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Notes

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Reactions of Hexafluorocyclotriphosphazene with Lithium Enolate Anions

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In recent years, the reactions of hexafluorocyclotriphosphazene ($P_3N_3F_6$) with alkyl-[1], alkynyl-[2], and aryllithium[3,4] reagents have been investigated. Thus, many compounds not available by direct synthesis[5] or the Friedel–Crafts reaction[5] may be prepared. In view of the fact that lithium enolate anions of ketones are known to react as nucleophilic reagents,[6] it would appear to be worthwhile to attempt reactions of these species with $P_3N_3F_6$. If successful, these reactions would yield phosphazenes with a ketone function in the exocyclic group which would be the precursors of a wide variety of organocyclophosphazenes derived from reactions of the carbonyl group. Therefore, we wish to report the synthesis and characterization of the pentafluorocyclotriphosphazene derivatives of acetophenone (I, $P_3N_3F_5CH_2C(O)C_6H_5$) and cyclohexanone (II, $P_3N_3F_5C_6H_9O$).

Experimental Section

All reactions were carried out under anhydrous conditions and a nitrogen atmosphere. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Hexafluorocyclotriphosphazene was prepared from hexachlorocyclotriphosphazene (El monte or Ethyl Corp.) by previously established procedures.[7] Diisopropylamine was purified by distillation over calcium hydride. Commercially available *n*-butyllithium, acetophenone, and cyclohexanone were used without further purification. NMR spectra in ($CDCl_3$) were obtained on a JEOL C60-HL spectrophotometer at 60 MHz (^1H) or 56.5 MHz (^{19}F). Tetramethylsilane (^1H) and fluorotrichloromethane (^{19}F) were used as internal standards. Infrared spectra were obtained on thin films using a Beckman IR-20A spectrophotometer with sodium chloride or polyethylene disks. Mass spectra were obtained on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Samples were introduced through the liquid inlet. Analytical samples were purified by preparative-layer chromatography (silica/pentane) or preparative VPC using a Gow Mac 69-100 chromatography equipped with a DC 200 Chromsorb column. Elemental analyses were performed by Robertson Laboratories.

Preparation of $P_3N_3F_5CH_2C(O)C_6H_5$ (I). To a stirred solution of 5.1 g (0.05 mol) of diisopropylamine in 20 mL of tetrahydrofuran (THF)[8] at −78 °C was added 21 mL of *n*-butyllithium in hexane (0.048 mol). After stirring for 20 min, 6.0 g (0.05 mol) of acetophenone in 20 mL of THF was added dropwise over a 1-h period.[6] After an additional hour of stirring, the solution was allowed to reach room temperature and was added dropwise to a stirred solution of 12.5 g (0.05 mol) of $P_3N_3F_6$ in 50 mL of THF. The clear solution gradually turned to a vivid yellow and finally a pale orange after 3 h under refluxing conditions. The solvent was removed under aspirator vacuum and the remaining oil was dissolved in diethyl ether and extracted with acidified water. Evaporation of the ether layer yielded a brown oil which was then distilled at 75–80 °C and 4–5 mmHg to give 8.45 g (48% of theory) of a water white oil. VPC analysis of the distillate showed it to be a 95/5 mixture of $P_3N_3F_5CH_2C(O)C_6H_5$ and acetophenone. Analytical sample purification was done by either preparative-layer chromatography or preparative VPC. Anal. Calcd for $P_3N_3F_5C_8H_7O$: C, 27.51; H, 2.01; mol wt 350. Found: C, 27.63; H, 2.19; mol wt 350 (mass spectrum).

NMR:[9] ^{19}F $\delta(PF_2)$ 62.0 (4 F, $J(PF) = 788$ Hz), $\delta(PFR)$ 58.0 (1 F, $J(PF) = 778$ Hz); ^1H $\delta(CH_2)$ 5.4 (2 H, $J(PH) = 15$ Hz), δ (C_6H_5) 7.5 (5 H). IR:[10] 3020 (m, CH str), 2950 (w, CH str), 1640 (s, CO str), 1580 (m, CC str), 1490 (m, CC str), 1450 (m, CH bend), 1270 (s, PN str), 1080 (s, PN^1 str), 1050, (m, CH bend), 1010 (m, CH bend), 980 (s, PF asym), 890 (s), 950 (s, PF sym), 840 (s, PF sym), 760 (s PF sym), 740 (m), 700 (s), 670 (m), 580 (w), 570 (w), 560 (w), 500 (s), 450 (s). Mass spectra:[11] 350 (100%, $P_3N_3F_5C_8H_7O^+$), 334 (6%, $P_3N_3F_5C_8H_7^+$), 247 (21%, $P_3N_3F_5OH^+$), 244 (9%, $P_3N_3F_5CH_2^+$), 230 (14%, $P_3N_3F_5^+$), 103 (70%, $C_6H_5CN^+$), 102 (80%, $C_6H_5C_2H^+$), 77 (54%, $C_6H_5^+$).

