

hexane, yielding white needles: mp 118–119°;  $[\alpha]_D -8.6^\circ$  ( $c$  7.0, methanol), pmr  $C_6H_4CH_3$ , s,  $\tau$  7.60,  $PCH_3$ , d,  $\tau$  8.02,  $J_{PC} = 13$  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)<sub>p</sub>-methylphenylphosphinate according to the general procedure described before.<sup>10</sup> The crude phosphine oxide was purified by distillation (kugelrohr, bp 150° (0.05 mm)) from a viscous black tar,<sup>46</sup> 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°,  $[\alpha]_D +6.6^\circ$  ( $c$  1.1, methanol), pmr  $PCH_3$ , d,  $\tau$  7.93,  $J_{PC} = 13$  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.<sup>10</sup>

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

Compd	Absolute config	Bp (mm), <sup>b</sup> °C	$[\alpha]_D^c$ deg (λ, nm)
1	R	40 (0.01)	+124 (325)
2	R	35 (0.02)	+87 (305)
3	R	40 (0.05)	+1000 (350) <sup>d</sup>
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	<i>a</i>	+144 (350) <sup>d</sup>

<sup>a</sup> See ref 44. <sup>b</sup> These temperatures are only approximate ( $\pm 10^\circ$ ), since the kugelrohr technique was employed. <sup>c</sup> All rotations were measured at  $c$  0.5–1.5 g/100 ml and refer to solvent decalin except where noted. <sup>d</sup> 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.<sup>9</sup> The physical properties of the phosphines are listed in Table II.

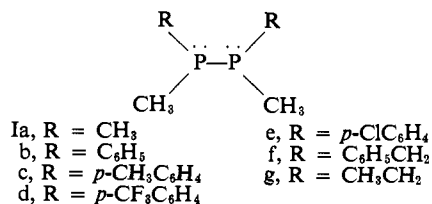
## Substituent Effects in the Inversion–Rotation Process of Diphosphines

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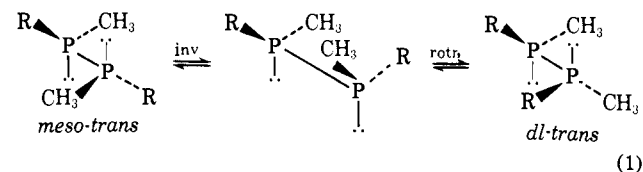
**Abstract:** Diphosphines of the type  $RCH_3PPCH_3R$  have been prepared and characterized by <sup>1</sup>H and <sup>31</sup>P magnetic resonance spectroscopy. The energetics of the inversion–rotation process have been examined as a function of the substituent ( $R = C_6H_5$ ,  $p$ - $CH_3C_6H_4$ ,  $p$ - $CF_3C_6H_4$ ,  $C_6H_5CH_2$ ) 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  $p_\pi$ - $d_\pi$  bonding in the transition state to inversion. The proton spectrum of tetramethyldiphosphine was found to be independent of temperature down to  $-65^\circ$ . 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<sup>2,3</sup> and Fluck



and Issleib<sup>4</sup> observed that the diastereomers produce distinct <sup>31</sup>P resonances. In previous work, we found that a diastereomeric differentiation is also exhibited

in the proton spectra of these diphosphines,<sup>5,6</sup> as well as in the spectra of the corresponding diarsines.<sup>6,7</sup> The proton resonances associated with the *dl* and *meso* forms were found to coalesce into an average spectrum above  $150^\circ$ .<sup>5-7</sup> 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.<sup>8</sup> In either case, the



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

(5) J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, **88**, 3669 (1966).

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

(7) J. B. Lambert and G. F. Jackson, III, *ibid.*, **90**, 1350 (1968).

(1) (a) Alfred P. Sloan Fellow, 1968–1970. This work was supported by the National Science Foundation (Grants GP-6611 and GP-9257) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-A4,5); (b) National Science Foundation Trainee, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1969; (c) National Science Foundation Undergraduate Research Participant, 1965–1966.

(2) L. Maier, *Angew. Chem.*, **71**, 574 (1959); *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

(3) L. Maier, *Ber.*, **94**, 3043 (1961).

