molecule. If both of these electrons are forced to occupy the 7a' orbital, we obtain the singlet state, and the energy parallels the triplet 7a' about 31 kcal higher. Thus on the HNO side of the molecule the separation between 7a' and 2a'' is sufficiently large virtually to overcome the added repulsion energy from a doubly occupied 7a' orbital and the singlet and triplet have the same energy. On the HON side of the molecule the separation is only half that on the other and the electrons prefer to be in different orbitals. The difference between the two ends of the NO is largely due to the greater size of the N AO's and the consequent greater interaction with the H.

We may look at the effects operating in these molecules in another way that is very useful. HNO is isoelectronic with O_2 and also with H_2CO, formaldehyde. We can envisage a partially united atom approach in which we start with O_2, move one proton out to get HNO, and then move a second to get H_2CO. Figure 5 shows qualitatively the changes in the energies of the important states. For O_2 the $^3\Sigma_g^-$ is lowest and the $^1\Delta_g$ is considerably higher. When one proton is moved out at an angle the degeneracy of the Δ state is split and the resulting $^3A''$ and $^1A'$ have about the same energy. By the time that two protons are placed off-center, the splitting of the original $^1\Delta_g$ is so large that the first excited triplet state of formaldehyde is much higher in energy than the singlet. It is also quite evident from the calculations reported here that the proton in HON cannot split the $^1\Delta_g$ state far enough to bring the $^1A'$ energy below the $^3A''$. These calculations have allowed us to put the graph originally given by Orgel[8] on a somewhat more quantitative level.

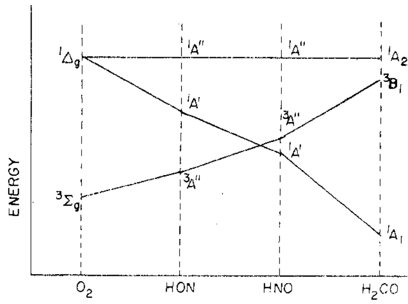

Figure 5. Qualitative representation of the energies in passing from O_2 to H_2CO.

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Registry No. HNO, 14332-28-6; HON, 35337-59-8.

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Photoreactions of Tetrafluorodiphosphine with Nonsubstituted Olefins and Perfluoroolefins[1]

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The photoreactions of P_2F_4 with C_2H_4, C_3H_6, 2-C_4H_8, C_6H_{10}, C_2F_4, and C_3F_6 have resulted in the formation of $F_2PCH_2CH_2PF_2$, $CH_3CHPF_2CH_2PF_2$, $CH_3CHPF_2CHPF_2CH_3$, $C_6H_{10}(PF_2)_2$, $F_2PCF_2CF_2PF_2$, and $CF_3CFPF_2CF_2PF_2$. No recoverable amount of comparable products was obtained in similar mixtures of P_2F_4 and 2-C_4F_8 or of P_2F_4 and C_6F_{10}. The new compounds were characterized by ir, nmr, and mass spectrometry. $C_6H_{10}(PF_2)_2$ displays temperature-dependent nmr spectra consistent with the trans isomer.

Introduction

The ability of P_2F_4 to generate PF_2 radicals has been established by physical means.[2,3] Although it has been suggested that the PF_2 radical might be involved in syntheses of certain compounds,[4-6] the chemical behavior of the PF_2 radical remains unexplored. In a recent communication[7] we reported the reaction of P_2F_4 with ethene in the presence of ultraviolet light, a reaction which did not proceed in the absence of uv light. We wish to report in this paper the reaction of P_2F_4 with olefins and perfluoroolefins which resulted in the preparation and characterization of 1,2-bis(difluorophosphino)propane ($C_3H_6P_2F_4$), 2,3-bis(difluorophosphino)butane ($C_4H_8P_2F_4$), *trans*-1,2-bis(difluorophosphino)cyclohexane ($C_6H_{10}P_2F_4$), 1,2-bis(difluorophosphino)perfluoroethane ($C_2F_4P_2F_4$), and 1,2-bis(difluorophosphino)perfluoropropane ($C_3F_6P_2F_4$) and the attempted syntheses of 2,3-bis(difluorophosphino)perfluorobutane ($C_4F_8P_2F_4$) and 1,2-bis(difluorophosphino)perfluorocyclohexane. Data for $C_2H_4P_2F_4$, reported earlier,[7] are included for comparison.

