LINEAR CORRELATION OF THE BARRIERS TO PYRAMIDAL INVERSION OF PHOSPHORUS WITH THE ³¹P CHEMICAL SHIFTS OF ACYLPHOSPHINES

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We have for the first time studied the dependence of the inversion barriers (ΔG^{\neq}) of phosphorus compounds directly on a parameter of the inversion center, i.e., the chemical shift of the nucleus $(\delta^{31} P)$. The possibility of such an approach was justified by the correlation both of ΔG^{\neq} [1, 2], and of $\delta^{31} P$ [3] for phosphorus compounds with one and the same characteristics (the bond angles and electronegativities of the substituent).

The acylphosphines (I-IX) were investigated in the range of variation of ΔG^{\neq} , accessible to dynamic NMR and in a fairly wide range of δ^{31} P (Table 1). Treatment of the obtained data (Fig. 1) by the method of least squares gives the equation:

$$\Delta G_{25^{\circ}} \neq \text{(kcal/mole)} = 28.3 \pm 0.3 \,\delta^{31}\text{P} \text{(ppm)}, \ r = 0.97$$
 (1)

The coefficient of determination is best for the parabolic relationship:

$$\Delta G_{250^{\neq}} = 31.3 + 0.6 \,\delta^{31}P + 0.005 \,(\delta^{31}P)^2, r = 0.99 \tag{2}$$

However, analysis of the remainder variances of Eqs. (1) and (2) at a 5% significance level (0.94 and 0.39, respectively) does not show any advantage for Eq. (2). The more simple equation (1) was therefore adopted.

The use of correlation (1) was especially important when the inversion barriers experimentally determined by dynamic NMR were hindered by high values of the merging temperature T_m (e.g., (XXII)) or made basically impossible by the absence of indicator groups (e.g., in Me_2PX , X = MeCO and CN). In such a case the inversion barrier was found from the kinetics of racemization of optically active phosphines or by quantum-chemical calculations [2, 5, 6].



Fig. 1. Dependence of the barriers to pyramidal inversion of phosphorus (ΔG^{\neq}) on the $\delta^{31} P$ chemical shifts of phosphorus. The dashed line shows the 95% confidence region for determination of ΔG^{\neq} by means of Eq. (1).

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Com- pound	x	Solvent	Δv,a Hz	r _m ,∘c	$\begin{array}{c} \Delta G_{25}^{\neq} \pm 0,3, \\ \text{kcal/mole} \end{array}$	δ³¹₽b (Ph₂O), ppm
(I) (II) (IV) (V) (VI) (VII) (VIII) (IX)	$\begin{array}{c} Me_2N\\ MeO\\ p-BrC_6H_4\\ Ph\\ FCH_2\\ Me\\ CF_3CHF\\ CF_3\\ (CF_3)_2CH \end{array}$	$\begin{array}{c} Ph_2O\\ Ph_2O\\ Ph_2O\\ Ph_2O\\ CCl_4\\ Ph_2O\\ CCl_4\\ Cl_2Cl_2\\ CH_2Cl_2\\ CH_2Cl_2\end{array}$	$2.8 \\ 3.8 \\ 4.0 \\ 4.1 \\ 4.5 \\ 4.8 \\ 4.5 \\ 2.8 \\ 3.6$	195 148 83 85 55 56 28 9 13	27,0° 23,4° 19,5 19,6° 17,7 17,8° 16,2 15,4 15,3	$\begin{array}{r} -8.0 \\ -16.9 \\ -26.1 \\ -26.5 \\ -32.0 \\ -38.7 \\ -40.9 \\ -41.2 \\ -47.1 \end{array}$

TABLE 1. Inversion Barriers of Phosphorus and ³¹P Chemical Shifts in Acylphosphines i-Pr₂PCOX

a) Observed group i-Pr.

b) Measured at 27°C from 85% phosphoric acid as external standard (negative values, downfield).

c) Repeated and refined data [4].

This can be done much more quickly and simply by means of Eq. (1) on the basis of the readily determined $\delta^{3\,1}P$.* Since the $\delta^{3\,1}P$ values depend largely on the type of substituent at the phosphorus [3], for compounds with substituents R differing from i-Pr conversion to the i-Pr₂PX series (X = acyl, CN) is necessary by the introduction of the increments of this substituent (IR), determined according to [7] from the $\delta^{3\,1}P$ value of the corresponding tertiary phosphine by means of Eqs. (3) and (4) (Table 2)

$$I_{\rm R} = \delta^{31} P \left(R_3 P \right) / 3 \tag{3}$$

$$I_{\rm X} = \delta^{31} P({\rm XPR}^{1} {\rm R}^{2}) - I_{{\rm R}^{1}} - I_{{\rm R}^{2}}$$
⁽⁴⁾

The calculation of the increment for the substituent is illustrated for the case of Me₂PCOMe, $\delta^{31}P = 19.7 \text{ ppm}$. Using I_{Me} and I_i-Pr (see Table 2), we change to the i-Pr₂PX series, $\delta^{31}P$ (with allowance for I_R) = 19.7 - 2I_{Me} + 2I_i-Pr = -34.3 ppm. From Eq. (1) we obtain: $\Delta G_{25} \circ^{\neq} = 28.3 + 0.3 \cdot (-34.3) = 18.0 \text{ kcal/mole}$.

