Barriers to Rotation about Carbon–Phosphorus Bonds in *tert*-Butylphosphines. ^{31}P–^{1}H Spin–Spin Coupling as a Probe of Molecular Geometry

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Abstract: The temperature dependence of the ^{1}H dnmr spectra yielded activation parameters for *tert*-butyl rotation in *tert*-butyldichlorophosphine ($\Delta H^{\ddagger} = 6.0 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -3 \pm 4$ eu, $\Delta G^{\ddagger} = 6.4 \pm 0.1$ kcal/mol at 125°K), di-*tert*-butylchlorophosphine ($\Delta H^{\ddagger} = 6.3 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = 0 \pm 4$ eu, $\Delta G^{\ddagger} = 6.3 \pm 0.1$ kcal/mol at 124°K), tri-*tert*-butylphosphine ($\Delta H^{\ddagger} = 9.0 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = 2 \pm 4$ eu, $\Delta G^{\ddagger} = 8.6 \pm 0.1$ kcal/mol at 170°K), and tri-*tert*-butylphosphine sulfide ($\Delta H^{\ddagger} = 9.5 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -5 \pm 4$ eu, $\Delta G^{\ddagger} = 10.5 \pm 0.1$ kcal/mol at 200°K). Reproducible albeit subtle changes in the ^{1}H dnmr spectra of *tert*-butyldichlorophosphine oxide and sulfide are also consistent with slowing *tert*-butyl rotation below −125°. For those phosphines having a "free" lone pair of electrons, the ^{1}H–^{31}P spin–spin coupling for a methyl gauche to the lone pair ($^3J_{\mathrm{PCCH}}$ = 15–21 Hz) is significantly different from a methyl trans to the lone pair ($^3J_{\mathrm{PCCH}}$ = 2–5 Hz), with the phosphine oxides and sulfides showing no such coupling constant dependence on geometry.

Knowledge regarding the dynamics of simple stereomutations (*i.e.*, bond rotation, atomic inversion, ring reversal) is important in understanding more completely the chemistry of relevant systems and in developing a general theory for predicting barriers to nondestructive rate processes. Although infrared, Raman, and microwave spectroscopy have been utilized in the determination of potential barriers ($\Delta H^{\ddagger}$) to rotation about carbon–nitrogen and carbon–phosphorus single bonds in relatively simple amines and phosphines (Table I), there exists a dearth of data regarding such rotational processes in more hindered homologous systems. Dynamic nuclear magnetic resonance (dnmr) spectroscopy has revealed interesting conformational dynamics in a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines in which the *tert*-butyl rotation and nitrogen inversion rate processes are coupled.[2] Contrasting behavior is observed in a series of *N*-*tert*-butyl-*N*-alkyl-*N*-chloramines for which nitrogen inversion and *tert*-butyl rotation proceed at different rates.[3,4] Estimates of the sixfold barrier to rotation about the phenyl–phosphorus bond in phenylphosphine (0.17–1.02 kcal/mol),[5a] phenyldichlorophosphine (0.7–4.1 kcal/mol),[5b] and diphenylchlorophosphine (0.5–3.4 kcal/mol)[5b] were obtained from T_1 measurements utilizing ^{31}P dnmr spectra. Conventional ^{1}H dnmr studies have revealed slow *tert*-butyl rotation in *tert*-butyldichlorophosphine ($\Delta G^{\ddagger} = 6.4 \pm 0.1$ kcal/mol at −148°)[6] and di-*tert*-butylchlorophosphine ($\Delta G^{\ddagger} = 6.3 \pm 0.1$ kcal/mol at −149°).[6a] Slow rotation about phosphorus–nitrogen bonds in a variety of compounds has also been observed by the dnmr technique.[7]

Table I. Barriers to Rotation ($\Delta H^{\ddagger}$) About Carbon-Nitrogen and Carbon-Phosphorus Bonds

Compd	$\Delta H^{\ddagger}$, kcal/mol	Ref
CH_3NH_2	2.0	*a*
$(CH_3)_3N$	4.4	*b*
CH_3NO_2	0.006	*c*
CH_3PH_2	1.96	*d*
$(CH_3)_2PH$	2.22	*e*
$(CH_3)_3P$	2.6	*f*
	3.58	*g*
CH_3PCl_2	3.37	*h*
CH_3POCl_2	4.45	*h*
CH_3POF_2	3.61	*h*
CH_3PSCl_2	3.17	*h*

[a] T. Nishikawa, T. Itoh, and K. Shimoda, *J. Chem. Phys.*, **23**, 1735 (1955). [b] D. R. Lide, Jr., and D. E. Mann, *ibid.*, **28**, 572 (1958). [c] E. Tannenbaum, R. J. Meyers, and W. D. Gwinn, *ibid.*, **25**, 42 (1956). [d] T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961). [e] R. Nelson, *ibid.*, **39**, 2382 (1963). [f] D. R. Lide and D. E. Mann, *ibid.*, **29**, 914 (1958). [g] J. R. Durig, S. K. Craven, and J. Bragin, *ibid.*, **53**, 38 (1970). [h] J. R. Durig and J. M. Casper, *J. Phys. Chem.*, **75**, 1956 (1971).