(4) E. Fluck and K. Issleib, *ibid.*, **98**, 2674 (1965).

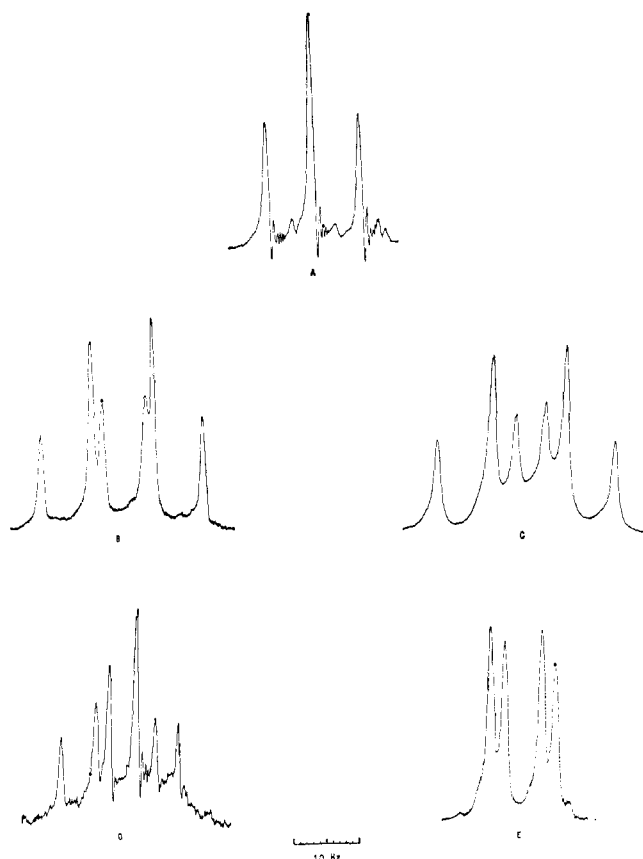


Figure 1. The 90-MHz nmr spectra of the methyl group attached to phosphorus without  $^{31}\text{P}$  irradiation for diphosphines of the type  $\text{RCH}_3\text{PPCH}_3\text{R}$ : (a) tetramethyldiphosphine, (b) 1,2-dimethyl-1,2-diphenyldiphosphine, (c) 1,2-dimethyl-1,2-bis(*p*-trifluoromethylphenyl)diphosphine, (d) 1,2-dimethyl-1,2-dibenzoyldiphosphine, (e) 1,2-dimethyl-1,2-di(*p*-tolyl)diphosphine.

value is lower than that observed for inversion of monophosphines.<sup>8</sup>

In the present study, we have examined the effect of the group R on the inversion-rotation process of I. Anet,<sup>9</sup> Mislow,<sup>10</sup> and their coworkers have previously studied substituent effects on inversion about nitrogen and sulfur, respectively. Substituted phenyl rings are utilized in our study in order to determine the nature of electron demand at phosphorus in the transition state. Nonaromatic R groups assist in determining the effect of  $p_\pi$ - $p_\pi$  conjugation. Addition of a sulfur atom to one of the phosphorus atoms produces a system with different possibilities of  $p_\pi$ - $d_\pi$  bonding from those in the original diphosphines, so that the importance of this factor may be assessed. Finally, low-temperature spectra have been examined in an attempt to resolve the rate process into its rotational and inversional components.

## Results

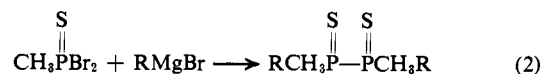
The diphosphines were prepared by the copper reduction of the corresponding disulfides,<sup>6,11</sup> which in turn were obtained by the reaction of methyl dibromophosphine sulfide with the appropriate Grignard reagent (eq 2). Typically, both *meso* and *dl* modifications

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

(9) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 357 (1967).

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

(11) N. H. Niebergall, *Angew. Chem.*, **72**, 210 (1960).



of the disulfide were isolated and converted to the diphosphine.