Experimental Section

General Techniques. Standard high-vacuum techniques were used throughout.[8] Apiezon N grease was used for joints in general, although Kel-F No. 90 was found to give cleaner products in experiments with fluorocarbons. Infrared spectra were obtained using a low-temperature infrared cell[8] and a 75-mm path length gas cell with KBr windows on a Beckman IR-20-A spectrometer. ^{31}P, ^{19}F, and ^1H nmr spectra of the neat liquids were obtained at 40.4, 94.1, and 100.1 MHz, respectively, with a Varian Associates XL-100-12 instrument. External standards were used for chemical shift measurements unless noted otherwise. Chemical shift values are given in ppm from 85% orthophosphoric acid, CCl_3F, and TMS. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer. A Rayonet photochemical reactor (Southern N.E. Ultraviolet Co., Middleton,

Table I. Nmr Data for Olefin (Perfluoroolefin) + P_2F_4 Addition Products

	^{1}H	^{31}P		^{19}F	
	δ,^{a} ppm	δ,^{a} ppm	J_{P-F}, Hz	δ,^{a} ppm	J_{P-F}, Hz
$C_2H_4P_2F_4$	+1.6	−234	1170	+98.7	1168
$C_3H_6P_2F_4$	+1.67, CH_3 +1.03, CH_2 CH	−234	1190	+88.3	1185
$C_4H_8P_2F_4$	+1.29, CH_3 +1.9, CH	−231 } −234 }	meso {1198 *d,l* {1193	+107 {^{b} meso, *d,l*}	1180
$C_6H_{10}P_2F_4$	+1.97	−234.1 large triplet^c	1218	+81.3	1174
	(+1.80, 2.14 at −60°)	−241.4 small triplet^c	1203		
$C_2F_4P_2F_4$		−227	$^1J_{PF}$ = 1258 $^2J_{PF}$ = 91 $^3J_{PF}$ = 20	+106, PF_2 +132, CF_2	J_{PF} = 1252 $^2J_{PF}$ = 86

[a] Sign conventions: ^{1}H, + = downfield from TMS; ^{19}F, ^{31}P, + = upfield from $CFCl_3$ or from 85% H_3PO_4. For sample temperatures, see text. [b] Complex overlapping multiplet–average positions are given. [c] See Figure 1 and text.

Conn.) containing reactor lamps RPR-3000A was used as the energy source. The photoreaction tube used consisted of a 200-ml quartz tube (45-mm o.d.) attached to a vacuum stopcock and a 10/30 joint to allow entry to the vacuum system.

Materials. P_2F_4 was prepared by the method of Centofanti and Rudolph.[9] Propene and butene-2 were obtained from Matheson (CP). The former was distilled through a −150° trap and the latter through a −78° trap before using. Cyclohexene was obtained commercially, dried over Linde molecular sieves, and distilled from a trap held at −78° to one held at −196°. The −78° fraction was used for the reaction. All perfluoroolefins were obtained from PCR, Inc. Gainesville, Fla. C_2F_4 was purified by passing it through a −84° trap to a −196° trap with pure C_2F_4 being retained in the −196° trap.[10] Perfluoropropene was distilled through traps held at −78, −130, and −196°. The contents of the −130° trap were used in the preparations. Perfluorobutene-2 was distilled through traps held at −78, −160, and −196°. The contents of the −160° trap were used in the reactions.

