facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture; (c) formerly Louisiana State University in New Orleans.
(2) A. B. Pepperman, Jr., and T. H. Siddall, III, *J. Org. Chem.*, **40**, 1373 (1975).
(3) N. Kreutzkamp and K. Storck, *Naturwissenschaften*, **47**, 497 (1960); *Chem. Abstr.*, **55**, 10360c (1961).
(4) S. A. Buckler and M. Epstein, *J. Am. Chem. Soc.*, **82**, 2076 (1960).
(5) E. K. Fields, *J. Am. Chem. Soc.*, **74**, 1528 (1952).
(6) S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 4215 (1960).
(7) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry", Academic Press, New York, N.Y., 1965, p 91.
(8) P. A. S. Smith, "The Chemistry of Open Chain Organic Nitrogen Compounds", W. A. Benjamin, New York, N.Y., 1965, p 294.
(9) R. C. Miller, C. D. Miller, W. Rogers, and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).
(10) V. S. Abramov, Y. A. Bochkova, and A. D. Polyakova, *Zh. Obshch. Khim.*, **23**, 1013 (1953); *Chem. Abstr.*, **48**, 8169 (1954).
(11) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, Amsterdam, 1967, pp 21–23.
(12) M. M. Sprung, *Chem. Rev.*, **26**, 297 (1940); R. W. Layer, *ibid.*, **63**, 489 (1963); I. T. Millar and H. D. Springall in N. V. Sidgwick, "The Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 1966, p 164.
(13) G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).
(14) Following paper in this issue: A. B. Pepperman, Jr., G. J. Bourdreaux, and T. H. Siddall, III.
(15) R. B. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).
(16) K. N. Campbell, C. H. Helbing, M. P. Florkowski, and B. K. Campbell, *J. Am. Chem. Soc.*, **70**, 3868 (1948).
(17) K. A. W. Parry, P. J. Robinson, P. J. Sainsbury, and M. J. Waller, *J. Chem. Soc. B*, 700 (1970).
(18) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).
(19) L. A. Bigelow and H. Eatough, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 80.
(20) C. W. C. Stein and A. R. Day, *J. Am. Chem. Soc.*, **64**, 2569 (1942).
(21) C. Shoppee, *J. Chem. Soc.*, 1225 (1931).

Decomposition Reactions of Hydroxyalkylphosphorus Compounds. III. Reaction of Benzylbis(α-hydroxybenzyl)phosphine Oxide with Benzaldehyde and *p*-Tolualdehyde[1a]

Armand B. Pepperman, Jr.,* and Gordon J. Boudreaux

Southern Regional Research Center,[1b] New Orleans, Louisiana 70179

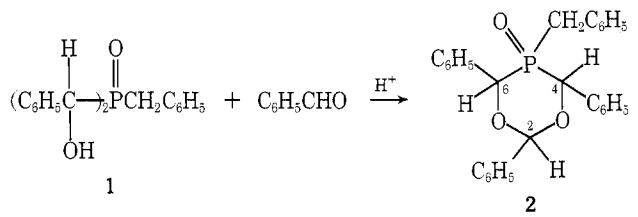
Thomas H. Siddall, III

University of New Orleans,[1c] New Orleans, Louisiana 70122

Received December 5, 1974

The reaction of benzylbis(α-hydroxybenzyl)phosphine oxide (1), a *dl*-diol, with benzaldehyde yielded both *dl* (**2a**) and meso (**2s**) cyclic acetals (5-benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-oxides). The interconversion of **2a** and **2s** was found to occur with the equilibrium constant expressed as $K_{dl} = 3.8 \pm 0.4$. The mechanisms proposed for both of these reactions involve P–C bond cleavage between the oxygen-substituted carbon and phosphorus. The reaction of **1** with *p*-tolualdehyde afforded, as the only isolable product (15% yield), a meso cyclic acetal (**13**) which had *two p*-tolyl groups adjacent to phosphorus (5-benzyl-4,6-di-*p*-tolyl-2-phenyl-1,3,5-dioxaphosphorinane 5-oxide). The production of **13** required P–C bond cleavage twice and the loss of 2 mol of benzaldehyde from **1**.

