preciable for strong D–A interaction even in the heterocycles.

The present calculation substantiated the classification of cyclic conjugation. An interesting chemical consequence is the inapplicability of the Hückel rule to some π-electron systems. The relative delocalizability is not dependent on the number of electrons but proportional to the frequency of the D–A alteration. This is fundamental in the heterocycles.

Our attention has been centered on the *relative* delocalizability of the D–A disposition isomers but not on the intrinsic delocalizability of each isomer. The possibility cannot be ruled out that noncyclic delocalization may control the relative delocalization of some isomers, of which the other properties may be determined by cyclic delocalizability, and vice versa.

Acknowledgment. The calculations were carried out by the Facom 230-28 computer of Gifu University and the Facom M200 computer of Nagoya University Computer Center.

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Interconversions among Alkoxyfluorophosphoranes: Effect of Differences in Apicophilicity on the Equilibrium Distribution of Substituents on 5-Coordinated Phosphorus

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Fluorine atoms and alkoxy groups (OR = OCH_2CF_3 or OCH_2CCl_3) redistribute readily on the 5-coordinated phosphorus center

resulting in interconversions among the series of alkoxyfluorophosphoranes $PhPF_{4-n}(OR)_n$. An equilibrium is reached after less than 2 days at room temperature. No phosphorylated species, exchange of phenyl groups, nor conversion to ionic isomers was observed. Quantitative molar distribution data were obtained from ^1H or ^{19}F NMR spectra of 15 equilibrated samples, prepared in various ways, for R = CH_2CF_3 and of 8 samples for R = CH_2CCl_3. All the mixed species are thermodynamically favored, the dialkoxydifluorophenylphosphoranes so strongly that their disproportionation products were never detected. Within the limits of detection by NMR (ca. 1%), the sorting of fluorine vs. alkoxy groups among equatorial sites and among apical sites can be treated independently and described respectively by $\bar{K}_1 = [PhPF_4][PhPF_2(OR)_2]/[PhPF_3(OR)]^2 = (5.6 \pm 0.5) \times 10^{-2}$ and $\bar{K}_3 = [PhPF_2(OR)_2][PhP(OR)_4]/[PhPF(OR)_3]^2 = (1.7 \pm 0.3) \times 10^{-2}$ (for R = CH_2CF_3). An upper limit was set for $K_2 = [PhPF_3(OR)][PhPF(OR)_3]/[PhPF_2(OR)_2]^2 < 10^{-4}$, which expresses a difference of apicophilicity of at least 10 kJ between the two substituents. It is suggested that the measuring of redistribution equilibria could provide a way of establishing the concept of apicophilicity on a thermodynamic basis.

Introduction

Although redistribution reactions are an important feature of phosphorus chemistry,[1] there appears to be no quantitative study yet of a redistribution equilibrium on a 5-coordinated phosphorus atom—nor on any other 5-coordinated trigonal-bipyramidal atom—though the occurrence of the redistribution phenomenon has often been recognized[2,3] in this fast developing field. The problem is of special interest since there are in the case of a bipyramidal arrangement of the substituents *two sets of distinct sites*—apical and equatorial—to be considered on the *same* central atom and there is no reason why two distinct substituents should distribute randomly between these two sets of sites. In other words, the position of the equilibrium is expected to be strongly dependent on the relative *apicophilicity*[4] of the exchangeable substituents. Conversely, the gathering of *equilibrium* data could provide a means of evaluating differences in apicophilicity on a quantitative *thermodynamic* basis.

We have shown previously that alkoxyfluorophosphoranes, although they can be stabilized with respect to their irreversible decomposition into phosphoryl derivatives, nevertheless undergo easy disproportionation reactions which preserve the pentacoordinate character of phosphorus.[2,5] For example, $PhPF_3(OCH_2CCl_3)$ irreversibly decomposes only by heating above 200 °C, while its disproportionation products $PhPF_4$ and $PhPF_2(OCH_2CCl_3)_2$ already appear after 1 h at room temperature. *t*-$BuOPF_4$ disproportionates at room temperature[3a] and $PF_4(OCH_2CF_3)$ below room temperature[2] (which prevents its isolation), while advantage has been taken of redistribution reactions to synthesize various *di*alkoxyfluorophosphoranes[6] as well as difluoro(trifluoromethyl)phosphorane $(CF_3)_3PF_2$.[3b] These reactions, which lead to interconversions among the series of alkoxyfluorophosphoranes, are often reversible, in which case they can be described in terms of redistribution equilibria, for example, in the case of the series $PhPF_{4-n}$-

