equatorial substitution where the "s" contribution to the bonding is likely to be much greater than in the axial bonds.[4,33] Precise values have not yet been obtained for all possible axial CF_3 coupling constants because of the difficulty of analysis of the nmr spectra of substituted phosphoranes which become very complex at low temperatures; however it seems clear that axial CF_3 groups tend to have a smaller $^2J_{PF}$ value than equatorial CF_3 groups.[26] The equatorial coupling constants may be well established by the large values of $^2J_{PF}$ demonstrated by the chlorophosphoranes and by $(CF_3)_2PCl_2[N(CH_3)_2]$.

The proposed exclusive equatorial CF_3 substitution in chlorophosphoranes arising from the present nmr studies is unfortunately at variance with vibrational studies on these molecules. Both CF_3PCl_4[34] and $(CF_3)_2PCl_3$[35] appear to have C_{3v} symmetry (axial CF_3 groups). The reason for this inconsistency is not known but may arise from the difference in physical state since vibrational studies were done on gaseous samples (except for some Raman data on the neat liquids)[34,35] whereas nmr studies involve dilute solutions. Further inquiry into this problem is warranted.

Acknowledgments. We thank the National Research Council of Canada for financial support of this work, and Dr. K. I. The and Dr. A. J. Tomlinson for some experimental assistance. We also thank one of the referees for his extensive comments on the nmr spectra and positional averaging processes.

Registry No. $(CF_3)_3PCl_2$, 420-72-4; $(CH_3)_2NH$, 124-40-3; $(CF_3)_3P[N(CH_3)_2]_2$, 51874-38-5; $CF_3PO_3H^-$, 51965-63-0; $(CF_3)_2PCl_3$, 353-77-5; $(CF_3)_2Cl_2PN(CH_3)_2$, 51874-47-6; $(CF_3)_3P(Cl)N(CH_3)_2$, 52021-56-4; $CF_3P(S)Cl_2$, 18799-78-5; $CF_3P(S)[N(CH_3)_2]_2$, 18894-82-1; $CF_3P(S)Cl[N(CH_3)_2]$, 51965-67-4; $CF_3P(O)Cl_2$, 51965-64-1; $CF_3P(O)[N(CH_3)_2]_2$, 51965-65-2; $CF_3P(O)Cl[N(CH_3)_2]$, 51965-66-3; $(CF_3)_2PN(CH_3)_2$, 432-01-9; CH_3OH, 67-56-1; CH_3SH, 74-93-1; H_2S, 7783-06-4; HCl, 7647-01-0.

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Investigation of the Reactions of Tetrafluorodiphosphine with Some 3-Substituted Propene Derivatives[1]

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The investigation of the reaction of P_2F_4 with $F_2PCH_2CH{=}CH_2$ and $H_2NCH_2CH{=}CH_2$ has resulted in the formation of the new compounds $F_2PCH_2CHPF_2CH_2PF_2$ and $F_2PNHCH_2CH{=}CH_2$. $(CH_3)_2NCH_2CH{=}CH_2$ reacts in the dark with P_2F_4 to give unidentified solid products. The formation of $PF_2CH_2CHPF_2CH_2PF_2$ proceeds by a free-radical path. The tribasic character of this compound has been demonstrated by the formation of a triadduct with B_2H_6. The relative Lewis basicities of the two kinds of phosphorus in $F_2PCH_2CHPF_2CH_2PF_2$ have been investigated by an nmr study of a 1:1 mixture of B_2H_6 and $F_2PCH_2CHPF_2CH_2PF_2$.

Introduction

The free-radical addition of P_2F_4 to the double bond of ethene has been recently reported.[2] In this investigation, the generality of the free-radical behavior of P_2F_4 toward double bonds has been tested in three propene derivatives with phosphorus or nitrogen in the 3 position.

Experimental Section

General Techniques. Standard high-vacuum techniques were used throughout. A uv wavelength of 3000 A was employed in all irradiations. *N,N*-Dimethylallylamine (Eastman) and allylamine (Aldrich) were dried over Linde 3A molecular sieves and were distilled prior to use. All nmr data were obtained on a Varian XL-100-12 spectrometer. Nmr chemical shifts were obtained by the tube-interchange technique. Ir data were obtained on a Beckman IR-20A spectrometer. Solid-phase ir spectra were obtained at −196° using a low-temperature cell.[3] Mass spectral data were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer operating at 70 eV. Expected isotope peaks were observed but are omitted for brevity in the data following, as are peaks of mass number 30 or less and others not essential to characterization.