Buckler has shown that the reaction of benzylbis(α-hydroxybenzyl)phosphine oxide (1) with benzaldehyde affords the cyclic acetal **2** as a mixture of isomers.[2] The isomers, when separated, had markedly different ir and NMR spectra and were identified from NMR spectra and symmetry considerations as one meso and one *dl* form.[3] Since the starting diol **1** was the *dl* form,[3] we studied the mechanism by which meso acetal was produced from *dl* diol.

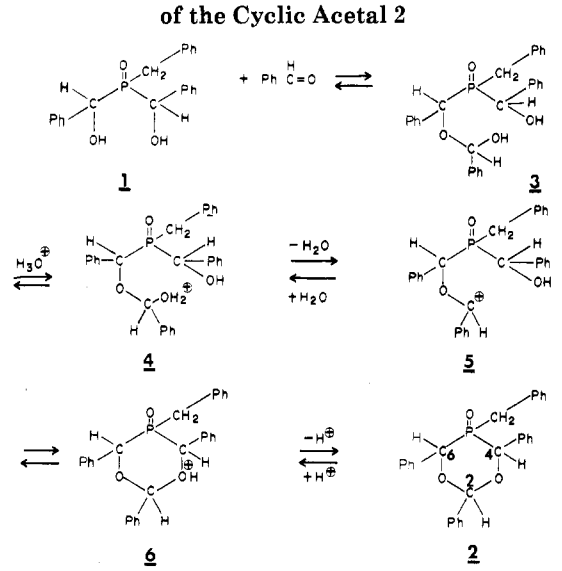


1 2

Results and Discussion

The expected mechanism for the formation of **2** is shown in Scheme I. Diol **1** plus benzaldehyde forms the intermediate hemiacetal **3**. It does not matter which carbon is involved, since in this step the absolute configuration at the carbon will be unchanged. This hemiacetal can be protonated at either of the two remaining hydroxyl groups. Elimination of water to form the carbonium ion and closure to the cyclic acetal **2** occurs readily. However, since the starting material **1** is the *dl* isomer and closure leads predominantly to the *dl* cyclic isomer, it follows that carbonium ion formation occurs predominantly at the carbon adjacent to the ether oxygen (**5**). This is as expected for carbonium ion stability, since the oxygen has free electron pairs capable of resonance stabilization of the carbonium ion while the phosphoryl group would destabilize the carbonium ion.

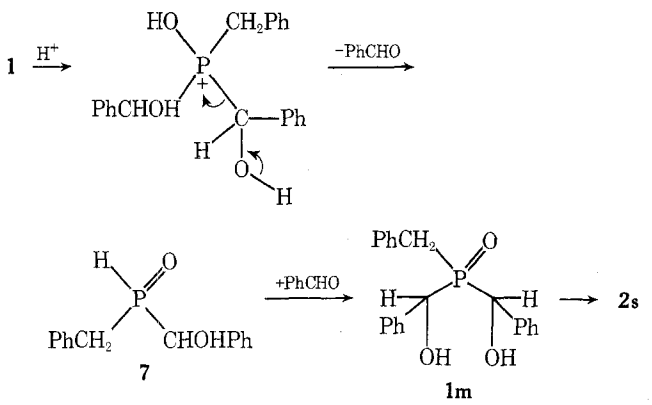
Scheme I
Mechanism for the Formation of the Cyclic Acetal 2



Therefore, the absolute configuration of the carbons adjacent to the phosphorus is not affected and the *dl* isomer is obtained.

The production of the meso isomer could occur by carbonium ion formation adjacent to the phosphorus. This would allow change of configuration at C-4 (or C-6) and produce the meso isomer. However, the large differences in relative carbonium ion stability (between C-2 and C-4 or C-6) make this possibility remote.