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Table I. NMR Data[a]

compd	δ_{OCH_2}	J_{HCOP}	J_{HCCF}	δ_F	J_{PF}	J_{FaFe}	δ_P
$PhPF_4$				−54.2	973		−51.7
$PhPF_3(OCH_2CF_3)$	4.45	10.0	8.3	−42.8 (a), −66.8 (e)	841 (a), 980 (e)	64	−54.2
$PhPF_2(OCH_2CF_3)_2$	4.27	10.3	8.3	−43.2	808		−58.5
$PhPF(OCH_2CF_3)_3$	4.19	8.4	8.3	−40.5	820		−57.2
$PhP(OCH_2CF_3)_4$	4.01	5.0	8.3				−58.7
$PhPF_3(OCH_2CCl_3)$	4.57	8.0		−41.7 (a), −65.7 (e)	839 (a), 974 (e)	64	−55.7
$PhPF_2(OCH_2CCl_3)_2$	4.62	7.5		−38.0	824		−59.1

[a] δ are taken positively toward decreasing fields with respect to Me_4Si (^1H), CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P). J is given in Hz and (a) and (e) refer to apical and equatorial sites.

$(OCH_2CF_3)_n$ of fluorine atoms with alkoxy groups. Alkoxyfluorophosphoranes appear to be appropriate for a *quantitative* study of redistribution equilibria because, contrary to their amino and some of their aryloxy analogues,[7] they show little tendency to convert into ionic species (which could prevent a study of equilibrium distributions in a homogeneous phase). The formation of an ionic isomer is only observed in the case of $PF_3(OCH_2CF_3)_2$, which is the only series member that can give the completely symmetrically substituted phosphorus anion and cation in $P(OCH_2CF_3)_4^+PF_6^-$.[2] This behavior was not found when the nonexchangeable phenyl group was present on phosphorus; this group moreover lowers the volatility of the compounds and facilitates the quantitative analysis of the equilibrium mixtures.[2]

Experimental Section

The alkoxyfluorophenylphosphoranes were prepared as previously reported.[6] All reactants and solvents were dried and redistilled under nitrogen before use, and their purity was checked by NMR. $PhPF(OCH_2CF_3)_3$ was accompanied by ca. 10% of $PhP(OCH_2CF_3)_4$ and used as such. After use, the reaction vessels and NMR tubes having contained fluorophosphorus compounds were decontaminated in an alcoholic solution of sodium hydroxide (NaOH–EtOH–H_2O 1:1:1).[8] The sample mixtures were prepared by condensing the desired amounts of the ingredients at low temperature directly into standard 5-mm NMR tubes; an equal volume of CH_2Cl_2 was then added. The sample tubes were filled so as to reduce the vapor phase to a minimum volume and sealed. They were kept at room temperature (22 °C) and periodically analyzed by ^1H or ^{19}F NMR on a JEOL C-60 HL spectrometer at −70 °C. Since the exchange rates became exceedingly slow at this temperature, the data correspond truly to equilibrium distributions at 22 °C. Additional data were sought for overall compositions, defined by $R = [OR]/[P]$ close to 2, with use of a Fourier-transform Bruker WH-90 spectrometer. The equilibrium data were collected after 4 weeks, i.e., long after the spectra ceased to show any evolution with time.