With allowance for $I_{
m R}$ we obtained satisfactory agreement between the inversion barriers calculated according to Eq. (1) and those obtained experimentally for unsymmetrically substituted acylphosphines (Table 3). This makes it possible to apply the correlation (1) to compounds for which it is not possible to determine ΔG^{\neq} by the NMDR method (Table 4). The soundness of the obtained results is confirmed by comparison with the experimental values of ΔG^{\neq} for similar compounds and with data from calculations by the CNDO/2 method (see the footnotes in Table 4). Whereas the applicability of Eq. (1) to mono- and diacylphosphines (Table 4) is not subject to doubt, with respect to the phosphines (XXIII, XXIV) and triacylphosphines (XXXII-XXXVIII) (Table 5) there is no such certainty, since there are no reliable criteria for assessing the reliability of the obtained ΔG^{\neq} values. The significant increase in the ΔG^{\neq} values obtained by means of Eq. (1) in (XXV) and (XXVI) compared with ΔG^{\neq} obtained by the NMDR method in (XXV) (see Table 5) can be explained by the large difference between $I_{t-BuCO} = -17.0$ ppm (see Table 2) and the I_{t-BuCO} values obtained by means of Eq. (4) for compounds (XXV-XXVII), i.e., -2.1, +5.9, and +10.1 ppm, respectively. The correlation (1) cannot therefore be applied to acylphosphines with a tert-alkyl-CO group. This is confirmed by the It-BuCO values obtained by means of Eq. (4) for compounds (XXVIII-XXXI), i.e., -33.2, -36.4, -53.2, and -60.4 ppm, respectively, although a decrease in the ΔG^{\neq} value is observed with the introduction of the SiMe3 group at the phosphorus atom (discovered earlier in [2]). Attempts to apply Eq. (1) to phosphines of the R_2PX type, where X = Ph and R_3E (E = Si, Ge, Sn) by means of the $\delta^{31}P$ values from [3, 16] were unsuccessful. Equation (1) cannot be applied to di- and tricyanophosphines on account of the absence of a reliable ICN value (see Table 2). For the activated vinylphosphine (XXXIX) we obtain acceptable agreement between the ΔG^{\neq} values calculated by means of Eq. (1) and those obtained experimentally. In the case of the vinylogs of acyl- and cyanophosphines, however, the correlation (1) is not observed (Table 6). It should be noted that the ΔG^{\neq} values in the acylphosphine (II)

^{*}The ³¹P chemical shifts depend little on the solvent [3], and it is therefore possible to use various published data on δ^{31} P.

TABLE 2. The ³¹P Chemical Shifts of Phosphines and the Increments of the Substituents, Calculated by Means of Eq. (3) [7]

R	ð³¹₽, R₃₽, ppm	I _R , ppm	R	δ³¹₽, R₃₽, ₽₽m	IR, ppn:
Me Et Bz C ₆ H ₁₁ <i>i</i> -Pr <i>t</i> -Bu Ph MeCO <i>t</i> -BuCO	61,6 19,5 11,7 -7,0 [3] -19,4 -62,6 7,5 -63,5 [8] -51,0 [8]	$\begin{array}{r} 20,5 \\ 6,5 \\ 3,9 \\ -2,3 \\ -6,5 \\ -20,9 \\ 2,5 \\ -21,2 \\ -17,0 \end{array}$	PhCO 3-MeC ₆ H ₄ CO 4-MeC ₆ H ₄ CO 1-C ₁₀ H ₇ CO 2-C ₁₀ H ₇ CO EtO ₂ C BuO ₂ C CN Me ₃ Si	$\begin{array}{c} -54.0 \ [9, 10] \\ -53.4 \ [9] \\ -53.2 \ [9] \\ -67.9 \ [9] \\ -53.5 \ [9] \\ -3.3 \ [11] \\ -3.9 \ [11] \\ 135.7 \ [3] \\ 251.0 \ [8] \end{array}$	18,0 17,9 17,7 22,6 17,8 1,1 ^c 1,3 ^c 45,2 ^d 83,7

a) Agrees with $I_{Me} = 21.0$ and $I_{Et} = 7.5$ ppm, obtained by means of Eq. (4) from $\delta^{31}P$ 48.5 ppm for Me₂PEt [3]. b) Coincides with $I_{Ph} = 2.5$ ppm, obtained by means of Eq. (4) from $\delta^{31}P$ 28.0 ppm for Ph₂PMe [3].

c) Close to $I_{MeO_2C} = -3.2 \text{ ppm} - \text{the average value obtained}$ by means of Eq. (4) for (XIV) (see Table 4). d) Differs significantly from ICN, obtained by means of Eq.