The  $^{31}\text{P}$  and  $^1\text{H}$  spectral data are presented in Tables I and II. The  $^{31}\text{P}$  shifts are in agreement with what literature data are available.<sup>2-4,12</sup> The  $^{31}\text{P}$  spectra almost always consist of two peaks (at higher field than 85% phosphoric acid), corresponding to the *meso* and *dl* forms of the diphosphine. With decoupling of  $^{31}\text{P}$  from  $^1\text{H}$ , the populations may be readily determined from the peak heights.

Table I. The  $^{31}\text{P}$  Chemical Shifts and Population Analyses for the Diphosphines  $\text{RCH}_3\text{P}-\text{PCH}_3\text{R}$  and the Monosulfide

R	Chemical shift, ppm, from external 85% phosphoric acid	Chemical shift (lit. <sup>a,b</sup> ), ppm	Populations (low to high field)
$\text{CH}_3$	+60.2	+59.5	
$\text{C}_6\text{H}_5$	+38.2	+38.2	0.59:0.41
	+41.7	+41.7	
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (?) <sup>c</sup>	+67.6		0.56:0.44
	+73.3		
<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$	+38.3		0.55:0.45
	+41.9		
<i>p</i> - $\text{ClC}_6\text{H}_4$	+36.4		0.56:0.44
	+38.3		
$\text{C}_6\text{H}_5\text{CH}_2$	+39.4		0.46:0.54
	+40.7		
$\text{CH}_3\text{CH}_2$	+45.9	+44.7	0.42:0.58
	+48.1	+46.2	
$\text{C}_6\text{H}_5$	-44.3	-43.7	
(monosulfide)	-37.4	-33.9	
	+33.7	+37.5	
	+39.8	+47.4	

<sup>a</sup> References 2-4. <sup>b</sup> K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962). <sup>c</sup> There is some doubt about the structure of this compound (*vide infra*).

Table II. Proton Chemical Shifts ( $\delta$  in parts per million) for the Diphosphines  $\text{RCH}_3\text{P}-\text{PCH}_3\text{R}$  and the Monosulfide

R	$\text{CH}_3\text{P}$	A <sup>a</sup>	B <sup>a</sup>
$\text{CH}_3$	Triplet 0.22-0.55		
$\text{CH}_3\text{CH}_2$	Multiplet 0.67-1.67		
$\text{CH}_3\text{CD}_2$	Multiplet 0.13-1.47		
<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$	Multiplet 0.52-0.97	Multiplet 6.46-7.13	Doublet <sup>b</sup>
B A			
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (?)	Multiplet 0.72-1.0	Multiplet 6.83-7.05	Doublet 1.75-1.79
B A			
<i>p</i> - $\text{ClC}_6\text{H}_4$	Singlet (broad) 0.97	Singlet (broad) 6.8	
A			
$\text{C}_6\text{H}_5\text{CH}_2$	Multiplet 0.47-0.88	Singlet 6.9	Multiplet 2.35-2.8
A B			
$\text{C}_6\text{H}_5$	Multiplet 0.7-1.1	Multiplet 6.6-7.1	
A			
$\text{C}_6\text{H}_5$	Multiplet 0.71-2.0	Multiplet 6.6-7.9	
A			
(monosulfide)			

<sup>a</sup> The letters A and B refer to specific protons in the R group, as specified in the first column. <sup>b</sup> Fluorine-19 spectrum.

(12) See Table I, footnote b.

A methyl group on phosphorus in a diphosphine usually gives rise to a "deceptively simple" triplet (Figure 1a), since the protons are coupled to both phosphorus atoms ( $^2J_{\text{HCP}}$  and  $^3J_{\text{HCPP}}$ ). If diastereoisomerism is possible, as in I (R not  $\text{CH}_3$ ), two overlapping methyl triplets, derived from the *meso* and the *dl* forms, are found (Figure 1b–1d). The sum of  $^2J$  and  $^3J$  is readily measured (Table III), and the distinct

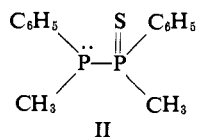
Table III. Sum of  $^2J_{\text{PCH}}$  and  $^3J_{\text{PPCH}}$  for  $\text{RCH}_2\text{P}-\text{PCH}_2\text{R}$  in Hertz

