The Effect of Structure on the Rate of Pyramidal Inversion of Acyclic Phosphines[1,2]

Raymond D. Baechler and Kurt Mislow

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received November 8, 1969*

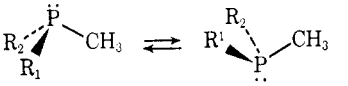
Abstract: Rate constants and activation parameters have been determined for the thermal racemization of a variety of acyclic phosphines. The results are discussed in terms of a pyramidal inversion mechanism. The rates are all cleanly first order and measurable at 130°, with $\Delta G^{\ddagger}_{130}$ falling into the range of 29–36 kcal/mol. Steric effects appear to be insignificant. The effect of substituents (R) in the series of phosphines with general formula (p-RC_6H_4)(C_6H_5)(CH_3)P on the rate of pyramidal inversion, though small, shows a remarkable correlation with similar substituent effects previously found for the pyramidal inversion of sulfoxides of general formula (p-RC_6H_4)-(p-$CH_3C_6H_4$)SO (Figure 1). In both systems, electron-withdrawing substituents in the *para* position result in a lowering of the energy barrier to pyramidal inversion.

There have been sporadic reports concerning the pyramidal instability of the phosphine pyramid at elevated temperatures.[3-8] However, no study has been reported which deals *systematically* with the effect of structural variations on the barrier to pyramidal inversion, as reflected in rates of thermal stereomutation. The present work was undertaken in an attempt to fill this gap, by a critical comparison of the rates of thermal racemization of a variety of optically active acyclic diarylalkyl-, dialkylaryl-, and trialkylphosphines.

The compounds selected for this study were readily available by reduction of the corresponding optically active phosphine oxides with hexachlorodisilane, a high yield reaction which has been shown to proceed with inversion of configuration and to afford phosphines of high optical purity.[9] All but one of the phosphine oxides were prepared by the Grignard synthesis[10] from diastereomerically pure menthyl $(S)_P$-methylphenylphosphinate.[11,12] Cyclohexylmethyl-n-propylphosphine oxide was prepared by catalytic hydrogenation of methylphenyl-n-propylphosphine oxide.[14]

The rates of thermal racemization of the phosphines in hydrocarbon solvents were determined polarimetrically. The results are collected in Table I. The rates were cleanly first order over the period of measurement, and no sign of decomposition could be detected in the product of racemization (see Experimental Section). For the racemization of allylmethylphenylphosphine (**3**) in benzene, activation parameters were determined: E_a = 32.2 kcal/mol, log A = 12.8. These values are close to those reported[3] for the racemization of methylphenyl-n-propylphosphine (**2**) in methylnaphthalene: E_a = 30.7 kcal/mol, log A = 12.4.

The results of the present study are most simply accounted for by the unimolecular process of pyramidal inversion, as shown below. A homolytic scission–recombination mechanism, such as found in the racemization of benzyl sulfoxides,[15] may be safely ruled out by the absence of decomposition products, by the close similarity in the k_{rac} values of **2** and **3**, and by the normal preexponential terms in the Arrhenius equations. It has also been shown[2] that intramolecular allylic shifts play no role in the racemization of **3**.



Inspection of the results in Table I reveals that the rates of racemization are not greatly affected by variations in structural parameters. This relative insensitivity of rates of pyramidal inversion parallels our previous observations in the pyramidal inversion of sulfoxides,[16] and may be understood on the same basis:[16] the force field for the inversion process[17,17a] within a given system ($R_1R_2R_3M$) is not, in general, grossly altered by variations in the structure of the substituents.[18]

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) For a preliminary account of a portion of this work, see R. D. Baechler, W. B. Farnham, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 5686 (1969).

(3) L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964).

(4) L. Horner and J. P. Bercz, *ibid.*, 5783 (1966).

(5) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, **88**, 3832 (1966).

(6) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *ibid.*, **90**, 6401 (1968).

(7) S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968).

(8) (a) W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 6878 (1969); (b) W. Egan, R. Tang, G. Zon, and K. Mislow, *ibid.*, **92**, 1442 (1970).

(9) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788, 7012 (1969).

(10) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968); R. A. Lewis and K. Mislow, *ibid.*, **91**, 7009 (1969).

(11) The high optical purity of the products afforded by this method helps to maximize the precision of the ORD measurements.

(12) *t*-Butylmethylphenylphosphine oxide was prepared[13] by reaction of this ester with *t*-butyllithium, although in significantly lower yield and optical purity than is typical[10] for the Grignard reactions.

