The Stereochemical Lability of Diphosphines and Diarsines

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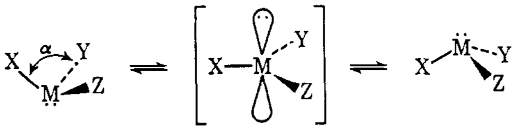
Abstract: Nuclear magnetic resonance experiments have been performed to detect pyramidal inversion about the heavy atom in diphosphines and diarsines. Doubling of the methyl and the phenyl resonances in the spectrum of 1,2-dimethyl-1,2-diphenyldiphosphine has been attributed to the presence in solution of diastereomeric modifications. The reversible coalescence of each doublet above 150° is interpreted in terms of an interconversion between the *meso* and the *dl* forms through inversion about phosphorus. Appropriate kinetic data have been gathered. Similar observations have been made with the arsenic analog of this system. The Arrhenius activation energies were found to be 26 ± 2 and 27 ± 1 kcal/mol for the diphosphine and the diarsine, respectively. Detailed consideration is given to viable mechanistic alternatives, such as bimolecular inversion and rotational isomerism.

Pyramidal inversion of configuration about a central atom M, surrounded by three substituents and a lone pair (eq 1), has been the subject of several theoretical studies during the past 30 years.[4] The magnitude of the barrier to inversion has been shown by these studies to be determined principally[4d] by the intergroup bond angles (α) and the corresponding bending force constants. Systems with central atoms from the second period (nitrogen, oxygen, carbon) generally have much smaller barriers than identically constituted molecules with central atoms from later periods (phosphorus, arsenic, sulfur, selenium, although probably not silicon or germanium). This dichotomy of behavior arises because the intergroup angles (α) for alkyl- and aryl-substituted second-period atoms (105–115°) require less distortion to achieve the 120° angle in the transition state than do the smaller (90–100°) angles from the later-period atoms.[5] Thus many attempts to generate optically active amines have been abortive, but numerous configurationally stable phosphorus, arsenic, and sulfur systems have been isolated.



(1)

The principal experimental techniques for characterization of pyramidal inversion have been loss of optical activity, provided resolution can be achieved, and dynamic nmr methods,[6] provided diastereomeric molecules or diastereotopic protons give rise to separate signals capable of site change. Since neither technique is general, experiments have come to lag somewhat behind theory. The extensive empirical study by Miller and coworkers[4d] has by itself supplied sufficient kindling to keep experimentalists at work in this field for some time. Because the configurational stability of second-period atoms is relatively low, only nmr techniques have proved fruitful for kinetic studies.[7] There are now considerable data by such methods on the subject of nitrogen inversion,[6] but an almost complete void in the fields of unimolecular carbon[8] and oxygen[9] inversions. The configurational stability of central atoms from beyond the second period has generally precluded use of the nmr method.[10] Loss of optical activity has thus proved useful in studies of inversion about phosphorus[11] and sulfur.[12]

In the present study, molecular systems are devised specifically for application of dynamic nmr methods to the study of inversion about group V elements other than nitrogen. Reduction in configurational stability has been achieved by the use of diphosphines and diarsines[10c,d] (*vide post*). Future papers in this series will be concerned with substituent effects, with the development of general systems for the study of all group V and group VI atoms, and with methods for observation of the low-barrier oxygen and carbon stereomutation.

Systems and Synthesis

Because of the high configurational stability of phosphorus and arsenic,[11,13–16] special bonding situations must be devised in order to place the barrier within

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(2) National Institutes of Health Predoctoral Fellow, 1966–1968 (F1 GM-33,876).

(3) National Science Foundation Undergraduate Research Participant, 1965–1966.

(4) (a) J. F. Kincaid and F. C. Henriques, *J. Am. Chem. Soc.*, **62**, 1474 (1940); (b) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952); (c) R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954); (d) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967); (e) A. Veillard, J.-M. Lehn, and B. Munsch., *Theor. Chim. Acta*, **9**, 275 (1968).

(5) Probably equivalent to such an explanation is one in terms of lone-pair hybridization.[4e] A discussion of various explanations for the difference in geometry between second- and later-period molecules is given by J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," John Wiley & Sons, Ltd., London, 1965, pp 52–54.