R	Downfield triplet	Upfield triplet
$\text{CH}_3$	14.0	(Only one triplet present)
$\text{C}_6\text{H}_5$	16.0	15.5
<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$	15.2	19.5
$\text{C}_6\text{H}_5\text{CH}_2$	12.6	14.4

values could be obtained by a more detailed analysis.<sup>13</sup> In 1,2-dimethyl-1,2-diphenyldiphosphine (Ib), the phenyl resonances are also separated into *dl* and *meso* regions.<sup>5,6</sup> The  $^{19}\text{F}$  spectrum of the *p*-trifluoromethylphenyl compound (Id) and the *p*-methyl spectrum of the tolyl compound (Ic) are also diastereomerically doubled. The methyl group on phosphorus in Ic gives a quartet (Figure 1e), in which all the separations are couplings, rather than chemical shifts. In this case, the *dl* and *meso* resonances must be superimposed. Diastereoisomerism is assured by the doubling of the aromatic methyl and the  $^{31}\text{P}$  resonances. The methyl group in the *p*-chlorophenyl compound (Ie) gives a broad, structureless band that could not be analyzed. Because of overlapping chemical shifts, the substituent resonances in the ethyl compound (Ig) do not give useful information, even with deuterium substitution in the methylene group.

If the compounds giving a pair of methyl triplets (Ib, Id, If) are irradiated at the  $^{31}\text{P}$  frequency, the proton spectra simplify to two chemically shifted singlets, as determined by observation of the spectra at 60 and 90 MHz for each case. These singlets coalesce to one peak at high temperatures. The kinetics of these processes were determined by complete line-shape analysis or by the coalescence-temperature method.<sup>14</sup> The spectral data and the activation parameters for the rate process are set out in Table IV. Since the *P*-methyl peaks in the *p*-tolyl case are not chemically shifted (the quartet is invariant with field), the kinetics were followed by the coalescence of the tolyl methyl doublet to a single line (Table IV). In all these systems, allowance was made in the kinetic analysis for temperature dependence of the chemical shifts and of the inherent line widths, if necessary.

The 1,2-dimethyl-1,2-diphenyldiphosphine monosulfide (II) was prepared in order to obtain a better idea



(13) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); E. G. Finer and R. K. Harris, *Mol. Phys.*, **12**, 457 (1967).

(14) Because of incomplete decoupling, a complete analysis could not be used with the benzyl compound (If).

Table IV. Free Energies of Activation and Spectral Parameters for Inversion-Rotation in Diphosphines of the Type  $\text{RCH}_2\text{P}-\text{PCH}_2\text{R}$

R	$T_c^a$ , °C	$\Delta\nu$ , Hz at 90 MHz	$\Delta G^\ddagger(155^\circ)$ , kcal/mol	$k/k_{\text{C}_6\text{H}_5}(155^\circ)$
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (?)	130 <sup>b</sup>	3.5 <sup>c</sup>	22.5 <sup>d</sup>	4
<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$	156 <sup>e</sup>	11.4 <sup>f</sup>	22.6 <sup>g</sup>	3.5
$\text{C}_6\text{H}_5$	153 <sup>b</sup>	10.7 <sup>h</sup>	23.6 <sup>g</sup>	1.0
		9.3 <sup>f</sup>		
$\text{C}_6\text{H}_5\text{CH}_2$	156 <sup>b</sup>	4.0 <sup>f</sup>	24 <sup>d</sup>	0.8

<sup>a</sup> Coalescence temperature. <sup>b</sup> Measured at 60 MHz. <sup>c</sup> Separation of peaks due to methyl on phenyl. <sup>d</sup> Coalescence temperature method. <sup>e</sup> Measured at 90 MHz. <sup>f</sup> Separation of peaks due to methyl on phosphorus. <sup>g</sup> Complete line-shape method. <sup>h</sup> Separation of *meta* protons in the phenyl-2,4,6-*d*<sub>3</sub> derivative.

of the effect of  $p_\pi$ - $d_\pi$  bonding on the inversion barrier. Unsymmetrical monosulfides of the type II can exist as two *dl* pairs that can interconvert by phosphorus inversion. There was no apparent change in the methyl or phenyl multiplets for this compound over the temperature range of 100–200°.