Another possibility, which seems more reasonable and for which there is precedent,[4] is the protonation of the phosphoryl oxygen with subsequent loss of benzaldehyde to form the secondary phosphine oxide, **7**. This could add to benzaldehyde[5] to form the meso diol **1m** (actually there are two meso forms of **1**[3]). The meso diol, on reaction with another mole of benzaldehyde, would form the meso acetal **2s**.



Decomposition of **1** through loss of benzaldehyde has already been demonstrated in a different type of reaction.[6,7]

Isomeric Stability. Only two isomers were obtained from the reaction, and since Eliel[8] has shown that the formation of 1,3-dioxanes yields thermodynamically controlled products, these isomers were probably the most thermodynamically stable of all the possible isomers. It is conceivable, therefore, that the meso acetal (**2s**) was formed from the *dl* acetal (**2a**) under the conditions of the reaction.

Each of the isomers was heated under reflux in benzene with a catalytic amount of *p*-toluenesulfonic acid. Aliquots were taken at prescribed intervals, the solid was recovered, and the NMR spectrum was obtained in $CDCl_3$. In this manner, it was possible to integrate directly the signals due to each isomer present. Within the limits of NMR detectability, only two isomers were observed as evidenced by the singlet at δ 6.25 for the *dl* form and the doublet at δ 6.02 for the meso form.[3] Since the other peaks of these two forms overlapped, only the signals for the protons at C-2 could be accurately integrated. The results of the equilibration of each isomer are shown in Table I.

The NMR study demonstrated that equilibrium is reached after 24–31 hr of heating in benzene under reflux with catalytic amounts of *p*-toluenesulfonic acid. An average of all the percentages, at equilibrium for both examples, yielded a value of 79.2% *dl* and 20.8% meso. The equilibrium constant for the interconversion can then be given by

$$K_{dl} = \frac{dl}{\text{meso}} = \frac{79.2}{20.8} = 3.8 \pm 0.4$$

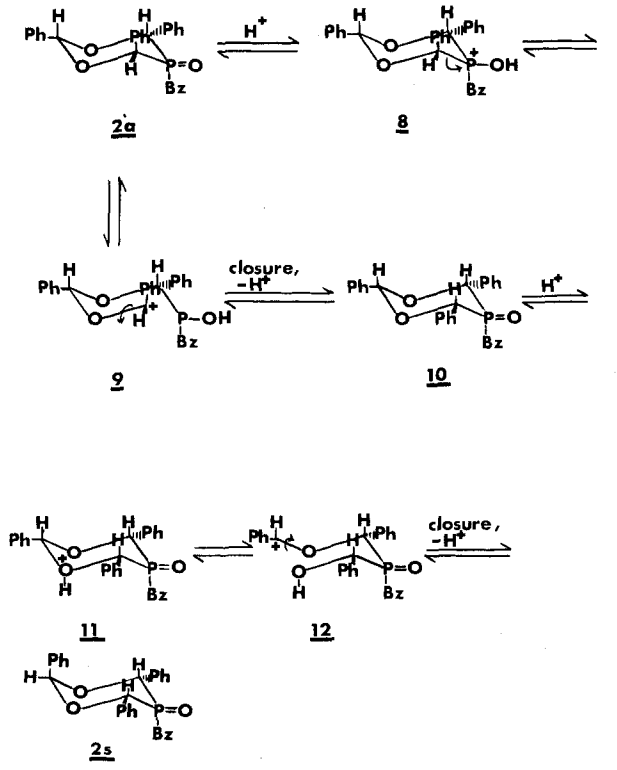
The error involved is expected to be within 10%.[9] Scheme II shows the probable mechanism for the interconversion of **2a** and **2s**.