(4) for MeP(CN)₂ [3], (XXI), and (XXII) (Table 4), respectively: 30.7, 22.0, and 20.5 ppm. This increment cannot therefore be used.

and its vinylog (XL) are almost identical,* whereas the ΔG^{\neq} value decreases in the transition from cyanophosphine (XXII) to its vinylog (XLII), i.e., the introduction of the CH=CH bridge in the first case does not alter and in the second case strengthens the effect of the substituent, which is expressed as a reduction of the inversion barrier of the phosphorus. These results are as yet difficult to explain.

Thus, the correlation (1) makes it possible to make a satisfactory estimate of the inversion barriers from the $\delta^{31}P$ values for phosphines of the R₂PX type, if the substituent X has a strong -M effect (COR, CO₂R, CONR₂, CN).

Some general considerations about the correlation (1) are given below. The significant decrease of the ΔG^{\neq} value in acylphosphines compared with tertiary phosphines [2, 6] is explained by $p-\pi$ conjugation between the electron pair of the phosphorus and the CO group in the planar transition state of the inversion [2, 4, 13]. Electronegative substituents at CO in (VII-IX), which activate conjugation, facilitate the inversion of the phosphorus in

TABLE 3. Inversion Barriers of Phosphorus in Acylphosphines, Obtained by the NMDR Method and Calculated by Means of Eq. (1) with Allowance for the Increments of the Substituents

				T _{III} ° C	δ ³¹ Ρ,	ppm	$\Delta G_{25^{\circ}}^{\neq}$, kcal/mole	
Compound	Solvent	Observed group	Δv, Hz		found in Ph ₂ O	withal- lowance for IR	found	calcu- lated (1)
<i>i</i> -Pr (Bz) PCOCF ₃ (X) <i>i</i> -Pr (Bz) PCOMe (XI) <i>t</i> -Bu (Bz) PCO ₂ CH (Me) CO ₂ Me (XII) <i>i</i> -Pr (Bz) PCOCHFCF ₃ (XIII)	CCl ₄ Ph ₂ O Ph ₂ O CCl ₄	CH ₂ <i>i</i> -Pr <i>t</i> -Bu ^a <i>i</i> -Pr	$25 \\ 1,8 \\ 5,0 \\ 4,5 \end{cases}$	$69 \\ 72,5 \\ 139 \\ 40$	-36,7 -27,9 -19,1 -34,1 b	-32,7 -38,3 -15,1 -44,5	17,1 19,7 23,1 16,9 ^c	18,5 17,0 23,8 15,0

a) Differs in chemical shift for the diastereomers.

b) The center of the signals of the diastereomers, which overlap at 30°.

c) Agrees with the value obtained for the analog (VII).

*In diaziridines the inversion barrier of the nitrogen decreases in the transition from the analogous N-methoxycarbonyl derivative to the corresponding vinylog [4].

TABLE 4. The ³¹P Chemical Shifts and Inversion Barriers in Monoacyl-, Diacyl-, and Cyanophosphines, Calculated by Means of Eq. (1) with Allowance for the Increments of the Substituents

	ð³¹₽,		
Compound	found in Ph ₂ O	with allow- ance for I _R	$\Delta G_{25^{\circ}}^{\neq}$, kca l/mole
t-Bu (Bz) PCO ₂ Me (XIV) t-Bu PCOCE (XV)	-19,5 -60.8		23,7 ^a 18.5 ^b
Ph ₂ PCOCF ₃ (XVI) Ph ₂ PCOC ₆ H ₄ Br-o (XVII) [12]	-17,9 -19,7 (CDCl ₃)	35,9 37,6	17,5 17,0 °
Ph ₂ PCOMe (XVIII) Me ₂ PCOMe (XIX) MeP(COMe) ₂ (XX) Me ₂ PCN (XXI) <i>i</i> -Pr ₂ PCN ^a (XXII)	$\begin{array}{r} -15.0 \\ +19.7 \\ -31.0 \\ +63.0 \\ +7.5 \end{array}$	-33,0 -34,3 -43,3 +9,0 -	18,4 [°] 18,0e 15,4 ^f 31,0 g 30,5

a) Practically coincides with the values obtained for the analogs (II) and (XII), cannot be determined on account of the large value of $\Delta\nu CH_2$ (28 Hz at 190°).

b) Comparable with the values obtained for the analogs (VIII) and (X).

c) Comparable with the value obtained for (III).

d) Agrees with the value obtained for Ph(i-Pr)PCOMe, $\Delta G_{110}^{\ddagger}$ °= 19.4 kcal/mole [13].