(6) G. Binsch, "Topics in Stereochemistry," Vol. III, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, in press. Also, see M. Saunders and F. Yamada, *J. Am. Chem. Soc.*, **85**, 1882 (1963), for a substantially different method for measuring inversion kinetics by nmr.

(7) However, see S. J. Brois, *J. Am. Chem. Soc.*, **90**, 508 (1968) and D. Felix and A. Eschenmoser, *Angew. Chem.*, **80**, 197 (1968).

(8) G. Fraenkel, D. T. Dix, and M. Carlson, *Tetrahedron Letters*, 579 (1968).

(9) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).

(10) The exceptions involve special bonding situations: (a) P. Haake and P. C. Turley, *ibid.*, **89**, 4611, 4617 (1967); (b) E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Commun.*, 58 (1966); (c) J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, **88**, 3669 (1966); (d) J. B. Lambert and G. F. Jackson, III, *ibid.*, **90**, 1350 (1968).

(11) L. Horner and H. Winkler, *Tetrahedron Letters*, 461 (1964).

(12) (a) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); (b) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966).

(13) B. Fontal and H. Goldwhite, *Tetrahedron*, 22, 3275 (1966).

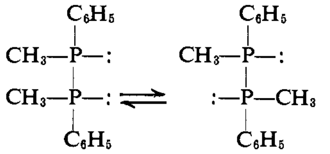
(14) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

(15) L. D. Quin and H. E. Shook, Jr., *Tetrahedron Letters*, 2193 (1965).

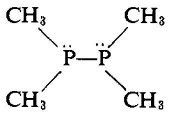
(16) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).

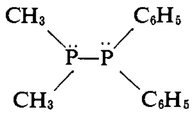
reach of the nmr method. The measurements of Horner and Winkler[11] indicate that simple tertiary phosphines are just out of range (∼30 kcal/mol) of nmr techniques. The use of diastereomeric diphosphines offers the twofold advantage of a symmetry handle necessary to observe configurational inversion and the possibility of a lower barrier due to p_π–d_π bonding in the transition state. Each of these advantages will be considered in turn.

The presence of two structurally identical chiral centers in 1,2-dimethyl-1,2-diphenyldiphosphine permits the existence of *meso* (Ia in its Fischer representation) and *dl* (Ib) modifications. The diastereomers may interconvert by inversion about a single phosphorus atom (eq 2). Each should have distinct spectral properties, which should merge at temperatures for which inversion becomes nmr fast. For molecules such as tetramethyldiphosphine (II) and 1,1-dimethyl-2,2-diphenyldiphosphine (III), which lack the symmetry handle of compound I, the inversion process is spectroscopically invisible by our methods.

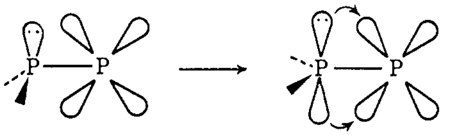

Ia Ib

(2)


II

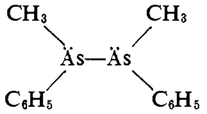

III

The phosphorus atoms in diphosphines are generally represented as being joined by a single σ bond. Each atom, however, offers a pair of nonbonding electrons for possible donation to the empty 3d orbitals on the adjacent phosphorus atom.[17] Specific evidence for such p_π–d_π bonding in diphosphines has come from ultraviolet spectroscopy.[18,19] Whereas the d orbitals appear not to have stringent stereochemical requirements for maximum overlap, the donor lone pair offers the best geometry (pure p) when the molecule is at the transition state to inversion (eq 3).[20] Thus p_π–d_π bonding stabilizes the transition state to inversion of diphosphines with respect to the ground state, but no such effect can be operative in monophosphines. The transition state to the simultaneous double inversion of both phosphorus atoms would have considerable triple-bond character (p_π–d_π overlap both ways), but the over-all energy is probably higher than that for the single inversion, because of additional requirements of substituent reorganization.[21] The extra stability of the bromine–bromine and the iodine–iodine bonds has been explained in terms of p_π–d_π overlap and an associated molecular orbital theory identical with that which would be used to describe the double-inversion transition state for diphosphines.[22]


ground state single-inversion transition state.