This report concerns the direct observation of slow *tert*-butyl rotation in a series of *tert*-butylphosphines using the ^{1}H dnmr method. The slow exchange dnmr spectra of the *tert*-butylphosphines having a "free" lone pair exhibit a dramatic difference between the ^{1}H–^{31}P spin–spin coupling constants for methyl gauche or trans to the lone pair. This coupling constant dependence on methyl group orientation is eliminated in the phosphine oxides and sulfides.

Results and Discussion

The ^{1}H dnmr spectrum of tri-*tert*-butylphosphine (7% v/v in vinyl chloride) at −35° (Figure 1) consists of a time-averaged doublet resonance centered at δ 1.28

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(1) Alfred P. Sloan Research Fellow, 1971–1974; Camille and Henry Dreyfus Teacher-Scholar, 1972–.

(2) (a) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 542 (1971); (b) C. H. Bushweller and W. G. Anderson, *Tetrahedron Lett.*, 129 (1972); (c) H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **27**, 5761 (1971).

(3) C. H. Bushweller and J. W. O'Neil, *Tetrahedron Lett.*, 3471 (1971).

(4) C. H. Bushweller, W. G. Anderson, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, 717 (1973).

(5) (a) S. J. Seymour and J. Jonas, *J. Magn. Resonance*, **8**, 376 (1972); (b) *J. Chem. Phys.*, **54**, 487 (1971).

(6) (a) C. H. Bushweller, J. A. Brunelle, W. G. Anderson, and H. S. Bilofsky, *Tetrahedron Lett.*, 3261 (1972); (b) J. B. Robert and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 4902 (1972).

(7) T. T. Bopp, M. D. Havlicek, and J. W. Gilje, *ibid.*, **93**, 3051 (1971); A. Hung and J. W. Gilje, *J. Chem. Soc., Chem. Commun.*, 662 (1972); E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *ibid.*, **92**, 5206 (1970).

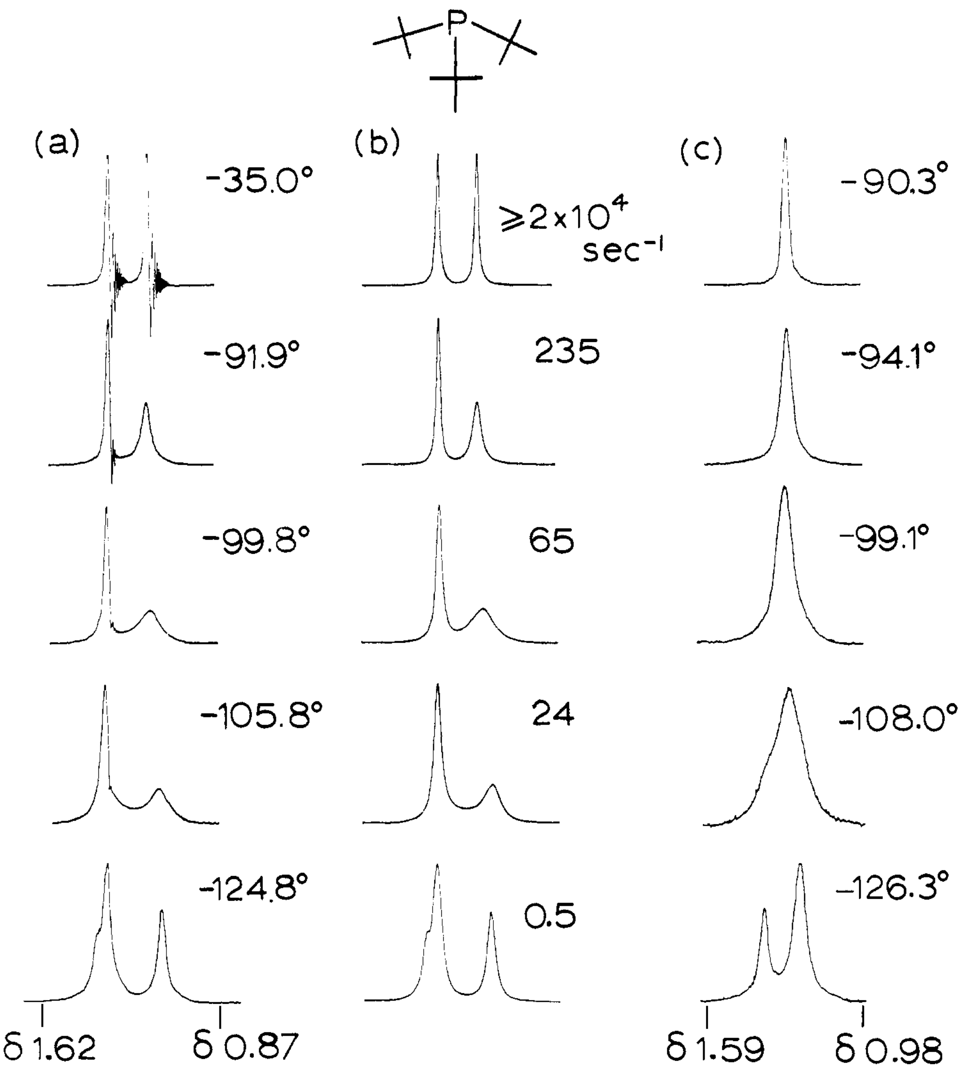
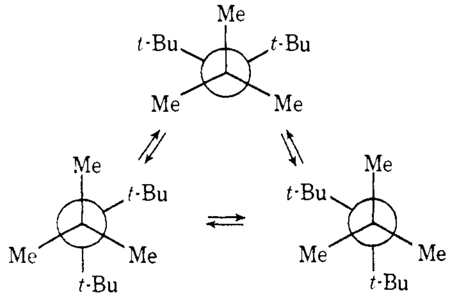