e) Agrees with the values obtained for the analogs (VI) and (XI) and compound (XVIII), calculation for (XIX) by the CNDO/2 method gives ΔG^{\neq} 22 [13] and 22.6 kcal/mole [14]. f) Agrees with the value obtained for PhP(i-PrCO)₂, ΔG^{\neq} =12 kcal/mole [2] if account is taken of the fact that replacement of Alk by Ph at P leads to a decrease of 2-3 kcal/mole in ΔG^{\neq} [5, 6]. Calculation for MeP(COH)₂ by the CNDO/2 method gives ΔG^{\neq} =18.8 kcal/mole [14]. g) By the CNDO/2 method, found ΔG^{\neq} = 31.9 kcal/mole [5]. h) Δvi -Pr = 10.0 Hz; T_m > 190°C; ΔG^{\neq} > 26 kcal/mole.

comparison with the mesomeric-positive substituents at CO in compounds (I) and (II), which concurrently weaken the $p-\pi$ conjugation with the phosphorus and thus impede inversion. The concurrent conjugation of the electron pair of the nitrogen with the CO group in (I) shows up as restricted amide rotation [4].

The $\delta^{31}P$ values depend little on temperature [18]; for (XIII), for example, $\Delta\delta^{31}P$ for variation of the temperature by 100°C amounts to only 0.2 ppm. It can therefore be considered that the observed decrease of ΔG^{\neq} and the downfield shift of $\delta^{31}P$ in the transition from (I) to (IX) (Table 1) and in the analogs (Tables 3 and 4) are directly related to the conjugation between the electron pair of the phosphorus and the substituent.

If the -I effect of the substituent XCO were responsible for ΔG^{\neq} , the order of variation of ΔG^{\neq} in the series (I-IX) would be opposite. With increase in the number of electronegative substituents in the triacylphosphines the -I effect already evidently appears, and this can be explained by the increase of the inversion barrier compared with the diacylphosphines. In addition, calculation for (XIX) [13, 14] with allowance for the COP conjugation gives ΔG^{\neq} values close to the experimental values (see footnote e in Table 4), and without allowance for this conjugation the obtained barriers are high ($\Delta G^{\neq} = 35.6$ kcal/mole [5]), as in tertiary phosphines [2, 6]. To judge from the Raman and IR spectra [19], however, the acylphosphines exist in one conformation having a plane of symmetry, i.e., an unconjugated conformation. This contradiction can be explained by the presence of the equilibrium:

If the fraction of the conjugated form (B) in the equilibrium is small (<10%), it could remain unrecorded in the vibrational spectra [19].

TABLE 5	• The	• * P	Chemi	cal Sł	hifts	and	Inver	sion	Barri	ers :	in
Carbamo	ylphos	phine	s and	Mono-	- and	Tria	cy1ph	nosphi	ines,	Calc	ula-
ted by	means	of Eq	. (1)	with	A110v	vance	for	the	Incren	nents	of
the Sub	stitue	nts									

	ð³1P, pj			
Compound	found in Ph ₂ O	with al- lowance for I _R	$\Delta G_{25^{\circ}}^{\neq},$ kcal/mole	
i-Pr ₂ PCONHPh ^a (XXIII) Ph ₂ PCONHPh (XXIV) [15] i-Pr ₂ PCOBu- t ^b (XXV) i-Pr(t -Bu)PCOBu- t ^c (XXVI) t-Bu ₂ PCOBu- t (XXVI) $m_{0}(SiMe_{3})PCOBu-t (XXVII) [8]C6H41 (SiMe_{3})PCOBu-t (XXIX) [8]Ph (SiMe_{3})PCOBu-t (XXXI) [8]P(COC6H4Me-3)3 (XXXII) [9]P(COC6H4Me-4)3 (XXXIV) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(COC6H4Me-4)3 (XXXVI) [9]P(CO2Et)3 (XXXVII) [11]P(CO2Bu)3 (XXVIII) [11]$	$\left \begin{array}{c} -21,5\\ -10,8\\ -15,1\\ -21,5\\ -31,7\\ +71,0\\ +45,0\\ +33,0\\ +107,0\\ -53,0\\ +107,0\\ -53,7\\ -53,2\\ -67,9\\ -53,5\\ -3,3\\ -3,9\end{array}\right $	$\begin{array}{c} -\\ -28,8\\ -\\ -7,1\\ -2,9\\ -46,2\\ -49,4\\ -66,2\\ -73,4\\ -31,0\\ -30,9\\ -30,8\\ -35,7\\ -30,8\\ -35,7\\ -30,9\\ -44,1\\ -14,3\\ \end{array}$	21,9 19,6 23,8 26,2 27,4 14,4 13,5 8,4 6,3 19,0 19,0 19,1 17,6 19,0 24,1 24,0	

a) Found: $\Delta vi-Pr = 1.9$ Hz; $T_m = 73^{\circ}C$, $\Delta G_{25}^{\neq}^{\circ} = 19.7$ kcal/mole. Not included in the correlation (1) on account of the sharp decrease of ΔG^{\neq} compared with (1), which may be due to the reversible dissociation of (XXIII) into phosphine and phenyl isocyanate.

b) Found: $\Delta vi-Pr = 3.1$ Hz, $T_m = 75^{\circ}C$, $\Delta G_{25}^{\neq} \circ = 19.2$ kcal/mole. c) It is not possible to determine the ΔG^{\neq} value on account of overlap of the signals for the i-Pr and t-Bu groups. d) For compounds (XXXII-XXXVIII), close to the ΔG^{\neq} values of the corresponding monoacylphosphines (III, IV, II, XII, XIV). Calculation of P(COH)₃ by the CNDO/2 method in relation to the angle of rotation about the C-P bond gives ΔG^{\neq} values between 14.4 and 41.6 kcal/mole [14].

