not definitive of mechanism.

In summary, we have not obtained any evidence that the 2-pyridyl cation participates in arynelike cycloaddition as might be expected from canonical structure **2b**. We have obtained products that appear to result from normal aromatic electrophilic substitution reactions.

Experimental Section

1,2,3,5-Thiatriazolo[5.4-*a*]pyridine 3-oxide (4) was prepared from 2-pyridylhydrazine following the method of Kauffmann and Marhan.[11]

Reaction of 4 in Toluene Containing Anthracene. A solution of 4 (1.0 g, 6.4 mmol) and anthracene (3.45 g, 19.4 mmol) in 30 mL of toluene was heated at reflux for 2 h. The solid that separated on cooling was collected and identified as anthracene on the basis of its melting point and mixture melting point with an authentic sample. The filtrate was extracted thrice with small portions of dilute aqueous HCl. The combined aqueous layer was washed once with diethyl ether, neutralized by addition of $NaHCO_3$, and extracted with diethyl ether. The dried ether extract was concentrated by evaporation at reduced pressure and the residue was examined by GC/MS with use of a Finnigan 4000 system. Of three major peaks, two had molecular mass 169 and were similar in fragmentation pattern. The third had base peak *m/e* 220; a product with the same mass spectrum was also obtained from reaction of 4 with furan (see below); it follows that the third product is derived strictly from 4.

One of the species of mass 169 was recognized to be 2-(*p*-tolyl)pyridine (8) by comparison of its GLC retention time and mass spectrum with those of an authentic sample (from Aldrich Chemical Co.); mass spectrum, *m/e* 169, 168, 167, 154, 141, 120. The other product of mass 169 was isolated by preparative GLC on a 10% UC W-98 on Chromosorb P column and was identified as 2-(*o*-tolyl)pyridine (7); mass spectrum, *m/e* 169, 168, 167, 154, 141, 120; NMR ($CDCl_3$) δ 2.37 (s, 3 H), 7.14–7.90 (m, 7 H), 8.51–8.74 (m, 1 H); picrate, mp 140–142 °C (lit.[16] mp 143 °C). The yields of 7 and 8 were 19% each.

The third major peak had the following mass spectrum: *m/e* 220 (base peak), 187, 156, 155, 78. Inasmuch as 4 has molecular mass 155, components from at least two molecules of 4 must be represented in this species. One possibility is di-2-pyridyl sulfone (mass 220). The peak at *m/e* 78 is probably the 2-pyridyl cation, at 156 di-2-pyridyl radical cation, at 155 the same less one protium, and at 187 the mass 220 species less O_2H.

An attempt to effect reaction of 4 with anthracene at reflux in benzene for 1 h was unsuccessful; only unreacted 4 and anthracene could be found in the cooled mixture.

Reaction of 4 in Furan. A mixture of 4 (0.60 g) with furan (5 mL) was sealed in a glass tube and heated for 2 h at 110 °C. The contents of the cooled tube were decanted, and the dark, sticky material adhering to the wall of the tube was removed by two washings with diethyl ether. The combined decantate and extracts were evaporated, leaving a dark, oily material which was examined by GC/MS. Three major components were revealed; one had parent peak *m/e* 145 and is discussed below; a second had *m/e* 172, 171, 156, 144, 118, 95, 79, 78, and is perhaps di-2-pyridyl ether; the third had parent peak *m/e* 220 and mass spectrum identical with that of the species formed from reaction of 4 with anthracene and toluene as discussed above. By preparative GLC on 10% UC W-98 on Chromosorb B, 2-(2-pyridyl)furan (11) was isolated; mass spectrum, *m/e* 145, 117, 116, 90, 89, 78; NMR ($CDCl_3$) δ 8.73–8.46 (m, 1 H), 7.50–7.83 (m, 3 H), 6.84–7.23 (m, 2 H), 6.50–6.63 (m, 1 H); IR (film) 1575, 1560, 1450, 1420, 1275, 1145, 1110, 980, 750 cm^{-1}; picrate mp 172–174 °C. The NMR spectrum and picrate melting point agree with those in literature data[17] for 11. The IR and picrate melting point are different than those reported[15] for 10. The yield of 11 by GLC was 30%.

Attempted Diazotization of 2-Aminopyridine. 2-Aminopyridine (0.011 mol) was recovered unchanged from exposure to 3-methylbutyl nitrite (0.01 mol) in a solvent of furan (0.033 mol) and CH_2Cl_2 (10 mL) for 30 min at reflux. Diazotization likewise failed to occur when acetic acid (0.011 mol) was present as well as the other species mentioned. A mixture of 2-aminopyridine (4.2 g), 3-methylbutyl nitrite (5.6 g), furan (27.2 g), trifluoroacetic acid (10.0 g), and CH_2Cl_2 (about 75 mL) was heated at reflux for 1 h; besides much 2-aminopyridine, isolated as its picrate (mp 213–215 °C), there was obtained 1.1 g of an oily material lacking characteristics of either 10 or 11. We did not try to employ the aprotic diazotization procedure of Doyle and Bryker.[18]

Registry No. 2, 35895-92-2; **4**, 78715-82-9; **5**, 1628-89-3; **7**, 10273-89-9; **8**, 4467-06-5; **11**, 55484-03-2; furan, 110-00-9; toluene, 108-88-3.

