

and dried (MgSO_4) and the solvent evaporated to give 4.7 g of a crude product which by vpc (12-ft SE-52, 41°) was shown to contain approximately 12% of the corresponding acid fluoride. Distillation gave 2.9 g (50%) of II, bp 115–116° (680 mm). Characteristic bands in the infrared were located at 692 (ϵ 43, cyclohexane),² 711 (ϵ 9, cyclohexane),² and 1315 cm^{-1} (neat). ¹⁹F magnetic resonance spectra data are recorded in Tables I and III. *Anal.* Calcd for $\text{C}_8\text{H}_{13}\text{F}_3$: C, 57.82; H, 7.88; F, 34.30. Found: C, 57.99; H, 7.86; F, 34.2.

Method B. *p*-Trifluoromethylbenzyl bromide²⁷ (9.0 g, 0.038 mole) and lithium aluminum hydride (0.8 g, 0.021 mole) in 30 ml of tetrahydrofuran were heated under reflux for 1 hr. On cooling, ice-cold water was added dropwise, and the metal hydroxides were dissolved in 2 *N* sodium hydroxide (25 ml). The organic layer was added to 60 ml of ether, washed with water (four 15-ml portions) and saturated sodium chloride solution (one 15-ml portion), and dried (MgSO_4). Distillation through an efficient fractionating column yielded 4.8 g (80%) of *p*-methylbenzotrifluoride, bp 128–129° (760 mm). The infrared spectrum contained intense bands at 1130, 1170, and 1340 cm^{-1} (neat). The pmr spectrum was identical with that published.²⁸ *Anal.* Calcd for $\text{C}_8\text{H}_7\text{F}_3$: C, 60.00; H, 4.41. Found: C, 60.25; H, 4.74. *p*-Methylbenzotrifluoride (4.4 g) in 10 ml of ethanol was hydrogenated using the procedure described for benzotrifluoride. The product (4.2 g) was shown by vpc (conditions as above) to consist of a 4:1 mixture of *cis*- and *trans*-4-methyltrifluoromethylcyclohexane which was separated by preparative vpc (12-ft, 20% Apiezon L, 108°) into the pure components (2.5 g, II; 0.5 g, III), the former being identical with the sample of *cis*-4-methyltrifluoromethylcyclohexane obtained by method A.

***trans*-4-Methyltrifluoromethylcyclohexane (III).** A 2:1 mixture of *cis*- and *trans*-4-methylcyclohexanecarboxylic acid²⁸ (8.5 g, 0.06 mole) was converted to a mixture (2:1) of the corresponding trifluoromethylcyclohexanes (7.5 g) by reaction with 20.5 g (0.19 mole) of sulfur tetrafluoride under the conditions described above. Preparative vpc (12-ft, 20% Apiezon L, 108°) yielded the

pure (99%) *trans* epimer (1.2 g), bp 118–119° (760 mm), identical in all respects with the sample obtained from method B above. Characteristic bands were present in the infrared at 692 (ϵ 62, cyclohexane)² and 1340 cm^{-1} (neat). Fluorine magnetic resonance data are collected in Tables I and III. *Anal.* Calcd for $\text{C}_8\text{H}_{13}\text{F}_3$: C, 57.82; H, 7.88; F, 34.30. Found: C, 57.50; H, 7.53; F, 34.8.

***trans*-4-*t*-Butyltrifluoromethylcyclohexane (IV).** *trans*-4-*t*-Butylcyclohexanecarboxylic acid²⁹ (4.3 g, 0.024 mole) was similarly treated with 8 g (0.074 mole) of sulfur tetrafluoride to give 3.8 g (76%) of IV, bp 85–86° (34 mm); n_D^{20} 1.4082. The infrared spectrum contained characteristic bands at 687 (ϵ 62, cyclohexane),² 1250, and 1340 cm^{-1} (neat). ¹⁹F magnetic resonance spectra details are included in Tables I and III. *Anal.* Calcd for $\text{C}_{11}\text{H}_{19}\text{F}_3$: C, 63.44; H, 9.20; F, 27.36. Found: C, 63.40; H, 9.27; F, 27.4.