The most basic oxygen in **2a**, the phosphoryl oxygen, is protonated to form **8**, which then ring opens with P–C bond cleavage to form the carbonium ion at C-4 (or C-6), **9**. The benzyl carbonium ion is further stabilized through delocalization of the charge by the oxygen lone pairs. The carbonium ion, being planar, can close in either of two ways, to reform **2a** or to form **10**, after the loss of a proton. The formation of **2s** from **10** occurs in the reverse of the acetal formation by bond cleavage at C-2. The phosphorus in **9** is shown in the trivalent form, which is the reactive species under acidic conditions.[6,7]

Table I
Isomeric Stability of Cyclic Acetal Isomers 2a and 2s

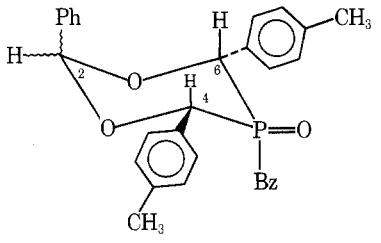
Hr of heating	Integration of singlet	Integration of doublet	% *dl*
	dl Isomer **2a**		
0	10.0		100
24	7.0	1.5	82
48	5.5	1.5	79
96	23.0	7.0	77
120	16.0	5.0	76
144	12.5	3.0	81
	Meso Isomer **2s**		
0		6.5	0
11	11.5	6.5	64
15	12.0	6.0	67
31	18.5	4.0	82
55	10.5	3.0	78

Scheme II
Equilibrium between 2a and 2s



Exchange Reactions. Oxide **1** was treated with *p*-tolualdehyde in an attempt to produce the cyclic acetal (or acetals) with the *p*-tolyl group at C-2. Another possible product from this reaction would be the exchange product wherein *p*-tolyl groups have replaced the phenyl groups in **1**. The procedure used was that described by Buckler[2] for the production of **2** from the reaction of **1** and benzaldehyde. The first solid isolated (15% yield) was an acetal

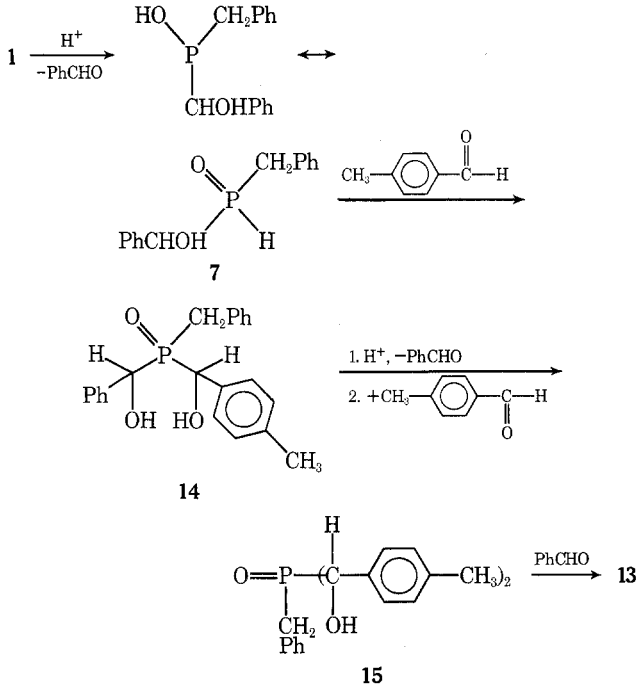
which contained *two* *p*-tolyl groups. The NMR spectrum of the product, **13**, exhibits a singlet for the tolyl methyl protons, a doublet (J = 15 Hz) for the benzyl methylene protons, and a doublet (J = 14 Hz) for the ring methine protons (at C_4 and C_6). The equivalence of the tolyl methyl groups can occur only if the *p*-tolyl groups are both adjacent to phosphorus, unless there is accidental chemical shift equivalence. However, as discussed earlier,[3] the simplicity of the NMR spectrum is diagnostic for the meso form and this requires both *p*-tolyl groups to be adjacent to phosphorus as any combination of *p*-tolyl and phenyl groups at C-4 and C-6 would yield a *dl* form. Nothing definitive can be said about the proton at C-2 as the signal is a broadened singlet which may indicate a small coupling to phosphorus. Using the reasoning developed earlier[3] for **2s**, the structure of **13** can be represented as below, where the configuration at C-2 is not designated.