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Mono- and Polyanhydride Formation by Reaction of 2,2,4,4,6,6-Hexachlorotriazatriphosphorine with Carboxylic Acid Salts under Mild Conditions

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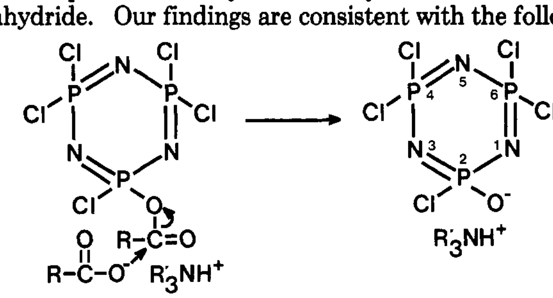
In the last decade several convenient uses of 2,2,4,4,6,6-hexachlorotriazatriphosphorine ($N_3P_3Cl_6$) in organic syntheses have been reported.[1-4] Moreover, $N_3P_3Cl_6$ has been extensively used for activating carboxylic acid in amide syntheses.[5-8] In this paper we report the reaction of $N_3P_3Cl_6$ with carboxilic acids neutralized by a tertiary amine. When the reaction was performed in organic solvents, at low temperature, a fast and quantitative formation of carboxylic acid anhydride was observed; consequently, $N_3P_3Cl_6$ was converted into the trialkylammonium salt of 2-hydroxy-2,4,4,6,6-pentachlorotriazatriphosphorine, a new cyclophosphazene derivative (2). The probable mechanism of reaction involves a compound of type 1 as an active intermediate that can undergo a nucleophilic attack by the carboxylate anion to form an anhydride. Our findings are consistent with the following



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stoichiometric pathway:

$$2RCOOH{\cdot}R'_3N + N_3P_3Cl_6 = (RCO)_2O + R'_3N{\cdot}HCl + 2$$

On the basis of IR evidence, we could establish that this reaction proceeds to completion within a few minutes in the temperature range −10–0 °C and can be carried out in a large variety of organic solvents. All the carboxylic acids tested (acetic, propionic, benzoic, p-toluic, succinic, ethylenediaminetetraacetic, phthalic, pyromellitic, and polyacrylic) were successfully converted into the corresponding anhydrides. Compound **2** has been isolated as the triethylammonium salt. It was found unable to promote further conversion of carboxlyic acid salts into anhydrides, although an unidentified and slow reaction could be observed.

The structure of **2** has been established on the basis of elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopy. In fact, the IR spectrum shows two strong bands at 1215 and 1170 cm^{-1}, attributed to the P=N and P—O⁻ bonds, two strong bands at 590 and 520 cm^{-1} related to the P–Cl bonds and the characteristic bands of Et_3N^+H ion. The ^1H NMR spectrum is consistent with that expected for triethylammonium ion, and the ^{31}P NMR spectrum shows a triplet centered at 1.93 ppm, attributed to the P atom in position 2, and a doublet centered at −21.09 ppm, attributed to P atoms in positions 4 and 6.

The reaction has been applied to the preparation of linear polyacrylic anhydride using a polyacrylic acid with M_r 150 000 as the starting material. In this case, the reaction was not quantitative, possibly because of steric hindrance, but the conversion of the carboxylic acid into anhydride was sufficiently large, ranging between 75 and 90%.

Experimental Section

Materials. $N_3P_3Cl_6$ was purchased from EGA-Chemie, West Germany, and was recrystallized from n-heptane, mp 113–114 °C. Polyacrylic acid, M_r 150 000, was supplied as an aqueous solution by Polyscience Inc. It was purified by dialysis, recovered by lyophilization, and dried at 50 °C under vacuum. Carboxylic acids were pure grade products; triethylamine, tri-n-butylamine, and pure grade solvents were purified and dried by standard methods. Isolated chemicals (Et_3NHCl and ArCOOCOAr) were identified by comparison of their IR spectra and melting points with those of authentic samples.

Physical Measurements. Melting points were taken in open capillary tubes and are uncorrected. The IR spectra were recorded by using a 577 Perkin-Elmer spectrophotometer. ^1H NMR and ^{31}P NMR spectra were recorded with a WP-80DS Bruker NMR spectrometer.