(13) R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, 1010 (1969).

(14) L. Horner, R. Luckenbach, and W. D. Balzer, *Tetrahedron Lett.*, 3157 (1968).

(15) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4861 (1968).

(16) D. R. Rayner, A. J. Gordon, and K. Mislow, *ibid.*, **90**, 4854 (1968).

(17) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967), and references cited therein.

(17a) NOTE ADDED IN PROOF. The calculated[17] energy barrier (V_i) to pyramidal inversion of trimethylphosphine (*ca.* 20 kcal/mol) appears to be underestimated by *ca.* 10–15 kcal/mol when comparison is made with the value now available for the simple trialkyl phosphine, **1**. By contrast, a recent SCF–LCAO–MO calculation (J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969)) performed on phosphine itself provides a very realistic inversion barrier of 37 kcal/mol.

(18) This statement assumes an invariance in the central coordinating atom (M), *i.e.*, the comparison is restricted to the *same* pyramidal system (phosphines, sulfoxides, etc.), and excludes the operation of special effects such as have been observed in compounds containing second or

Table I. First-Order Rate Constants for Thermal Racemization[a] of Phosphines $(R_1)(R_2)(CH_3)P$

R_1	R_2	Compd	$k^f \times 10^5$, sec^{-1}	$\Delta G^{\ddagger}_{130}$, kcal/mol	Period of observn[g]	k/k' [h]
C_6H_{11}	n-C_3H_7	**1**	0.0427	35.6	0.5	1.0
C_6H_5	n-C_3H_7	**2**	3.34[i]	32.1	2	78.0
C_6H_5	CH_2=$CHCH_2$	**3**	1.44	32.8	2	33.6
		3[b]	1.69	32.6	1	39.5
		3[c]	7.48		3	
		3[d]	28.0		4	
C_6H_5	t-C_4H_9	**4**	1.61	32.7	4	37.7
C_6H_5	p-$CH_3OC_6H_4$	**5**	17.0	30.8	5	397
C_6H_5	p-$CH_3C_6H_4$	**6**	30.6	30.3	3	716
C_6H_5	p-$CF_3C_6H_4$	**7**	145	29.1	4	3400
C_6H_5	β-$C_{10}H_7$	**8**[b,e]	64.8	29.7	5	1520

[a] In decalin (*cis*:*trans* 2:1) at 130.0 ± 0.3°, except as noted. [b] In benzene at 130.0 ± 0.3°. [c] In benzene at 145.0 ± 0.3°. [d] In benzene at 160.0 ± 0.3°. [e] Benzene was used for **8** because of the insolubility of this phosphine in decalin. [f] The estimated error in rate constants is ±1.5%. [g] In units of $t_{1/2}$ (half-life). [h] Rate constant k for $(R_1)(R_2)(CH_3)P$, relative to that (k') for compound **1**, at 130°. [i] This value is in good agreement with the rate constant (3.78×10^{-5} sec^{-1}) previously reported[3] for the racemization of **2** in decalin at 130°.

Steric effects appear to play no significant role, as evidenced by the close similarity in the rates of racemization of *t*-butylmethylphenylphosphine (**4**) and the unbranched analogs, **2** and **3** (Table I). This observation parallels the previous finding[16] that in the pyramidal inversion of sulfoxides, steric effects play only a minor role. Thus, for example, values of k_{rac}[210] for methyl *p*-tolyl and adamantyl *p*-tolyl sulfoxides differ only by a factor of 3. Similarly, only a minor rate acceleration accompanies the replacement of the methyl by a *t*-butyl group in N-methylaziridine.[20]

The absence of major steric effects in pyramidal inversion processes for the systems discussed above is in contrast to the very large rate accelerations which have been observed for pyramidalinve rsion in 1-*t*-butyl-2,-2,3,4,4-pentamethylphosphetane[7] (a factor of about 10^4 relative to the 1-methyl analog[21]) and N-*t*-butyldiphenyloxaziridine[22] (a factor of *ca.* 8×10^3 relative to the N-methyl analog). However, in these systems the nonbonded repulsive interactions between the methyl groups in the phosphetane, or phenyl groups in the oxaziridine, and the *t*-butyl group on phosphorus or nitrogen, which are more important in the pyramidal ground state than in the planar transition state, may provide the driving force for the rate acceleration. That such B strain may be operative follows from two further lines of evidence. First, the close similarity between the rate constant for the conversion of *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane to the *cis* isomer[23] (1.1×10^{-5} sec^{-1} at 130° [24]) and the rates of inversion ($0.5k_{rac}$) of the acyclic analogs **2** and **3** would be surprising in view of the demonstrated *deceleration* in rates of pyramidal inversion which accompanies the incorporation of the inversion center (M) in a small ring system,[25,26] were it not for a compensating steric *acceleration*. Second, although ring strain[25,26] *slows* the rate of inversion of the 1-methylphosphetane relative to an acyclic trialkylphosphine (**1**),[21] the rate of inversion of the 1-*t*-butylphosphetane at 130° is *ca. 500 times faster* than the rate of inversion of the acyclic analog.[27] Again a pronounced steric acceleration is plainly in evidence. Moreover, in the phosphetanes, rate acceleration due to B strain is clearly dominant over rate deceleration due to angle strain.