EXPERIMENTAL

The NMR spectra were recorded on the following spectrometers: Tesla BS-487C (¹H, 80 MHz, with HMDS as internal standard); JNM-C-60-HL (¹⁹F, 56.546 MHz, with trifluoroacetic acid as external standard); JNM-4H-100 (³P, 40.5 MHz, with 85% phosphoric acid as external standard). The concentrations of the samples were \sim 15%. The tubes were filled in an atmosphere of argon. During dynamic measurements the temperature in the spectrometer sample unit was monitored against standard samples (methanol and ethylene glycol). The inversion rate constants were determined at the temperature corresponding to the merging of the exchanging groups: $k = \pi \Delta v / \sqrt{2}$, for a spectrum of the AB type $k = \pi / \sqrt{2} (\Delta v^2 + 6J^2)^{1/2}$, Δv was extrapolated to T_m . The change in the free energy of activation was obtained by means of Eyring's equation: $\Delta G^{\neq} T_m = 4.57$ Tm (10.32 + log T - log k), $\Delta G^{\neq} {}_{25} \circ = \Delta G^{\neq} T_m + R$ (Tm - 298.15). The

TABLE 6.	Inversion 1	Barrier	s of	Phosphor	rus i	n Activated.	Vinyl-
phosphines	, Obtained	by the	NMDR	& Method	and	Calculated	Ъу
Means of H	Eq. (1)						

		Tm		∆G ≢ _0,k	ΔΔG 7 .		
Compound	Hz	°C	∿™P,PP ™	found	calcula- ted Eq.1	kcal/mole	
i-Pr ₂ PCF=C(CF ₃) ₂ (XXXIX) i-Pr ₂ PCH=CHCO ₂ Me(trans) (XL) Ph ₂ PCH=CHCO ₂ Me (XLI) [17] i-Pr ₂ PCH=CHCN(cis) (XLII)	4,5 4,6 4,4	168 157 145	-15,9 -3,2 +11,0 +0,6	24,3 23,7 - 23,1	23,5 27,3 26,2 28,4	0,8 3,6 - 5,3	

a) In Ph20, observed group i-Pr.

error in the determination of ΔG^{\neq} was not greater than 0.3 kcal/mole with allowance for $\Delta v \pm 1$ Hz and $T_m \pm 3^{\circ}C$. The IR spectra of the pure liquids were recorded on UR-20 and UR-10 spectrometers in the region of 4000-400 cm⁻¹ with an accuracy of ± 1 cm⁻¹ in cuvettes with potassium bromide windows.

All the syntheses and physicochemical investigations of the compounds were carried out without access to air and moisture in an atmosphere of argon. The glass apparatus was evacuated (1 torr), heated by a burner flame, and filled with dry argon. Only absolute solvents and freshly distilled reagents were used in the work.

The synthesis of the initial phosphines and compounds (I, II, IV, VI, VIII, IX, XI, XII, XV, XIX) was described in [4], and the synthesis of compounds (XVI, XVIII, XX) was described in [20].

<u>p-Bromobenzoyldiisopropylphosphine (III)</u>. To 1.82 g (8 mmole) of N-morpholinomethyldiisopropylphosphine [21] in 15 ml of ether we added a solution of 1.9 g (8 mmole) of pbromobenzoyl chloride in 10 ml of ether at 20°C. The mixture was stirred for 0.5 h, and the precipitate was filtered off and washed with ether. The solvent was distilled, and the residue was distilled under vacuum. We obtained 0.43 g (17%) of a lemon-yellow liquid; bp 135°C (2 mm Hg), vCO 1640 cm⁻¹. PMR spectrum (carbon tetrachloride, δ , ppm, J, Hz): 0.94 (Me_A, J_{HH} = 7.0, J_{HP} = 13.5), 1.04 (Me_B, J_{HH} = 7.0, J_{HP} = 13.0), 2.09 (HCP, J_{HCP} = 3.0), 7.64 m (Ph).

<u>Fluoroacetyldiisopropylphosphine (V).</u> By the method in [4], from 0.74 g (6.2 mmole) of diisopropylphosphine and 0.6 g (6.2 mmole) of $ClCOCH_2F$ in 25 ml of ether in the presence of pyridine we obtained 0.8 g (72%) of a lemon-yellow liquid; bp 52°C (4 mm Hg), vCO 1675 cm⁻¹, m/z 178 (M⁺). PMR spectrum (carbon tetrachloride, δ , ppm, J, Hz): 1.07 (Me_A, J_{HH} = 7.0, J_{HP} = 12.9), 1.13 (Me_B, J_{HH} = 7.0, J_{HP} = 14.0), 2.18 (HCP, J_{HCP} = 3.0), 4.62 (CH₂, J_{HCCP} = 2.0, J_{HF} = 46.0).