(3)

The arguments of symmetry and of p_π–d_π overlap are analogous for 1,2-dimethyl-1,2-diphenyldiarsine (IV).


IV

The synthesis of diphosphine I was patterned after the method of Maier.[23–25] Diarsine IV was prepared by a procedure similar to that of Reesor and Wright.[26]

Results and Discussion

The proton-decoupled phosphorus-31 spectra of diphosphines similar to I were found by Maier[23] and by Fluck and Issleib[27,28] to contain two peaks, attributed by them to the *dl* and *meso* forms. No temperature studies were reported. The proton spectrum of I without solvent contains multiplets at δ 6.6–7.1 and 0.7–1.1 ppm, respectively, due to the aromatic protons (complicated by nonequivalence of ring positions[29]) and to the methyl protons (complicated by unequal couplings to the two phosphorus atoms). With irradiation at the ^{31}P frequency, the methyl protons collapse to two sharp peaks in the ratio of 45 to 55 ± 2 (low to high field; see Figure 1a) and separated by 7.0 Hz at 60 MHz. Synthesis of I with deuterium atoms in the *ortho* and *para* positions of the phenyl rings simplifies the aromatic region to two broad peaks from the remaining *meta* protons in the ratio of 57 to 43 ± 2 (low to high field; see Figure 1b) and separated by 6.4 Hz at 60 MHz (10.7 Hz at 100 MHz in a separate experiment).

The aromatic region was examined as a function of temperature with tri-*n*-butylphosphine sulfide as solvent and the methyl region with biphenyl as solvent. Both doublets coalesce to single peaks above 180° (Figure 1). The coincidence of coalescence temperatures (152 ± 3° at 60 MHz) is attributed to the near identity of peak separation (*vide supra*). Kinetics were determined by a complete line-shape analysis over the entire temperature range following the method of Gutowsky, Holm, and

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(17) For a general discussion on the subject of p_π–d_π bonding in phosphorus compounds, see R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965, Chapter 3; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., Amsterdam, 1967, Chapter 1.

(18) A. H. Cowley, *Chem. Rev.*, **65**, 618 (1965).

(19) L. R. Grant and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).

(20) If the intergroup angle (α) in the ground state were 90°, the lone pair would reside in a nondirectional s orbital, for which p_π–d_π is not possible. The actual value of 95–100° admits of some overlap in the ground state because of additional p character in the lone pair orbital.[5]

(21) Interpretation of the kinetic results presented in the next section does not depend on a choice between the single-inversion and the double-inversion transition state.

(22) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955); R. G. Pearson, *ibid.*, **85**, 3533 (1963).

(23) L. Maier, *Angew. Chem.*, **71**, 574 (1959); *Ber.*, **94**, 3043 (1961); *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

(24) N. K. Patel and H. J. Harwood, *J. Org. Chem.*, **32**, 2999 (1967).

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

(26) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 382 (1957).

(27) E. Fluck and K. Issleib, *Ber.*, **98**, 2674 (1965).

(28) V. Mark, M. M. Crutchfield, C. H. Dungan, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1967, pp 24, 247.

(29) G. Shaw, J. K. Becconsall, R. M. Canadine, and R. Murray, *Chem. Commun.*, 425 (1966).