Figure 1. The ^1H dnmr spectra (60 MHz) of tri-*tert*-butylphosphine (7% v/v in vinyl chloride): (a) normal experimental spectra; (b) theoretical spectra as a function of the rate of *tert*-butyl rotation; (c) experimental spectra with irradiation at the ^{31}P resonant frequency (~24.3 MHz).

exhibiting time-averaged coupling to ^{31}P ($^3J_{PCCH}$ = 9.8 Hz). This spectrum is consistent with all three methyl groups of each *tert*-butyl moiety being rendered equivalent due to rapid rotation about the carbon–phosphorus bond (eq 1). Lowering the temperature effects



(1)

changes in the dnmr spectrum consistent with slowing *tert*-butyl rotation (Figure 1). Under conditions of slow *tert*-butyl rotation (*e.g.*, −124.8°; Figure 1), the spectrum consists of two overlapping doublet resonances at δ 1.24 (6 H, $^3J_{PCCH}$ = 13.4 Hz) and at 1.37 (3 H, $^3J_{PCCH}$ = 2.4 Hz). The upfield component of the 3 H doublet is superimposed on the low-field component of the 6 H doublet. The time-averaged spectrum observed at −35.0° possesses a chemical shift and ^1H–^{31}P spin-spin coupling constant which are exactly weighted time averages of the respective values observed at −124.8°, *i.e.*, the variation of chemical shifts and coupling constants with temperature is negligible. The small doublet (3 H, δ 1.37, $^3J_{PCCH}$ = 2.4 Hz) is assigned to the methyl group of *tert*-butyl which is trans to the lone pair on phosphorus (eq 1). The larger doublet is assigned to the two other methyl groups gauche to the phosphorus lone pair. Using these slow exchange nmr parameters, a series of theoretical dnmr spectra were calculated as a function of the rate of *tert*-butyl rotation using the computer program DNMR3[8] (Figure 1). A series of first-order rate constants (k) as a function of temperature for the conversion of any one of the three equivalent rotamers to another (eq 1) is given in Table II. A least-squares fit of a plot of ln (k/T) *vs.* $1/T$ gave the activation parameters compiled in Table III. It is apparent that the major contributor to the free energy of activation ($\Delta G^{\ddagger}$) for C–P bond rotation in tri-*tert*-butylphosphine is the enthalpy of activation ($\Delta H^{\ddagger}$) with a small entropy of activation ($\Delta S^{\ddagger}$). Subsequent examination of the ^1H dnmr spectrum of tri-*tert*-butyl-

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[8] D. A. Kleier and G. Binsch, *J. Magn. Resonance*, 3, 146 (1970).