<u> α -Monohydroperfluoropropionyldiisopropylphosphine (VII)</u>. Into a mixture of 1.77 g (15 mmole) of diisopropylphosphine and 1.51 g (15 mmole) of triethylamine in 25 ml of ether at -40°C we bubbled 2.2 g (17 mmole) of FCOCHFCF₃. The temperature of the mixture was brought to 20°C, the precipitate was filtered off, the ether was distilled, and the residue was distilled under vacuum. We obtained 2 g (54%) of a lemon-yellow liquid; bp 41°C (1.5 mm Hg), vCO 1682 cm⁻¹, m/z 246 (M⁺). PMR spectrum (diphenyl ether, δ , ppm, J, Hz): 0.93 (Me_A, J_{HH}= 7.0, J_{HP} = 13.8), 0.98 (Me_B, J_{HH} = 7.5, J_{HP} = 15.0), 2.08 (HCP, J_{HCP} = 2.25), 4.55 (HCF, J_{HCCP} = 2.0, J_{HF} = 46.0, J_{HCCF} = 7.5).

<u>Trifluoroacetyl-tert-butylbenzylphosphine (X)</u>. Into a solution of 0.26 g (11 mmole) of dimethylamino-tert-butylbenzylphosphine [21] in 35 ml of ether at -40° C we bubbled 1.5 g (11 mmole) of trifluoroacetyl chloride. The precipitate was filtered off and washed with ether. The solvent was evaporated, and the residue was distilled under vacuum. We obtained 0.28 g (37%) of a lemon-yellow liquid; bp 75°C (1 mm Hg), vCO 1690 cm⁻¹, m/z 276 (M⁺). PMR spectrum (carbon tetrachloride, δ , ppm, J, Hz): 1.12 (Me₃C, J_{HCCP} = 13.0), 2.92 (H_A, J_{HP} = 2.0, J_{gem} = 14.0), 3.48 (H_B, J_{HP} = 3.0), 7.21 (Ph).

<u> α -Monohydroperfluoropropionylisopropylbenzylphosphine</u> (XIII). Similarly, from 0.90 g (4 mmole) of dimethylaminomethylisopropylbenzylphosphine [21] and 0.67 g (4 mmole) of ClCOCH-FCF₃ in 25 ml of ether at 20°C we obtained 0.45 g (38%) of a lemon-yellow liquid; bp 90°C (1 mm Hg), vCO 1682 cm⁻¹, m/z 294 (M⁺). PMR spectrum (carbon tetrachloride, δ , ppm, J, Hz) (mixture of diastereomers): 0.96 (Me¹, J_{HH} = 7.0, J_{HP} = 13.0), 1.0 (Me², J_{HH} = 7.0, J_{HP} = 13.0), 2.2 (HCP, J_{HCP} = 1.5), 2.75 (CH₂¹, J_{gem} = 14.0), 3.07 (CH₂², J_{gem} = 14.0), 4.67 (HCF, J_{HCF} = 46.0), 7.1 (Ph). ¹⁹F NMR spectrum (carbon tetrachloride, δ , ppm, J, Hz): -2.9 (CF, J_{CF}-CF₃ = 12.0), -4.4 (CF₃, J_{CF₃}-P = 7.3, J_{HF} = 7.1, J_{FCCP} = 36.4).

Methoxycarbonyl-tert-butylbenzylphosphine (XIV). By the method in [4], from 4.8 g (27 mmole) of tert-butylbenzylphosphine and 3 g (32 mmole) of methyl chloroformate in 50 ml of ether at -10°C in the presence of 6.4 g (28 mmole) of N-(β -ethoxycarbonylethyl)proline methyl ester [obtained by the reaction of *l*-proline S-methyl ester with ethyl acrylate in ether, colorless liquid, bp 117°C (3 mm Hg), $n_D^{2°}$ 1.4578, $[\alpha]_{546}^{2°}$ -90° (C 10.5, MeOH), m/z 230 (M⁺)] we isolated 4.3 g (67%) of a colorless liquid; bp 135°C (3 mm Hg), vCO 1685 cm⁻¹, m/z 238 (M⁺). PMR spectrum (carbon tetrachloride, δ , ppm, J, Hz): 1.11 (Me₃C, J_{HCCP} = 12.0), 2.75 (H_A, J_{HP} = 0, J_{gem} = 15.5), 3.26 (H_B, J_{HP} = 4.0), 3.57 (MeO), 7.14 (Ph).