Preparation and Properties of 1,2,3-Tris(difluorophosphino)propane. In a typical reaction, 1.27 mmol of P_2F_4[4] and 0.65 mmol of $PF_2CH_2CH{=}CH_2$[5] were condensed at −196° into a 100-ml quartz reaction tube and allowed to warm to room temperature (both reactants were completely vaporized). The reaction mixture was then irradiated for 20 min. During the course of the irradiation, formation of a green-yellow solid on the sides of the reaction vessel was observed as well as the formation of a liquid in the bottom of the reaction tube. The reaction mixture was condensed to −196° and then distilled through traps held at 0, −45, and −196°. No material was apparent in the trap held at 0°. The trap held at −196° held 0.73 mmol of material which was identified (ir) as a mixture of PF_3 and P_2F_4. The trap held at −45° contained 0.48 mmol (mass) of a colorless liquid of low volatility (vp = 1 mm at 25.9°) which was subsequently identified as $PF_2CH_2CHPF_2CH_2PF_2$. The yield of $PF_2CH_2CHPF_2CH_2PF_2$ based on the amount of $PF_2CH_2CH{=}CH_2$ used was 73.5%. The liquid slowly decomposes to a yellow solid if allowed to stand at room temperature as indicated by the presence of a solid, yellow residue after transfer. In the absence of uv irradiation, no $F_2PCH_2CHPF_2CH_2PF_2$ was obtained from the reaction mixture. After extended irradiation (1.5 hr) no product was obtained, presumably a result of decomposition. The gas-phase ir of $PF_2CH_2CHPF_2CH_2PF_2$ shows the following absorption bands (relative intensity and tentative assignment in parentheses) (cm^{-1}): 2880 (vw, ν(C–H)), 1395 (w, $\delta_s(PCH_2)$), 1373 (w), 1350 (w, δ(HCH)), 1022 (m), 990 (w), 811 (s, ν(P–F)), 663 (m, ν(P–C)). The solid-phase ir shows absorption bands at 2890 (m, ν(C–H)), 2823 (w,

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ν(C–H)), 1400 (w, δ_s(PCH_2)), 1015 (m, b), 767 (s, b, ν(PF)), 724 (s, ν(PC)), 465 (m, δ(FPF)). The mass spectrum displays the following principal *m/e* values (relative intensities and assignments in parentheses): 248 (3.1, $PF_2CH_2CHPF_2CH_2PF_2^+$, molecular ion), 229 (0.7, $C_3H_5P_3F_5^+$), 179 (70, $C_3H_5P_2F_4^+$), 160 (1.4, $C_3H_5P_2F_3^+$), 141 (2, $C_3H_5P_2F_2^+$), 125 (2, $C_2HP_2F_2^+$), 110 (13.3, $C_3H_5PF_2^+$), 91 (75.8, $C_3H_5PF^+$), 83 (1.3, $PF_2CH_2^+$), 77 (6.6, $C_2H_3PF^+$), 71 (25, $PC_3H_4^+$), 69 (100, PF_2^+), 65 (59.1, $PFCH_3^+$), 64 (2.6, $PFCH_2^+$), 55.4 (1.7, metastable), 50 (5.8, PF^+), 46.4 (0.8, metastable), 41 (66.6, $C_3H_5^+$), 31 (1.8, P^+). Peaks corresponding to the loss of hydrogen from major fragments were also present as expected.

Preparation of $H_3BPF_2CH_2CHPF_2BH_3CH_2PF_2BH_3$. In a typical reaction, 0.48 mmol of $PF_2CH_2CHPF_2CH_2PF_2$ and 2.46 mmol of B_2H_6 were condensed at −196° in a reaction tube. The reactants were allowed to warm to room temperature and stand for 5 min. The volatiles were then recondensed to −196° and the above process was repeated two times. The volatile products of the reaction were distilled through traps held at −78 and −196°. No material was recovered from the −78° trap. The trap held at −196° contained 1.72 mmol of B_2H_6. This corresponds to a 1.54:1 reaction ratio of B_2H_6 to $PF_2CH_2CHPF_2CH_2PF_2$. A colorless nonvolatile liquid remained in the reaction tube. The liquid decomposed slowly at room temperature to a yellow solid. The liquid was subsequently identified as $H_3BPF_2CH_2CHPF_2BH_3CH_2PF_2BH_3$. The liquid-phase ir spectrum of $H_3BPF_2CH_2CHPF_2BH_3CH_2PF_2BH_3$, obtained between sodium chloride plates, shows the following absorption bands (relative intensities and tenative assignments in parentheses) (cm^{-1}): 2905 (w, ν(CH)), 2880 (w, ν(CH)), 2405 (m, ν(BH)), 2360 (m, ν(BH)), 1395 (w, δ_s(PCH_2)), 1340 (w, δ(HCH)), 1040 (m), 980 (w), 888 (s, ν(PF)), 730 (m, ν(P–C)).

Preparation of a B_2H_6-$PF_2CH_2CHPF_2CH_2PF_2$ Mixture Deficient in B_2H_6. An nmr sample consisting of 0.25 mmol of $PF_2CH_2CHPF_2CH_2PF_2$ and 0.25 mmol of B_2H_6 was prepared by condensing these amounts into an nmr tube. The reactants were allowed to warm to room temperature and stand for 3 min and were recondensed to −196°. This process was repeated two more times before condensing the contents to −196° and sealing the nmr tube. The same procedure was used to prepare a sample with B_2H_6 and $F_2PCH_2CHPF_2CH_2PF_2$ in ratio of 0.5:1.