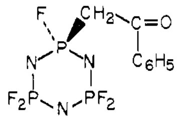
Preparation of $P_3N_3F_5C_6H_9O$ (II). The same procedure was employed as the one outlined above except that cyclohexanone was used in place of acetophenone. The resulting oil was distilled at 60–70 °C and 4–5 mmHg to yield 5.2 g (33% of theory) of a water white oil. Purity, as established by VPC, was again approximately 95%. Anal. Calcd for $P_3N_3F_5C_6H_9O$: C, 21.95; H, 2.75; mol wt 327. Found: C, 22.00; H, 2.92; mol wt 327 (mass spectrum).

NMR:[9] ^{19}F $\delta(PF_2)$ 61.0 (4 F, $J(PF) = 760$ Hz), $\delta(PFR')$ 59.0 (1 F, $J(PF) = 765$ Hz); ^1H $\delta(CH_2)$ 1.9 (8 H, br d), $\delta(CHP)$ 5.5 (2 H, $J(PH) = 4$ Hz). IR:[10] 2900 (m, CH str), 2830 (w, CH str), 1680 (m, CO str), 1440 (m), 1360 (w), 1330 (w), 1270 (s, PN str), 1100 (s, PN^1 str), 1060 (m), 1040 (m), 1000 (m), 940 (PF asym), 840 (PF sym), 750 (PF sym), 550 (w), 500 (s), 450 (s). Mass spectra:[11] 327 (31%, $P_3N_3F_5C_6H_9O^+$), 247 (82%, $P_3N_3F_5OH^+$), 230 (20%, $P_3N_3F_5^+$), 97 (9%, $C_6H_9O^+$), 80 (95%, $C_6H_8^+$), 79 (100%, $C_6H_7^+$).

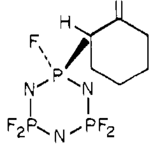
Both new compounds are reasonably stable under normal laboratory conditions. The expected derivatives of the ketones are formed in reactions with dinitrophenylhydrazine and butyllithium.

Results and Discussion

The fluorine-19 NMR data indicate[4] the presence of the $P_3N_3F_5$ function in both compounds I and II. The proton NMR spectra indicate substantially deshielded alkyl groups ($\delta \sim 5.5$ ppm). The integrated areas along with the strong perturbation of the chemical shifts establish that the phosphazene moiety is attached in a position α to the carbonyl function. The observation of normal ketone reactions and the ketone band in the infrared spectra reinforce this conclusion. Therefore, these molecules can be depicted as



I



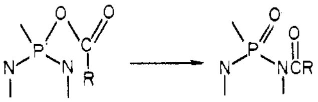
II

The strong perturbation of the PCH proton chemical shifts reflects a combination of the strong electron-withdrawing effect of the $P_3N_3F_5$ moiety[12] and possible anisotropic effects associated with the phosphorus atom. The difference[13] in J_{PCH} in the two compounds probably relates to geometric factors.

In addition to the normally expected bands from the phosphazene[3] and ketone functions, there are some significant perturbations in the infrared spectra of I and II. One would expect that substitution in the α position of a ketone with a strong electron-withdrawing function would lead to a significant increase in the carbonyl frequency.[14] However, in each case an approximately 50 cm^{-1} decrease is observed. We attribute this decrease to an intramolecular donor/acceptor interaction between an endocyclic nitrogen lone pair of electrons and the electropositive carbon center in the carbonyl group. Similar intramolecular nitrogen/carbonyl effects have been observed in the infrared spectra of cyclic amino ketones.[15] If one considers the phosphazene ring to have three-center (PNP) π molecular orbitals with nodes at the phosphorus atoms,[16] then this perturbation will affect only one of the three such regions in a cyclotriphosphazene. The loss of the ability of the nitrogen lone pair to interact with phosphorus centers will weaken the phosphorus–nitrogen bond in this region.[17] Therefore, one observes a strong phosphorus–nitrogen stretching vibration in the normal region (1270 cm^{-1}) and a significantly lower value associated with the phosphorus–nitrogen bonds deprived of the nitrogen lone pair interaction. Furthermore the phenyl multiplet in the ^1H NMR of I does not show significant separation between the ortho, meta and para protons indicating a decrease in the positive nature of the carbonyl carbon.

The prominent peaks in the mass spectra of I and II are dominated by ligand fragmentation processes. In both cases the $P_3N_3F_5OH^+$ ion is prominent. One can envision the formation of this ion via the elimination of the appropriately substituted acetylene, i.e., elimination of phenylacetylene from the molecular ion of I. The ion derived from the acetylene is observed in each case. It is also of interest to note the large $C_6H_5CN^+$ ion in the mass spectrum of I.