Reaction of P_2F_4 with C_2H_4. In a typical reaction, 1.9 mmol of P_2F_4 and 1.01 mmol of C_2H_4 were frozen into the photoreaction tube. The contents were allowed to warm to room temperature with no visible reaction occurring. Maintaining the reaction tube in the dark for 2 hr and subsequent distillation as described below did not result in the recovery of any product of low volatility. However, heating the reaction tube in a tube furnace at 300° for 2 hr or irradiating the tube in the photoreactor for periods of 1–6 hr at 3000 Å resulted in the recovery of $P_2F_4C_2H_4$ in approximately 50% yield. Separation and purification were carried out by distillation of the volatile products through traps held at −63, −84, and −196°. The pure product was obtained in the trap held at −84°. This separation was greatly improved when the trap at −84° was packed with glass beads, pure product being obtained in a 20–30-min distillation. The reaction tube contained an orange-gold film which had been deposited on the sides of the tube during the reaction. The amount of film formed did not necessarily depend on the reaction time and may have indicated a difference in the degree of purity of the reactants. The −196° trap contained a mixture of small amounts of PF-containing products (preliminary data suggest PF-substituted derivatives of C_2H_4 dimers or trimers; further investigation is under way to identify these compounds), P_2F_4, F_2POPF_2, PF_2H, and PF_3. Distillation of the mixture in the −196° trap through traps held at −112, −126, −145, −160, and −196° resulted in P_2F_4 in the −126° trap, PF_3 (<0.01 mmol) in the −196° trap, and equimolar amounts (0.06 mmol) of PF_2H and F_2POPF_2 being collected in the −160 and −145° traps, respectively. The small amounts of PF_2H and F_2POPF_2 collected and the fact that equimolar amounts were obtained indicate that abstraction of a hydrogen by the $PF_2\cdot$ radical is not a competing reaction of enough significance to allow obtaining the abstraction product as a main product, as this result suggests reaction with trace amounts of H_2O.[2b] The mass spectrum of $F_2PCH_2CH_2PF_2$ is reported elsewhere as are experimental molecular weight, vapor pressure data, and a description of the nmr spectra (^{1}H, ^{31}P, ^{19}F).[7] The values for the coupling constants and chemical shifts are included in the tabulation in Table I. The ir absorption bands and tentative assignments are shown in Table II.

Reaction of P_2F_4 with Other Olefins. The experimental procedure used in each case was essentially the same as that described for the photolysis above. Quantities used, reaction times, products, and product yields are summarized in Table III. In each case, trace amounts of F_2PH and F_2POPF_2 were obtained; in no case was there indication of significant hydrogen abstraction from the olefin or of reaction prior to photolysis. Other volatile materials included the product, unreacted starting materials, and PF_3 from the decomposition of P_2F_4. In each case a solid orange-gold film remained in the reaction vessel. Ir data are summarized in Tables II and IV. Nmr data are included in Table I.

Mass Spectra and Other Physical Data. The mass spectral data following include only the major peaks essential to identification of products. Isotope peaks and fragmentation peaks due to hydrogen loss etc. were in every case present as expected as were those due to fragmentation of the hydrocarbon or fluorocarbon moiety. Assignments and relative intensities of peaks are included in parentheses following each mass number.

$C_3H_6P_2F_4$. Mp ∼−147°, glass-like solid. Vapor pressures (mm): 0.0°, 16.60; 6.1°, 25.30; 11.3°, 33.00; 15.1°, 36.30; 19.2°, 51.00; log $P = -1835.6/T + 7.97$. Mass spectrum: 180 ($C_3H_6P_2F_4^+$, 5.9), 161 ($C_3H_6P_2F_3^+$, 0.5), 111 ($C_3H_6PF_2^+$, 30.6), 92 ($C_3H_6PF^+$, 0.6), 73 ($C_3H_6P^+$, 4.3), 69 (PF_2^+, 100), 50 (PF^+, 3.1), 45 (CH_2P^+, 2.4), 42 ($C_3H_6^+$, 5.5).

$C_4H_8P_2F_4$. Mp ∼−120°, glass. Vapor pressures: −23.0°, 1.7 mm; 0.0°, 6.5 mm; 18.7°, 17.2 mm. *Anal.* Calcd: C, 24.70; H, 4.10. Found: C, 23.33; H, 4.16. Mass spectrum: 194 ($C_4H_8P_2F_4^+$, 2.5), 175 ($C_4H_8P_2F_3^+$, 0.4), 125 ($C_4H_8PF_2^+$, 20.3), 106 ($C_4H_8PF^+$, 0.7), 97 ($C_2H_4PF_2^+$, 1.9), 91 ($C_3H_5PF^+$, 1.8), 87 ($C_4H_8P^+$, 1.8), 77 (C_2H_3PF, 2.9), 69 (PF_2^+, 39.3), 65 (CH_3PF^+, 2.5), 56 ($C_4H_8^+$, 9.3), 55 ($C_4H_7^+$, 100).