Preparation of Allylaminodifluorophosphine. In a typical reaction, 1.65 mmol of P_2F_4 was condensed at −196° into a 200-ml reaction bulb connected *via* a stopcock to a 500-ml reaction bulb into which 1.58 mmol of allylamine was condensed. The reactants were allowed to warm to room temperature (both reactants completely vaporized) and the connecting stopcock was opened. The immediate formation of a yellow cloud of solids was observed. The reaction was allowed to proceed for 10 sec and then condensed to −196°. The volatile products were distilled through traps held at −45, −63, and −196°. A mixture of brown, yellow, and orange solids remained in the reaction bulb. No material was recovered from the trap held at −45°. The trap held at −196° contained 0.94 mmol of PF_3 with a trace of P_2F_4 (ir). The trap held at −63° contained 0.37 mmol (mass) of a colorless liquid of low volatility which was subsequently identified as $PF_2NHCH_2CH{=}CH_2$. The yield of $PF_2NHCH_2CH{=}CH_2$ based on the amount of allylamine used was 23.4%. The vapor pressure of $PF_2NHCH_2CH{=}CH_2$ was approximately 8.5 mm at room temperature. Fairly rapid decomposition of $PF_2NHCH_2CH{=}CH_2$ at room temperature to a yellow solid prevented obtaining accurate vapor pressure data. A similar reaction in a quartz tube which was irradiated with uv light for periods from 5 min to 1.5 hr proceeded in the same fashion resulting in the same products. The yield of this reaction was lower, presumably due to decomposition of $PF_2NHCH_2CH{=}CH_2$ while standing at room temperature over a longer period of time. The gas-phase ir spectrum of $PF_2NHCH_2CH{=}CH_2$ showed the following absorption bands (relative intensities and tentative assignments in parentheses) (cm^{-1}): 3420 (m, ν(N–H)), 3045 (w, ν(C–H olefinic)), 3010 (vw, ν(C–H olefinic)), 2995 (w, ν(C–H)), 2960 (w, ν(C–H)), 2940 (w, ν(C–H)), 1648 (w, ν(C=C)), 1450 (w, δ(CH_2)), 1404 (ms, δ($=CH_2$)), 1356 (m, δ(HCH)), 1230 (m, δ(CH_2)), 1132 (m, ?), 1076 (s, ν(PN–C)), 1025 (m, ?), 990 (m, δ(HCC in $CH_2=$)), 923 (ms, δ(HCC in =CH–)), 820 (s, ν(P–F)), 788 (s, ν(P–NC)), 610 (vw, ?), 538 (m, δ(FPF)). The mass spectrum of $PF_2NHCH_2CH{=}CH_2$ displayed the following principal *m/e* values (relative intensities and assignments in parentheses): 125 (38.4, $PF_2NHCH_2CHCH_2^+$, molecular ion), 124 (70.9, $PF_2NC_3H_5^+$), 112 (1.9, $PF_2NC_2H_5^+$), 106 (7.0, $PFNC_3H_6^+$), 99 (34.8, $PF_2NCH_4^+$), 98 (57.0, $PF_2NCH_3^+$), 97 (5.1, $PF_2NCH_2^+$), 96 (20.9, PF_2NCH^+), 86 (2.4, $PNC_3H_5^+$), 85 (2.7, $PNC_3H_4^+$), 78 (6.7, $PFNCH_2^+$), 69 (61.6, PF_2^+), 56 (52.3, $NC_3H_6^+$), 50 (5.3, PF^+), 46 (3.0, PNH^+), 31 (0.9, P^+), 28 (100, CH_2N^+), 25.1 (1.2, metastable). Other peaks of low mass number corresponding to fragmentation of the allylamine moiety were also observed.

Reaction of P_2F_4 with $(CH_3)_2NCH_2CH{=}CH_2$. In a typical reaction 1.07 mmol of P_2F_4 and 0.61 mmol of $(CH_3)_2NCH_2CH{=}CH_2$ were condensed at −196° into a 100-ml quartz tube. As the reaction mixture slowly warmed to room temperature, a rapid reaction indicated by the formation of a cloud of brown solids was observed. The volatile products were distilled through traps held at −63 and −196°. Some brown solid remained in the reaction tube. The trap held at −63° contained 0.41 mmol of $(CH_3)_2NCH_2CH{=}CH_2$ (ir). The trap held at −196° contained a PF_3-P_2F_4 mixutre (ir). An 0.81-mmol sample of P_2F_4 and 0.79 mmol of $(CH_3)_2NCH_2CH{=}CH_2$ condensed at −196° into a 100-ml quartz reaction tube also resulted in the formation of a brown cloud upon warming. Irradiating the resulting gaseous reaction mixture for 14 min, 40 min, and 2 hr and 50 min, with examination of the products by distillation after each irradiation period, resulted in no new volatile products and recovery of only starting materials and PF_3. The brown solids remaining in the reaction tubes were not identified.