<u>Dimethylcyanophosphine (XXI)</u>. A mixture of 3 g (30 mmole) of finely divided silver cyanide powder and 2.2 g (20 mmole) of dimethylchlorophosphine was kept at 20°C for 24 h. The product was blown under a vacuum of 1 torr at 60°C (bath temperature) for 30 min into a cooled (-78°C) tube with a tap. We obtained 1.3 g (65%) of a colorless liquid readily oxidized and spontaneously ignited in air; mp 0°C.

Diisopropylcyanophosphine (XXII). Method A. Into a solution of 2.55 g (20 mmole) of diisopropylphosphine and 1.6 g (20 mmole) of pyridine in 50 ml of ether at 17°C we bubbled 1.2 g (20 mmole) of cyanogen chloride for 15 min. The reaction mixture was heated to 30°C, and a copious white precipitate separated. The precipitate was rapidly filtered and washed with 10 ml of ether. The ether was distilled from the filtrate, and the residue was distilled under vacuum. After a second distillation we obtained 1 g (33%) of a colorless liquid; bp 34-35°C (1 mm Hg), $n_D^{2^\circ}$ 1.4501, $\nu C \equiv N$ 2177 cm⁻¹ (vw), m/z 143 (M⁺) [22]. PMR spectrum (Freon 113, δ , ppm, J, Hz): 1.25 (MeA, JHH = 7.03, JHP = 12.4), 1.15 (MeB, JHH = 6.8, JHP = 17.8), 2.6 (HCP, JHCP = 3.0).

Method B. By a method similar to that used for the synthesis of (III), from 2.44 g (14 mmole) of N-dimethylaminodiisopropylphosphine [21] and 0.96 g (15 mmole) of cyanogen chloride in 20 ml of ether we obtained 1.29 g (65%) of diisopropylcyanophosphine (XXII).

Pivaloylisopropyl-tert-butylphosphine (XXVI). By the method in [4], from 0.66 g (5 mmole) of isopropyl-tert-butylphosphine, 0.58 g (6 mmole) of triethylamine, and 0.61 g (5 mmole) of ClCOBu-t in 20 ml of ether we obtained 0.59 g (55%) of a lemon-yellow liquid; bp 50°C (2 mm Hg), vCO 1665 cm⁻¹, m/z 216 (M⁺). PMR spectrum (diphenyl ether, δ , ppm, J, Hz): 1.0 (Me₃C, J_{HCCP} = 11.25), 1.04 (Me₃CCO), 2.01 (HCP, J_{HCP} = 2.5). The signals of the methyl groups of the isopropyl substituent overlap with the signals of the tert-butyl group. ³¹P NMR spectrum (diphenyl ether, δ , ppm): -21.5 ppm.

<u>Methyl trans- β -Diisopropylphosphinoacrylate (XL)</u>. To 2.6 g (21 mmole) of diisopropylphosphine in 30 ml of ether at -20°C we added a solution of 1.7 g (20 mmole) of methyl propiolate in 15 ml of ether. As the temperature was brought to 20°C, the color of the mixture changed from light-yellow to brown. The ether was rapidly distilled, and the residue was distilled under vacuum. We obtained 0.65 g (16%) of a colorless liquid; bp 64-65°C (1 mm Hg), $n_D^{2^\circ}$ 1.4971, vCO 1730, vC = C 1605 cm⁻¹, m/z 202 (M⁺) [22]. PMR spectrum (tetrachloroethylene, δ , ppm, J, Hz): 1.04 (Me_A, J_{HH} = 7.28, J_{HP} = 15.4), 1.0 (Me_B, J_{HH} = 7.34, J_{HP} = 12.0), 1.81 (HCP, J_{HCP} = 2.5), 3.62 (MeO), 6.15 (H_{α}, J_{HP} = 8.2, J_{H α H $\beta}$ = 17.2), 7.30 (H $_{\beta}$, J_{HP} = 4.0).}

<u>cis- β -Diisopropylphosphinoacrylonitrile (XLII)</u>. Similarly, from 1.32 g (11 mmole) of diisopropylphosphine and 0.6 g (12 mmole) of cyanoacetylene in 30 ml of ether at -40°C we obtained 0.5 g (28%) of a colorless liquid; bp 72.5-73.5°C (1 mm Hg), n_D^{2°} 1.5005, vC \equiv N 2228 cm⁻¹, m/z 169 (M⁺) [22]. PMR spectrum (tetrachloroethylene, δ , ppm, J, Hz): 1.58 (Me_A, J_{HH} = 7.12, J_{HP} = 15.4), 1.52 (Me_B, J_{HH} = 7.12, J_{HP} = 11.5), 1.69 (HCP, J_{HCP} = 2.5), 6.47 (H_{\alpha}, J_{HP} = 20.5, J_{H\alpha}H_{\beta} = 12.8), 7.36 (H_{\beta}, J_{HP} = 4.1).

CONCLUSIONS

A linear correlation was obtained between the barriers to pyramidal inversion of the phosphorus and the ³¹P chemical shifts of acyldiisopropylphosphines. It was shown that it can be applied to various acyl-, diacyl-, triacyl-, and cyanophosphines if the increments of the ³¹P chemical shifts of the substituents are taken into account.