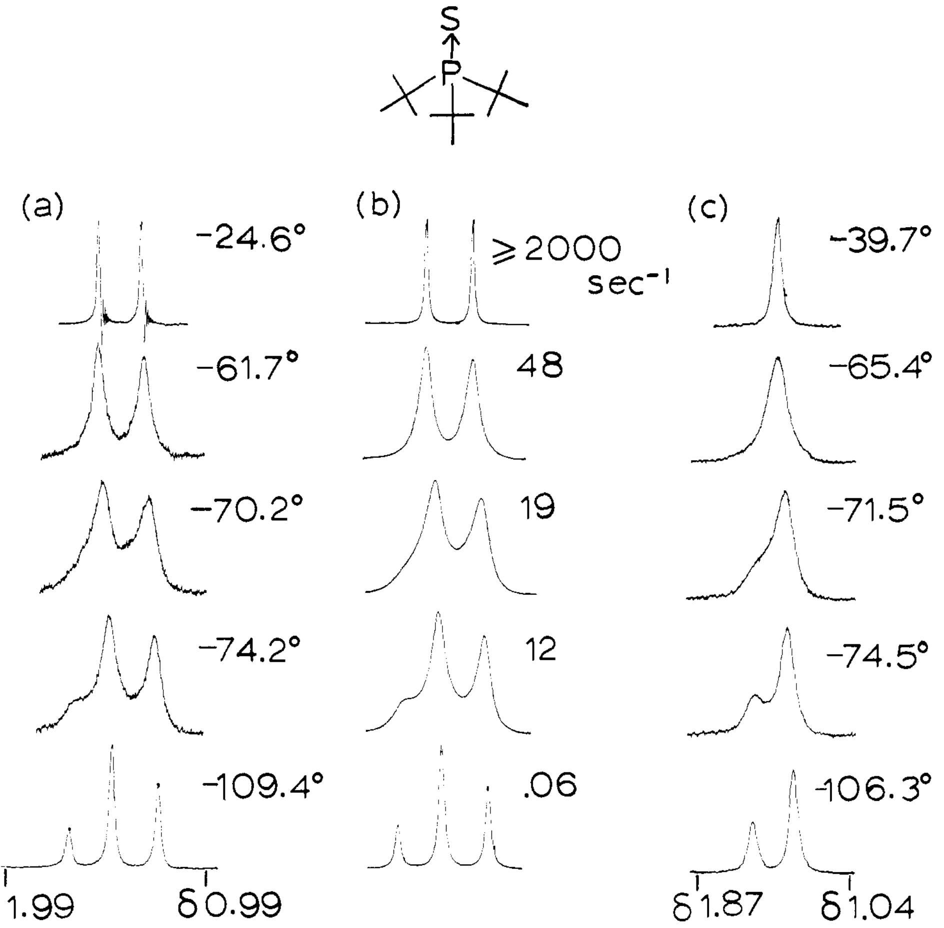


Figure 2. The ^{1}H dnmr spectra (60 MHz) of tri-*tert*-butylphosphine sulfide (0.12 *M* in vinyl chloride): (a) normal experimental spectra; (b) theoretical spectra as a function of the rate of *tert*-butyl rotation; (c) experimental spectra with irradiation at the ^{31}P resonant frequency (~24.3 MHz).

Table II. Rate Constants for *tert*-Butyl Rotation in Tri-*tert*-butylphosphine

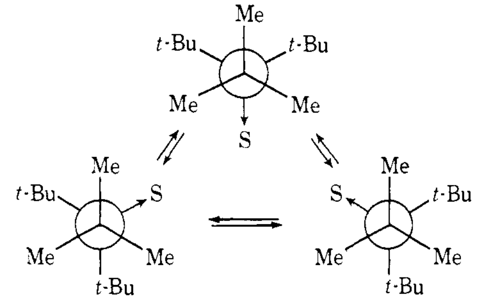
Temp, °C	−84.1	−89.0	−91.9	−96.4
k, sec^{-1}	660	325	235	130
Temp, °C	−99.8	−103.4	−105.8	−111.9
k, sec^{-1}	65	38	24	9.0
Temp, °C	−116.2	−119.5		
k, sec^{-1}	4.0	1.7		

Table III. Activation Parameters for *tert*-Butyl Rotation in *tert*-Butylphosphines

Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)
$(t\text{-Bu})_3$P	9.0 ± 0.4	2 ± 4	8.6 ± 0.1 (−103)
$(t\text{-Bu})_3$PS	9.5 ± 0.4	−5 ± 4	10.5 ± 0.1 (−72)
$(t\text{-Bu})$PCl$_2$	6.0 ± 0.4	−3 ± 4	6.4 ± 0.1 (−148)
$(t\text{-Bu})_2$PCl	6.3 ± 0.4	0 ± 4	6.3 ± 0.1 (−149)
t-BuPOCl$_2$			~7 (−130)
t-BuPSCl$_2$			~7 (−130)

phosphine with irradiation at the ^{31}P resonant frequency (~24.3 MHz) revealed a separation of the time-averaged *tert*-butyl singlet resonance at high temperatures into two singlets of relative intensity 1:2 at low temperatures (Figure 1). This is, of course, also consistent with slowing *tert*-butyl rotation on the dnmr time scale (eq 1) and the direct observation of one methyl trans (δ 1.37) and two methyls gauche to the lone pair (δ 1.24).

Perusal of the ^{1}H dnmr spectrum of tri-*tert*-butylphosphine sulfide (0.12 *M* in vinyl chloride) at −24.6° (Figure 2) also revealed a time-averaged doublet resonance (δ 1.43, $^3J_{\mathrm{PCCH}}$ = 13.8 Hz) consistent with rapid *tert*-butyl rotation on the dnmr time scale (eq 2).



(2)

At lower temperatures (Figure 2), the spectrum is transformed into two overlapping doublet resonances at δ 1.56 (3 H, methyl trans to sulfur, $^3J_{\mathrm{PCCH}}$ = 13.3 Hz) and at 1.34 (6 H, two methyls gauche to sulfur, $^3J_{\mathrm{PCCH}}$ = 14.0 Hz) consistent with slow *tert*-butyl rotation. The changes in the ^{1}H dnmr spectrum of tri-*tert*-butylphosphine sulfide are analogous to those for tri-*tert*-butylphosphine except that the ^{1}H–^{31}P spin–spin coupling constants for methyl gauche and trans to sulfur are now almost equal. In a manner exactly analogous to tri-*tert*-butylphosphine, theoretical ^{1}H dnmr spectra were generated as a function of the rate of *tert*-butyl rotation (Figure 2; Table IV), and the