Results and Discussion

The general physical and chemical properties of the new compounds have been included in the Experimental Section. Although elemental analysis has not been obtained, the unequivocal identification of the compounds by spectroscopic means has been completed as described below.

Synthesis of 1,2,3-Tris(difluorophosphino)propane. The reaction of $F_2PCH_2CH{=}CH_2$ with P_2F_4 has resulted in the preparation of $F_2PCH_2CHPF_2CH_2PF_2$. The reaction proceeds when irradiated with uv light. The product does not form in the absence of uv light. On the basis of the preceding and the known formation of PF_2 radicals from P_2F_4 at this frequency,[6] it has been concluded that the reaction involves a free-radical addition of P_2F_4 to the double bond in $PF_2CH_2CH{=}CH_2$. The free-radical behavior of P_2F_4 has been observed in the reaction of P_2F_4 with ethene.[2]

The new potential tridentate ligand $PF_2CH_2CHPF_2CH_2PF_2$ has been unequivocally characterized by ir, mass spectral, and nmr data. The ir assignments (Experimental Section) are in good agreement with the proposed structure. Also, the absence of ν(C=C) and vinyl C–H stretching bands indicates the absence of a double bond and suggests addition to the double bond of $F_2PCH_2CH{=}CH_2$ has occurred.

The mass spectrum shows a peak at *m/e* 248 which corresponds to the molecular ion. Other peaks correspond to successive loss of F, PF_2, and H and fragmentation of the carbon skeleton. In addition to these and the parent peak, the mass spectrum exhibits two metastable peaks. The metastable peak at *m/e* 46.4 indicates that the transition from *m/e* 91 to 65 occurs with loss of a neutral fragment of mass 26, corresponding to loss of C_2H_2 and consistent with assignments of $CH_2CHCH_2PF^+$ and CH_3PF^+ to the 91 and 65 peaks. The metastable peak at *m/e* 55.4 indicates that the transition from *m/e* 91 to 71 occurs *via* loss of a neutral fragment which in this instance is HF. The isotope peaks (not included) are consistent with the *m/e* assignments. The spectrum is entirely consistent with the assigned structure.

The proton nmr spectrum (100.1 MHz, −60°) consists of a broad unsymmetrical peak at δ ~2.1 ppm downfield of TMS. No further detail could be resolved, though the asymmetry suggests more than one proton environment. The fluorine nmr spectrum (94.1 MHz, −60°, Figure 1C) consists of two 1:1 doublets which are 2:1 in total area. This pattern is consistent with the presence of three PF_2 moieties, two of which are equivalent. One doublet is centered at δ_a +99.3 ppm from $CFCl_3$. The other, less intense doublet

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(6) J. H. Current, J. K. Burdett, L. Hodges, and V. Dunning, *J. Phys. Chem.*, 74, 4053 (1970).

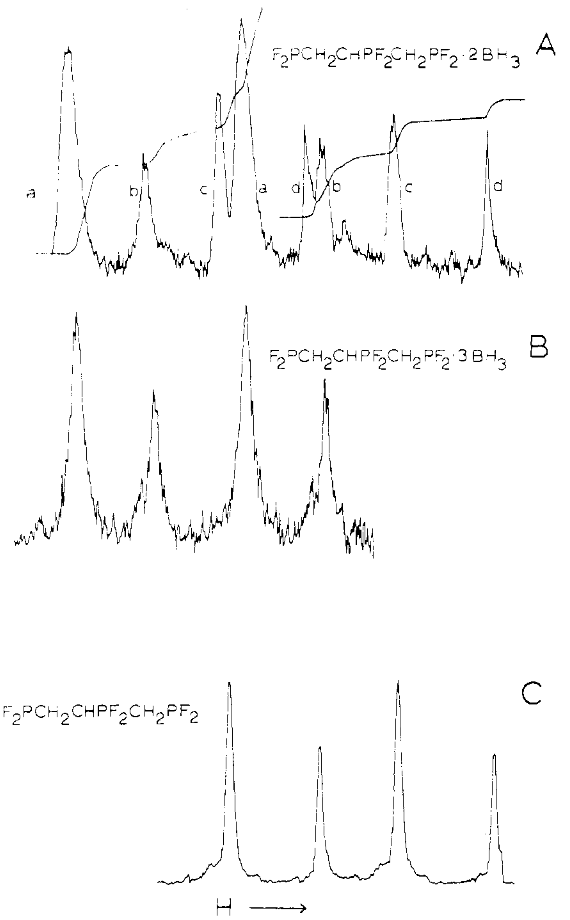
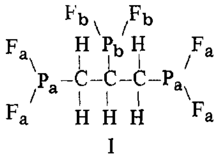


Figure 1. ^{19}F nmr spectra of $F_2PCH_2CHPF_2CH_2PF_2$ neat and in 1:3 and 1:2 complexes with BH_3.