$C_6H_{10}P_2F_4$. Mp ∼−112°, glass. Vapor pressure: 12 mm at 24°. Mass spectrum: 220 ($C_6H_{10}P_2F_4^+$, 4.5), 201 ($C_6H_{10}P_2F_3^+$, 1.3), 151 ($C_6H_{10}PF_2^+$, 37.6), 131 ($C_6H_9PF^+$, 1.2), 113 ($C_6H_{10}P^+$, 0.7), 97 ($C_2H_4PF_2^+$, 1.4), 83 ($C_6H_{10}^+$, 10.0), 81 ($C_6H_9^+$, 100), 69 (PF_2^+, 27.1).

$C_2F_4P_2F_4$. Mass spectrum: 238 ($C_2F_4P_2F_4^+$, 16.4), 169 ($C_2F_4PF_2^+$, 5.9), 150 ($C_2F_5P^+$, 59), 138 ($P_2F_4^+$), 4.1 (C_2F_6 or CF_3PF_2 are not likely since 139 isotope peak was negligible)), 131 ($C_2F_4P^+$, 26), 119 ($P_2F_3^+$, $C_2F_3^+$, $C_2F_4P_1^+$, 4.7), 100 ($C_2F_4^+$, $P_2F_2^+$, 10), 88 (PF_3^+, CF_4^+, 0.6), 81 (CF_2P^+, $C_2F_3^+$, 4.7), 69 (PF_2^+, CF_3^+, 100).

$C_3F_6P_2F_4$. Mass spectrum: 288 ($C_3F_6P_2F_4^+$, 0.2), 231 ($C_3F_7P_2^+$, 0.1), 219 ($C_2F_7P_2^+$, 0.7), 200 ($C_3F_7P^+$, $C_2F_6P_2^+$, 0.3), 193 ($C_3F_5P_2^+$, 0.1), 181 ($C_3F_6P^+$, 1.7), 169 ($C_2F_6P^+$, 1.7), 150 ($C_3F_6^+$, $C_2F_5P^+$, 0.2), 138 ($P_2F_4^+$, CF_5P^+, 2.3), 119 ($C_2F_5^+$, CF_4P^+, 0.8), 100 ($C_2F_4^+$, CF_3P^+, 0.8), 93 ($C_3F_3^+$, $C_2F_5P^+$, 0.4), 88 (PF_3^+, CF_4^+, 42.2), 81 ($C_2F_3^+$, CF_2P^+, 3.0), 69 (PF_2^+, CF_3^+, 100).

Attempted Reaction of P_4F_4 with C_4F_8 or C_6F_{10}. A small amount of the familiar orange-gold solid deposit formed in the reaction on photolysis of mixtures of varying ratio, but no volatile products other than starting materials and PF_3 were recovered in either case.

Results and Discussion

The reaction products obtained in these reactions were all obtained as colorless liquids which gradually attain a yellow coloration on standing in the vacuum line at room temperature and leave a yellow solid residue on transfer from a room-

Table II. Infrared Spectra of Alkane Derivatives[a]

