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Reaction of Hexachlorocyclotriphosphazene with Amides to Form Nitriles

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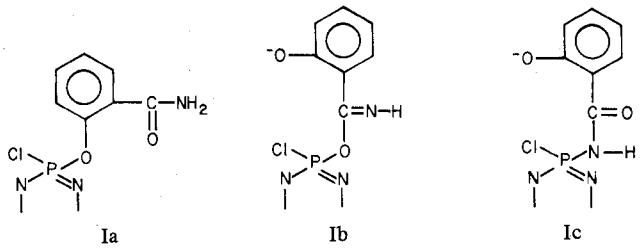
Hexachlorocyclotriphosphazene, $N_2P_3Cl_6$, is known to act as a reagent for the formation of nitriles when heated with salts of organic acids.[1-3] $N_3P_3Cl_6$ has also been shown to act as an activator for the formation of amides in the reaction between organic acids and amines.[4] Both of these reactions were believed to involve an initial step which resulted in an unstable phosphazene–carboxylate adduct which either rearranged to the nitrile or was displaced by an amine to form an amide. Recently, such an adduct was isolated by forming a stable spiro compound using salicylic acid as a reagent.[5] Isolation of this compound led us to attempt isolation of an analogous spiro compound for salicylamide. The product obtained was not the spiro derivative predicted but rather a phosphazene derivative which had the amide group rearranged to a nitrile.

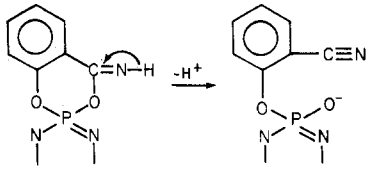
Caglioti et al. had reported the synthesis of salicylamide in high yields from the reaction between salicylic acid, ammonia, and $N_3P_3Cl_6$.[4] The reaction times utilized were relatively short, 5–10 min, and no nitrile products were reported. The proposed initial step in this reaction was on attack by the carboxylate anion on a phosphorus atom followed by a rapid nucleophilic attack on the carboxyl carbon atom by the amine to yield the amide. Our work would seem to indicate that the aryloxy group of the salicylamide may be the initial attacking group.

There are three possible products from the initial attack by salicylamide on a phosphazene: Ia, Ib, and Ic.



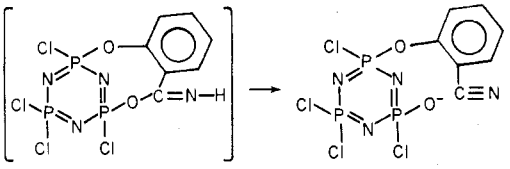
Ia Ib Ic

None of these compounds could be isolated or detected in the reaction mixture. However, the first product which could be isolated is shown as II. From the structure of II the most probable intermediate would be III, and III could only arise from Ia or Ib. At this time there is no physical evidence to distinguish which of these two compounds is the correct intermediate.



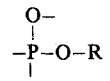
III II

It was possible that the intermediate was of an "Ansa"[6,7] type, IV to yield V. However, the ^{31}P NMR spectrum of the



IV V

product is an AB_2 type which indicates that II is the correct structure and not V. The doublet centered at −6.9 ppm



and the triplet at +18.55 ppm (PCl_2) were intergrated at 1:2 respectively and are within the range of phosphazene–phosphorus absorptions.[8]

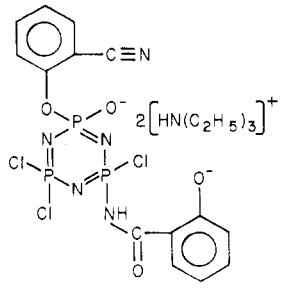
Although there are no previously reported examples of carbonyl oxygen attack on phosphazenes to yield products such as Ib and III, this mode of attack has been well documented in the formation of spiro phosphoranes.[9,10] Also this mode of attack has been hypothesized for the mechanism of the reaction of amino acid esters with $N_3P_3Cl_6$.[11]

The intermediate III is the same type as that proposed by Cherbuliez et al. for the alcoholysis of a phosphate derivative which begins as a nitrile and yields an amide.[12]