Peak assignment in the NMR spectra was achieved on the basis of the chemical shifts and characteristic spin multiplicity patterns of the ^1H, ^{19}F, and ^{31}P spectra of isolated or enriched compounds (Table I) and further checked by material balance calculations. The formalism, techniques for quantitatively evaluating the molecular distributions, equilibrium constants and thermochemical data, with standard errors and data reduction procedures, are detailed in previous papers.[1,9]

Results

Exchange of Fluorine Atoms with 2,2,2-Trifluoroethoxy Groups on the Phenylphosphorane Center. The *mono*alkoxytrifluorophenylphosphorane $PhPF_3(OCH_2CF_3)$ was obtained by allowing the trimethylsilyl ether $Me_3SiOCH_2CF_3$ to react with an equimolar amount of tetrafluorophenylphosphorane, $PhPF_4$.[5] The low-temperature ^{19}F NMR spectrum of the freshly prepared reaction mixture showed the presence of $PhPF_3(OCH_2CF_3)$ and Me_3SiF only, but after a few hours at room temperature, one observed the reappearance of the doublet corresponding to $PhPF_4$ and the simultaneous development of a new doublet at 43.22 ppm, corresponding to the *di*alkoxydifluorophenylphosphorane $PhPF_2(OCH_2CF_3)_2$. The areas of these two doublets stayed in a constant 2:1 ratio. These observations were confirmed by ^{31}P NMR, which showed the appearance of the quintet due to $PhPF_4$ and of the triplet due to $PhPF_2(OCH_2CF_3)_2$ in addition to the initial quartet for $PhPF_3(OCH_3CF_3)$. After ca. 2 days at room temperature, there was no further detectable evolution of the spectra, which then remained unchanged for several months, thus establishing that an equilibrium situation had been reached. The reaching of an equilibrium was further affirmed by the obtaining of the same signals, with the same relative peak area, i.e., molar distribution, after 2 days at room temperature, from an equimolar mixture of $PhPF_4$ and $PhPF_2(OCH_2CF_3)_2$.

Similarly, the *tri*alkoxyfluorophenylphosphorane $PhPF(OCH_2CF_3)_3$ underwent a disproportionation reaction at room temperature, as shown by the appearance in the ^1H NMR spectrum, in addition to the initial doublet of quadruplets due to $PhPF(OCH_2CF_3)_3$, of the two doublets of quadruplets whose chemical shifts and coupling constants are identical with those measured on independently prepared samples of $PhPF_2(OCH_2CF_3)_2$ and $PhP(OCH_2CF_3)_4$.[6]

Since the phenyl group does not take part in these exchange reactions, one can describe them as a redistribution of two substituents on a phosphorus center having four exchangeable sites only: in such cases there are five possible products. Three independent equilibrium constants are necessary to determine and describe such a system completely; we have chosen to use the constants related to the disproportionation of the three mixed species (where brackets denote concentrations):

$$2PhPF_3(OR) \rightleftharpoons PhPF_4 + PhPF_2(OR)_2$$

$$2PhPF_2(OR)_2 \rightleftharpoons PhPF_3(OR) + PhPF(OR)_3$$

$$2PhPF(OR)_3 \rightleftharpoons PhPF_2(OR)_2 + PhP(OR)_4$$

$$K_1 = [PhPF_4][PhPF_2(OR)_2]/[PhPF_3(OR)]^2$$

$$K_2 = [PhPF_3(OR)][PhPF(OR)_3]/[PhPF_2(OR)_2]^2$$

$$K_3 = [PhPF_2(OR)_2][PhP(OR)_4]/[PhPF(OR)_3]^2$$

In order to evaluate these constants on a thorough experimental basis, we prepared samples whose overall compositions, $R = [OCH_2CF_3]/[P]$, were in the range from $R = 0.36$ to $R = 3.90$. The methods by which these samples were prepared were varied deliberately. Thus some samples were obtained by allowing $PhPF_4$ and $Me_3SiOCH_2CF_3$ to react in various ratios, so as to obtain mixtures of alkoxyfluorophosphoranes. Other samples were prepared by mixing various amounts of $PhPF_4$ with $PhPF_2(OCH_2CF_3)_2$, of $PhPF_4$ with a mixture of tri- and tetraalkoxyfluorophosphoranes (90% and 10%, respectively), and of $PhPF_2(OCH_2CF_3)_2$ with $PhP(OCH_2CF_3)_4$. We also examined the disproportionation of isolated samples of mono- and dialkoxyphosphoranes as well as the equilibration

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Table II. Experimental and Calculated (in Parentheses) Molecular Distributions of Alkoxyfluorophosphoranes in System II at Equilibrium at 22 °C