Replacement of the cyclohexyl group in the trialkylphosphine **1** by a phenyl group (**2**) results in a 78-fold increase in rate. It is suggested that in **2** the planar transition state of racemization is stabilized, relative to the ground state, by $(p\text{–}p)\pi$ delocalization involving the lone pair of electrons on phosphorus.[28] Similar observations have been made in the analogous phosphetane[29] and aziridine[30,31] systems.[32] Introduction of a second aryl group (**5**–**8**) results in a further, though smaller, increase in rate. The tenfold increase in rate of racemization in going from **2** to **6** parallels the 15-fold increase in rate of racemization when the change is from methyl *p*-tolyl sulfoxide to phenyl *p*-tolyl sulfoxide.[16]

higher row elements bonded to pyramidal phosphorus[6,89,18a] or sulfur,[19] and which are presumably due to $(p\text{–}d)\pi$ conjugation.

(18a) Note Added in Proof. In the pyramidal inversion of isopropylphenyltrimethylsilylphosphine, the $\Delta G^{\ddagger}_{62}$ value of 18.9 kcal/mol represents a lowering in the inversion barrier of nearly 14 kcal/mol, relative to the closely analogous compound **4** (R. D. Baechler and K. Mislow, unpublished results).

(19) P. Koch and A. Fava, *J. Amer. Chem. Soc.*, **90**, 3867 (1968).

(20) S. J. Brois, *ibid.*, **89**, 4242 (1967).

(21) Based on an estimate from a kinetic run at 193° (S. E. Cremer, private communication).

(22) F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 1086 (1969).

(23) These configurational assignments are the reverse of those originally reported[7] (S. E. Cremer, private communication).

(24) Calculated from the reported[7] activation parameters.

(25) See, for example, S. J. Brois, *Trans. N. Y. Acad. Sci.*, **31**, 931 (1969).

(26) There is evidence that ring strain may raise the inversion barrier in other cyclic phosphines. A comparison of the barriers for the acyclic monoarylphosphines, **2**–**4**, with the value of $\Delta G^{\ddagger}_{170}$ *ca.* 36 kcal/mol reported[8b] for 3-methyl-1-phenylphospholane, indicates a ring strain effect of approximately 4 kcal/mol even in the five-membered ring systems.

(27) This estimate is based on a comparison with the acyclic trialkylphosphine **1**, with the added assumption that substitution of a *t*-butyl group for a *n*-propyl group in **1** has a negligible effect on the rate of inversion, as in the case for **4** and **2**.

(28) Evidence from fluorine nuclear magnetic resonance shifts also indicates that phosphorus is a weak π donor in aromatic phosphines of the type under discussion [J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 5236 (1968)]; *cf.* also R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 2.

(29) At *ca.* 160°, *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane is converted to the *cis* isomer at a rate about 10^3 times greater than that of the conversion of the *trans*- to the *cis*-1-methyl analog.[21] As discussed above, a steric factor is also involved.

(30) F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 352 (1967).

(31) The effect is greater in the aziridines[30] than in the phosphines, presumably because of more effective overlap of the benzene π system with the lone pair on nitrogen than with that on phosphorus in the transition state.

(32) Surprisingly, the effect of substituting an aryl for an alkyl group in a dialkyl sulfoxide seems to have only a minor effect on the rate of pyramidal inversion.[16]

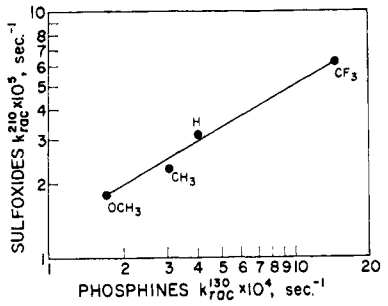


Figure 1. Correlation of log k_{rac} values of arylmethylphenylphosphines and aryl *p*-tolyl sulfoxides (aryl = *p*-RC_6H_4). See ref 35.