***cis*-4-*t*-Butyltrifluoromethylcyclohexane (V).** *cis*-4-*t*-Butylcyclohexanecarboxylic acid²⁹ was treated with 10 g (0.10 mole) of sulfur tetrafluoride as described previously, to give 6.8 g of oil which by vpc (12-ft SE-52, 80°) was shown to contain V contaminated with intermediate acid fluoride (*ca.* 10%). The latter was removed by distillation which gave 4.1 g (57%) of *cis*-4-*t*-butyltrifluoromethylcyclohexane, bp 89–90° (37 mm), 70–72° (18 mm); n_D^{20} 1.4119. Characteristic bands in the infrared were located at 703 cm^{-1} (ϵ 31, cyclohexane),² 1225, and 1292 cm^{-1} (neat). The ¹⁹F magnetic resonance spectra data are recorded in Tables I and III. *Anal.* Calcd for $\text{C}_{11}\text{H}_{19}\text{F}_3$: C, 63.44; H, 9.20; F, 27.36. Found: C, 63.49; H, 8.96; F, 27.6. Repetition of the above reaction at 125–130° for 24 hr gave a product (85% yield) which by vpc (conditions as above) was shown to be uncontaminated with acid fluoride, but which consisted of a mixture of *cis*-4-*t*-butyltrifluoromethylcyclohexane (retention time 13.9 min) and its *trans* epimer (12.7 min).

Acknowledgment. The author is grateful to Dr. T. M. Spotswood and Mr. L. Paltridge for running the ¹⁹F nmr spectra. This project was supported, in part, by a grant awarded by the Australian Research Grants Committee.

(29) H. H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959).

(27) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1768 (1949).

(28) "Nmr Spectra Catalog," Varian Associates, Vol. I, Palo Alto, Calif., 1962, Spectrum No. 190.

Conformational Analysis of Tritolylphosphines¹

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Abstract: The dependence of dipole moments and ultraviolet absorption spectra on constitution in the series tris(4-methylphenyl)phosphine (1), tris(3-methylphenyl)phosphine (2), and tris(2-methylphenyl)phosphine (3) has been accounted for by a model in which the C–P–C bond angle remains constant at 102° while the angle of torsion around the phosphorus–phenyl bond varies with the position of the substituent methyl group. The present interpretation is at variance with a previous conclusion in which this dependence was rationalized by invoking a variation in the C–P–C bond angle.

In a recent study, Schindlbauer² observed the dependence of dipole moments and absorption spectra on constitution in the series of isomeric tritolylphosphines which is reported in Table I, and from these findings concluded that the C–P–C bond angle varies as indicated in Table I. The spread in bond angles was presumed to arise from repulsive interaction effects which increase in the series 1 to 3.

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67.

(2) H. Schindlbauer, *Monatsh. Chem.*, **96**, 1793 (1965).

The extraordinary flattening of the phosphorus pyramid claimed² for 3 (see Table I) led us to reexamine Schindlbauer's calculations. In a molecule R_3P with threefold symmetry, assuming that the observed moment μ acting along the C_3 axis equals the resultant of the partial moments, the relation between μ and the group moments μ_R is given by

$$\mu = 3\mu_R \cos \theta \quad (1)$$

where θ is the angle between μ and μ_R (see Figure 1).

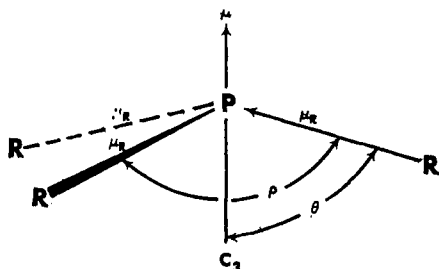


Figure 1.

If ρ is the angle between μ_R 's, it can be shown that

$$3 \cos^2 \theta = 1 + 2 \cos \rho \quad (2)$$

Thus, given the observed value of μ and values for μ_R , one may calculate the angle between group moments, ρ .