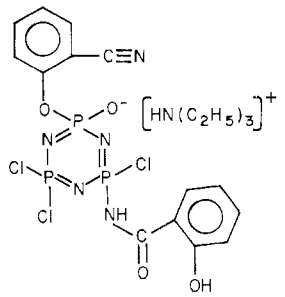
Further support for the intermediate Ib is that the times necessary for the preparation of phenoxy phosphazene esters are very long, 1–4 days, compared to the times of reactions involving carboxylate groups, 15–30 min.[8-13]

If more than 1 equiv of salicylamide was reacted with $N_3P_3Cl_6$, the product which could be isolated had the structure VI. Neither an increase in temperature, an increase in the concentration of salicylamide, nor changing solvents resulted in the addition of more than two salicylamide groups to a phosphazene. The reasons for this limitation to substitution are unclear. Solubility is not a factor, as the reaction results in the precipitation only of triethylammonium chloride. Steric factors would seem to be the only explanation at this time. The

careful heating of VI results in the formation of VII.



VI



VII

Infrared evidence would indicate that the second salicylamide group initially has an amido nitrogen–phosphorus bond as shown. This is confirmed when VI is converted to VII by heat. The uv spectra and the infrared spectra of VI and VII differ only in the OH region and in those regions of absorption for triethylammonium ion. The presence of a phenolic OH group in VII can be confirmed by ferric chloride or aminoantipyrine reactions. Attempts to further react VII into a spiro ring system by heating result in phosphazene ring degradation and the evolution of *o*-cyanophenol and salicyl chloride.

Salicylic acid as well as other 3-hydroxy acids have been found to limit the degree of substitution to only two groups per phosphazene.[5,14] The analogue of VII for salicylic acid, however, was found to have a phenoxy–phosphorus bond rather than a carboxy–phosphorus bond.

The possibility that conversion of the amide to a nitrile preceded substitution was very real. However, attempts to prepare *o*-cyanophenoxyhexachlorocyclotriphosphazene under conditions similar to those used in the salicylamide reactions resulted in no detectable substitution.

Experimental Section

All solid reagents were dried in a vacuum oven overnight before use. $N_3P_3Cl_6$ (Hooker) was recrystalized from *n*-heptane to mp 113 °C. Triethylamine was dried over potassium hydroxide and then distilled just before use. All solvents were dried over calcium hydride. ^{31}P NMR spectra were obtained with the use of a Joel 100 spectrometer operating at 40.29 MHz and measured vs. external H_3PO_4.

The Reaction between Stoichiometric Quantities of Salicylamide and $N_3P_3Cl_6$. A mixture of 5.0 g of $N_3P_3Cl_6$ (0.014 37 mol), 1.971 g of salicylamide (0.014 37 mol), and 4.354 g of triethylamine (0.0431 mol) was refluxed under N_2 gas for 3 h in 100 ml of tetrahydrofuran (THF). At the end of this time the warm THF was filtered to yield 3.78 g of triethylammonium chloride. Filtrate (50 ml) was removed on a rotary evaporator and the remaining solution was poured into 400 ml of ligroin, bp 35–60 °C. The resultant precipitate was filtered and dried, then dissolved in 50 ml of pure THF followed by precipitation into 400 ml of ligroin: yield 5.69 g of a white solid; mp 137 °C; mol wt by mass spectrum 411, parent peak ($M - (C_2H_5)_3NH^+$) and a weak set of peaks at 510–514 amu; calculated 513. Anal. Calcd for $N_3P_3Cl_4(OC_6H_4CN)(O)HN(C_2H_5)_3$: Cl, 27.68; P, 18.12. Found: Cl, 27.47; P, 18.17. The ultraviolet spectrum of this compound in CH_2Cl_2 had the following characteristic peaks: λ_{max} 288 (log ϵ, 3.93), 279 (log ϵ, 3.285), 236 (log ϵ, 3.93), 232 (log ϵ, 3.967). Based on the 232 peak and the log ϵ for 2-cyanoanisole, the molecular weight was calculated to be 511. The infrared spectrum of this compound showed a strong cyanide peak at 2215 cm^{-1} with the concurrent loss of the set of peaks at 1600–1700 cm^{-1} present in pure salicylamide. ^1H NMR of this solid gives a triplet centered at δ 1.4, a quartet centered at δ 3.2, and a complicated multiplet at δ 7.6 with an integration of 9:6:4, respectively. The ^{31}P NMR shows a triplet centered at −6.88 ppm and a doublet centered at +18.53 ppm.