R	$PhPF_4$	$PhPF_3(OR)$	$PhPF_2(OR)_2$	$PhPF(OR)_3$	$PhP(OR)_4$	10^2K_1	10^2K_3
0.36[a]	64.2[a]	35.8	d				
0.40[b,g]	(61.29)[c]	(37.42)	(1.29)				
0.56[g]	47.1	49.9	3.0[e]			5.67 ± 1.42	
0.55[g]	(47.87)	(49.27)	(2.87)				
0.79[h]	30.0	61.0	9.0			7.25 ± 1.46	
0.78[h]	(29.56)	(62.88)	(7.56)				
0.82[j]	27.1	63.6	9.3			6.23 ± 1.25	
0.81[j]	(27.45)	(64.09)	(8.45)				
1.00[g]	16.4	67.8	15.8			5.64 ± 0.90	
0.98[g]	(17.13)	(67.74)	(15.13)				
1.00[h]	16.2	67.9	15.9			5.59 ± 1.05	
1.00[h]	(16.11)	(67.78)	(16.11)				
1.10[g]	11.0	68.0	21.0			4.99 ± 0.75	
1.09[g]	(12.03)	(66.93)	(21.03)				
1.45[g]	2.8	49.1	48.1[e]			5.59 ± 1.20	
1.46[g]	(2.73)	(48.54)	(48.73)				
1.56[g]	1.7	40.6	57.7[e]			5.95 ± 1.19	
1.56[g]	(1.63)	(40.74)	(57.63)				
1.61[i]	1.2	36.6	62.2[e]			5.57 ± 1.11	
1.61[i]	(1.21)	(36.57)	(62.21)				
1.68[h]	d	32.3	67.7				
1.67[h]	(0.82)	(31.36)	(67.82)				
1.86[h]	d	13.5	86.5				
1.84[h]	(0.12)	(13.75)	(86.12)				
2.00[g]		d	100.0	d			
2.00[g]		<1.0	>98	<1.0		$K_2 < 10^{-4}$	
2.10[i]			90.0[a]	10.0	d		
2.09[i]			(91.02)[f]	(8.97)	(0.02)		
2.28[j]			71.7	28.3	d		
2.27[j]			(73.17)	(26.67)	(0.17)		
2.54[i]			46.3	52.7	1.0[e]		1.67 ± 0.61
2.58[i]			(43.21)	(55.57)	(1.21)		
2.65[i]			36.4	61.7	1.9[e]		1.82 ± 0.46
2.70[i]			(32.26)	(65.48)	(2.26)		
3.09[i]			6.5	78.2	15.3		1.63 ± 0.41
3.10[i]			(6.27)	(77.46)	(16.27)		
3.38[i]			1.5	59.3	39.2[e]		1.67 ± 0.81
3.39[i]			(1.42)	(58.16)	(40.42)		
3.70[i]			d	30.0	70.0		
3.72[i]			(0.18)	(27.64)	(72.18)		
3.90[i]			d	10.0	90.0		
3.89[i]			(0.03)	(10.95)	(89.02)		
4.00					100.00		

[a] Calculated from the NMR data. [b] Calculated from the ingredients. [c] Calculated from $\overline{K}_1 = (5.65 \pm 0.36) \times 10^{-2}$. [d] Not detected by NMR. [e] Measurement made on a Fourier transform apparatus with accumulation. [f] Calculated from $\overline{K}_3 = (1.70 \pm 0.26) \times 10^{-2}$. [g] Sample prepared from $CF_3CH_2OSiMe_3$ and $PhPF_4$. [h] Sample prepared from $PhPF_2(OCH_2CF_3)_2$ and $PhPF_4$. [i] Sample prepared from $PhPF_2(OCH_2CF_3)_2$ and $PhP(OCH_2CF_3)_4$. [j] Sample prepared from $PhPF_4$, $PhPF(OCH_2CF_3)_3$, and $PhP(OCH_2CF_3)_4$.

of an enriched sample of trialkoxyphosphorane.