Comparison of the rates of racemization of **5**, **6**, and **7** reveals that, although substituent effects are small, there is an unmistakable trend in the direction of rate acceleration with increasing electron-withdrawing power of the substituent; the effect correlates with σ_p ($\rho \approx 1.0$). This direction is opposite to that which might have been predicted on the basis of a simple inductive effect[33,34] but is consistent with the view that (p–p)π conjugation affects the barrier to inversion (see above). The direction of the substituent effects observed in the pyramidal inversion of arylmethylphenylphosphines parallels the previously found[16] direction of substituent effects in pyramidal inversion of aryl *p*-tolyl sulfoxides. Moreover, there is a linear correlation between the log k_{rac} values for the two systems which is depicted in Figure 1.[35,37]

Similar trends have been observed in the pyramidal inversion of *para*-substituted 1-aryl-2,2-dimethylaziridines.[38] However, the effect is more pronounced in the aziridines,[39] supporting the view that delocalization of the lone pair on nitrogen is more effective than delocalization of the lone pair on phosphorus or sulfur (see above).

The present work demonstrates the utility of substituent constants for correlative purposes in pyramidal inversion processes.

Experimental Section[40]

Procedure for Kinetic Runs. The kinetics were carried out by the sealed tube method. Stock solutions of the phosphines (*c* 0.5–1.5 g/100 ml) in benzene (Baker and Adamson) or decalin (Aldrich, *cis*:*trans* 2:1) were prepared as follows. The solvents were dried and deoxygenated by refluxing and distillation over sodium–potassium alloy under a steady stream of dry nitrogen. After rapid distillation (kugelrohr), the pure phosphine was rinsed with solvent into a volumetric flask. In order to ensure the exclusion of oxygen,[41] solvents and solutions were stored under nitrogen and transferred by syringe, and all manipulations were performed in a plastic drybag under a nitrogen atmosphere. Aliquots (3.2 ml) of the stock solution were placed in micro Carius tubes. Each sample tube was then degassed using several cycles of immersion in liquid nitrogen, evacuation, and thawing to room temperature. The tubes, eight to ten in number, were sealed under vacuum and placed in a high-temperature Colora Ultra Thermostat circulating oil bath preset and maintained throughout the duration of the run at a set temperature within ±0.2°. After a 15–20 min initial equilibration period,[42] the "zero-time" tube was withdrawn and immediately quenched in ice water. The remaining tubes were withdrawn at intervals ranging from 5 min to 24 hr, as desired.[43] The solutions were transferred directly from the sealed tubes into a 1-cm ORD cell for the determination of the rotation (α) of the partially racemized phosphine. For a given phosphine, the rotations were all measured at a wavelength (within the range 310–350 nm) at which a high specific rotation could be obtained without significant absorbance. The first-order rate constants for racemization were calculated from the slope ($-k_{rac}/2.303$) obtained from the best straight line plot of log α *vs. t*. Even in cases where the racemization was followed for over 5 half-lives, no deviation from linearity was observed.[44] For allylmethylphenylphosphine (**3**), the Arrhenius activation energy, E_a, was calculated from the slope ($E_a/2.303R$) of the best straight line plot of log k_{rac} *vs.* T^{-1}. The preexponential factor (A) was obtained from the Arrhenius equation, $\ln k = \ln A - E_a/RT$. The activation free energies, $\Delta G^{\ddagger}_{130}$, were obtained from the Eyring equation, $\ln k = \ln (kT/h) - \Delta G^{\ddagger}/RT$. The homogeneity of the phosphine was verified by glpc both before and after racemization, using a 2-ft 10% silicone gum rubber SE 30 on 60–80 Chromosorb W column. The racemized phosphines were characterized by reoxidation with hydrogen peroxide to the phosphine oxides, which were in every case identical (by glpc analysis) with authentic samples. In this manner the presence of any decomposition of the phosphines accompanying racemization was excluded.