13

The next solid collected (10% yield) was primarily a mixture of the *dl* diol and *dl* acetal as evidenced by its NMR spectrum, which showed exchangeable protons and at least two signals for the tolyl methyl groups. Eventually 11% of starting **1** was recovered while the rest of the reaction mixture remained as a viscous oil.

While **13** is not the major product of this reaction, its formation must arise from the loss of benzaldehyde from **1**. The loss of benzaldehyde leads to the formation of the secondary phosphine oxide **7**, which then reacts with *p*-tolualdehyde to form the mixed diol **14**. The mixed diol can lose benzaldehyde and react with *p*-tolualdehyde to form the diol **15**. The meso form of **15** would react with benzaldehyde to form **13**. It is not surprising that most of the reaction mixture could not be resolved, as the *dl* forms of **14** and the meso and *dl* forms of **15** can react with either benzaldehyde or *p*-tolualdehyde to form many different cyclic acetals.



14

15

In an attempted exchange reaction, **2a** was heated at 80° (refluxing benzene) with an equimolar quantity of *p*-tolualdehyde in the presence of a catalytic amount of *p*-toluenesulfonic acid. Fractional crystallization of the solid product yielded 75% of unchanged starting material while the filtrates afforded 13% of a solid which was identified as a mixture of acetals having an average of one *p*-tolyl group per acetal. These results further demonstrate the lability of these cyclic acetals, since they will exchange one aldehyde group for another.

Mechanistic Implications. The production of the *dl* and meso acetals (**2a** and **2s**, respectively) from the *dl* diol (**1**) revealed that some mechanism other than the classical acetal-forming mechanism (Scheme I) was involved. The interconversion of the acetals indicated one way in which **2s** was formed. The exchange of *p*-tolualdehyde for part of the benzaldehyde in **2a** showed that aldehyde exchange processes do occur. The isolation of the meso acetal **13** from the treatment of **1** with *p*-tolualdehyde demonstrated that benzaldehyde is being lost from **1**. Based on these results, we concluded that the meso acetal **2s** could be formed from the *dl* diol **1** through the intermediate formation of the secondary phosphine oxide **7**, which adds to free benzaldehyde to form the meso diol **1m**. Closure through the classical acetal mechanism affords the meso acetal **2s**. Previous observations[6,7] suggest that the loss of benzaldehyde from **1** might be thermally induced rather than acid catalyzed.

Experimental Section

Reagent grade chemicals and solvents were used without further purification. Other chemicals and solvents were purified as stated. Benzene was dried for 24 hr or more over Linde molecular sieve 4A[10] before use.

The ir spectra were taken on a Perkin-Elmer 137[10] with NaCl optics. Solid samples were run as KBr pellets using about 1% of the sample. The NMR spectra were taken on a Varian A-60A[10] or Jeolco MH-60-II.[10] Elemental analyses were performed by Enviro Analytical Laboratory, Knoxville, Tenn., and Galbraith Laboratories, Inc., Knoxville, Tenn. All melting points are uncorrected.

Benzylbis(α-hydroxybenzyl)phosphine Oxide (1). The preparation of **1** was carried out exactly as described by Buckler.[2] The physical properties of **1** are reported in the earlier publication.[3]

5-Benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-Oxide (2). The preparation of **2** was carried out in a manner similar to Buckler's procedure.[2] The meso (**2s**) and *dl* (**2a**) isomers were separated and identified according to the reported procedure.[3]

Interconversion of 2a and 2s. For this study, 0.5 g of the appropriate isomer (either **2a** or **2s**) was heated to reflux in 100 ml of dry benzene with one or two crystals of *p*-toluenesulfonic acid (TsOH). Aliquots (20 ml) were taken at predetermined intervals, the benzene was removed in vacuo, and the solid present was collected by washing with anhydrous ethyl ether onto a filter. The NMR spectrum of the solid in $CDCl_3$ was obtained and the signals of the protons at C-2 due to each isomer were carefully integrated. The results of these experiments are shown in Table I.