The samples were kept at room temperature and analyzed by NMR. ^{19}F NMR was used for the composition domain $0 \leq R \leq 2$. The measurements were made at low temperature to avoid the coalescence of signals due to the fast exchange of the fluorine atoms between apical and equatorial sites in $PhPF_3OCH_2CF_3$. ^1H NMR proved to be more convenient for analyzing the samples in the composition domain $2 \leq R \leq 4$. $PhPF_3(OCH_2CF_3)$ appears in less than 1 h at room temperature in the samples prepared from $PhPF_4$ and $PhPF_2(OCH_2CF_3)_2$. Similarly, $PhPF(OCH_2CF_2)_3$ is formed rapidly from $PhPF_2(OCH_2CF_3)_2$ and $PhP(OCH_2CF_3)_4$. A striking feature of this study is that the simultaneous presence of more than three species (other than $PhPF_4$, $PhPF_3(OCH_2CF_3)$, and $PhPF_2(OCH_2CF_3)_2$ when $0 \leq R \leq 2$ or $PhPF_2(OCH_2CF_3)_2$, $PhPF(OCH_2CF_3)_3$, and $PhP(OCH_2CF_3)_4$ when $2 \leq R \leq 4$) was never detected. Furthermore, the presence of disproportionation products was never detected in a sample of $PhPF_2(OCH_2CF_3)_2$, even after several months at room temperature. For overall compositions close to $R = 2$, we never observed more than two simultaneous species: this implies that only an upper limit can be estimated for K_2 on the basis of the detection limit of the NMR (better than 1%). The exchange of the phenyl group, the formation of ionic isomers, and the decomposition to phosphorylated species were never observed, even after several months at room temperature.

Table I gives the NMR data relevant to the interconverting series of alkoxyfluorophosphoranes. Table II displays the molar distributions in the equilibrated samples. Equilibrium constants K_1 and K_3 were computed for nine and four samples, respectively; they show no significant dependence upon the sample compositions. The upper limit for K_2 was evaluated to be 10^{-4}. The self-consistency of the K values was checked by comparing the experimentally determined molar distributions with those computed from the weighted averaged constants. Further agreement is found when the overall compositions of the samples as determined from the weight of the ingredients are compared with those obtained from the NMR measurements.

Exchange of Fluorine Atoms with 2,2,2-Trichloroethoxy Groups on the Phenylphosphorane Center. The

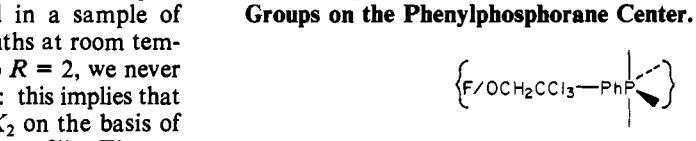

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Table III. Experimental and Calculated Molecular Distributions of Alkoxyfluorophosphoranes in System I at Equilibrium at 22 °C

R	$PhPF_4$	$PhPF_3(OCH_2CCl_3)$	$PhPF_2(OCH_2CCl_3)_2$	10^2K_1
0.11[a]	89.0[a]	11.0	[d]	
(0.12)[b]	(88.08)[c]	(11.83)	0.08	
0.57[e]	46.4	50.0	3.6	6.68 ± 1.7
(0.56)	(46.86)	(50.27)	(2.86)	
0.81[e]	27.6	63.5	8.9	6.09 ± 1.5
(0.84)	(25.13)	(65.73)	(9.13)	
0.87[e]	23.4	65.7	10.8	5.85 ± 1.2
(0.88)	(22.55)	(66.90)	(10.55)	
0.97[f]	17.1	68.3	14.4	5.28 ± 1.1
(0.96)	(17.86)	(68.27)	(13.86)	
1.31[e]	4.1	60.5	35.4	3.96 ± 1.0
(1.35)	(4.30)	(56.40)	(39.30)	
1.38[e]	3.9	53.9	42.2	5.66 ± 1.4
(1.40)	(3.45)	(53.10)	(43.45)	
1.66[f]	[d]	34.0	66.0	
(1.65)	(0.89)	(33.22)	(65.89)	
1.90[e]	[d]	10.0	90.0	
(1.90)	(0.06)	(9.88)	(90.06)	
2.00			100.00	