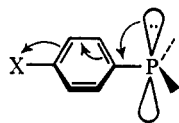
The proton spectra of tetramethyldiphosphine (Ia) and of 1,2-dimethyl-1,2-di(*p*-tolyl)diphosphine (Ic) were examined down to  $-65^\circ$  in toluene-*d*<sub>8</sub> in order to detect possible rotational transformations. The spectrum of the tetramethyl compound was unchanged over the temperature range from  $-65$  to  $+180^\circ$ . The spectrum of the *p*-tolyl compound remained unchanged from  $-65^\circ$  to about  $+100^\circ$ , at which temperature the above-mentioned coalescence phenomena set in.

## Discussion

The factors that influence atomic inversion have been enumerated by previous workers.<sup>9,10</sup> (1) Sterically bulky groups on the central atom will decrease the inversion barrier under certain circumstances, because the  $sp^2$  transition state relieves steric strain. (2) If the central atom is incorporated into a small ring, angle strain is increased in the transition state, and the barrier is raised. (3) Conjugative effects ( $p_\pi$ - $p_\pi$  and  $p_\pi$ - $d_\pi$ ) will lower the barrier, because in the transition state the lone pair is in a pure *p* orbital that possesses optimal symmetry for overlap. (4) Electronegative substituents increase the *s* character of the lone pair on the central atom and hence raise the barrier. (5) Finally, substituents bearing lone pairs will increase the barrier, because lone pair-lone pair repulsion is greatest in the transition state.

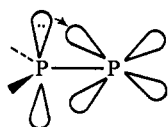
Steric and electronegativity factors are nearly constant in our series of compounds, and angle strain is not applicable. Electronic factors (3) and (5) are therefore expected to dominate. If the rate process is predominantly a rotation about bonds, electronic factors should be minimal.<sup>15</sup> The substituted phenyl series (Ib, Ic, and Id) is sterically constant, but electronically variable. In an atomic inversion, the effect of the phenyl group should be one of acceleration, since the lone pair is best situated for overlap at the transition state. An electron-withdrawing *para* substituent should enhance this effect. The rate data in Table IV are consistent with this picture, but the changes are extremely small. Thus, replacement of the nonconjugating benzyl group with a phenyl group lowers the barrier about 0.5 kcal/

(15) For documentation of this statement, see M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Am. Chem. Soc.*, **91**, 6677 (1969).

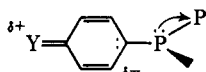


mol.<sup>16</sup> The *p*-CF<sub>3</sub> group lowers the barrier a slight bit more. Mislow and coworkers have observed a similar effect on the barrier to inversion of sulfoxides<sup>10</sup> and monophosphines.<sup>17</sup> The *p*-CH<sub>3</sub> group does not fit into this series.<sup>18</sup> It is found to convey a small rate enhancement to the rate process. Such an observation is inconsistent with a rate-determining bond rotation, but it is also contrary to the expected phenyl effect.

To clarify these observations, we must explore what influence the substituted phenyl series has on *p*<sub>π</sub>-*d*<sub>π</sub> overlap. In monophosphines, the barrier to inversion has been found to be much higher than can be observed by nmr methods.<sup>17,19</sup> We attributed the lower barrier for inversion of diphosphines to stabilization of the transition state through *p*<sub>π</sub>-*d*<sub>π</sub> bonding between the phosphorus atoms.<sup>5-7</sup> This effect appears to be dominant for these molecules.<sup>20</sup> Thus, introduction of a



C<sub>6</sub>H<sub>5</sub> or *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub> group on phosphorus has only a small effect, because it serves not only to lower the barrier by direct (*p*<sub>π</sub>-*p*<sub>π</sub>) conjugation, but also to decrease the *p*<sub>π</sub>-*d*<sub>π</sub> overlap. The *p*<sub>π</sub>-*p*<sub>π</sub> effect is also reduced because of poor overlap between the *p* orbitals on carbon and on phosphorus. The "normal" effect of an electron-donating group, such as CH<sub>3</sub>, is to decrease the rate, because of increased electron density adjacent to the inverting atom.<sup>10</sup> This interaction is greater in the



transition state than in the ground state. In the diphosphine system, there is room for alleviation of the electron repulsion by overlap of the lone pair on phosphorus with the empty *d* orbitals on the adjacent phosphorus atom. Since relief of this repulsion would be greater in the transition state than in the ground state, the "normal" rate-retarding effect should not be observed. The small rate acceleration might be explained by an enhancement of *p*<sub>π</sub>-*d*<sub>π</sub> bonding between phosphorus