Tentative assignment	$C_2H_4P_2F_4$(g)	$C_2H_4P_2$-F_4(s)	$C_3H_6P_2F_4$(g)	$C_3H_6P_2F_4$(g)	$C_4H_8P_2F_4$(g)	$C_4H_8P_2F_4$(s)	$C_6H_{10}P_2$-F_4(g)	$C_6H_{10}P_2F_4$(s)
C–H str	2955 w	2912 m	2972 m	2960 s	2980 s	2980 s	2940 s	2925 s
	2910 m		2941 w	2938 m	2945 m	2940 m	2870 m	
	2800 vw		2895 w	2918 w	2885 m	2910 sh		
				2880 m		2880 m		2850 mw
	1645 vw		1625 vw	1580 w, br	1620 vw	1580 w, br		1590 vvw
CH_2 bend		1420 w	1460 m	1455 s	1455 s	1460 sh	1450 m	1445 m
						1450 s		
	1410 m		1400 sh	1440 s				
		1397 s	1380 m	1380 m	1380 m	1380 m	1375 w	1382 w
			1298 vw	1300 w	1310 vw	1310 w		
			1255 w	1260 w	1245 w	1255 w	1265 w	
CH_2 twist and skel vib	1197 m	1199 s	1208 w	1210 m	1200 w	1195 w		1195 w
	1175 s	1181 s	1165 w	1170 s	1110 w	1160 w		1170 w
				1085 sh				1095 w
	1072 m	1084 w	1080 w	1080 m	1010 m	1110 w	1020 w	1065 m
		1040 vvw		1025 m		1035 m		1033 w
	1008 w		990 w	985 m	980 m	1010 m		985 w
						980 w		
	960 m	950 m		940 w	940 w	945 m	910 m	900 m
				890 m		885 vw		872 m
P–F str			825 s, sh	815 s, sh	840 s, sh	800 s, sh		
	822 vvs	793 vvs	812 vvs	780 vvs	815 vvs	775 vvs	813 vvs	799 vvs
	750 sh	770 s, sh		755 s				730 w
	737 s	740 m	732 m	737 s	725 s	730 s	730 m	715 m
		710 s	691 s	695 m	683 s	685 s	710 w	695 sh
C–P str and skel vib				672 s				
	708 s	670 mw	675 sh	665 sh	650 s	650 s		
	465 m	470 m		470 m	480 m	480 m		504 m
	425 w			440 w				460 w

[a] Intensity designations: w, weak; m, moderate; s, strong; v, very.

Table III. Photoreactions of P_2F_4 with Olefins

Olefin (mmol)	P_2F_4 (mmol)	Photolysis time	Product	Yield, %	Temp of product trap, °C
C_2H_4 (1.01)	1.90	6 hr	$F_2PCH_2CH_2PF_2$	50	−84
C_3H_6 (0.89)	1.71	1 hr	$F_2PCH_2CH(PF_2)CH_3$	21	−78
2-C_4H_8 (1.34) (cis or cis, trans)	1.10	2 hr	$F_2PCH(CH_3)CH(CH_3)PF_2$	25	−78
C_6H_{10} (0.47)	1.13	20 min	$F_2P\overline{CHCH_2CH_2CH_2CH_2CH}PF_2$	62	−23
C_2F_4 (0.88)	1.76	4–6 hr	$F_2PCF_2CF_2PF_2$	~10	−112
C_3F_6 (0.50)	0.86	7 hr	$F_2PCF_2CF(CF_3)PF_2$	~6	−95
2-C_4F_8 (0.45) (cis,trans)	0.5–0.9	2–7 hr			
C_6F_{10} (0.35)	0.78	1/3–2 hr			

Table IV. Infrared Spectra of Perfluoroalkane Derivatives

$C_2F_4P_2F_4$(g)	$C_2F_4P_2F_4$(s)	$C_3F_6P_2F_4$(g)
1710 vw		
		1635 vw
		1350 w
	1300 w	1270 w
1225 w, br		1240 m
	1260 vw	1195 m
1129 s		
1106 s		1100 w
		1090 w
	985 vw	1015 m
	947 vw	915 s
	904 vw	
	825 w, sh	830 s, sh (ν(PF))
844 vvs (ν(PF))	798 m	820 vvs
778 w	785 sh	
	762 w	720 vw
660 vvw		650 vw
570 m		
527 vvw		
462 m	495 w	475 m
450 m		

temperature vessel. Accordingly they are best stored at reduced temperature and utilized in such a fashion as to limit exposure to higher temperature, at least as liquids. Some yellow coloration was in general observed in the liquids after storage at −78° over a 24 hr period. Though not specifically tested in any case other than $C_6H_{10}P_2F_4$, it is anticipated that these compounds will show comparable air and moisture sensitivity to other alkylfluorophosphines. In the one case tested, exposure to the atmosphere resulted in loss of the compound (mass spectrum).