[a] Calculated from the NMR data. [b] Calculated from the ingredients. [c] Calculated from $\bar{K}_1 = (5.31 \pm 0.51) \times 10^{-2}$. [d] Not detected by NMR. [e] Sample prepared from $PhPF_2(OCH_2CCl_3)_2$ and $PhPF_4$. [f] Sample prepared from $CCl_3CH_2OSiMe_3$ and $PhPF_4$.

system yielded comparable, though less complete, results, which support the conclusion of this study. The formation of $PhPF_3(OCH_2CCl_3)$ from $PhPF_4$ and $PhPF_2(OCH_2CCl_3)_2$ is already noticeable after a few minutes at room temperature while the reverse reaction, disproportionation of $PhPF_3(OCH_2CCl_3)$, is much slower and takes several hours to become significant. Identical mixtures of $PhPF_{4-n}(OCH_2CCl_3)_n$ (n = 0–2) were obtained after 2 days at room temperature by equilibration of either a sample of pure $PhPF_3(OCH_2CCl_3)$ or an equimolar mixture of $PhPF_4$ and $PhPF_2(OCH_2CCl_3)_2$. The ready formation of a mixture of mono- and dialkoxyphosphoranes by adding $PhPF_4$ to a mixture of the di- and trialkoxy derivatives shows that the redistribution phenomenon occurs over the full composition domain $0 < R < 4$. Again, and most significantly, no evidence has been found for the redistribution of the dialkoxydifluoro species $PhPF_2(OCH_2CCl_3)_2$ within the detection limits of the NMR.

The quantitative evaluation of the equilibrium constants from low-temperature ^{19}F NMR was straightforward for $0 < R < 2$ and was performed on eight distinct samples prepared in various ways (see Table III).

On the contrary, the evaluation of equilibrium constants for the composition domain $2 < R < 4$ proved difficult and was not pursued: the inertia of $PhPF_2(OCH_2CCl_3)_2$ to further substitution, probably due to steric hindrance, makes it difficult to obtain the tri- and tetraalkoxy species.[6] Thus only 5% of $PhPF(OCH_2CCl_3)_3$ is formed with 95% of $PhPF_2(OCH_2CCl_3)_2$ after 40 h of heating at 150 °C of a 5:1 $Me_3SiOCH_2CCl_3$–$PhPF_4$ mixture. More prolonged heating inevitably leads to contamination by species such as $PhP(O)F(OCH_2CCl_3)$ and $PhP(O)(OCH_2CCl_3)_2$.

Since a quantitative description of the system can again be achieved, to the level of approximation imposed by the detection limits, by consideration of two separate subsystems (see Discussion) related to the exchanges between the equatorial and apical positions, respectively, one expects only three species to be present at any one time. Table III collates the quantitative molar distributions measured at equilibrium, as well as those calculated from the averaged constant $\bar{K}_1$.

Discussion

Redistribution Equilibria on 5-Coordinated Bipyramidal Phosphorus. The present study confirms that redistribution reactions can occur easily, even at room temperature, on 5-coordinated phosphorus. The experimental conditions required are much more gentle than those needed for redistributions on 3- and 4-connected phosphorus centers. Thus the exchanges of fluorine vs. alkoxy groups on 3- and 4-coordinated phosphorus, although general, necessitate heating to 80 °C for 24 h to become noticeable and 6–8 weeks at this temperature to reach an equilibrium.[10,11] Redistribution reactions on 5-coordinated species are thus much more likely to interfere with the isolation of mixed species in a pure state[2,3] than those on 3- and 4-coordinated species.