Preparation of the Phosphine Oxides. With the exception of the precursor to **4**,[12] all the phosphine oxides were prepared by the Grignard synthesis[10] from diastereomerically pure menthyl $(S)_p$-methylphenylphosphinate and were therefore of high optical purity. The preparation and physical properties of the phosphine oxide precursors to phosphines **2**,[10] **3**,[45] **4**,[13] **5**,[10] and **8**[10] have been described before. Cyclohexylmethyl-*n*-propylphosphine oxide was prepared by the quantitative catalytic (rhodium-on-charcoal) reduction[14] of **2** in ethanol at 100° (24 hr) under 1500 psi of hydrogen. The precursors to phosphines **6** and **7**, also prepared by the Grignard procedure, have not been described before.

(−)-(*S*)-Methylphenyl-*p*-tolylphosphine Oxide. This compound was prepared by reaction of *p*-tolylmagnesium bromide and menthyl $(S)_p$-methylphenylphosphinate according to the general procedure described before.[10] The crude phosphine oxide was purified by chromatography on silica gel, eluting with benzene and chloroform, and the product thus obtained was crystallized from benzene–

(33) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(34) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem.*, in press.

(35) The data for the phosphines are taken from the present work (Table I) and those for the sulfoxides from ref 16. The racemization of the sulfoxides refers to solvent *p*-xylene. The rates for "racemization" of the achiral molecules, bis-*p*-tolyl sulfoxide and diphenylmethylphosphine,[36] were estimated by interpolation from the individual Hammett plots (using σ_p) of the other three substituents (R = CH_3O, CH_3, CF_3 for the phosphines, and R = CH_3O, H, CF_3 for the sulfoxides).

(36) Though racemization, defined as an interconversion of enantiomers, is excluded for these two molecules, pyramidal inversion results in an interchange of enantiotopic groups, and the barriers could therefore be estimated, in principle, by measurements made under chiral conditions (*e.g.*, in a chiral solvent), without recourse to labeling.

(37) The slope of the line, 0.58, is the ratio of ρ values and is a measure of the sensitivity of the sulfoxide relative to the phosphine system to changes in σ_p of the substituent.

(38) J. Andose, J.-M. Lehn, K. Mislow, and J. Wagner, *J. Amer. Chem. Soc.*, in press.

(39) Thus, the N-*p*-trifluoromethylphenyl compound inverts *ca.* 10^3 times as fast as the N-*p*-anisyl analog at −60°.

(40) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Unless otherwise noted, pmr spectra were recorded on a Varian A-60A spectrometer, and refer to *ca.* 10% solution in deuteriochloroform, with tetramethylsilane as internal standard. Optical rotations at the D line were measured on a Schmidt and Haensch visual polarimeter using a 2-dm tube, and at other wavelengths on a Cary 60 spectropolarimeter with a 1-cm cell.

(41) This is particularly essential for compound **3** which undergoes an oxygen-catalyzed decomposition, and for compound **1** which, even in dilute solution, is very sensitive to oxidation.

(42) For phosphines **7** and **8**, whose half-lives are short at 130°, an equilibration of only 10 min was sufficient.

(43) As indicated in Table I, measurements were typically obtained over a period of at least 3 half-lives. For compound **1**, a duration of only 0.5 half-life was acceptable, due to the slow rate of racemization at 130°, $t_{1/2}$ *ca.* 450 hr. However, a sample of **1** was further racemized at a higher temperature (170°) in order to examine for any trace of decomposition accompanying racemization.

(44) In the case of methylphenyl-β-naphthylphosphine (**8**), a correction was required for a slight constant residual rotation (less than 10% of the initial rotation). To minimize the effects of an exceptionally rapid racemization under the conditions of reduction, presumably by silicon tetrachloride catalysis,[9] the reaction of the corresponding phosphine oxide with hexachlorodisilane was terminated after an unusually short period (2 min). Moreover, to avoid subjecting this rather nonvolatile phosphine to high temperature (and hence thermal racemization), the material was used without distillation. The residual rotation found after racemization is thus most likely due to a trace of unreacted phosphine oxide.

(45) A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

hexane, yielding white needles: mp 118–119°; $[\alpha]D$ −8.6° (*c* 7.0, methanol), pmr $C_6H_4CH_3$, s, τ 7.60, PCH_3, d, τ 8.02, J_{PCH} = 13 Hz. The material was homogeneous by tlc on silica gel and by glpc.

Anal. Calcd for $C_{14}H_{15}PO$: C, 73.02; H, 6.58; P, 13.45. Found: C, 73.11; H, 6.45; P, 13.51.

