound whose identity could not be established conclusively. Although benzoic acid in the presence of pyridine also gave benzonitrile and benzoic anhydride, benzoic acid alone gave benzoyl chloride and no benzonitrile. Reaction of $(NPCl_2)_3$ with the sodium salts of acetic, lauric, *p*-methoxybenzoic and *p*-chlorobenzoic acids also gave the corresponding nitriles and the acid anhydrides.

II. Experimental

The $(NPCl_2)_3$, m.p. 114.0,[11] was obtained from Albright and Wilson, Ltd., Birmingham, England. The sodium benzoate was anhydrous U.S.P. grade, dried at 105° to constant weight before use.

A mixture of 13.35 g. (0.0384 mole) of $(NPCl_2)_3$ and 50.00 g. (0.347 mole) of sodium benzoate (1:9 mole ratio) were ground together and placed in a 250 ml. round bottom flask fitted to a condenser, drying tube, liquid N_2 trap and a trap containing standard NaOH. A precision thermometer was suspended in the inner condenser tube with its bulb immersed in the reaction mixture. Flask temperature was increased gradually by means of a manually-controlled heating mantle; mantle and reaction mixture temperatures were recorded during the run. No indication of reaction was noted until the mantle temperature reached 110–120°. At this point, the reaction temperature, which had been about 30° below mantle temperature, rose sharply to about 240° and heating was terminated. The reaction temperature spurt occurred about 45 minutes after heating was begun and over-all reaction time was 60 minutes. Simultaneously with the temperature increase the mixture began to react vigorously and a colorless liquid was observed to be forming and condensing. It was apparent that the reaction began as soon as the $(NPCl_2)_3$ melted. [A similar reaction with benzoic acid gave a temperature rise when 110–120° was reached but one of lesser magnitude, the reaction temperature, at its maximum, remaining below mantle temperature.]

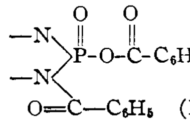
After completion of reaction, no material was found in the cold trap, the normality of the NaOH solution was unchanged, and the flask and contents weighed the same as before reaction. The products were treated with CCl_4 and the residue was extracted with additional CCl_4 for 90 hr. in a Soxhlet extractor. The combined CCl_4 solutions were distilled up to 77° at atmospheric pressure, the residue transferred to a small still pot and again distilled up to 77° at atmospheric pressure. A final distillation was then done at 35° and 1–2 mm. pressure, using a Dry Ice trap. There resulted 22.91 g. of residue, 0.49 g. of material in the trap and 6.91 g. of benzonitrile, n^{20}_D 1.5282, lit. value n^{20}_D 1.5289. The benzonitrile was further confirmed by infrared analysis. The residue was subjected to vacuum sublimation at 60° and 1 mm. pressure for 48 hr. to give 19.61 g. of a white, crystalline compound m.p. 41.2°, hydrolyzable to benzoic acid, and identified as benzoic anhydride, literature m.p. 42°.

The CCl_4-insoluble reaction products were extracted with anhydrous methanol to remove NaCl and unreacted sodium benzoate. The extract was treated with dilute H_2SO_4 to isolate the latter as benzoic acid. This gave 4.29 g. of a crystalline material, m.p. 122°, and identified as benzoic acid, indicating that 5.07 g. of sodium benzoate had not reacted. Also extracted by the methanol was 11.23 g. of a white crystalline compound containing no phosphorus, 57.9% Cl (Cl calcd. for NaCl, 60.3%) and further identified by X-ray diffraction as NaCl. The methanol-insoluble residue was found to contain some NaCl, which a second extraction removed completely giving a white, water-soluble residue, which contained no chlorine, and 2.4, 27 and 18.8% of N, P and Na, respectively (flame photometry).

The reactions with the sodium salts of acetic, *p*-methoxybenzoic, lauric and *p*-chlorobenzoic acids were carried out in similar fashion. In all cases, the corresponding nitrile and acid anhydride were positively identified by infrared spectra and refractive index.

III. Discussion

The following reactions are proposed as leading to the observed formation of nitriles. The first step involves the usual nucleophilic substitution reaction, $(NPCl_2)_3 + 6C_6H_5COONa \rightarrow [NP(OOCC_6H_5)_2]_3 + 6NaCl$. The presence of two groups, oxygen-bonded to phosphorus, results in a tautomeric rearrangement to



(I)

Such a rearrangement has been shown[12] to take

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[1] Presented at the Symposium on Inorganic Polymers sponsored by the Division of Inorganic Chemistry at the 136th Meeting, American Chemical Society, Atlantic City, September 13–18, 1959.

[2] F. Goldschmidt and B. Dishon, *J. Poly. Sci.*, **3**, 481 (1948).

[3] B. Dishon, THIS JOURNAL, **71**, 2251 (1949).

[4] F. P. Otto and R. W. Barrett, U. S. Patent 2,580,587, Jan. 1, 1952.

[5] C. J. Brown, *J. Poly. Sci.*, **5**, 465 (1950).

[6] D. Lipkin, U. S. Patents 2,192,921, Mar. 12, 1940 and 2,214,769, Sept. 17, 1940.