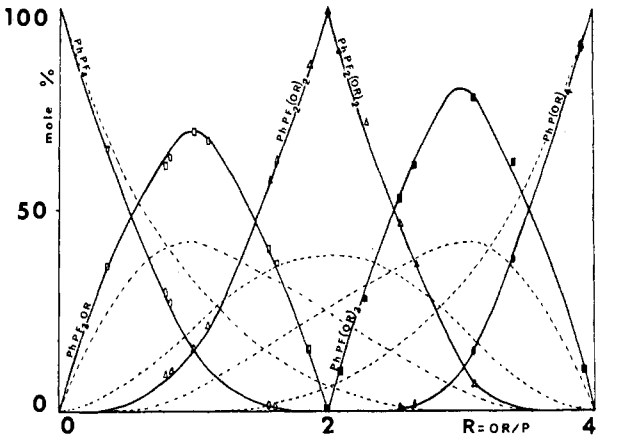
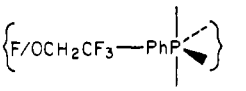


Figure 1. Equilibrium distribution of alkoxyfluorophosphoranes in system II at 22 °C. The full lines correspond to the equilibrium; the dotted lines to the random case in which $K_1 = K_3 = {}^3/_8$ and $K_2 = {}^4/_9$.

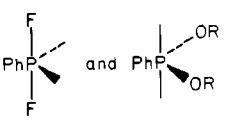
The plot of molar distributions at equilibrium vs. overall compositions for systems



II

(Figure 1) shows that these distributions (full lines) strongly deviate from random sorting among the four sites (dotted lines). There is a definite "accident" for $R = 2$, where the proportions of mono and trialkoxyfluorophosphorane become too low to be detected in the NMR. That there nevertheless is no rupture of continuity at $R = 2$, and that it is only the value of K_2 which is very low, is shown by the fact that the exchange of substituents between apical and equatorial sites occurs readily if one mixes two compounds (or two previously equilibrated samples, one having an R value <2 and the other an R value >2: since as little as 1 mole % of the disproportionation products of $PhPF_2(OR)_2$ could have been detected, an upper limit of K_2 can be set at 10^{-4}.

As a result, and *within the limits of detection* of the analytical method used, this means that for the composition domain $0 < R < 2$ the apical sites are exclusively occupied by fluorine atoms and that for $2 < R < 4$ the equatorial sites are exclusively occupied by alkoxy groups. In other words, only the equatorial sites are to be considered for the exchange of the two substituents for $0 < R < 2$ and only the apical sites are to be considered for $2 < R < 4$: The four-site system can thus be decomposed into two adjacent subsystems having two exchangeable sites only, on centers consisting respectively of



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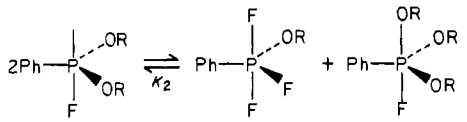
One can thus describe independently the redistribution reactions among equatorial sites on the one hand and among apical sites on the other and can calculate the equilibrium distributions for any value of R from K_1 alone for $0 < R < 2$ or from K_3 alone for $2 < R < 4$.

From this viewpoint, K_2 relates the apical subsystem to the equatorial subsystem and can be considered an "intersystem" constant. So far, intersystem constants have been used to describe exchange processes between two chemically *distinct* central atoms, which therefore offer two distinct types of sites. In this study the two types of sites are borne by the same central atom. Constant K_2 is directly related to the difference in affinity of the fluorine atoms and alkoxy groups for the apical and equatorial sites, as pictured by the equilibrium



Constant K_1 suffices in the above approximation to describe the equilibrium distribution among equatorial sites. Its average value, $\bar{K}_1 = (5.6 \pm 0.5) \times 10^{-2}$, and the related exchange enthalpy (after the statistical factor is taken into account)[1,9] $\Delta H_1 = 1.8$ kJ/mol of reactant, show that the monoalkoxyphosphorane is more stable than if it resulted from random distribution of the two substituents among these two sites; similarly one finds $\bar{K}_3 = (1.7 \pm 0.3) \times 10^{-2}$ and $\Delta H_3 = 3.3$ kJ. Both $\bar{K}_1$ and $\bar{K}_3$ compare closely with $K = (1.8 \pm 0.2) \times 10^{-2}$ found for the exchange of F vs. OMe on the two-site $CH_3P(O)<$ center.[10] We take this as further support for the idea that the positions of such redistribution equilibria depend more on the nature of the substituents exchanged than on the exact nature and functionality of the center at which they occur.[12] No significant variations in the product ratio were found in an exploratory survey of possible solvent effects (CH_2Cl_2, toluene, OEt_2, CH_3CN).