LITERATURE CITED

R. D. Baechler and K. Mislow, J. Am. Chem. Soc., <u>93</u>, 773 (1971).
 K. Mislow, Trans. New York Acad. Sci., Ser. II, <u>35</u>, 227 (1973).

- V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. van Wazer, Topics in Phosphorus 3. Chemistry, Vol. 5, New York-London-Sydney, Chap. 4 (1967).
- R. G. Kostyanovskii, Yu. I. Él'natanov, K. S. Zakharov, and L. M. Zagurskaya, Dokl. 4. Akad. Nauk SSSR, 219, 137 (1974); R. G. Kostyanovskii, Yu. I. Él'natanov, L. M. Zagurskaya, K. S. Zakharov, and A. A. Fomichev, Izv. Akad. Nauk SSSR, Ser. Khim., 1891 (1972); R. G. Kostyanovskii, Yu. I. Él'natanov, L. M. Zagurskaya, and K. S. Zakharov, Izv. Akad. Nauk SSSR, Ser. Khim., 1893 (1972); R.G. Kostyanovskii, Yu. I. El'natanov, and L. M. Zagurskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 901 (1975); R. G. Kostyanovskii, K. S. Zakharov, M. Zaripova, and V. F. Rudchenko, Izv. Akad. Nauk SSSR, Ser. Khim., 875; (1975) R. G. Kostyanovskii (Kostyauovsky), K. S. Zakharov, M. Zarpo, and V. F. Rudchenko (Rudtchenko), Tetrahedron Lett., 4207 (1974).
- A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, J. Am. Chem. Soc., 93, 5. 6507 (1971).
- A. Rauk, L. C. Allen, and K. Mislow, Angew. Chem., Int. Ed., 9, 400 (1970). 6.
- 7.
- S. O. Grim, W. McFarlane, and E. F. Davidoff, J. Org. Chem., <u>32</u>, 781 (1967). G. Z. Becker, Anorg. Allg. Chem., <u>423</u>, 242 (1976); G. Becker, <u>Z</u>. Anorg. Allg. Chem., 8. 430, 66 (1977).
- G. D. Macdonell, A. Radhakrishna, K. D. Berlin, J. Barycki, R. Tyka, and P. Mastalerz, 9. Tetrahedron Lett., 857 (1978).
- D. Kost, F. Cozzi, and K. Mislow, Tetrahedron Lett., 1983 (1979). 10.
- A. W. Frank and G. L. Drake, Jr., J. Org. Chem., <u>36</u>, 3461 (1971). 11.
- M. Dankowski, K. Praefske, S. C. Nyburg, and W. Wong-ng, Phosphorus and Sulfur, 3, No. 12. 3, 275 (1979).
- W. Egan and K. Mislow, J. Am. Chem. Soc., 93, 1805 (1971). 13.
- D. A. Dougherty, K. Mislow, and M. H. Whangbo, Tetrahedron Lett., 2321 (1979). 14.
- D. H. M. M. Thewissen and H. P. M. M. Ambrosius, Recueil, 99, No. 11, 344 (1980). 15.
- 16. H. Schumann and H. J. Kroth, Z. Naturforsch, 32b, 513 (1977).
- N. E. Waite, J. C. Tebby, R. S. Ward, and D. H. Williams, J. Chem. Soc., 1100 (1969). 17.
- 18. M. D. Gordon and L. D. Quin, J. Magn. Reson., 22, 149 (1976).
- E. R. Razumova, Yu. I. Él'natanov, Sh. M. Shikhaliev, and R. G. Kostyanovskii, Izv. 19. Akad. Nauk SSSR, Ser. Khim., 97 (1978).
- R. G. Kostyanovskii, V. V. Yakshin, S. L. Zimont, and I. I. Chervin, Izv. Akad. Nauk 20. SSSR, Ser. Khim., 188, 391 (1968).
- R. G. Kostyanovskii, Yu. I. Él'natanov, and Sh. M. Shikhaliev, Izv. Akad. Nauk SSSR, 21. Ser. Khim., 249 (1977); 1590 (1979).
- 22. R. G. Kostyanovskii (Kostyanovsky), V. G. Plekhanov, Kh. Khafizov, L. M. Zagurskaya, G. K. Kadorkina, and Yu. I. Él'natanov, Org. Mass Spectrom., 7, 1113 (1973); R. G. Kostyanovskii (Kostyanovsky), A. P. Pleshkova, V. N. Voznesenskii (Voznesensky), and Yu. I. El'natanov, Org. Mass Spectrom., 15, 397 (1980).
- I. L. Knunyants, E. G. Bykhovskaya, V. I. Frosin, and Yu. A. Sizov, Inventor's Certi-23. ficate No. 239952; Byull. Izobr., 12, 15 (1969). J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Reson-
- 24. ance Spectroscopy, Pergamon (1966).