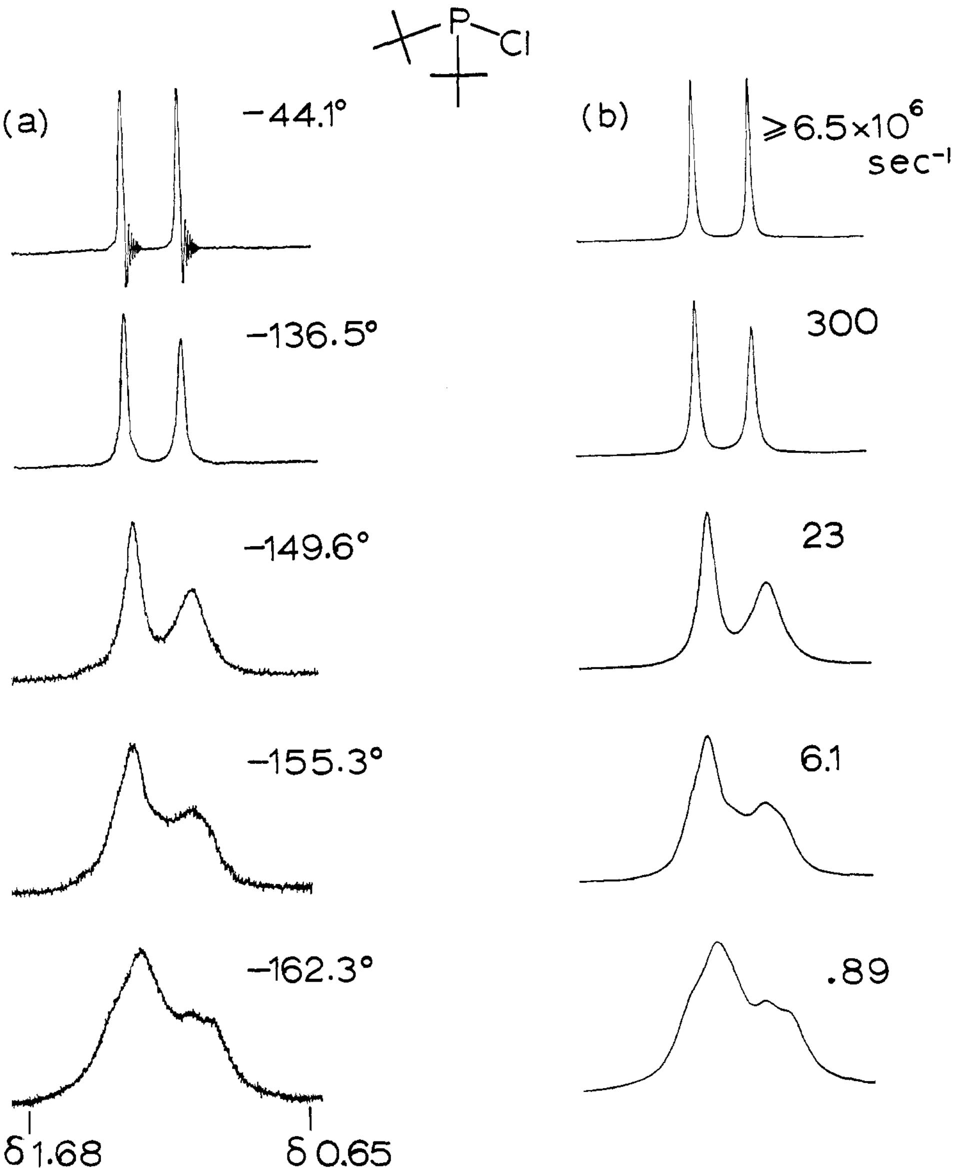


Figure 3. The ^{1}H dnmr spectra (60 MHz) of di-*tert*-butylchlorophosphine (5% v/v in vinyl chloride): (a) experimental spectra, (b) theoretical spectra as a function of the rate of *tert*-butyl rotation.

Table IV. Rate Constants for *tert*-Butyl Rotation in Tri-*tert*-butylphosphine Sulfide

Temp, °C	−61.7	−63.0	−66.9	−70.2	
k, sec^{-1}	48	44	27	19	
Temp, °C	−72.1	−74.2	−76.7	−79.6	−84.5
k, sec^{-1}	16	12	8.5	5.6	3.0

Table V. Rate Constants for *tert*-Butyl Rotation in *tert*-Butyldichlorophosphine

Temp, °C	−136.2	−138.6	−142.4	−144.7	−146.1
k, sec^{-1}	90	59	39	25	24
Temp, °C	−148.2	−148.5	−149.1	−151.0	−153.3
k, sec^{-1}	14	13	12	7.5	4.2
Temp, °C	−155.3	−156.3	−159.5		
k, sec^{-1}	2.6	1.6	1.2		

derived activation parameters are listed in Table III. The ^{1}H dnmr spectra of tri-*tert*-butylphosphine sulfide with irradiation at the ^{31}P resonant frequency reveal a transition into two singlets of relative intensity 1:2 under slow exchange conditions, again consistent with slowing *tert*-butyl rotation (Figure 2).

The ^{1}H dnmr spectrum of *tert*-butyldichlorophosphine has been reported previously and our results[6a] are in substantial agreement with those of other workers.[6b] Under conditions of slow exchange, the *tert*-butyl resonance consists of two overlapping doublets at δ 1.15 (6 H, methyls gauche to lone pair, $^3J_{\mathrm{PCCH}}$ = 20.7 Hz) and at 1.27 (3 H, methyl trans to lone pair, $^3J_{\mathrm{PCCH}}$ = 5.3 Hz). A complete dnmr line-shape analysis gave the rate constants in Table V and the activation parameters in Table III.