Calculation of μ_R is illustrated in Figure 2 for the case of **2**. Vector addition of partial moments gives

$$\mu_R^2 = \mu_P^2 + \mu_C^2 - 2\mu_P\mu_C \cos \delta \quad (3)$$

where μ_P is the partial moment acting along the phosphorus-phenyl bond axis, μ_C is the partial moment acting along the phenyl-methyl bond axis, and δ is the angle between μ_P and μ_C . Taking δ as equal to 180, 120, and 60° for **1**, **2**, and **3**, respectively, and given esti-

Table I. Reported^a Properties of Isomeric Tritolylphosphines

R in R ₃ P	Dipole moment, μ (D.) ^b	Absorption spectrum ^c λ_{\max} , m μ	Log ϵ	Calcd C-P-C bond angle, deg
4-Methylphenyl (1)	2.14	262	4.06	100
3-Methylphenyl (2)	1.65	263	4.04	105
2-Methylphenyl (3)	0.53	275	4.05	117

^a Reference 2. ^b In benzene at 20°. ^c In 96% ethanol.

mates of μ_P and μ_C (see below), it is thus possible to calculate μ_R . Defining γ as the angle between μ and μ_P , and ω as the C-P-C bond angle, it can be shown that the same relationship obtains between γ and ω as between θ and ρ :

$$3 \cos^2 \gamma = 1 + 2 \cos \omega \quad (4)$$

Schindlbauer² arrived at his calculated values of "bond angles" by equating the direction of μ_R with the direction of the phosphorus-phenyl bond moment (μ_P). However, the directions of μ_R and μ_P are not necessarily coincidental; see Figures 1 and 2. In fact, as will be discussed in detail below, the unstated but implicit assumption² that $\rho = \omega$ and $\theta = \gamma$ imposes a condition which is met in all conformations of **1** and triphenylphosphine (**4**), where the direction of μ_R coincides with that of μ_P , but in two and only two conformations of **2** and **3**, where the directions do not coincide. Since Schindlbauer's reported values of "bond angles" (Table I) refer in actuality to angles between group moments (ρ) rather than to bond angles (ω), and since $\rho = \omega$ only in two conformations of **2** and **3**, the conclusion² of pyramidal flattening is based on limited premises.

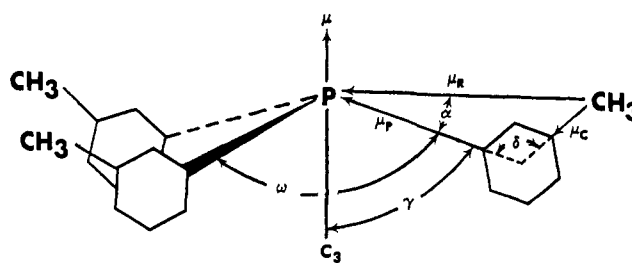


Figure 2.

The data² presented by Schindlbauer may however be rationalized on the basis of a model in which the bond angle ω remains fixed and in which the only variable is the angle of torsion around the phosphorus-carbon bond. In setting up this model, we have made the following assumptions.

(A) The bond angle ω remains invariant. This assumption is based on the remarkably small variation observed for X-P-X bond angles in substituted phosphines³ where, regardless of the nature of the substituent on phosphorus, the bond angle assumes a value of about $102 \pm 2^\circ$. From dipole moment measurements, the C-P-C bond angle in **4** is estimated⁴ to be 102° . In the crystalline state, the bond angles of **4** are reported⁵ to be 103.6, 103.3, and 102.1° . Accordingly, we have taken $\omega = 102^\circ$ for all C-P-C angles in compounds **1-4** and have assumed that this value does not significantly change with torsion around the P-C bond.

(B) Threefold symmetry has been arbitrarily assigned to all molecules of structure R₃P which are considered in this paper.⁶ The simplifying assumption that a C₃ axis passes through the phosphorus atom while contrary to at least one observation (*i.e.*, that **4** is asymmetric in the crystalline state)^{5,7} is hopefully a reasonable approximation to the description of the unknown conformation of the molecule in solution.^{8,9} Any other description would not only be equally arbitrary, but would in addition require the introduction of complicating and, in the last analysis, equally unjustifiable assumptions. Granted threefold symmetry, molecules containing substituent groups R with axial symmetry,¹⁰ *i.e.*, *p*-tolyl in **1**, phenyl in **4**, and mesityl in the comparison compound

(3) In trimethylphosphine, \angle C-P-C is $99.1 \pm 0.2^\circ$ [D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958)]; in phosphorus trifluoride, \angle F-P-F is $104 \pm 4^\circ$ [L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935)]; in phosphorus trichloride, \angle Cl-P-Cl is $100.1 \pm 0.3^\circ$ [P. Kisiuk and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950)]; in phosphorus tribromide, \angle Br-P-Br is $100 \pm 2^\circ$ [A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937)]; in phosphorus triiodide, \angle I-P-I is $100-105^\circ$ [O. Hassel and A. Sandbo, *Z. Physik. Chem.*, **B41**, 75 (1938)]. Sutton, *et al.*, also noted the remarkable constancy of the bond angle in all group V trihalides.