Redistribution Equilibria as a Possible Thermodynamic Approach to Apicophilicity. The term "apicophilicity" describes an empirical notion related to the observed preferential sorting of distinct substituents between apical and equatorial positions in a trigonal bipyramid. It has been defined as the change in *energy* when these groups exchange apical and equatorial positions in a trigonal bipyramid[4] and integrates many factors including electronegativity, inductive effects, π contributions to bonding, ring spanning effects, etc. This difference in energy determines which isomer will be most stable and, when a substitution reaction on four-connected phosphorus occurs via five-connected phosphorus slowly enough for apical vs. equatorial exchange processes to take place, which will be the final product. Even although apicophilicity has thus been defined on a thermodynamic basis, most of the information available on apicophilicity differences has thus far been based on kinetic or reactivity data. Trippett, for example, compares the *activation* free energies of a process in which the various groups R, whose apicophilicities are to be compared, have to change from equatorial to apical positions during the transition state. This approach intrinsically cannot provide the ΔG values required by the definition; moreover, in using $\Delta G^{\ddagger}$ values, one compares differences in energy between stable states and hypothetical transition states, i.e., activation barriers, and one has thus to assume that the transition state—and reaction mechanism—do not depend on R. Many of these apicophilicities were estimated with compounds in which phosphorus bears small, strained, or sometimes sterically hindered cycles, for which the structures and transition states are expected to depart strongly from bipyramidal geometry. In such cases, the exchange often forced the cycles from their preferred apical–equatorial to the less favorable equatorial–equatorial positions as well as causing changes in orientation (i.e., availability for π contribution) of lone pairs. The contributions of all these factors, which have been carefully discussed by Trippett,[4] to $\Delta G^{\ddagger}$ have to be assumed to be independent of the substituents whose apicophilicities are to be evaluated.

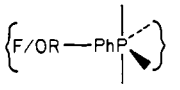
A chemical probe has been suggested for the estimation of relative apicophilicities by assuming that the attack of the most apicophilic nucleophiles at tetrahedral phosphorus would lead to substitution without (or with little) pseudorotation of the intermediate trigonal bipyramid and with inversion of configuration at phosphorus, while the poorly apicophilic nucleophiles would lead, via pseudorotating intermediates, to retention of configuration at phosphorus.[13] Finally, Cavell has classified various substituents by checking (with low-temperature NMR spectra) which substituent occupies which position in isolable mixed-pentacoordinated species.[14] These last methods provide no energy difference values.

The study presented in this paper provides a thermodynamic approach to apicophilicity by means of the equilibrium constant K_2. An even more direct expression of the relative apicophilicities of the two substituents could be given by

$$K_{ap} = [F_a](a)/[F_e](e)$$

where $[F_a]$ and $[F_e]$ represent the molarities of fluorine atoms in the apical and equatorial sites, and (a) and (e) the number of apical and equatorial sites available for exchange (2 and 2 on the phenylphosphorane center), which gives, for less than 1% disproportionation products detected, $K_{ap} > 4 \times 10^2$.

Unfortunately, in the case of the



III

system analyzed here, these constants are too high to be evaluated by NMR, and the rates of the reactions are too slow to allow straightforward calorimetric measurements. So far, we can therefore only set upper limits on ΔH_2 of −10 kJ for both OCH_2CF_3 and OCH_2CCl_3 (from K_2 with the usual assumption that ΔS is negligible in redistribution reactions)[1,9] to represent the extra stability of the $PhPF_2(OR)_2$ species relative to a random distribution of the fluorine atoms and alkoxy groups among the four exchangeable sites. Substituents more amenable to such measurements are presently being sought.

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Registry No. $PhPF_4$, 666-23-9; $PhPF_3(OCH_2CF_3)$, 40563-07-3; $PhPF_2(OCH_2CF_3)_2$, 63325-04-2; $PhPF(OCH_2CF_3)_3$, 63325-05-3; $PhP(OCH_2CF_3)_4$, 63325-06-4; $PhPF_3(OCH_2CCl_3)$, 36219-95-1; $PhPF_2(OCH_2CCl_3)_2$, 43227-68-5.

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