is centered at δ_b +106.2 ppm from $CFCl_3$. (The subscripts a and b that appear in chemical shift and coupling constants refer to structure I). The chemical shift of the more intense


$F_2P_a{-}CH_2{-}CH(P_bF_2){-}CH_2{-}P_aF_2$

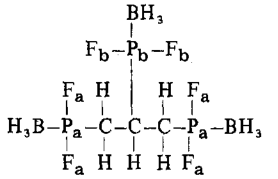
I

doublet which results from the "a" fluorine signal is in close agreement with the value found in the similar compound $PF_2CH_2CH_2PF_2$ (δ +98.7 ppm).[2] The more intense doublet arises from the splitting of the nmr signal of the four equivalent "a" fluorines by the "a" phosphorus nucleus which is directly attached to them ($J_{P_aF_a}$ = 1181 Hz). The less intense doublet arises from the splitting of the nmr signal of the two equivalent "b" fluorines by the "b" phosphorus nucleus ($J_{P_bF_b}$ = 1219 Hz). PF coupling constants are appropriate for the PF_2 moiety.[7] Further splitting by other magnetically active nuclei could not be resolved.

The phosphorus nmr spectrum (40.5 MHz, −60°) consists of two 1:2:1 triplets which are 2:1 in total area. This supports the above assignment of three PF_2 moieties, two of which are equivalent. The larger triplet is centered at δ_a −232.9 ppm from 85% H_3PO_4. The less intense triplet is located at δ_b −214.6 ppm from 85% H_3PO_4. The chemical shift of the more intense triplet which corresponds to the "a" phosphorus is in close agreement with the value found for the similar compound $PF_2CH_2CH_2PF_2$ (δ −234 ppm).[2] This triplet arises from the splitting of the nmr signal of the two equivalent "a" phosphorus nuclei by the two "a" fluorines attached to each ($J_{P_aF_a}$ = 1138 Hz). The less intense triplet arises from the splitting of the nmr signal of the "b" phosphorus nucleus by the two "b" fluorine nuclei ($J_{P_bF_b}$ = 1172 Hz). No further detail could be resolved.

Synthesis of $H_3BPF_2CH_2CHPF_2BH_3CH_2PF_2BH_3$. The tribasic character of $PF_2CH_2CHPF_2CH_2PF_2$ has been demonstrated by the formation of $H_3BPF_2CH_2CHPF_2BH_3CH_2PF_2BH_3$ *via* the interaction of $PF_2CH_2CHPF_2CH_2PF_2$ and excess B_2H_6. The triadduct has been characterized by stoichiometric, ir, and nmr data. The experimental 1.54:1 stoichiometric ratio of B_2H_6 to $PF_2CH_2CHPF_2CH_2PF_2$ is in excellent agreement with the expected 1.50:1 ratio for a triadduct. The shift of the P-F stretching frequency from 811 cm^{-1} in the free ligand to 888 cm^{-1} in the triadduct is consistent with adduct formation.[8] The characteristic B-H absorption band confirms the presence of a B-H bond.

The proton nmr spectrum (100.1 MHz, +20°) consists of a broad (~500 Hz) unsymmetrical multiplet centered at ~0.15 ppm downfield of TMS. No splitting could be assigned or resolved. That splitting was not observed is likely due to two contributing factors. First, due to the unstable nature of the triadduct at higher temperatures, the spectrum was obtained on the neat liquid at the lowest possible temperature and viscosity effects would tend to broaden the signal observed. Second, close overlapping of the nonequivalent BH_3 proton multiplets together with the broadness expected of this signal resulting from quadrupolar broadening by the boron obscures the individual peaks. The fluorine nmr spectrum (94.1 MHz, +20°, Figure 1B) consists of two 1:1 doublets which are 2:1 in total area, just as in the free ligand. Both are shifted to lower field in the adduct and the peaks are broadened significantly relative to those of the free ligand. The more intense doublet is centered at δ_a +85.2 ppm from $CFCl_3$ ($J_{P_aF_a}$ = 1198 Hz). (See structure II for a, b atom designations.) The less intense doublet is centered at δ_b +91.1 ppm from $CFCl_3$ ($J_{P_bF_b}$ = 1202 Hz). The splitting arises in a manner analogous to that discussed for the free ligand. The signal broadening is due to quadrupole relaxation by the boron nuclei which are bound to the phosphorus atoms.


$H_3B{-}P_aF_2{-}CH_2{-}CH(P_bF_2BH_3){-}CH_2{-}P_aF_2{-}BH_3$

II

The phosphorus nmr spectrum (40.5 MHz, +20°) consists of a broad 1:2:1 triplet centered at δ −159.2 ppm (85% H_3PO_4) (J_{P-F} = 1198 Hz). The apparent collapse of two distinct phosphorus signals in the free ligand to a single broad triplet in the triadduct is thought to be a result of two factors both associated with adduct formation. The attachment of BH_3 groups to all three phosphorus atoms causes their magnetic environments to become more nearly equivalent than in the free ligand, thereby reducing the chemical shift difference. The quadrupolar broadening effect of the boron nuclei results in significantly less sharp signals. These factors,

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(7) J. F. Nixon, *Advan. Inorg. Chem. Radiochem.*, **13**, 364 (1970).