Procedure for Detection of Anhydride Formation. Carboxylic acid (2 mequiv) was dissolved in CH_2Cl_2 (6–10 mL) with the addition of Et_3N or $(n\text{-}Bu)_3N$ (2 mmol). With stirring $N_3P_3Cl_6$ (1 mmol) was added as a solid to the carboxlyate solution kept in a cold bath (−10–0 °C). Immediately after dissolution (about 1 min), the reaction mixture was put into an IR cell (path length 0.1 mm), and the spectrum was recorded. The total operation time was ~8 min. The IR spectra were identical with those obtained at longer reaction times.[9]

Preparation of Benzoic Anhydride. Benzoic acid (4.88 g, 0.04 mol) was dissolved in dry Et_2O (100 mL) and was neutralized by addition of 4.04 g (0.04 mol) of Et_3N. The solution was cooled to −10 °C, and then 6.94 g (0.02 mol) of $N_3P_3Cl_6$ was added with stirring. Immediately an exothermic reaction took place, with consequent formation of a white precipitate. The mixture was kept for 20 min at −10 °C and then filtered. The insoluble product (yield 2.60 g, 0.019 mol) was identified as pure $Et_3N{\cdot}HCl$. The clear solution was passed through a silica gel chromatographic column and eluted by dry Et_2O. Pure benzoic anhydride (0.42 g, 0.018 mol) was recovered from the eluate, while the triethylammonium salt of the halocyclophosphazene derivative was completely retained by the column.

Preparation of Polyacrylic Anhydride. Polyacrylic acid (4.2 g) and 10.9 g of $n\text{-}Bu_3N$ were dissolved at room temperature in 100 mL of CH_2Cl_2. $N_3P_3Cl_6$ (10.15 g) was added with stirring to the salt solution. After 30 min, 200 mL of Et_2O was added to the clear reaction mixture. A gelatinous precipitate of crude polymeric product was obtained. It was recovered by filtering under dry nitrogen and by washing extensively with CH_2Cl_2.[10] Finally, the product was dried at 50 °C under vacuum (yield 3.9 g). The polyacrylic anhydride was linear, as proved by its easy solubility in N,N-dimethylformamide.[11] The conversion of its carboxylic groups into anhydride, measured according to ref 12, amounted to 85 ± 5%. IR (KBr) 1805 (s, sharp), 1760 (s, sharp), 1700 (m, sh), 1620 (w), 1030 cm^{-1} (s, br).

Preparation of $(N_3P_3Cl_5O^-)(C_2H_5)_3N^+H$. $N_3P_3Cl_6$ (13.92 g, 0.040 mol) was added with stirring to 5.08 g (0.020 mol) of pyromellitic acid neutralized by 8.08 g (0.080 mol) of Et_3N in 100 mL of CH_2Cl_2 at 0 °C. After 10 min the mixture was evaporated to dryness under vacuum. The solid was extracted with 100 mL of cold benzene, from which 18.2 g of crude product was recovered. Crystallization from Et_2O–n-hexane yielded 16.4 g (0.038 mol): mp 85–87 °C; IR (KBr) 2910 (s), 2835 (m), 2700 (m), 2500 (w), 1460 (m), 1400 (w), 1375 (m), 1218 (vs, br), 1170 (vs, br), 590 (vs, sharp), 545 (m, sh), 520 cm^{-1} (vs. sharp). ^1H NMR (CD_2Cl_2–$(CH_3)_4Si$) δ 1.37 (9 H, t, J = 7 Hz, $3CH_3$), 3.12 (6 H, m, J = 7 Hz, $3CH_2$); 10.71 (1 H, br, ^+NH]; ^{31}P NMR (CD_2Cl_2–H_3PO_4, 85%) δ 1.93 (1 P, t, J = 44 Hz, $P(O^-)Cl$), −21.09 (2 P, d, J 44 Hz, $2PCl_2$).

Anal. Calcd for $(N_3P_3Cl_5O^-)(C_2H_5)_3N^+H$: C, 16.72; H, 3.72; Cl, 41.23; N, 13.01; P, 21.60. Found: C, 17.02; H, 3.79; Cl, 40.20; N, 13.19; P, 21.92.

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Registry No. 2 (R′ = Et), 78685-93-5; acetic acid, 64-19-7; propionic acid, 79-09-4; p-toluic acid, 99-94-5; succinic acid, 110-15-6; ethylenediamine tetraacetic acid, 60-00-4; phthalic acid, 88-99-3; pyromellitic acid, 89-05-4; benzoic acid, 65-85-0; polyacrylic acid, 9003-01-4; acetic anhydride, 108-24-7; propionic anhydride, 123-62-6; p-toluic anhydride, 13222-85-0; succinic anhydride, 108-30-5; ethylenediamine tetraacetic anhydride, 23911-25-3; phthalic anhydride, 85-44-9; pyromellitic anhydride, 89-32-7; benzoic anhydride, 93-97-0; polyacrylic anhydride, 25301-00-2; $N_3P_3Cl_6$, 940-71-6.

(9) Only in the case of polyacrylic acid was the final IR spectrum obtained in about 25 min at room temperature.

(10) The polymeric anhydride remains soluble in CH_2Cl_2 solution but becomes insoluble in the same solvent precipitated once by Et_2O.

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Reactivity of an (Arylthio)thiocarbonyl Radical. Intramolecular Addition to the Azido Group

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In a previous paper we reported that the reduction of aryldiazonium tetrafluoroborates (**1**) with iodide ions in the presence of carbon disulfide led to (arylthio)thiocarbonyl radicals (**2**) by addition of the corresponding aryl radicals to the sulfur atom of carbon disulfide.[1] Radical

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