Contrary to a previous report,[6b] the ^{1}H dnmr spectrum of di-*tert*-butylchlorophosphine (5% v/v in vinyl chloride) exhibits significant changes at low temperatures (Figure 3).[6a] The sharp doublet (δ 1.19, J_{PCCH} = 12.2 Hz) observed at −44.1° is consistent with fast *tert*-butyl rotation. At much lower temperatures, the spectrum collapses in a manner roughly analogous to the other phosphines discussed above giving a rather ill-defined spectrum under conditions of slow exchange (−162.3°; Figure 3) *but entirely consistent with slowing*

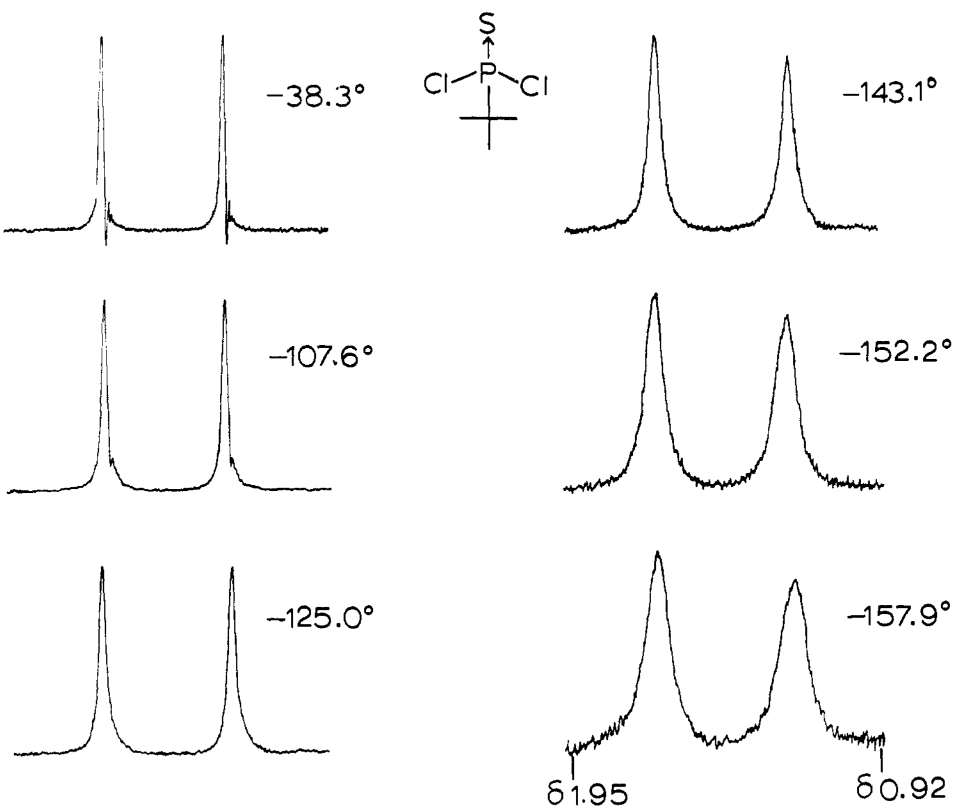
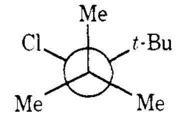


Figure 4. The ^{1}H dnmr spectra (60 MHz) of *tert*-butyldichlorophosphine sulfide (0.3 M in 2:1 v/v vinyl chloride–bromotrifluoromethane).

tert-butyl rotation. An iterative approach to calculating the slow exchange spectrum of di-*tert*-butylchlorophosphine resulted in an excellent fit using ^{1}H resonances at δ 1.12 (3 H, methyl gauche to lone pair, $^{3}J_{\mathrm{PCCH}}$ = 15.9 Hz), 1.22 (3 H, methyl gauche to lone pair, $^{3}J_{\mathrm{PCCH}}$ = 16.6 Hz), and at 1.24 (3 H, methyl trans to lone pair, $^{3}J_{\mathrm{PCCH}}$ = 4.5 Hz). It is gratifying that the fast exchange ^{1}H chemical shift and ^{1}H–^{31}P coupling constant (*e.g.*, at −44.1°) are essentially exact weighted averages of the selected slow exchange values. In addition, the necessity of invoking three chemical shifts, *i.e.*, three nonequivalent methyls, is consistent with the asymmetry experienced by a static *tert*-butyl in di-*tert*-butylchlorophosphine (**1**). Further support of



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our slow-exchange peak assignments came from excellent fits of theroetical to experimental dnmr spectra obtained in the intermediate exchange region (Figure 3). A series of rate constants for *tert*-butyl rotation is found in Table VI, and derived activation parameters are found in Table III.

Also contrary to a previous report,[6b] we have detected changes albeit subtle but reproducible in the ^{1}H dnmr spectrum of *tert*-butyldichlorophosphine oxide (0.3 M in 2:1 v/v vinyl chloride–bromotrifluoromethane) and *tert*-butyldichlorophosphine sulfide (0.3 M in 2:1 v/v vinyl chloride–bromotrifluoromethane). A representative series of spectra is shown in Figure 4 for *tert*-butyldichlorophosphine sulfide. The time-averaged doublet resonance of *tert*-butyldichlorophosphine sulfide at −38.3° (δ 1.45, $^{3}J_{\mathrm{PCCH}}$ = 26.6 Hz; Figure 4) undergoes a differential broadening of the upfield component beginning at about −125° and ending at about −140° (Figure 4). Such behavior is consistent with slowing *tert*-butyl rotation with a very small chemical shift difference between nonequivalent methyls and almost identical $^{3}J_{\mathrm{PCCH}}$ for the methyl groups gauche and trans to oxygen or sulfur. The fast exchange ^{1}H dnmr spectrum of *tert*-butyldichlorophosphine oxide (δ 1.39, $^{3}J_{\mathrm{PCCH}}$ = 25.1 Hz) is subject to essentially the same behavior as the analogous sulfide. The barriers to *tert*-butyl rotation in *tert*-butyldichlorophosphine oxide and sulfide are estimated to be 7 ± 1 kcal/mol.