(8) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 2436 (1969).

together with quite similar P-F coupling of the nonequivalent phosphorus atoms with the fluorine atoms (1198 and 1202 Hz from the fluorine spectra), result in the unresolved spectrum observed.

The boron nmr spectrum (32.1 MHz, +20°) consists of a single broad peak centered at δ +44.0 ppm from $BF_3\cdot O(CH_2CH_3)_2$. This indicates that the two potentially different boron nuclei are approximately magnetically equivalent. Failure to observe B-H or B-P splitting is apparently due to a combination of close overlap of the two types of borane as well as the viscosity effect alluded to in the discussion of the ^1H nmr spectrum, though "thermal decoupling"[9] may also be a factor.

Relative Lewis Basicity of Phosphorus Sites in $PF_2CH_2CHPF_2CH_2PF_2$. The ^{19}F nmr spectrum of a sample containing $F_2PCH_2CHPF_2CH_2PF_2$ and B_2H_6 in a 1:1 ratio (1:2 = $F_2PCH_2CHPF_2CH_2PF_2$:BH_3) is shown in Figure 1A. The spectrum is made up of four 1:1 doublets (a, b, c, and d). Chemical shifts and coupling constants are as follows: (a) +84.8 ppm, 1242 Hz; (b) +90.6 ppm, 1245 Hz; (c) +96.2 ppm, 1212 Hz; (d) +102.8 ppm, 1238 Hz. These peaks can be assigned on the basis of chemical shifts similar to those in the free ligand (Figure 1C) and in the completely bound ligand (Figure 1B), the additional breadth arising from coordination of the PF_2 group to BH_3, and relative peak areas. The results are that a and b correspond to the bound PF_2 groups and c and d to the free PF_2 groups. Further, a and c correspond to the terminal PF_2 groups while b and d correspond to the unique PF_2 group on the basis of the 2:1 area ratios (Figure 1A). Although thermodynamic data are required quantitatively to compare the relative basicities of the two base sites, some qualitative statements can be made. There cannot be a large difference in basicity at the two sites because both sites are observed bound and free in a borane-deficient sample rather than one site being entirely bound. Statistically, the terminal PF_2 groups should be favored over the secondary site in a 2:1 ratio; that is, for equal base strengths, the area ratio expected is 2:1 = a:b. The observed ratio is 2.7:1 indicating that the terminal sites are slightly more basic than is the unique site. The ^{31}P nmr spectrum also clearly shows two different triplet sets and their relative breadths imply that one corresponds to a bound set of PF_2 sites and the other to an unbound set, but the signals overlap severely and thus do not provide the detailed information provided by the fluorine spectrum. The latter observation is consistent with the spectra of both the free and the completely bound compounds.

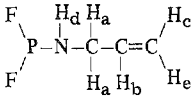
In the ^{19}F nmr spectrum of a 1:1 molar sample of BH_3 and $PF_2CH_2CHPF_2CH_2PF_2$ the signal corresponding to the bound terminal PF_2 site is clearly apparent while that for the bound unique PF_2 site is not discernible above the noise. The intensity of the observed signal is such that, assuming comparable peak widths, the presence of the bound unique PF_2 group should be clearly apparent if both bound species were present in the statistically expected ratio of 2:1. On the other hand, signals for both unbound sites are observed as well, with area ratio not greatly different from 2:1, implying that both sites have been removed from the free ligand "pool" nearly equally. The net implication of this experiment is of a very slight preference for the terminal PF_2 site, as suggested by the data above for the 2:1 mixture. Any difference in basicity between the two sites appears to be small enough so as to have no dramatic effect on the coordination chemistry of the compound $F_2PCH_2CHPF_2CH_2PF_2$.

Synthesis of Allylaminodifluorophosphine. The reaction of allylamine with P_2F_4 has resulted in the formation of $PF_2NHCH_2CH{=}CH_2$. Unlike the reaction involving P_2F_4 and $PF_2CH_2CH{=}CH_2$, this reaction does not proceed by a free-radical path. This has been concluded on the basis that the reaction yields the same product when irradiated with uv light as is formed in the absence of uv light. Since cleavage of an N-H bond and the formation of a solid have been observed in this reaction, a mechanism involving formation of amine salts is feasible.

The new compound $PF_2NHCH_2CH{=}CH_2$ has been unequivocally characterized by ir, mass, and nmr spectral data. In the ir spectra, the absorption bands at 3045, 1648, 990, and 923 cm^{-1} indicate the presence of a vinyl group. The absorption band at 3420 cm^{-1} indicates the presence of an N-H bond. The lack of a second band (ν_{asym}(N-H)) in the ir spectrum eliminates the presence of an NH_2 group in the molecule. A PF_2 group is indicated by the absorption bands at 820 and 538 cm^{-1}.