(4) G. Klages and R. Langpape, *Z. Elektrochem.*, **63**, 533 (1959).

(5) J. J. Daly, *Z. Krist.*, **118**, 332 (1963); *J. Chem. Soc.*, 3799 (1964).

(6) Threefold symmetry has been established for a number of closely related molecules:⁷ tris(4-methylphenyl)arsine [J. Trotter, *Can. J. Chem.*, **41**, 14 (1963)]; tris(2,5-dimethylphenyl)arsine [J. Trotter, *Acta Cryst.*, **16**, 1187 (1963)]; triphenylbismuthine [J. Wetzel, *Z. Krist.*, **104**, 305 (1942)].

(7) However, one may question the relevance of X-ray structural information to the problem at hand, *i.e.*, the conformation of the molecule in solution.

(8) In their study of the conformations and polarities of triphenyl derivatives of group Vb elements, Aroney, *et al.*,⁹ also assumed threefold symmetry and conformational homogeneity for triphenylphosphine in solution.

(9) M. J. Aroney, R. J. W. LeFevre, and J. D. Saxby, *J. Chem. Soc.*, 1739 (1963).

(10) The methyl group is viewed as having conical symmetry.

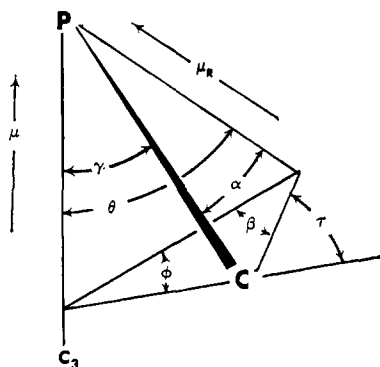


Figure 3.

(see below) tris(2,4,6-trimethylphenyl)phosphine (**5**), may in principle assume (a) an infinite number of chiral (dissymmetric) conformations (*i.e.*, structures differing in the degree of torsion about the P-C bond) of symmetry C_3 , in which the benzene rings are tilted in the same sense and by the same amount, and (b) two achiral (nondissymmetric) conformations of symmetry C_{3v} . In one of the C_{3v} conformations, the axes which pass through the center of and are perpendicular to the planes of the benzene rings intersect at the C_3 axis. In the other C_{3v} conformation, the planes containing the benzene rings intersect at the C_3 axis. Molecules containing substituent groups R which are not axially symmetric, *i.e.*, *m*-tolyl in **2** and *o*-tolyl in **3**, may also assume (a) an infinite number of chiral conformations of symmetry C_3 , and (b) two achiral conformations of symmetry C_{3v} . In both of the C_{3v} conformations, the planes containing the benzene rings intersect at the C_3 axis; however in one conformation the three methyl groups are directed into the pyramid, *i.e.*, toward the C_3 axis (*endo* conformation), whereas in the other they are directed away from the C_3 axis (*exo* conformation; for example, see Figure 2).

(C) While there exists no reason *a priori* to suppose that any one of the compounds **1-5** is conformationally homogeneous in solution, we have arbitrarily assumed that **2** and **3** may be represented by a single conformation. Although conformational heterogeneity does not affect μ in those compounds in which the group R has axial symmetry (**1**, **4**, and **5**), the observed moment in compounds with nonaxial ligands (**2** and **3**) will be the summation of the different moments of the various conformers

$$\mu_{\text{obsd}}^2 = \sum_i N_i \mu_i^2$$

where N_i and μ_i are the mole fraction and moment of the *i*th conformer, respectively. The assumption of conformational homogeneity, like the assumption of threefold symmetry, while difficult to justify on the basis of published experimental evidence, is unavoidable if a solution to the problem is to be achieved.⁸ Provided that **2** and **3** exist predominantly in one conformation, the unique solution to the problem at least approximates the geometry of the major conformer. By the same token, we have not employed the "freerotation" model¹¹ on the assumption that it does not realistically reflect the conformational picture encountered in **1-5** (see below).