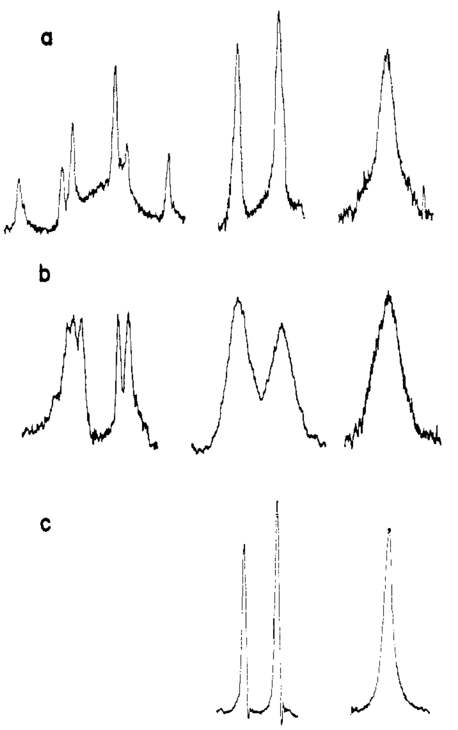

Figure 1. (a) The 60-MHz spectrum of the methyl region of 1,2-dimethyl-1,2-diphenyldiphosphine (left to right) at 105° without ^{31}P decoupling, at 120° with decoupling (slow exchange), and at 200° with decoupling (fast exchange); a broad impurity resonance just right of center in the spectra gives the impression of poor phasing or asymmetry. (b) The 60-MHz spectrum of the phenyl region of 1,2-dimethyl-1,2-diphenyldiphosphine (left to right) at 110° without deuterium labeling, at 137° with deuterium in the *ortho* and *para* positions, and at 200° with the same deuterium labeling. (c) The 60-MHz spectrum of 1,2-dimethyl-1,2-diphenyldiarsine at 115° and at 200° (left to right). The peak spacings at slow exchange are given in the text. The kinetic data for the rate processes may be found in Table I.

Borcic[30] (Table I). The Arrhenius activation energy and frequency factor were found to be 26 ± 2 kcal/mol and $10^{14 \pm 1}$ sec^{-1}, respectively.

Table I. Kinetic Data for the Stereomutation of Phosphorus and Arsenic

Diphosphine I[a]			Diarsine IV[b]		
T, °C	τ_A,[c] sec	τ_B, sec	T, °C	τ_A, sec	τ_B, sec
140	0.4	0.3	147	0.55	0.68
146	0.25	0.19	152.5	0.39	0.48
149	0.195	0.15	157.5	0.27	0.33
153[d]	0.163	0.125	162	0.185	0.23
160	0.091	0.070	167.5	0.133	0.164
162	0.071	0.055	173[d]	0.098	0.121
168	0.058	0.045	178.5	0.068	0.083
			182	0.051	0.063
			187	0.038	0.047
			189	0.031	0.038
			198	0.015	0.0186

[a] Changes in the phenyl peaks; the methyl peaks gave similar results. [b] Changes in the methyl peaks. [c] Mean lifetime (reciprocal of the first-order rate constant). [d] Coalescence temperature.

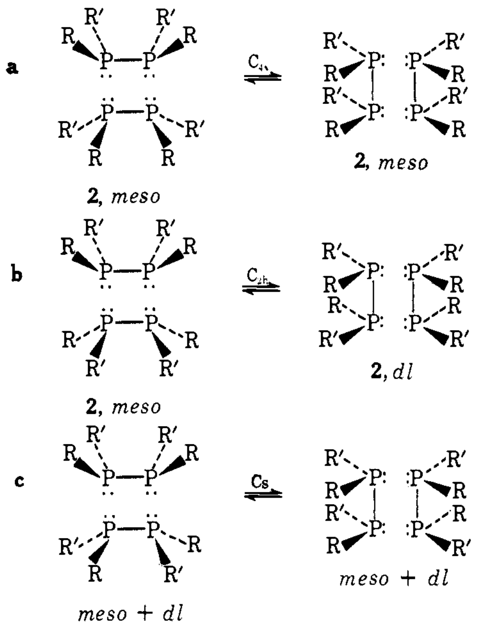

Figure 2. A four-centered ligand-exchange reaction between two diphosphine molecules of the type I may follow three distinct paths: (a) two *meso* molecules with like substituents over one another (C_{4v} transition state); (b) two *meso* molecules with unlike substituents over one another, or two *dl* molecules (C_{2h} transition state); (c) one *meso* and one *dl* molecule (C_s transition state).

The nmr spectrum of 1,2-dimethyl-1,2-diphenyldiarsine contains a multiplet at δ 6.5–7.2 ppm due to the phenyl protons and a doublet with components in the ratio 45 to 55 (low to high field; see Figure 1c) at δ 0.70–0.78 ppm due to the methyl protons. Arsenic-75 ($I = {}^3/_2$) gives no observable coupling with the methyl protons because of quadrupolar averaging. Above 200°, the components collapse to a single peak (Figure 1). The coalescence temperature at 60 MHz was found to be 173°. The kinetic analysis by the complete line-shape method (Table I) gave an Arrhenius activation energy of 27 ± 1 kcal/mol and a preexponential factor of $10^{14 \pm 1}$ sec^{-1}.