The mass spectrum contains a strong peak at *m/e* 125 which is the molecular ion. The metastable peak at *m/e* 25.1 indicates that the transition from *m/e* 125 to 56 occurs. This transition corresponds to the loss of PF_2 from the parent ion. The intense *m/e* 56 peak demonstrates that the allylamine moiety remains basically intact in the compound. The assigned isotope peaks are consistent with the *m/e* assignments. The remainder of the fragmentation pattern (see Experimental Section) is fully consistent with the assigned structure.

The proton nmr spectrum (100.1 MHz, −60°) consists of a broad absorption [δ values are subscripted with letters designating the proton nuclei which are responsible for the signal (structure III)] at δ_a 3.08 ppm, a broad doublet centered at δ_d 3.12 ppm, a multiplet centered at δ_{ce} 4.55 ppm, and a broad absorption centered at δ_b 5.09 ppm. All chemical shifts are downfield of TMS. The doublet arises from the splitting of the "d" proton by the phosphorus. ($J_{PNH} \approx 47$ Hz: value is approximate because half of the doublet is buried under the δ_a signal. The assignment is supported by the J_{PNH} coupling assignment from the ^{31}P spectrum.) The observed areas of the signals support the above assignments. The assignments are also supported by relative chemical shift values characteristic of vinyl groups.[10]



III

The fluorine nmr spectrum (94.1 MHz, −60°) consists of a doublet centered at δ +68.1 ppm from $CFCl_3$. This is consistent with the existence of a PF_2 group in the molecule. The doublet arises from the splitting of the fluorine signal by the phosphorus nucleus (J_{PF} = 1212 Hz). Chemical shift values for similar compounds have been reported: $PF_2N(CH_3)_2$, δ +65.5 ppm from $CFCl_3$;[11] $F_2PN(CH_2CH{=}CH_2)_2$, δ +63.7 ppm from $CFCl_3$.[12]

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[9] H. L. Hodges and R. W. Rudolph, *Inorg. Chem.*, 11, 2845 (1972).

[10] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967.

[11] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

[12] G. H. Dungan and J. R. Van Wazer, "Compilation of Reported ^{19}F NMR Chemical Shifts," Wiley-Interscience, New York, N. Y., 1970.

The phosphorus nmr spectrum consists of a triplet of doublets centered at -137.8 ppm (85% H_3PO_4). This is consistent with the existence of a PF_2NH group. The phosphorus signal is split into a triplet by the two equivalent fluorine nuclei ($J_{P-F} = 1172$ Hz). Each member of this triplet is then split into a doublet by the "d" proton nucleus attached to the nitrogen ($J_{PNH_d} = 47$ Hz). A comparable chemical shift value of -143 ppm (85% H_3PO_4) has been reported for $PF_2N(CH_3)_2$. The assignments are also supported by agreement of the J_{P-F} coupling from the ^{19}F spectrum.

Reaction of P_2F_4 with $(CH_3)_2NCH_2CH{=}CH_2$. Since a free-radical process was evident in the formation of $PF_2CH_2CHPF_2CH_2PF_2$ and an apparent N-H bond cleavage with formation of amine salts occurred in the formation of $PF_2NHCH_2CH{=}CH_2$, the interaction of P_2F_4 with $(CH_3)_2NCH_2CH{=}CH_2$ was investigated as it was thought that by elimination of the N-H bond as a reaction site, the reaction could proceed by free-radical addition. However, this was not found to be the case. Results indicate a non-free-radical reaction yielding an unidentified brown solid, unreacted $(CH_3)_2NCH_2CH{=}CH_2$, and PF_3.

Acknowledgments. We thank A. Srinivasan and G. Kodama for assistance in obtaining nmr data. Some of the spectra were obtained using equipment of the University of Utah. Financial support of the College of Science and University Research Council at Utah State University, the U. S. Army Research Office (Durham), and the Research Corp. is greatly appreciated.

Registry No. P_2F_4, 13824-74-3; $PF_2CH_2CH{=}CH_2$, 52124-33-1; $PF_2CH_2CHPF_2CH_2PF_2$, 52124-34-2; B_2H_6, 19287-45-7; $F_2PCH_2CHPF_2CH_2PF_2\cdot 3BH_3$, 52124-35-3; $F_2PCH_2CHPF_2CH_2PF_2\cdot 2BH_3$, 52124-36-4; $H_2NCH_2CH{=}CH_2$, 107-11-9; $PF_2NHCH_2CH{=}CH_2$, 52124-37-5.