(11) O. Fuchs, *Z. Physik. Chem.*, **B14**, 339 (1931).

(D) On the basis of assumptions A and B, the partial moment μ_P was derived from the experimentally determined dipole moment of **4** by equating μ_P with μ_R in eq 1 and 2 ($\rho = \omega = 102^\circ$). Of the various dipole moments reported for **4**, 1.39,¹² 1.42,¹³ 1.44,⁴ 1.45,¹⁴ 1.50,⁹ and 1.54 D.,¹⁵ the value of 1.44 D. has been selected, not only because it seems the most representative value within the experimental uncertainty of the determination, but also because the dipole moment of **1** found by the same workers⁴ can be accounted for by using 1.44 D. and a reasonable value of μ_C (see below).

As shown by independent calculations, the choice of μ_C significantly affects the estimated angle of torsion. Given $\rho = 102^\circ$, the value of μ_R calculated from that of μ reported² for **1** (2.14 D.) is 1.62 D. Since the C-methyl and C-phosphorus bond axes are collinear ($\delta = 180^\circ$) and since the phenyl \rightarrow phosphorus and methyl \rightarrow phenyl partial moments μ_P and μ_C , which are assumed to act along the two axes, are equally signed,^{2,4,15} taking Schindlbauer's value² of $\mu_P = 1.17$ it follows that $\mu_C = \mu_R - \mu_P = 1.62 - 1.17 = 0.45$ D. If, contrary to assumption A of a constant C-P-C bond angle, ω in **1** is allowed to vary, given again Schindlbauer's values² of $\mu = 2.14$ D. and $\mu_P = 1.17$, and taking² $\mu_C = 0.36$ D., substitution of $\mu_R (= \mu_P + \mu_C)$ in eq 1 and 2 yields $\rho = \omega = 100^\circ$. Within the limits of error of the underlying measurements, the difference between the two estimates of ρ (102 and 100°) and of μ_C (0.45 and 0.36 D.) is probably not significant. On the other hand, the dipole moments reported⁴ by Klages and Langpape for **1** (1.92 D.) and **4** (1.44 D.) are consistent with values of $\mu_P = 1.09$ D. and $\mu_C = 0.36$ D., on assumption A that $\omega = \rho = 102^\circ$ in *both* **1** and **4**. Since this result is in satisfactory agreement with literature values cited¹⁶ for μ_C , we have accordingly used $\mu_C = 0.36$ D. and $\mu_P = 1.09$ D. in all of our calculations.

Results and Discussion

If in a symmetrically substituted triarylphosphine R_3P ¹⁷ the substituent groups R are axially symmetric, as they are in **1**, **4**, and **5**, the vector μ_R will be collinear with the P-C bond axis and the angle α between μ_R and μ_P equals zero. Accordingly, $\rho = \omega$ and $\theta = \gamma$ in all conformations. Under these conditions the total moment μ will be unaffected by torsion of the benzene ring around the P-C bond axis. However, for molecules such as **2** and **3** in which the substituent groups R are not axially symmetric, the vector μ_R will not be collinear with the P-C bond axis, and α is not zero. Accordingly, in such cases, $\omega \neq \rho$ and $\gamma \neq \theta$ in all but two conformations, both of which are chiral. One of these conformations is that in which a plane defined by μ_R and μ_P is perpendicular to a plane defined by the C_3 axis and the bisector of α ; the other is its mirror image. The relationship among μ , μ_R , and the angle of torsion τ may be visualized by reference to Figure 3. For a given substituent, α and γ are constants, the former because

(12) G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

(13) H. Goetz, F. Nerdel, and K.-H. Wiechel, *Ann. Chem.*, **665**, 1 (1963).

(14) E. Bergmann and W. Schütz, *Z. Physik. Chem.*, **B19**, 401 (1932).

(15) H. Schindlbauer and G. Hajek, *Chem. Ber.*, **96**, 2601 (1963).

(16) H. Lumbruso and G. Dumas, *Bull. Soc. Chim. France*, 651 (1955).