The observed spectral changes are consistent with the pyramidal inversion mechanism of eq 1 and 2, whereby the *dl* and the *meso* diastereomers are in rapid, reversible equilibrium.[21] The experiments comprise the first kinetic observation of arsenic stereomutation, and the second[11] for phosphorus. The pyramidal inversion mechanism, however, is not the only explanation consistent with the data presented thus far. Two viable mechanistic alternatives will be discussed in detail, together with the data pertinent to their proposed exclusion.

If two diphosphine molecules engage in a four-centered ligand exchange, three distinct reaction pathways may be recognized (Figure 2; transition states may also be imagined in which the P–P bonds bisect each other perpendicularly). One molecule each of *meso* and *dl* diphosphine will reorganize to another *dl–meso* pair (Figure 2c). Two *dl* molecules will always give two *meso* molecules (Figure 2b), but the reaction of two *meso* forms can occur with either of two geometries. If the reactants line up with like substituents over one another (Figure 2a), the transition state possesses C_{4v} geometry, and two new *meso* molecules would be produced. Unlike ligands over one another (C_{2h}, Figure 2b), however, will produce two *dl* molecules, in the microscopic reverse of the *dl–dl* reaction. Thus a

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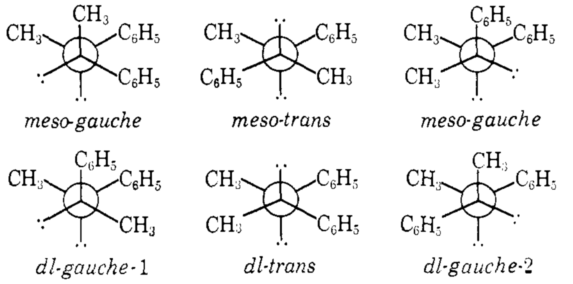
(30) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 5085 (1965).

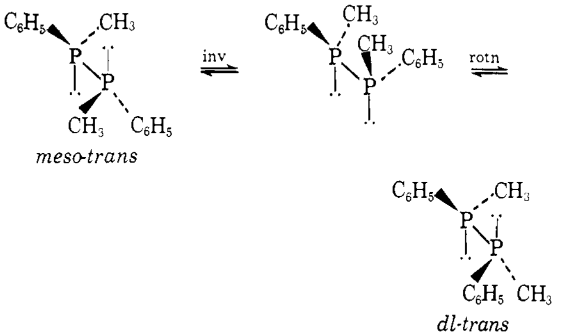
bimolecular ligand reorganization, with precedent,[13,31] can serve to interconvert the *meso* and the *dl* forms of the diphosphine or, in a similar manner, the diarsine.

Two lines of reasoning have been used to exclude this possibility. The rate of the bimolecular reaction should be concentration dependent, whereas the unimolecular inversion should not be affected by concentration changes. The reaction rate for the diarsine IV was measured at 131 and 142° for 7, 11, 21, 30, 63, 72, 86, and 93 mol % solutions in biphenyl. There was no observable effect on the rate at either temperature. Similar experiments with the diphosphine I for 14, 24, 56, and 80 mol % solutions in biphenyl could give no evidence for a bimolecular component in the rate constant.

The second line of reasoning considers coupling across the phosphorus–phosphorus bond. A methyl group in I is coupled unequally to the two phosphorus atoms. Thus in tetramethyldiphosphine (II) $^2J_{\mathrm{PCH}} = \pm 2.90$ Hz and $^3J_{\mathrm{PPCH}} = \pm 11.25$ Hz, even though the methyl groups appear as a triplet.[32] If the bimolecular process depicted in Figure 2 were responsible for the observed spectral changes, the coupling information from a methyl group to the further phosphorus atom ($^3J_{\mathrm{PPCH}}$) would be lost,[30] and the methyl triplet in II would become a doublet at high temperatures. The spectrum of tetramethyldiphosphine was observed up to 180° without loss of the triplet structure. The retention of the three-bond coupling confirms the fact that the observed rate process occurs without cleavage of the phosphorus–phosphorus bond.