[7] M. A. W. Hoffmann, *Bull. soc. chim. France*, **44**, 374 (1885).

[8] W. Couldridge, *ibid.*, **50**, 535 (1888); *J. Chem. Soc.*, **53**, 398 (1888).

[9] C. J. Brown, U. S. Patent 2,374,646, May 1, 1945.

[10] H. Bode, K. Butow and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).

[11] Lit. values vary between 113.5–114.0°.

[12] H. N. Stokes, *Am. Chem. J.*, **18**, 629, 780 (1896); **20**, 740 (1898). A. M. de Ficquelmont, *Compt. rend.*, **202**, 423 (1936): *Ann. Chim.*, **12**, 169 (1939). R. A. Shaw, *Chem. and Ind.* (*London*), [**13**], 412 (1959).

place when $(NPCl_2)_3$ is hydrolyzed. The product, instead of being the anticipated triphosphonitrilic acid, $[NP(OH)_2]_3$, is instead trimetaphosphimic acid, $[HNP(O)OH]_3$.

The presence of the ≡P-O group in (I) enhances the dissociation of the $—OCOC_6H_5$ group which, together with excess sodium benzoate, will split out benzoic anhydride and leave a substituted-metaphosphimate structure. We believe that this will rearrange to split out benzonitrile with concurrent formation of a P–O–P bond in place of the P–N–P, all without rupture of the ring structure.

This type of reaction has been shown to occur by Narath, Lohman and Quimby[13] who studied the hydrolysis of trimetaphosphimate ion and found the reaction to proceed largely through intermediate ring compounds with oxygen replacing the original imide linkages successively and at decreasing rates.

The nitrile formation mechanism presented above would give, if occurring for all $NPCl_2$ units, the stoichiometry

$$(NPCl_2)_3 + 9C_6H_5COONa \longrightarrow 3C_6H_5CN + 3(C_6H_5CO)_2O + (NaOPO_2)_3 + 6NaCl \quad (1)$$

The sodium benzoate reaction was studied carefully and efforts were made to isolate and identify all reaction products. The reaction mixture, 13.35 g. (0.0384 mole) of $(NPCl_2)_3$ and 50.00 g. (0.347 mole) of sodium benzoate represented a 1:9 mole ratio. For complete reaction in accord with (1), there should have been formed 0.115 mole each of benzonitrile and benzoic anhydride, 0.038 mole of sodium trimetaphosphate and 0.230 mole of NaCl. Actually, 0.035 mole of sodium benzoate (about 10% of the starting weight) was recovered, indicating incompleteness of some reaction. However, 0.192 mole of NaCl and 0.090 mole of benzoic anhydride were found, quantities quite close to those expected. The amount of benzonitrile isolated (0.067 mole) was approximately $^2/_3$ of theoretical, indicating that the elimination-rearrangement to give this compound did not occur for the third nitrogen in the ring. This finding, too, is in accord with the results obtained by Narath, Lohman and Quimby, who found that hydrolysis of the third nitrogen takes place very slowly.

The phosphorus-containing reaction product which, for complete reaction, would be sodium trimetaphosphate, could not be identified as such. Thus, X-ray diffraction showed it to be amorphous and its infrared absorptions did not correspond with those reported by Corbridge and Lowe[14] for various metaphosphates. The compound was found to contain 2.4% nitrogen, further confirmation of the fact that substitution by oxygen was not complete. It is probable that greater reaction time would give complete conversion to the metaphosphate.

The fact that reaction of phosphonitrilic chloride with benzoic acid did not give benzonitrile can be attributed to the HCl formed as a by-product of the nucleophilic substitution reaction. The use of pyridine as an acid acceptor precludes the formation of benzoyl chloride as a secondary reaction and leads to the nitrile.

Recently, Burg[15] reported a reaction between $(NPCl_2)_3$ and silver perfluoroacetate in which CF_3CN and $(CF_3CO)_2O$ were formed. Burg gave for this reaction the equation

$$(NPCl_2)_3 + 3AgOOCCF_3 \xrightarrow[\text{suddenly}]{135°} 3AgCl + {}^3/_2(CF_3CO)_2O + \frac{1}{x}[(NPCl)_2O]_x$$

and 10% yield of CF_3CN, together with minor amounts of some other products. This differs somewhat from our results in several respects. We found substantially all the chlorine present as NaCl, our acid anhydride was in accord with equation 1, the nitrile was a major reaction product, and our results indicate that at completion of reaction, the phosphorus will exist as a trimetaphosphate.

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[13] A. Narath, F. H. Lohman and O. T. Quimby, THIS JOURNAL, **78**, 4493 (1956); also paper given at 135th Am. Chem. Soc. Meetings, Boston, Mass., April, 1959.

[14] D. E. C. Corbridge and E. J. Lowe, *Anal. Chem.*, **27**, 1383 (1955).

[15] A. B. Burg, "Inorganic Polymers Involving Phosphorus, Nitrogen and Boron," given at the 134th Am. Chem. Soc. Meetings, Chicago, Sept. 7–12, 1958. Also private communication.