(16) There is a significant experimental error in the values  $\Delta G^\ddagger$  in Table IV ( $\pm 1$  kcal/mol), but the differences are determined fairly accurately.

(17) R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970).

(18) As noted in Table I, there is a possibility that Ic does not have the proposed structure. The <sup>31</sup>P chemical shift, the splitting of the methyl resonances (Figure 1e), and the activation energy are out of line. Nonetheless, the form of the <sup>31</sup>P spectrum, the chemical shifts and the integrals in the <sup>1</sup>H spectrum (Table II), and the mass spectrum of the antecedent disulfide (see Experimental Section) are entirely consistent with the diphosphine representation. If Ic is rejected because of these conflicting data, the remainder of the series (Ib, Id, If) follows the same basic pattern as do the phosphines reported by Mislow and coworkers.<sup>17</sup>

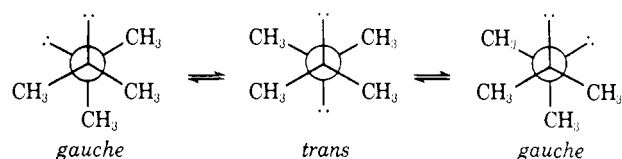
(19) For a review, see D. Gagnaire and M. St.-Jacques, *J. Phys. Chem.*, **73**, 1678 (1969).

(20) Acceleration of atomic inversion by *p*<sub>π</sub>-*d*<sub>π</sub> overlap has since been observed in several other cases also: P. Koch and A. Fava, *J. Am. Chem. Soc.*, **90**, 3867 (1968); E. W. Abel and J. P. Crow, *J. Organometal. Chem.*, **17**, 337 (1969); W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 6878 (1969).

atoms.<sup>18</sup> The effects in the substituted phenyl series may thus be explained in terms of a balance between direct *p*<sub>π</sub>(C)-*p*<sub>π</sub>(P) conjugation and perturbations on the *p*<sub>π</sub>(P)-*d*<sub>π</sub>(P) overlap between phosphorus atoms. It should be emphasized that the conclusions are tentative, since the sampling is small.

As mentioned in the previous section, the proton spectrum of 1,2-dimethyl-1,2-diphenyldiphosphine monosulfide (II) is invariant with temperature up to 200°. The two *dl* pairs would be expected to give separate spectra that would coalesce if inversion of the trivalent phosphorus atom became fast on the nmr time scale. Since the *meso* and *dl* forms of I are so close in energy for all cases (Table I), it is doubtful that the two *dl* forms of II differ significantly. The invariance of the spectrum must then be attributed to slow inversion about the trivalent phosphorus.<sup>21</sup> The sulfur atom donates *p* electrons to the *d* orbitals of the pentavalent phosphorus atom, so that any *p*<sub>π</sub>-*d*<sub>π</sub> bonding between phosphorus atoms must be correspondingly reduced. The trivalent phosphorus atom therefore more nearly resembles a monophosphine, with concomitant stability of configuration. Experiments with optically active materials should be carried out in order to substantiate this proposed effect.<sup>21b</sup>

The high-temperature changes in the nmr spectra of diphosphines have been interpreted as if the atomic inversion were rate determining. Some of the observations, indeed, are contrary to the expected behavior had bond rotation been rate determining.<sup>21a</sup> Since rotations about formal single bonds have generally been observed at low temperatures, we examined the proton spectra of Ia and Ic down to -65°. If a discrete process of phosphorus-phosphorus bond rotation exists, it might be expected to manifest itself in this temperature range. Previously, rotation about P-N, N-S, N-O, N-N, and S-S bonds have been studied by nmr spectroscopy below 0° (Table V). Neither diphosphine exhibited any changes between -65 and +50°. For the case of tetramethyldiphosphine (Ia), one may conclude either that P-P rotation is rapid in this range or that the molecule exists entirely as the *trans* rotational