The stability of I and II is in marked contrast to that of carboxylic acid derivatives of phosphazenes. The interaction of the benzoate anion with $P_3N_3Cl_6$ yields the trimetaphosphate anion and benzonitrile.[5,18] The mechanism for this reaction is believed to proceed through ring nitrogen lone pair attack on the carbonyl carbon followed by rearrangement to the phosphonyl function and N-substituted phosphazane (see below). While we observe evidence for nitrogen lone pair–carbonyl interaction in I and II, we do not observe the facile rearrangement which occurs in the benzoate reaction.



Registry No. I, 63915-14-0; II, 63915-13-9; $P_3N_3F_6$, 15599-91-4; acetophenone, 98-86-2; cyclohexanone, 108-94-1.

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(10) In cm^{-1}.

(11) Only high-intensity peaks are reported. Several low-intensity, high-mass fragments are in the spectrum of I. Several high-intensity, low-mass fragments due to the organic groups of both I and II are also omitted.

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Synthesis and Characterization of Mixed-Halide, Partially Oxidized Potassium Tetracyanoplatinates

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The detailed understanding of the metallic state of highly conducting one-dimensional (1-D) inorganic complexes has been thwarted by the paucity of materials available for study.[1-4] This has been especially true for the study of systematic variations due to disorder,[5] metal, ligands, Fermi energy, etc.[1,2] For this reason it seemed appropriate to synthesize $K_2Pt(CN)_4X_{0.3}{\cdot}3H_2O$ (X = Cl, Br),[1] **1**, with a variable mixture of chloride and bromide in the tetragonal lattice and study the ramifications of such a structural modification on the physical properties. Herein we report on the synthesis of $K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O$, **2**, by slow evaporation of an aqueous solution of 440 mg of $K_2Pt(CN)_4$, 59.7 mg of $K_2Pt(CN)_4Br_2$, and 49.8 mg of $K_2Pt(CN)_4Cl_2$.

Complex **1** (X = Cl, Br) can be synthesized by a variety of techniques including electrochemical oxidation[6] in the presence of KX or effectively partially oxidizing[1,7] $K_2Pt(CN)_4$ with X_2 (X = Cl, Br) in aqueous solution. The former method, however, cannot be utilized to prepare **2** since even in the presence of excess bromide, **1** (X = Cl) will preferentially form.[8]

Complex **2** was obtained in 66% yield from $Pt^{II}(CN)_4{}^{2-}$, *trans*-$Pt^{IV}(CN)_4Cl_2{}^{2-}$, **3**, and *trans*-$Pt^{IV}(CN)_4Br_2{}^{2-}$, **4**, via eq 1. The microanalytical data of **2** support the mixed-halogen

$$50K^+ + 21Pt^{II}(CN)_4{}^{2-} + 2\textit{trans}\text{-}Pt^{IV}(CN)_4Br_2{}^{2-} + 2\textit{trans}\text{-}Pt^{IV}(CN)_4Cl_2{}^{2-} \xrightarrow{H_2O} 25K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O \quad (1)$$

$K_2Pt(CN)_4Br_{\sim 0.16}Cl_{\sim 0.16}{\cdot}xH_2O$[9] formulation. Powder x-ray diffraction data of **2** clearly show that **2** is neither a simple mixture of **1** (X = Cl and Br) nor an ordered system with alternating unit cells containing chloride and bromide (as well as the vacant site typically associated with **1**) as neither doublets indexed[11] to the *P4mm* space group of **1**[12] nor a unique new power diffraction pattern was observed. This was confirmed from analysis and refinement of the lattice constants taken from single-crystal x-ray data.[13] The derived unit cell parameters for **2** are a = 9.851 (2) Å, c = 5.766 (1) Å, and V = 559.6 (2) Å^3.[13] The c axis lies approximately halfway between the values reported by Williams et al. for **1** (X = Br)[12b] and **1** (X = Cl)[12a] which suggest an intermediate oxidation between $K_2Pt(CN)_4Br_{0.30}$ and $K_2Pt(CN)_4Cl_{0.33}$.[14] Reflections for **1** (X = Cl or Br) were not observed.

These lustrous metallic gold appearing needle crystals exhibit ν_{CN} at 2148 cm^{-1} (Nujol) and no evidence for ν_{PtX}. This is consistent with the structure of **1**, where only disordered ionic halides are observed,[1,12] and the infrared spectra in the ν_{CN} region for **1** (X = Br,[1,15] Cl[1,15b]) and $M_{1.75}Pt(CN)_4{\cdot}xH_2O$ (M = K, Cs).[15b] Thus, **2** is best described by the tetragonal *P4mm* structure of **1** except that the ~60% occupied halogen sites