The second possible alternative to the unimolecular inversion mechanism is one involving rotational isomers. 1,2-Dimethyl-1,2-diphenyldiphosphine can exist in six staggered rotational conformations. The doublets in the nmr spectra could conceivably arise from two rotamers, each with one type of methyl (phenyl). The spectral changes with temperature would then be attributed to a transition from slow to fast rotation about the phosphorus–phosphorus bond, by which means the rotamers are interconverted. There are two distinct variations of this mechanism. (1) The interconverting species are rotamers of a single diastereoisomer. Such a possibility is exemplified by an equilibrium between the *dl-trans* and one (not both) of the *dl-gauche* isomers. (2) The interconverting species are rotamers of the different diastereoisomers. Such a model necessarily requires a phosphorus inversion (eq 4). In fact, the mechanism is identical with that previously termed "pyramidal inversion," except that the rate-determining step has become the rotation.





(4)

Rotation mechanism 1 requires at least 45% abundance of a *gauche* form. Because of the larger substituent–substituent and lone pair–lone pair interactions in the *gauche* rotamers, the *trans* form should predominate.[18] A considerable amount of data has accumulated concerning the structure of diphosphines (Table II). As yet, no study has produced evidence for the presence of a *gauche* isomer.[33] Evidence against this mechanism also comes from the extensive ^{31}P nmr investigations of diphosphines.[23,27] Of the three types of diphosphines studied, exemplified by compounds I–III, all can exist in different rotational forms, but only type I can exist as diastereoisomers. Almost invariably,[23,27] the type I diphosphines give two peaks in the ^{31}P spectrum, but in no case was doubling observed for type II or type III diphosphines. Similarly, the proton spectrum of tetramethyldiphosphine gives only one sharp peak when decoupled from ^{31}P.[34] The spectral doubling thus seems to be associated with the presence of diastereoisomers. Mechanism 1 can therefore be eliminated with a high degree of certainty.

Table II. Structural Data on Diphosphines and Diphosphine Disulfides

Molecule	Method	Result	Source
P_2H_4	Nmr	*trans* or rapid rotation	*a*
P_2Cl_4	Ir/Raman	*trans*	*b*
P_2I_4	X-ray[c]	*trans*	*d*
	Ir/Raman	*trans*	*e*
P_2F_4	Ir/Raman	*trans* (?)	*f*
	Nmr	*trans* and slow rotation	*g*
$P_2(CH_3)_4$	Nmr	*trans* or rapid rotation	*h*
$(P{=}S)_2(CH_3)_4$	X-ray[c]	*trans*	*i*
$(P{=}S)_2(CH_3)_2(C_6H_5)_2$	X-ray[c]	*trans*	*j*

[a] R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961). [b] S. G. Frankiss and F. A. Miller, *Spectrochim. Acta*, **21**, 1235 (1965). [c] Solid-state data, not directly applicable to solutions. [d] Y. C. Leung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956). [e] S. G. Frankiss and F. A. Miller, *Spectrochim. Acta*, **23A**, 543 (1967). [f] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966). [g] F. A. Johnson and R. W. Rudolph, *J. Chem. Phys.*, **47**, 5449 (1967). [h] Reference 32. [i] C. Pedone and A. Sirigu, *J. Chem. Phys.*, **47**, 339 (1967). [j] P. J. Wheatley, *J. Chem. Soc.*, 523 (1960).

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(31) L. Maier, *Fortsch. Chem. Forsch.*, **8**, 1 (1967).

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

(33) Even molecules with small substituents, such as P_2F_4, do not appear to have *gauche* contributors, in contrast to the analogous nitrogen systems, *cf.* C. B. Colburn, F. A. Johnson, and C. Haney, *J. Chem. Phys.*, **43**, 4526 (1965).

(34) The proton spectrum of tetramethyldiarsine also contains only one peak, *cf.* R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964); however, see M. Green and D. Kirkpatrick, *Chem. Commun.*, 57 (1967).