Table VI. Rate Constants for *tert*-Butyl Rotation in Di-*tert*-butylchlorophosphine

Temp, °C	−136.5	−143.0	−146.7	−149.6
k, sec^{-1}	300	75	39	23
Temp, °C	−153.1	−155.3	−158.8	
k, sec^{-1}	9.5	6.1	2.2	

In the case of *tert*-butyldiphenylphosphine (7% v/v in vinyl chloride), *tert*-butyl peak (δ 1.12, $^{3}J_{\mathrm{PCCH}}$ = 12.7 Hz) broadening occurred below −120°, but no peak separation was observed.

In perusing the barriers compiled in Table III, it is important to realize that for the compounds in Table III the barriers to pyramidal inversion of tricoordinate phosphorus are at least 30 kcal/mol.[9] In the phosphine oxides and sulfides, the pyramidal geometry is locked *via* bonding to oxygen or sulfur. Thus, at the temperatures relevant to this study (Figures 1–4), pyramidal inversion at phosphorus would not affect the dnmr

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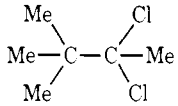
(9) R. D. Baechler, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970), and references therein.

spectra and *tert*-butyl rotation in *tert*-butylphosphines (Table III) may be assumed to occur with a fixed pyramidal phosphorus, *i.e.*, *via* a threefold potential barrier. This is in contrast to a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines in which *tert*-butyl rotation and nitrogen inversion are coupled rate processes and the common transition state for rotation and in version may involve a *planar* nitrogen.[2]

The barriers to *tert*-butyl rotation in Table III show a clear dependence on steric bulk. Coordination of the phosphorus lone pair to sulfur increases the barrier slightly in tri-*tert*-butylphosphine sulfide as compared to the free phosphine. The similarity in the barriers for di-*tert*-butylchlorophosphine and *tert*-butyldichlorophosphine is analogous to the comparable *tert*-butyl rotational barriers in **2** ($\Delta G^{\ddagger}$ = 10.8 kcal/mol at −61°) and **3** (11.4 kcal/mol at −58°)[10] indicating that *tert*-butyl–methyl and chlorine–methyl vicinal nonbonded repulsions are comparable for a given system. The significant effect of bond length is illustrated in a comparison of the barriers to *tert*-butyl rotation in *tert*-butyldichlorophosphine ($\Delta G^{\ddagger}$ = 6.4 kcal/mol at −148°) and *tert*-butyldichloramine ($\Delta G^{\ddagger}$ = 9.4 kcal/mol at −92°).[4]



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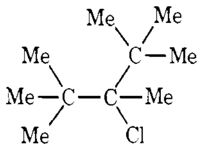

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In addition to the direct observation of slow rotation about carbon–phosphorus bonds, the dnmr spectra of static *tert*-butyl in the phosphines having a "free" lone pair show a significant dependence of $^3J_{\mathrm{PCCH}}$ on orientation of methyl gauche or trans to the lone pair. The results are summarized in Table VII. It is clear from the data in Table VII that the $^3J_{\mathrm{PCCH}}$ for a methyl group trans to a "free" lone pair is generally much smaller than that for methyl gauche to a lone pair. Incorporation of the lone pair into a coordinate covalent bond to sulfur washes out this dependence, *e.g.*, see tri-*tert*-butylphosphine sulfide in Table VII. The rationale for this behavior is not immediately clear although a hyperconjugative weakening of the carbon–methyl bond trans to the lone pair could account for the effect (eq 3).

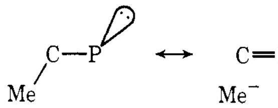

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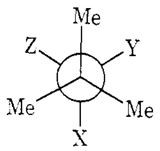
Table VII. ^{1}H–^{31}P Spin–Spin Coupling Constants for Methyl Groups in *tert*-Butylphosphines

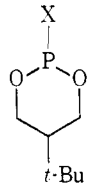


Compd	$^3J_{\mathrm{PCCH}}$(t), Hz[a]	$^3J_{\mathrm{PCCH}}$(g), Hz[b]
X = lone pair, Y = Z = *t*-Bu	2.4	13.4
X = S, Y = Z = *t*-Bu	13.3	14.0
X = lone pair, Y = Z = Cl	5.3	20.7
X = lone pair, Y = *t*-Bu, Z = Cl	4.5	15.9, 16.6

[a] ^{1}H–^{31}P spin–spin coupling constant for methyl trans to lone pair or oxygen or sulfur. [b] For methyl gauche to lone pair or sulfur or oxygen.

