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The Preparation of a Carboxylic–Phosphazene Salt

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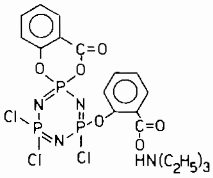
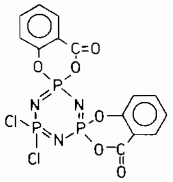
An acid substituted phosphazene has been postulated as the reactive intermediate in the formation of nitriles[1,2,3] or amides[4] as the result of the reaction between acid salts and hexachlorocyclotriphosphazene. This intermediate has never been detected nor isolated. We wish to report the first isolation of an acid–phosphazene salt which has the type of bonding only previously postulated.

It is possible to isolate, in 76% yield, compound I from a mixture of salicylic and, hexachlorocyclotriphosphazene and triethylamine in tetrahydrofuran. The compound can be isolated as a triethylammonium salt of the free acid group or can be sublimed to give compound II and triethylammonium chloride.



(I)



(II)

It should be noted that no nitrile or amide product could be detected in the reaction mixture. Thus, this is the first case reported where an acid salt reacting with hexachlorocyclotriphosphazene has not resulted in one of these products. This unusual product is attributed to the formation of a stable six-membered exocyclic spiro ring. The six-membered spiro ring at a phosphazene phosphorus has been shown to be a very stable arrangement compared to a five-membered spiro ring.[5] This is similar to the stability of a similar ring for phosphate chemistry.[6,7]

Compound I is a white crystalline solid which decomposes if slowly heated to 125 °C, but which melts at 142 - 143 °C, if heated rapidly. It is readily soluble in CH_2Cl_2 but is insoluble in ether or benzene. It is not soluble in water but is soluble in 1*N* sodium hydroxide.

^1H NMR in $CDCl_3$ shows the presence of methyl protons at 1.2δ, methylene protons at 3.0δ, and phenyl protons at 7.5 - 8.6δ. These are in a ratio of 9:6:8. The ammonium proton was not observed below 11.0δ.

Hydrolysis of I in hot aqueous pyridine yields two equivalents of salicylic acid and three equivalents of chloride. The infrared spectrum of I shows the presence of both cyclic ester carbonyl groups and phenyl ether groups.[8] The P=N stretch was found at 1193 cm^{-1}. The U.V. spectra in CH_2Cl_2 was consistent with a salicylate derivative λ_{max} 288 (log ϵ 3.67), 234 (log ϵ 4.37).

Treatment of a solution of I with ferric chloride–HCl solution does not give the characteristic color for a phenolic group. Treatment of a solution of I with aminoantipyrine also does not give any color change characteristic of a phenolic group. For these reasons the second salicyl group is presumed bonded through the phenolic oxygen with a triethylammonium salt of the free acid group.

Elemental analyses for $N_3P_3Cl_3(C_3H_4O_3)_2HN(C_2H_5)_3$: calcd. %P, 15.11; found, 15.17. Calcd. % Cl, 17.28; found, 17.21.

Sublimation of I at .02 mmHg at 90 °C for one week gave triethylammonium hydrochloride. This residue was found to have no triammonium peak in the infrared region of 2700 - 2500 cm^{-1} and to have a similar spectrum to I in the 1750 - 1600 cm^{-1} region. This compound was found to be 12.20% Cl, consistent with the formula $N_3P_3Cl_2(C_3H_4O_3)_2$ (calculated 12.24% Cl). On the basis of the above data this compound was assigned the structure shown as II.

We hope that the isolation of this new class of phosphazene derivatives will allow for a more clear interpretation of the reaction mechanism for reactions involving acid salts and hexachlorocyclotriphosphazenes.

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