(17) The following analysis applies with equal force to other symmetrically trisubstituted pyramidal molecules such as amines, arsines, bismuthines, sulfonium ions, carbanions, etc.

α depends only on μ_C , μ_P , and μ_R (Figure 2) which are themselves quantities fixed by the nature of R, and the latter because γ depends only on ω (eq 4), a quantity which is held to be constant at 102° ; it follows that $\gamma = 63.8^\circ$. Torsion takes place about the P-C bond axis and as it does the vector μ_R precesses, the angular variation being a function of θ , the angle subtended between the C_3 axis and μ_R . The points of intersection of the lines of action of $\mu(C_3)$, μ_R , and μ_P in a plane which is perpendicular to the P-C bond axis form a triangle with angles β and φ as shown in Figure 3; β and φ are functions of α , γ , and θ as expressed in eq 5 and 6.

$$\cos \beta = \frac{\cos \gamma - \cos \alpha \cos \theta}{m \sin \alpha} \quad (5)$$

$$\cos \varphi = \frac{\cos \alpha - \cos \gamma \cos \theta}{m \sin \gamma} \quad (6)$$

where $m = (\cos^2 \alpha + \cos^2 \gamma - 2 \cos \alpha \cos \gamma \cos \theta)^{1/2}$. The angle of torsion τ is given by

$$\tau = \beta + \varphi \quad (7)$$

The angle of torsion is defined with reference to the two achiral conformations of **2** and **3**: in the *exo* conformation, $\tau = 0^\circ$ and $\theta = \gamma + \alpha$, whereas in the *endo* conformation, $\tau = 180^\circ$ and $\theta = \gamma - \alpha$. From the reported² values of μ and the relationships given in eq 1-7, granted the assumptions stated above, computed values of τ are 87.9° for **2** and 36.5° for **3**. Thus, both molecules are chiral (C_3) and closer in geometry to the *exo* than to the *endo* conformation, **3** more so than **2**. A comparison with the calculated dipole moments of the achiral conformations further illustrates the preceding point: whereas μ_{obsd} of **2** (1.65 D.) lies midway between μ_{calcd} of *exo-2* (0.84 D.) and μ_{calcd} of *endo-2* (2.52 D.), μ_{obsd} of **3** (0.53 D.) lies much closer to μ_{calcd} of *exo-3* (0.36 D.) than to μ_{calcd} of *endo-3* (2.04 D.).

It is instructive to compare μ_{obsd} of **2** and **3** with μ_{calcd} corresponding to the two chiral conformations for which $\rho = \omega = 102^\circ$ and $\theta = \gamma = 63.8^\circ$. In **2**, $\mu_{\text{calcd}} = 1.73$ D. and the conformations have $\tau = 93.4^\circ$; in **3**, $\mu_{\text{calcd}} = 1.27$ D. and the conformations have $\tau = 94.8^\circ$.

The angles of twist calculated for **2** and **3** straddle the τ value of 59° calculated⁹ for the parent compound **4**.¹⁸ However, considering the many assumptions which underlie the present estimates and related⁹ computations, any critical comparison of these τ values would be sheer speculation. Accordingly, the calculated values of τ should be taken as no more than rough measures of the torsional angles.

The principal conclusion of the present study is thus that the dipole moments of the tritolyphosphines may be accounted for by assuming various degrees of torsion around the P-C bond while maintaining a constant C-P-C bond angle. This conclusion is buttressed by a crucial observation: the dipole moment of **5** (1.37 D.) is close to the range of dipole moments reported for **4** by several investigators^{4,12-14} (1.39-1.45 D.). This result is entirely consonant with our contention, for the

(18) On the basis of their studies of the Raman and infrared spectra of **4**, E. Steger and K. Stopperka [*Chem. Ber.*, **94**, 3023 (1961)] have suggested that the structure of **4** may have the C_{3v} symmetry in which the planes of the three phenyl rings intersect at the C_3 axis, *i.e.*, $\tau = 0^\circ$.

partial moments of the phenyl and mesityl groups in **4** and **5**, respectively, would be expected to be the same to a first approximation.¹⁹ By contrast, if increased *ortho* substitution on the benzene rings of **4** were to spread the C-P-C bond angle, as supposed by Schindlbauer,² the dipole moment of **5** should be even smaller than that of **3**, *i.e.*, of the order 0-0.5 D. Our finding is clearly incompatible with this conclusion.