The identification of the compounds has been accomplished by means of mass, ir, and nmr spectrometry. Because there remained some possible ambiguity concerning the nmr spectra of $C_4H_8P_2F_4$, analysis is also reported. Vapor pressure data are recorded in the Experimental Section, as are approximate melting points, for those compounds for which sufficient material was obtained. Melting points are approximate because the samples all freeze as glasses at quite low temperatures.

Mass Spectra. Molecular ions were observed for each of the compounds studied and the fragmentation patterns were in each case entirely consistent with the assigned formulas. Principal peaks are recorded in the Experimental Section.

Infrared Spectra. Spectra obtained for both vapor-phase and solid-phase (−196°) samples are summarized in Tables II and IV. The spectra in each case confirm the absence of the olefinic linkage both by the absence of the characteristic =CH stretching band above 3000 cm^{-1} and by the C=C band in the 1650-cm^{-1} region found in asymmetric olefins. In addition the very strong band at approximately 800 cm^{-1} is characteristic of the P–F stretching mode. The unresolved shoulder on the high-frequency side suggests the presence of both symmetric and asymmetric stretching typical of the PF_2 moiety as rotational structure is eliminated in the solid phase. This band is shifted to somewhat lower frequency in all the solid spectra relative to the gas spectra, a feature consistent with other difluorophosphine derivatives.[12]

The spectra of the perfluoroolefin derivatives are similarly consistent with the assigned structures, although the spectral regions are not susceptible to comparable fingerprint techniques. The C═C stretching band of perfluoropropene at 1790 cm^{-1} is absent, however, and the very strong band in the 800-cm^{-1} region, indicative of the PF_2 group, is present.

Nmr Spectra. In each case the gross features on the nmr spectra conform to those expected for the assigned structures. Coupling constants and chemical shifts are consistent with those observed in comparable compounds.[11] The good agreement between values obtained for coupling constants while observing different nuclei supports these assignments (Table I). Essential characteristics of these spectra for each compound follow except for $C_2H_4P_2F_4$ which has been previously described.[7]

$C_3H_6P_2F_4$. The ^{1}H spectrum (−60°) consists of two broad doublets of approximately equal area at δ 1.67 and 1.03 ppm from TMS. The breadth of the signals suggests unresolved splitting. Peak complexity also prevented resolution of the CH and CH_2 signals at δ 1.03. The ^{31}P spectrum (−50°) displayed a 1:2:1 triplet due to coupling with two ^{19}F nuclei. Again, further coupling was not resolved nor was there indication of two distinct ^{31}P environments. The ^{19}F spectrum (−40°) displayed a 1:1 doublet consistent with the ^{31}P signal. Each of the doublet peaks was further split to what appeared as a quintet of doublets ($J_q \simeq 12$ Hz, $J_d \simeq 4$ Hz), but it is likely a more complex pattern due to contributions from second-order coupling with the protons and/or $^2J_{PF}$ and a slight difference in fluorine environments due to molecular asymmetry.

$C_4H_8P_2F_4$. The ^{1}H spectrum (−50°) displayed peaks due to methyl and methine protons but splitting due to other nuclei resulted in broad, complex peaks, the centers of which were not accurately assignable. The ^{31}P spectrum (−50°) displayed *two* 1:2:1 triplets slightly offset from one another but with very similar P–F coupling constants. The ^{19}F spectrum displayed a basic doublet each member of which consisted of at least 11 lines at −60°. By −40°, two pairs of lines in each member of the doublet coalesced, suggesting some differentiation of rotamers at low temperature. No further collapse was noted up to +30°. The spectrum is clearly derived from two different species in the sample because the halves of the doublet are superimposable rather than the mirror images expected if the splitting were due entirely to second-order coupling effects. This is consistent with the two species observed in the ^{31}P spectrum. As the addition to the double bond of 2-butene is nonstereospecific (the same product mix arises from pure *cis*-2-butene or from a mixture of *cis*- and *trans*-2-butene as shown by the identical nmr and ir spectra), one would expect a mixture of *d*, *l*, and meso isomers of $C_4H_8P_2F_4$. Small chemical shift differences between the *d*, *l* pair and the meso form are expected based on a wide variety of data from proton spectra of threo and erythro mixtures.[13]