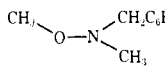
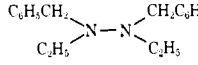
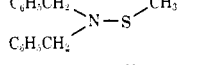
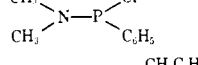
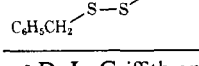


isomer. Contributions from a *gauche* form with slow rotation are specifically excluded.<sup>22</sup> The results with 1,2-dimethyl-1,2-di(*p*-tolyl)diphosphine may be interpreted in a similar fashion. There are six rotational isomers to be considered,<sup>6</sup> of which the four *gauche* forms may be excluded<sup>22</sup> on the basis of the above experiments with tetramethyldiphosphine. These experiments once again<sup>6</sup> point to a mechanism that is limited to an interconversion between the *trans-meso* and the *trans-dl* forms (eq 1). The substituent effects

(21) (a) If bond rotation were the rate-determining process in these systems, I and II should have similar behavior. The contrary was observed. (b) The spectral invariance, however, could be caused by an exact superposition of resonances or by a biased equilibrium.

(22) The *cis*-eclipsed form should also give a single triplet, but such a form need not be considered since it has been shown to be at a maximum in the torsional process; cf. M. S. Gordon, *J. Am. Chem. Soc.*, **91**, 3122 (1969); M. J. Caudillo and S. H. Bauer, *Inorg. Chem.*, **8**, 2086 (1969).

**Table V.** Coalescence Temperatures for Torsional Processes about X-Y Bonds

Compound	X-Y	$T_c$ , °C	Source
	O-N	-25	a, b
	N-N	-51	c
	N-S	< -100	d
	N-P	-50	e
	S-S	< -95	f

<sup>a</sup> D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 5055 (1968). <sup>b</sup> In all of these cases there is an ambiguity between bond rotation and atomic inversion, but the temperature ranges are nonetheless characteristic of the barrier for the slower process. <sup>c</sup> J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 706 (1969). <sup>d</sup> J. M. Lehn and J. Wagner, *ibid.*, 1298 (1968). <sup>e</sup> A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Am. Chem. Soc.*, **90**, 4185 (1968). <sup>f</sup> H. Kessler and W. Rundel, *Ber.*, **101**, 3350 (1968).

are best interpreted in terms of a rate-determining atomic inversion, although a merged mechanism cannot be excluded.

### Experimental Section

Nuclear magnetic resonance spectra were taken on the Bruker HFX-10 90-MHz spectrometer<sup>23</sup> and on Varian Models A-60 and T-60 spectrometers. Phosphorus-31 decoupling was effected with an NMR Specialties Model SE-60B heteronuclear decoupler on the Varian A-60 and with an RF Communications, Inc., 805 10-W power amplifier on the Bruker HFX-10. Mass spectra were obtained from the Denver Research Institute and the Morgan-Schaefer Corporation, as well as from a CEC Model 21-104 mass spectrometer. Kinetic analyses were carried out on CDC 3400 and 6400 computers equipped with a Calcomp plotting accessory.

**1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide (Ib).** To a Grignard reagent prepared from 9 g of magnesium and 59 g of bromobenzene in 120 ml of anhydrous ether, 50 g of methylidibromophosphine sulfide<sup>6</sup> in 100 ml of anhydrous ether was added dropwise with stirring and cooling (0°). Upon completion of the addition, the reaction mixture was refluxed for 1 hr. The precipitate remaining after hydrolysis with 200 ml of 10% sulfuric acid-ice was collected by filtration and washed with water to remove magnesium salts. The aqueous solution was extracted three times with ether, and the combined ether extracts were dried over CaCl<sub>2</sub>. The oil remaining after removal of the ether by distillation was combined with the solid collected earlier and extracted with 95% ethanol. The "meso" solid, which is not soluble in ethanol, was collected by filtration (mp 206–208°, lit.<sup>2</sup> mp 206–208°). The "dl" solid crystallized from the ethanol solution after standing several days (mp 145–146°; lit.<sup>2</sup> mp 145–146°). The mass spectrum of

(23) We thank the National Science Foundation for an equipment grant to purchase this instrument.

these solids exhibited the correct value for the parent peak (*m/e* 294).