We now turn to a reexamination of the reasons given² for the variation in the ultraviolet absorption spectra of the tritolyphosphines. The changes in this series (Table I) had earlier been ascribed² to an increased flattening of the phosphorus pyramid as the C-P-C angle was supposedly increasing in the series 1-3; this increased flattening was believed² to lead to an increase in π -electron overlap of the benzene rings with the phosphorus atom, accompanied by an increase in the s character of the phosphorus orbitals involved in P-C σ bonding.²⁰ In the light of our conclusion, the results in Table I must now be reinterpreted in terms (a) of a change in angle of torsion τ in the series 1-3, and/or (b) of an effect owing to the change in substitution pattern in the series 1-3. In the parent compound **4**, extensive conjugation between the benzene rings,²¹ possibly involving the phosphorus 3d orbitals,²² has been suggested to account for the position of the absorption band, λ_{max} 261 m μ ($\log \epsilon$ 4.02). Whether this band be assigned to a $\pi \rightarrow \pi^*$ transition²³ or to an $n \rightarrow \pi^*$ transition,^{13,24} the amount of overlap between the π -orbital system of the benzene rings and the available orbitals on phosphorus is likely to be some function of the angle of torsion. This may explain the rather similar spectra of **1**, **2**, and **4** (λ_{max} 261-263 m μ) ($\log \epsilon$ 4.02-4.06) and the red shift exhibited by **3** (Table I). Alternatively, the red shift noted for **3** may simply result from an inductive *ortho* effect; the marked further red shift observed for **5**, λ_{max} 312 m μ ($\log \epsilon$ 4.20), lends credence to this latter view. Even if the mesityl groups in **5** were twisted entirely out of conjugation and the molecule were to assume a C_{3v} conformation ($\tau = 0^\circ$),¹⁸ such an extreme spectral effect would not be expected on the basis of a loss in conjugation alone; on the other hand, inductive effects might well account for the observation, since the ultraviolet absorption spectrum of mesitylene is strongly red shifted relative to that of benzene while the spectral characteristics of the two compounds are otherwise similar with respect both to band shape and band intensity.²⁵

(19) In **5**, the components of $\mu_C(\text{ortho})$ perpendicular to the P-C bond axis exactly cancel each other. The components of $\mu_C(\text{ortho})$ parallel to the P-C bond axis ($\mu_C \sin 30^\circ$) are opposite in direction to $\mu_C(\text{para})$ and in combination cancel the latter since $\mu_C(\text{para}) = -2\mu_C(\text{ortho}) \sin 30^\circ$, assuming that the scalar value of $\mu_C(\text{para})$ equals that of $\mu_C(\text{ortho})$. Accordingly, $\mu_{\text{phenyl}} = \mu_{\text{mesityl}}$.

(20) According to Schindlbauer,² "Das würde bedeuten, dass... eine Änderung der Hybridisierung erfolgt, wie sie beim Phosphor häufig beobachtet wird, und damit eine Änderung der Bindungswinkel." We are not aware of any evidence for significant changes in hybridization of phosphorus in tricoordinated compounds of that element, any more than for significant changes in the bond angle (102°) of such compounds.

(21) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952); H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

(22) J. E. Bissey and H. Goldwhite, *Tetrahedron Letters*, 3247 (1966).

(23) H. Schindlbauer, *Monatsh. Chem.*, **94**, 99 (1963); H. Schindlbauer and H. Hagen, *ibid.*, **96**, 285 (1965).

(24) G. Shaw, *Chem. Commun.*, 425, (1966); C. N. R. Rao, J. Ramachandran, M. S. C. Iah, S. Somasekhara, and T. V. Rajakumar, *Nature*, **183**, 1475 (1959).