$C_6H_{10}P_2F_4$. The ^{1}H nmr spectrum at −60° consisted of two principal overlapping envelopes corresponding to the axial and equatorial protons of the cyclohexane ring. These two envelopes gradually narrowed and coalesced as the temperature reached +30° (Figure 1). The ^{31}P spectrum also displayed temperature variation. At −60°, a basic triplet with second-order fine structure was observed. A second triplet gradually developed as the temperature was increased (Figure 1). The ^{19}F spectrum consisted of a basic doublet due to P–F coupling. Each member of the doublet consisted of a complex pattern which was a mirror image of the other again indicating second order behavior. No temperature dependence was apparent.

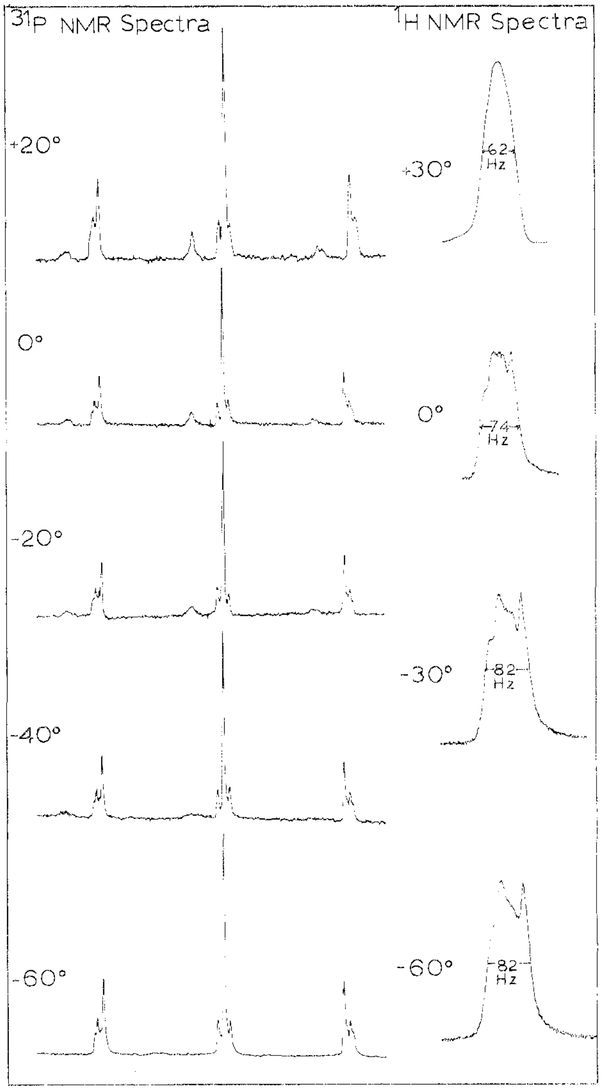

Figure 1. Temperature dependence of the ^{31}P and ^{1}H nmr spectra of $C_6H_{10}P_2F_4$.

It is expected from many studies of free-radical additions to cyclohexene that the addition gives the 1,2 adduct[14] and from structural studies of substituted cyclohexanes that the trans isomer is formed.[15] The formation of the trans isomer is supported by the ^{31}P spectra. At −60° a single conformer is apparently present with only one phosphorus environment. Only the trans isomer allows both PF_2 groups to be either equatorial or axial at one time. (The cis form demands that one be axial and one equatorial in any conformation, with two triplets of equal area at different chemical shifts expected at temperatures below rapid ring inversion.) Increasing the temperature of the sample results in the appearance and gradual increase in the relative area of a second triplet being slightly downfield from the first triplet but having an almost identical value for the P–F coupling constant. The second triplet appears to be due to the increasing concentration with greater freedom of motion of the other trans conformer. Temperature dependence of the cis isomer spectrum is also expected but should manifest itself in a collapse of the two triplets observed at low temperature to one at higher temperatures since the two PF_2 groups would be interchanging axial–equatorial positions. (Rapid exchange at still higher temperature should also bring about the coalescence of the separate triplets in the ^{31}P spectrum of the trans isomer as well. This aspect was not further pursued.) Thus a trans isomer is indicated as expected. It is also expected that the diequatorial form of the molecule will dominate at low temperature due to steric interactions. The ^1H spectrum provides qualitative support for this. Although accurate integration of the peaks is prevented by their overlap, the broad peak thought to be due to the axial protons[16] appears to be greater in area at low temperature than that due to equatorial protons. The ratio expected of the diequatorial conformer is 6:4 = axial:equatorial. In *trans*-1,2-dimethylcyclohexane the energy advantage of diequatorial over diaxial was estimated at about 3.4 kcal/mol[15] and no temperature dependence over the range −128 to +30° was noted.[17] It is of interest that the barrier to conformational inversion is apparently lower in the bis(difluorophosphino) derivative than in dimethylcyclohexane.