The remaining diphosphine disulfides (Ia, Ic, Id, Ig) were prepared in an analogous manner, with the exception of Ie and If. The physical constants of the products are given in Table VI. Small

**Table VI.** Properties of Diphosphines with the Structure RCH<sub>2</sub>P-PCH<sub>2</sub>R

R	Mp (A <sup>a</sup> ), °C	Lit. mp (A), °C	Mp (B <sup>b</sup> ), °C	Lit. mp (B), °C	<i>m/e</i> , <sup>c</sup> parent peak
CH <sub>3</sub>	226–228	227 <sup>d</sup>			
C <sub>6</sub> H <sub>5</sub>	206–208	206–208 <sup>d</sup>	145–146	145–146	294
CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	208–210		132.8		338
CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	187–192 <sup>e</sup>		137–141 <sup>e</sup>		446
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	183–184	188–189 <sup>d</sup>	120–123	120–123 <sup>d</sup>	338
CH <sub>3</sub> CH <sub>2</sub>	150–153 <sup>e</sup>	159–160 <sup>d</sup>	96–103 <sup>e</sup>	103–104 <sup>d</sup>	214
ClC <sub>6</sub> H <sub>4</sub>	209–211		45–50 <sup>e</sup>		378

<sup>a</sup> The less-soluble solid. <sup>b</sup> The more-soluble solid. <sup>c</sup> In each case, the correct value for the parent peak was found. <sup>d</sup> Reference 3. <sup>e</sup> This material was a waxy solid that may not have been completely pure, although no spurious lines were found in the mass spectrum, particularly with *m/e* greater than the parent peak.

variations in the procedures are detailed elsewhere.<sup>24</sup> Preparation of the corresponding *p*-methoxyphenyl compound was unsuccessful.<sup>24</sup>

**1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide (If).** The procedure is identical with that for Ib, up to the drying of the ether extracts over CaCl<sub>2</sub> (9 g of Mg, 47 g of benzyl chloride, 50 g of methylidibromophosphine sulfide). The oil remaining after removal of the ether by distillation was slowly added to 75 ml of 10% NaOH for the removal of phosphinic acids. The resulting solution was extracted three times with 200-ml portions of benzene, and these extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The oil remaining after removal of the benzene was combined with the solid collected earlier (*vide supra*) and extracted with 95% ethanol. The "dl" isomer (mp 120–123°; lit.<sup>2</sup> mp 120–123°) was collected by crystallization from ethanol after removal of the insoluble materials. Fractional crystallization of the insoluble materials from acetone yielded tri-benzylphosphine sulfide (mp 265–268°; lit.<sup>2</sup> mp 268–269°) and the desired "meso" product (mp 183–184°; lit.<sup>2</sup> mp 188–189°). The preparation of Ie was carried out in an analogous fashion (Table IV).<sup>24</sup>

**1-Bromoethane-1-*d*<sub>2</sub>** was prepared according to the procedure of Shiner.<sup>25</sup>

The diphosphines were prepared by the reaction of the appropriate diphosphine disulfide with copper dust in a manner described previously.<sup>6</sup>

**1,2-Dimethyl-1,2-diphenyldiphosphine Monosulfide (II).**<sup>2,26</sup> As described earlier, 1,2-dimethyl-1,2-diphenyldiphosphine was prepared by reaction of its disulfide with copper dust. The sealed nmr tube containing 0.295 g of the diphosphine was opened under a nitrogen atmosphere in a drybox, 0.370 g of the disulfide was added, and the tube was resealed. This mixture was then heated at 220° for 16 hr in a silicone oil bath. The crude reaction product was used directly for the nmr experiments.

(24) G. F. Jackson, III, Ph.D. Dissertation, Northwestern University, 1969.

(25) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953).

(26) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).