Rotation mechanism 2, on the other hand, does require the presence of diastereoisomers, and it does not require the presence of the unstable *gauche* forms. Thus none of the above evidence can be quoted in its disfavor. Both pyramidal inversion and bond rotation are integral parts of the model detailed in eq 4. One can conclude, therefore, that this equation represents the rate process that gives rise to the observed spectral changes. No fundamental decision can be made as to which step is rate determining. If the inversion step is slower, then the reported rate parameters indeed refer to the stereomutation of phosphorus and arsenic. The less likely reverse conclusion, that rotation is the slow step, nonetheless sets the experimentally observed values of 26 and 27 kcal/mol as upper limits to the barriers for inversion in diphosphines and diarsines. Either alternative thus demands an unusually rapid pyramidal inversion about trivalent phosphorus or arsenic.

Experimental Section

Nuclear magnetic resonance spectra were taken on Varian Model T-60, A-60, and HA-100[35] spectrometers. Phosphorus-31 decoupling was effected with an NMR Specialties Model SD-60B heteronuclear decoupler. Mass spectra were obtained from the Denver Research Institute and the Morgan–Schaefer Corp. Kinetic analyses were carried out on Control Data Corp. 3400 and 6400 computers equipped with the Calcomp plotting accessory.

Methyldibromophosphine.[23] A 40 in. × 25 mm heavy-walled Pyrex tube fitted with ground-glass joints was packed with a mixture of 15–16 g of red phosphorus, 4–5 g of copper dust, and 20–25 g of asbestos wool with about 2 in. of clean asbestos on each end. The tube was heated, first under a slow stream of nitrogen at 150° for 1 hr, and next at 350° for 3–4 hr under a slow stream of hydrogen. Methyl bromide was then introduced in a slow stream with the product condensing after 10–15 min onto a 105° distillation takeoff adapter that led to a round-bottomed flask. The unreacted methyl bromide and byproduct gases were bubbled through concentrated sodium hydride solution and allowed to pass out an exhaust hood. A typical 4-hr run yielded 20–30 g of methyldibromophosphine.

Methyldibromophosphine sulfide and *dl*- and *meso*-1,2-dimethyl-1,2-diphenyldiphosphine disulfides were prepared by the procedure of Maier.[23] The mass spectrum of the disulfide contained a parent peak at the correct value of *m*/*e* 294.

1,2-Dimethyl-1,2-diphenyldiphosphine.[25] The *meso*- or *dl*-disulfide was heated under vacuum with an excess of copper dust. The product diphosphine was caused to distill directly into an nmr tube attached as a side arm to the evacuated reaction vessel. The tube was sealed under vacuum to prevent reactions with the atmosphere. Spectral analysis indicated purity of about 90%. The two diastereomeric disulfides give identical mixtures of diphosphines.

Aniline-N,N-2,4,6-d_5 was prepared by the method of Best and Wilson.[36]

Bromobenzene-2,4,6-d_3.[37] Freshly distilled aniline (19.5 g, 0.21 mol) was diazotized in 210 ml of water and 22.5 ml of concentrated sulfuric acid by the addition of sodium nitrite (14.7 g, 0.21 mol) in 10 ml of water with the temperature of the solution maintained at 0–10° for 20 min. The diazonium solution was added dropwise over 80 min to a slurry of cuprous bromide, with a current of steam bubbled through the reaction mixture to codistill the product. The aqueous distillate was neutralized and extracted with ether. The ether extracts were dried and distilled to give a 51% yield of bromobenzene-2,4,6-d_3 (bp 154–158°), which was pure by vpc analysis.

1,2-Dimethyl-1,2-diphenyldiarsine was prepared by the method of Reesor and Wright[26] from phenylarsonic acid by way of arsenobenzene. Details may be obtained from the doctoral dissertation of G. F. Jackson, III (Northwestern University, 1969). The mass spectrum of the diarsine contained a parent peak at the correct value of *m*/*e* 334.

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(36) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 28 (1938).

(37) The procedure was modeled after a synthesis of *p*-bromotoluene, *cf.* L. A. Bigelow, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1951, pp 136–137.