The ^1H nmr spectrum is consistent with the phosphorus spectrum in that the apparent differentiation between axial and equatorial hydrogens at low temperatures diminishes until at ambient probe temperature the signals very nearly coalesce.

$C_2F_4P_2F_4$. The ^{19}F signal due to the PF_2 fluorine nuclei was observed at −60° as a doublet due to P–F coupling, with each member of the doublet exhibiting a complex pattern. Similarly, the CF_2 proton signal was observed as a basic doublet due to P–C–F coupling, again with a complex pattern for each member of the doublet. The ^{31}P signal (−50°) appeared as a triplet of triplets of triplets with apparent parameters as given in Table I. Since this spin system is at simplest an $A_2A'_2M_2M'_2XX'$ system with possible magnetic distinction between all members of the two chemical shift equivalent sets of fluorines, that such an apparently simple spectrum is observed is fortuitous. The J values in Table I are surely average values. Nonetheless, the appearance of signals appropriate to all the basic structural characters of the molecule supports the assignment of that structure.

$C_3F_6P_2F_4$. Insufficient quantities of this product were obtained to obtain nmr spectra.

General Discussion. A number of potentially useful ligand molecules are preparable by means of the photoaddition of P_2F_4 to olefins. The generality of the reaction to give useful yields is indicated by the formation of significant product in relatively short periods of time in reactions with ethene, with a terminal olefin, propene, with a nonterminal olefin, 2-butene, and a cyclic olefin, cyclohexene. The ease of addition diminishes, as expected on steric grounds, in the sequence ethene, propene, and 2-butene as demonstrated by the poorer overall yields and by the greater time required to produce them. Cyclohexene reacts by far the most readily of the hydrocarbon compounds.

The potential utility of the reaction in producing perfluoro ligands of the same general types is also demonstrated; however, the yields are much poorer. Although longer reaction periods can be used, there is a point of diminishing returns in that the P_2F_4 decomposes over long reaction periods and the gold-colored film which was produced in all these reactions apparently impeded the photolysis. Whether this is due to absorption or reflection of light due to the mirror-like finish formed on the reaction tube is not known.

Addition to perfluoroolefins has been shown to occur most readily by nucleophilic reagents.[18] This follows from the highly electronegative fluorine atoms leaving a partial positive charge on the reactive carbon sites. The attacking phosphorus atom is also expected to bear a partial positive charge, also because of the attached fluorine atoms, so that the resistance to addition of P_2F_4 to the perfluoroolefins relative to the hydrocarbons is not surprising. A similar resistance to addition to highly halogenated olefins was noted in reactions of $(CF_3)_4P_2$.[19] The relative reactivity of C_2F_4, C_3F_6, and C_4F_8 is also consistent with other experience[20] and is probably due to a combination of steric and electronic effects.

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Registry No. $C_3H_6P_2F_4$, 53432-50-1; $C_4H_8P_2F_4$, 53432-51-2; $C_6H_{10}P_2F_4$, 53432-52-3; $C_2F_4P_2F_4$, 53432-53-4; $C_3F_6P_2F_4$, 53432-54-5; C_3H_6, 115-07-1; 2-C_4H_8, 107-01-7; C_6H_{10}, 110-83-8; C_2F_4, 116-14-3; C_3F_6, 116-15-4; P_2F_4, 13824-74-3; ^{31}P, 7723-14-0.

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