A Reaction between an Excess of Salicylamide and $N_3P_3Cl_6$. A mixture of 5.0 g of $N_3P_3Cl_6$ (0.014 37 mol), 7.88 g of salicylamide (0.0575 mol), and 14.54 g of triethylamine (0.1437 mol) in 100 ml of THF was refluxed under N_2 gas for 120 h. The resultant solution was filtered to yield 5.39 g of triethylammonium chloride. The solvent was removed on a rotary evaporator at room temperature to yield 9.75 g of a cloudy oil. This oil was washed with 100 ml of cold absolute ethenol then dried in a vacuum oven at 1 mm for 24 h. The oil was examined by infrared and ultraviolet spectroscopy. The infrared spectrum has a set of peaks at 3440, 3350, and 3180 cm^{-1} and also a strong absorption at 2215 and 1660 and 1625 cm^{-1}. The ultraviolet spectrum of this compound was very similar to that described in the reaction above but there were shifts to shorter wavelengths for two of the peaks: λ_{max} 285, 279, 227 with only a slight shoulder at 236. The shifts to 285 and 227 were those which could be expected if a second salicylamide group is bonded to the phosphazene without rearranging to a cyano group. ^1H NMR of this oil gave a triplet centered at δ 1.4, a quartet centered at δ 3.30, and a very complex series of peaks at δ 7.2–7.9. Integrated ratios were 9:6:4, respectively. Anal. Calcd for $[N_3P_3Cl_3(O)(OC_6H_4CN)(NHCOC_6H_4O)]^{2-}[(C_2H_5)_3NH^+]_2$: Cl, 14.94; P, 13.02. Found: Cl, 15.15; P, 12.69.

Gentle heating of this oil in heptane followed by evaporation of the solvent yielded 8.85 g of a solid residue which decomposed at 92 °C. The uv spectrum of this compound was almost identical with that of the oil, but significant differences existed in the infrared spectrum of the solid. The OH region showed only two strong absorptions at 3400 and 3195 cm^{-1}. Also a decrease in the intensity occurred for the band at 1490 cm^{-1}, which is present for most triethylammonium salts. Anal. Calcd for $[N_3P_3Cl_3(O)(OC_6H_4C{\equiv}N)(NHCOC_6H_4OH)]^-[(C_2H_5)_3NH]^+$: P, 15.17. Found: P, 15.10. The ^1H NMR of this compound had absorptions in the same regions as described above but integrated ratios were 9:6:8, respectively. This compound was found to give a blue color when mixed with ferric chloride solution and a deep red-orange when stirred with aminoantipyrine.

Reactions in which the quantity of salicylamide was increased or refluxing benzene, xylene, or dioxane was used did not yield a greater quantity of oil or triethylammonium chloride than the reaction described above. Refluxing for 5 or 10 days also did not increase the yield. In all cases a maximum of 5.85 g of triethylammonium chloride (3 equiv) was obtained.

Hydrolysis in base of the solid product from these reactions resulted in the isolation of 1 equiv of 2-cyanophenol and salicylic acid accompanied by orthophosphate formation.

If the solid product is heated in a vacuum to 180 °C, decomposition occurs and salicyl chloride and 2-cyanophenol can be isolated by fractional condensation on a vacuum line at 0.1 Torr.

Attempted Reaction of 2-Cyanophenol with $N_3C_3Pl_6$. A mixture of 5.0 g of $N_3P_3Cl_6$ (0.014 37 mol), 11.9 g of 2-cyanophenol (0.10 mol), and 10.1 g of triethylamine (0.1 mol) in 100 ml of THF was refluxed under N_2 for 72 h. No solid was precipitated and 97.8% of unreacted $N_3P_3Cl_6$ was recovered.

Acknowledgment. We wish to acknowledge the Faculty Development Fund of The Pennsylvania State University for partial support for this work.

Registry No. $N_3P_3Cl_6$, 940-71-6; salicylamide, 65-45-2; $N_3P_3Cl_4(OC_6H_4CN)(O)HN(C_2H_5)_3$, 59728-85-7; $[N_3P_3Cl_3(O)(OC_6H_4CN)(NHCOC_6H_4O]^{2-}[(C_2H_5)_3NH^+]_2$, 59728-87-9; $[N_3P_3Cl_3(O)(OC_6H_4CN)(NHCOC_6H_4OH)]^-[(C_2H_5)_3NH]^+$, 59728-88-0.

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