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Experimental Section

Tris(2,4,6-trimethylphenyl)phosphine was prepared according to a modification of the procedure previously developed by Worrall²⁸ for the synthesis of triarylphosphines. Phosphorus trichloride (8.22 g, 0.06 mole) was added to a solution of powdered sodium (13.8 g, 0.6 g-atom) and freshly distilled bromomesitylene (38.8 g, 0.18 mole) in 300 ml of dry benzene. The solution turned greyish green on heating; it was allowed to reflux for 12–14 hr. The still warm, green solution was filtered by gravity to yield a clear yellow filtrate from which, after removal of solvent, 6.8 g (30%) of yellow solid was obtained. Crude yields in various runs ranged from 22 to 31%. The yellow solid was purified by chromatog-

raphy on a silica gel column prepared with petroleum ether (30–60°) and eluted with 10% benzene–petroleum ether. After several recrystallizations from absolute ethanol, about 1 g of product was obtained, white needles, mp 191.6–192.8° (lit.²⁷ mp 206°); dipole moment²⁸ in benzene at 25°, 1.37 ± 0.04 D.; $\lambda_{\text{max}}^{\text{ethanol}}$ 312 m μ (log ϵ 4.20).

*Anal.*²⁹ Calcd for C₂₇H₃₃P: C, 83.46; H, 8.56; P, 7.97; mol wt, 389. Found: C, 83.10; H, 8.63; P, 8.35; mol wt, 356.

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Racemization and Cleavage of Sulfoxides by Methyllithium^{1,2}

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Abstract: Reaction of optically active aryl methyl sulfoxides with methyllithium in dimethoxyethane followed by hydrolysis affords arene and partially racemized starting sulfoxide. A mechanism is suggested to account for these transformations in which the initially formed arenesulfinylmethide ion suffers reversible elimination to methylene sulfine (CH₂SO) and aryl carbanion. Alternative mechanisms are also discussed.

The racemization of sulfoxides may be induced by heating,⁴ by photochemical means,⁵ and by treatment with hydrogen chloride,⁶ sulfuric acid,⁷ polyphosphoric acid,⁸ nitrogen tetroxide,⁹ and acetic anhydride.¹⁰ However, no report has thus far appeared in which the base-catalyzed racemization of sulfoxides has been claimed. Quite to the contrary, it has been emphasized by several investigators that the sulfoxide pyramid retains its configurational integrity even under conditions where base-catalyzed α -hydrogen isotope exchange takes place. Thus Cram and Pine¹¹ observed that stereomutation of 2-octyl phenyl sulfoxide by reaction with potassium *t*-butoxide in *t*-butyl alcohol or dimethyl sulfoxide at 60° proceeds exclusively by epimerization at carbon, not at sulfur, and they noted¹² their failure to racemize optically active benzyl *o*-carboxyphenyl sulfoxide with strong base. Similarly, Oae and co-workers observed no racemization in the reaction of

(+)-methyl *p*-tolyl sulfoxide with potassium *t*-butoxide in *t*-butyl alcohol or dimethyl sulfoxide at 105–135°, conditions under which base-catalyzed hydrogen isotope exchange on both methyl groups is appreciable.¹³

We have found that reaction of optically active aryl methyl sulfoxides with methyllithium in dimethoxyethane (DME) under homogeneous conditions at room temperature, followed by hydrolysis, leads to recovery of partially racemized sulfoxide; salient results are collected in Table I.¹⁴ The rate of racemization of methyl phenyl sulfoxide in DME ($[\text{CH}_3\text{Li}]/[\text{C}_7\text{H}_5\text{SO}] = 1$) is first order in sulfoxide, $k_{\text{rac}}^{25} = (1.8 \pm 0.3) \times 10^{-6} \text{ sec}^{-1}$. As indicated in Table I, only a portion of the sulfoxide was recovered, extensive cleavage to arene having taken place. Under the reaction conditions employed, conversion of sulfoxides to arenes takes place in yields upward of 30% (Table I).¹⁵ As might be ex-

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(14) The optically active sulfoxides listed in Table I were prepared by reaction of menthyl methanesulfinate¹⁵ with the corresponding arylmagnesium bromides. Since reaction with *p*-tolylmagnesium bromide (see Experimental Section) yields (+)-(*R*)-methyl *p*-tolyl sulfoxide,¹⁶ and since the Grignard reaction is known to proceed with inversion,¹⁷ it follows that the menthyl methanesulfinate prepared by this procedure is enriched in the diastereomer which has the *R* configuration at sulfur and that all five (+)-aryl methyl sulfoxides listed in Table I have the *R* configuration.

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