Contribution from the Research Resources Center and the Department of Biochemistry, University of Illinois at the Medical Center, Chicago, Illinois 60612, and from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Cyclic Phosphates with Substitution or with Conjoined or Fused Rings

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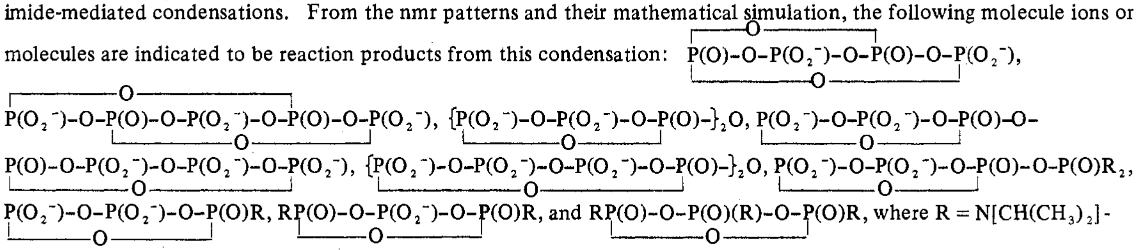
Conditions are reported for optimization of the nine detectable products obtained from orthophosphoric acid by carbodiimide-mediated condensations. From the nmr patterns and their mathematical simulation, the following molecule ions or molecules are indicated to be reaction products from this condensation: $\mathrm{P(O)-O-P(O_2^-)-O-P(O)-O-P(O_2^-)}$, $\mathrm{P(O_2^-)-O-P(O)-O-P(O_2^-)-O-P(O)-O-P(O_2^-)}$, $\mathrm{\{P(O_2^-)-O-P(O_2^-)-O-P(O)-\}_2O}$, $\mathrm{P(O_2^-)-O-P(O_2^-)-O-P(O)-O-P(O)-O-P(O_2^-)-O-P(O_2^-)-O-P(O_2^-)}$, $\mathrm{\{P(O_2^-)-O-P(O_2^-)-O-P(O_2^-)-O-P(O)-\}_2O}$, $\mathrm{P(O_2^-)-O-P(O_2^-)-O-P(O)-O-P(O)R_2}$, $\mathrm{P(O_2^-)-O-P(O_2^-)-O-P(O)R}$, $\mathrm{RP(O)-O-P(O_2^-)-O-P(O)R}$, and $\mathrm{RP(O)-O-P(O)(R)-O-P(O)R}$, where $\mathrm{R = N[CH(CH_3)_2]\text{-}[C(O)NHCH(CH_3)_2]}$ for condensation with diisopropylcarbodiimide and is the equivalent urea derivative for other carbodiimides. Upon hydrolysis of the condensation product mixtures, the compounds $\mathrm{RP(O_2^-)-O-P(O_2^-)-O-P(O_2^-)R}$, $\mathrm{RP(O_2^-)-O-P(O_2^-)-O-P(O_3^{2-})}$, and $\mathrm{RP(O_2^-)-O-P(O_3^{2-})}$ were produced in addition to some of the usual inorganic chain and ring phosphates. The products obtained by condensation of the tri- and tetrametaphosphoric acids are also discussed.



Although the condensed phosphates[1] make up one of the more important families of chemical compounds (having broad significance to biochemistry[2] as well as many industrial applications[2]), our knowledge of them is still woefully incomplete. In spite of the fact that straight-chain and simple-ring phosphates have been recognized for about a century, individual members of each of these series of compounds up to about the decaphosphate have been separated only quite recently.[3] The situation with respect to oligophosphates containing branching PO_4 groups has until now been almost purely speculative. It has been suggested[4] that the 1,5-μ-oxo-tetrapolyphosphate anion (structure I, given below), must serve as an intermediate in the solvolysis of the P_4O_6 cage molecule. Also, on the basis of hydrolysis products, the orthophosphatyltrimetaphosphate structure (ester IV) was claimed.[5] Unfortunately, because of substituent exchange reactions occurring during the hydrolysis process, this type of structure proof is not very satisfactory for the condensed phosphates and their derivatives. Therefore, we must conclude that, prior to the work described herein, there has been no acceptable evidence for the existence of branched oligophosphates, although it surely seemed reasonable to assume that they exist.

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(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Wiley-Interscience, New York, N. Y., 1958.

(2) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. II, Wiley-Interscience, New York, N. Y., 1961. Also see any general text on biochemistry.

(3) (a) E. J. Griffith and R. L. Buxton, *J. Amer. Chem. Soc.*, **89**, 2884 (1967), and references therein, for chain phosphates; (b) T. Glonek, J. R. Van Wazer, M. Mudgett, and T. C. Myers, *Inorg. Chem.*, 11, 567 (1972), for ring phosphates. Small amounts of both rings and chains through the decaphosphate have been isolated in our laboratory by eluting various phosphate condensation products from an anion-exchange column.

(4) *E.g.*, G. Burkhardt, M. P. Klein, and M. Calvin, *J. Amer. Chem. Soc.*, 87, 591 (1965). For a proper interpretation of this chemistry, see J. R. Van Wazer and S. Norval, *ibid.*, 88, 4415 (1966). For another example showing branched phosphates in hypothetical reactions, see p 694 of ref 1.

(5) R. Ratz and E. Thilo, *Justus Liebig Ann. Chem.*, 572, 173 (1951).