Reaction of 1 with *p*-Tolualdehyde. A solution of 7 ml of *p*-tolualdehyde, 27 ml of dry benzene, a crystal of TsOH, and 3.52 g (0.01 mol) of **1** was heated under reflux for 20 hr. Only 0.08 ml of water had collected (theoretical 0.18 ml) but reflux was stopped and the benzene was removed in vacuo. The oily residue was dissolved in 40 ml of ether and put aside. The white solid which formed was collected in two fractions, the first (0.72 g) melting at 185–196° and the second (0.45 g) at 142–170°. Recrystallization of these solids from 2-propanol–dioxane yielded, as the only pure product, the meso acetal 5-benzyl-4,6-di-*p*-tolyl-2-phenyl-1,3,5-dioxaphosphorinane 5-oxide (0.7 g, 15% yield). A second recrystallization from methanol–dioxane afforded the analytical sample **13**: mp 218–220°; ir (KBr) 3.27 (aromatic CH), 3.40 and 3.47 (aliphatic CH), 6.6, 6.7, and 6.9 (aromatic C=C), 8.4 and 8.48 μ (P=O); NMR ($CDCl_3$) δ 2.3 (s, 6 H, CH_3), 3.14 (d, J = 15 Hz, 2 H, PCH_2), 5.35 (d, J = 14 Hz, 2 H, PCHO), 5.96 (s, 1 H, OCHO), 6.75–7.75 (m, 18 H, aromatics).

Anal. Calcd for $C_{30}H_{29}O_3P$: C, 76.94; H, 6.20; P, 6.62. Found: C, 76.91; H, 6.31; P, 6.65.

The filtrates from these recrystallizations were evaporated to dryness and the recovered solid was shown to be a mixture of *dl* diols and *dl* acetals by NMR. There were clearly exchangeable protons and at least two different aromatic methyl groups in the NMR spectrum of the solid. Also 11% of the starting **1** was recovered and identified by its ir and NMR spectra.

Reaction of 2a with *p*-Tolualdehyde. An exchange reaction was attempted wherein **2a** (0.88 g, 2 mmol) was heated with an equimolar amount of *p*-tolualdehyde (0.24 g, 2 mmol) in refluxing benzene with one or two crystals of TsOH for 24 hr. After the reaction mixture was cooled for 1 hr, the solid present was collected (0.45 g), washed with ether, and identified as unchanged **2a** by its NMR spectrum (51% recovery). The filtrate was dried in vacuo and the solid which formed was collected by washing with ether (0.26 g, 29.5% yield based on one *p*-tolualdehyde group per acetal). The second solid was shown to contain 30% of the *p*-tolualdehyde moiety by its NMR spectrum. A third crop of solid (0.07 g, 8% yield) was shown to contain about 60% of the *p*-tolualdehyde moiety. These percentages of *p*-tolualdehyde are expressed in terms of one of the benzaldehyde groups being replaced by *p*-tolualdehyde and were arrived at by taking the integration of the aromatic protons signal and dividing by 19 (the number of aromatic protons if there are three phenyl groups and one *p*-tolyl group). The integration of the aromatic methyl region was divided by 3 and the ratio of the integration per hydrogen in the methyl region to that value in the aromatic region was used as the measure of incorporation of the *p*-tolualdehyde group in the acetal. Recrystallization of the latter two solids removed most of **2a** as crystalline compound (0.18 g of 0.30 g). The filtrates were allowed to evaporate to dryness at room temperature and the solid was collected by washing with ether. This solid (0.11 g) contained 75% of one *p*-tolualdehyde group per acetal.