(+)-(*S*)-Methylphenyl-*p*-trifluoromethylphenylphosphine Oxide. This compound was prepared by reaction of *p*-trifluoromethylphenylmagnesium bromide with menthyl $(S)_P$-methylphenylphosphinate according to the general procedure described before.[10] The crude phosphine oxide was purified by distillation (kugelrohr, bp 150° (0.05 mm)) from a viscous black tar,[46] followed by chromatography on silica gel, eluting with benzene, chloroform, and finally acetone. White crystals were obtained from benzene–hexane. This product had mp 137°, $[\alpha]D$ +6.6° (*c* 1.1, methanol), pmr PCH_3, d, τ 7.93, J_{PCH} = 13 Hz, and was homogeneous by tlc and glpc.

Anal. Calcd for $C_{14}H_{12}F_3PO$: C, 59.16; H, 4.26; F, 20.05; P, 10.90. Found: C, 59.62; H, 4.19; F, 19.57; P, 10.96.

(46) The rather poor yield (*ca.* 20%) in this preparation is not at all typical for the Grignard synthesis.[10]

Table II. Physical Properties of Phosphines $(R_1)(R_2)(CH_3)P$

Compd	Absolute confign	Bp (mm),[b] °C	$[\alpha]$,[c] deg (λ, nm)
1	*R*	40 (0.01)	+124 (325)
2	*R*	35 (0.02)	+87 (305)
3	*R*	40 (0.05)	+1000 (350)[d]
4	*R*	60 (0.05)	+340 (330)
5	*S*	140 (0.05)	+112 (330)
6	*S*	120 (0.1)	+25 (330)
7	*S*	90 (0.01)	−85 (340)
8	*S*	*a*	+144 (350)[d]

[a] See ref 44. [b] These temperatures are only approximate (±10°), since the kugelrohr technique was employed. [c] All rotations were measured at *c* 0.5–1.5 g/100 ml and refer to solvent decalin except where noted. [d] Solvent benzene.

Preparation of the Phosphines. All of the phosphines listed in Table I were prepared by hexachlorodisilane reduction of the corresponding oxides, following the general procedure described before.[9] The physical properties of the phosphines are listed in Table II.

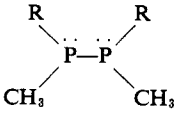
Substituent Effects in the Inversion–Rotation Process of Diphosphines

Joseph B. Lambert,[1a] George F. Jackson, III,[1b] and David C. Mueller[1c]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received November 8, 1969*

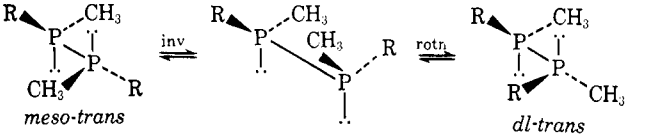
Abstract: Diphosphines of the type RCH_3PPCH_3R have been prepared and characterized by ^1H and ^{31}P magnetic resonance spectroscopy. The energetics of the inversion–rotation process have been examined as a function of the substituent (R = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CF_3C_6H_4$, $C_6H_5CH_2$) in order to determine the nature of electronic demand at phosphorus in the transition state. The monosulfide of 1,2-dimethyl-1,2-diphenyldiphosphine exhibits a temperature-invariant nmr spectrum. These results are interpreted in terms of p_π–d_π bonding in the transition state to inversion. The proton spectrum of tetramethyldiphosphine was found to be independent of temperature down to −65°. Either the *gauche* rotational isomer is completely absent, or rotation is fast in these diphosphines throughout the entire observable temperature range. These results require an unusually rapid inversion about phosphorus, in comparison to the rate of stereomutation of monophosphines.

Diphosphines of the type I may exist in *meso* and *dl* diastereomeric forms. Maier[2,3] and Fluck



Ia, R = CH_3
b, R = C_6H_5
c, R = *p*-$CH_3C_6H_4$
d, R = *p*-$CF_3C_6H_4$
e, R = *p*-ClC_6H_4
f, R = $C_6H_5CH_2$
g, R = CH_3CH_2

and Issleib[4] observed that the diastereomers produce distinct ^{31}P resonances. In previous work, we found that a diastereomeric differentiation is also exhibited in the proton spectra of these diphosphines,[5,6] as well as in the spectra of the corresponding diarsines.[6,7] The proton resonances associated with the *dl* and *meso* forms were found to coalesce into an average spectrum above 150°.[5–7] The mechanism of interconversion involves an inversion of configuration about phosphorus and a rotation about the phosphorus–phosphorus bond (eq 1). An experimental decision as to which step is rate determining was not made.[6] In either case, the



(1)

Arrhenius activation energy for inversion about phosphorus could not be greater than 26 kcal/mol. Such a

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