Although both the signs of $^3J_{\mathrm{PCCH}}$(t) and $^3J_{\mathrm{PCCH}}$(g) for all the compounds in Table VII are given as positive, identical theoretical ^{1}H d$_{\mathrm{nmr}}$ spectra under conditions of slow, intermediate, and fast exchange can be generated using negative values for both $^3J_{\mathrm{PCCH}}$(t) and $^3J_{\mathrm{PCCH}}$(g). However, by analogy with other data for ethylphenylphosphine[11a] and di-*tert*-butylfluorophosphine,[11b] it is most likely that the signs of $^3J_{\mathrm{PCCH}}$(t) and $^3J_{\mathrm{PCCH}}$(g) are positive. Although the use of different relative signs for $^3J_{\mathrm{PCCH}}$(t) and $^3J_{\mathrm{PCCH}}$(g) gave good fits of theoretical to experimental spectra under slow exchange conditions, it was impossible to obtain theoretical spectra for medium and fast exchange rates which were superimposable on the experimental spectra indicating that the relative signs of the two $^3J_{\mathrm{PCCH}}$ are not different.

A significant dependence of ^{1}H–^{31}P spin–spin coupling constants on geometry has also been observed in diphosphines,[12] *N*,*N*-dimethylaminophosphines,[7,13] 6-rings containing phosphorus (**4**),[14] and in **5**.[15]



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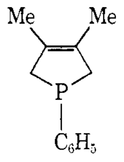
X = OMe, Cl, C_6H_5, NMe_2



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Experimental Section

The ^{1}H dnmr spectra were obtained using a Varian HR-60A nmr spectrometer equipped with a custom-built variable-temperature probe.[16] Heteronuclear spin decoupling was performed using an NMR Specialties SD-60B heteronuclear spin-decoupler.

Tri-*tert*-butylphosphine and tri-*tert*-butylphosphine sulfide were obtained from Orgmet, Inc., and used without further purification.

***tert*-Butyldichlorophosphine and di-*tert*-butylchlorophosphine** were obtained from Strem Chemicals, Inc., and were used without further purification.

***tert*-Butyldiphenylphosphine** (bp 120–125° (0.01 mm)) was obtained by the reaction (N_2 atmosphere) of *tert*-butyl lithium (~2 *M* in pentane) with diphenylchlorophosphine in anhydrous ether

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initially at −78° and then refluxed for 2 hr. The product gave an expected ^1H nmr spectrum (acetone-d_6) for *tert*-butyl (δ 1.12; $^3J_{PCCH}$ = 12.7 Hz) with a measured ratio of phenyl to *tert*-butyl protons of 1.08 (calcd, 1.10).

tert-**Butyldichlorophosphine oxide** was prepared by the method of Kinnear and Perren.[17]

tert-**Butyldichlorophosphine sulfide** was prepared by the method of Crofts and Fox.[18]

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Kinetics and Mechanism of the Hydrolysis of Pentaaryloxyphosphoranes

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Abstract: The rates of hydrolysis of pentaphenoxy- and of some substituted pentaphenoxyphosphoranes have been measured in 75% dimethoxyethane–25% water, largely by stopped-flow techniques. The reaction in neutral and alkaline solution is subject to strong electrical and steric effects; these effects are less pronounced in acid. The kinetic data and especially the large steric effect suggest that the reaction takes place by way of a hexacoordinated phosphorus intermediate or transition state.

The hydrolysis of phosphate esters may proceed either through expansion of the coordination number of phosphorus to five (through an hydroxyphosphorane intermediate) or by contraction of the coordination number to three (monomeric metaphosphate intermediate).[1] Much evidence has been accumulated for both mechanisms;[1-3] in particular, the demonstration of pseudorotation[4-6] as a necessary concomitant of the hydrolysis of certain phosphate esters shows that hydroxyphosphoranes are intermediates (as contrasted to transition states) in the hydrolysis of at least some phosphates.

Because of the role that phosphoranes play in the hydrolysis of phosphate esters, the mechanisms of hydrolysis of phosphoranes themselves are of interest. Two general pathways come prominently to mind: ionization to phosphonium salts and expansion of the phosphorus valency shell to form hexacoordinated intermediates. These mechanisms are illustrated below for the hydrolysis of pentaphenoxyphosphorane.

$$(C_6H_5O)_5P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_6H_5O)_4P^+ + C_6H_5O^-$$

$$(C_6H_5O)_4P^+ + H_2O \xrightarrow{k_2} (C_6H_5O)_4POH + H^+$$

$$(C_6H_5O)_4POH \xrightarrow{k_3} (C_6H_5O)_3P{=}O + C_6H_5OH$$

and

$$(C_6H_5O)_5P + H_2O \xrightarrow{k_1} (C_6H_5O)_5POH^- + H^+$$

$$(C_6H_5O)_5POH^- \xrightarrow{k_2} (C_6H_5O)_3P{=}O + C_6H_5OH + C_6H_5O^-$$

Both phosphonium salts[2] and anions of hexacoordinated phosphorus[7] are well known. Ramirez[8] and his collaborators and Denney and his collaborators[9] have reported that the hydrolysis of phosphoranes is rapid, and Ramirez's group has postulated,[10] on the basis of product studies and especially on the basis of observed base catalysis in the hydrolysis of a 1,2-oxaphosphetane,[10] that the reactions take place by way of intermediates or transition states that involve hexacoordinated phosphorus. We have now carried out a kinetic study of the hydrolysis of pentaaryloxyphosphoranes in 75% dimethoxyethane–25% water that strongly reinforces this conclusion for the compounds under study. Pentaaryloxyphosphoranes hydrolyze very rapidly, so

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