Registry No.—*dl*-**1**, 55145-51-2; **2a**, 36871-89-3; **2s**, 55176-81-3; **13**, 55145-52-3; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0.

References and Notes

(1) (a) Taken in part from the Ph.D. Dissertation of Armand B. Pepperman, Jr., Louisiana State University in New Orleans, 1973; (b) one of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture; (c) formerly Louisiana State University in New Orleans.
(2) S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 4215 (1960).
(3) A. B. Pepperman, Jr., and T. H. Siddall, III, *J. Org. Chem.*, **38**, 160 (1973), and references cited therein.
(4) R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).
(5) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, Amsterdam, 1967, pp 21–23.
(6) A. B. Pepperman, Jr., and T. H. Siddall, III, *J. Org. Chem.*, **40**, 1373 (1975).
(7) Preceding paper in this issue: A. B. Pepperman, Jr., and T. H. Siddall, III.
(8) E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.*, **90**, 3444 (1968).
(9) R. H. Bible, Jr., "Interpretation of NMR Spectra", Plenum Press, New York, N.Y., 1965, p 28.
(10) Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Steric Effects in the Hydrolysis of Methyl- and *tert*-Butylphenylphosphinic Chloride and Fluoride[1]

Richard J. Brooks and Clifford A. Bunton*

Department of Chemistry, University of California, Santa Barbara, California 93106

Received December 31, 1974

In aqueous acetone methylphenylphosphinic chloride and fluoride are much more reactive than the corresponding *tert*-butylphenylphosphinic halides in solvolysis and reaction with hydroxide ion. With the *tert*-butyl compounds, the fluoride is the more reactive toward hydroxide ion, but the chloride is more reactive in solvolysis, and solvolysis of the fluoride is very slow and autocatalyzed. All the reactions appear to be SN2 (P) displacements and have negative $\Delta S^{\ddagger}$, and steric hindrance by the *tert*-butyl group markedly increases $\Delta H^{\ddagger}$. Solvolysis of methylphenylphosphinic fluoride follows the Grunwald–Winstein equation with $m \sim 0.4$, but plots of log k against Y are curved for *tert*-butylphenylphosphinic chloride, although in the more aqueous solvents the plot is linear with $m \sim 0.6$.

Nucleophilic displacement at a phosphinyl group generally follows an associative, SN2 (P) mechanism, for both solvolysis and reaction in the presence of good nucleophiles, e.g., hydroxide ion.[2] However, it is sometimes possible to use bulky substituents to force a change to a dissociative, SN1 (P) mechanism.[5]

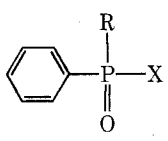
Part of the evidence for this mechanistic change came from markedly different solvent effects upon dissociative and associative reactions, based upon solvent nucleophilicities and the use of the Winstein–Grunwald mY equation. This equation was initially applied to SN reactions at saturated carbon.[6]

Substituent effects upon reaction rates and activation parameters have been rationalized in terms of steric and electronic effects upon nucleophilic attack on phosphorus. Inversion of configuration at phosphorus has been demonstrated,[7] although there is evidence in some reactions for build-up of a pentacovalent intermediate.[8]

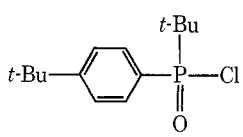
Electrophilic catalysis is often observed, and reactions of esters and fluorides are catalyzed by Brønsted and Lewis acids.[3-5,9a,b]

The aim of the present work was to compare reactions of phosphinyl chlorides and fluorides, because the strength of the P–F bond should make a dissociative mechanism less probable, but strong electron withdrawal by fluoride should assist a reaction in which bond making dominates, and the difference in the importance of bond making and breaking should make the fluorides much more discriminating than the chlorides to nucleophilic attack.

The compounds used were



Ia, X = F
b, X = Cl
R = Me, *t*-Bu



II

so that steric effects were varied, but electronic effects were approximately constant.