Alkaline Cleavage Reactions of Tetraalkylphosphonium Salts

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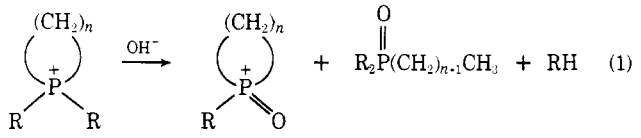
Abstract: Several representative tetraalkylphosphonium salts have been decomposed with potassium hydroxide in 70% aqueous dimethyl sulfoxide, a solvent greatly enhancing the nucleophilic activity of the hydroxide ion. The effects of ring size of cyclic phosphonium salts on cleavage products and rates are clearly evident with ring opening paralleling ring strain. Alcohols have been discovered to accompany phosphine oxide formation, but no alkenes resulting from Hofmann elimination were observed to form. The role of pseudorotation of pentacovalent intermediates is discussed in light of experimental findings.

The stereochemistry[1] and kinetics[2] of base-cleavage reactions of saturated cyclic systems containing phosphonium phosphorus as the only hetero atom has recently received considerable attention. The leaving groups employed in these studies have been either benzyl, phenyl, or alkoxy and therefore, except for the highly strained four-membered ring system,[1f,2,3] competition between exocyclic and ring cleavage at phosphorus (eq 1) is usually not observed[4,5] since the sta-



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bilities of the ejected phenyl,[6] benzyl,[6] and alkoxy[7] anions greatly exceed those of aliphatic anions and thus control product formation. If compounds of the type **1** are cleaved, where the R substituents are permitted to be aliphatic groups of similar leaving ability as compared to the ring carbons bonded to phosphorus, a method of assessing ring strain is made available. We have chosen to investigate the cleavage of four-, five-, and six-membered rings in this way. This study also attempts to supply information which is generally lacking with respect to the reactivity of tetraalkylphosphonium salts toward nucleophilic displacement.

Ring Cleavage. Table I shows the results of cleavage

Table I. Cleavage Results for Some Cyclic Phosphonium Salts

Bromide salt	% ring cleavage[a,b]	—% ring retention— By glpc[a,b]	By gas vol[b]
1a, n = 5, R = Me	0.08	99.9	98
1b, n = 5, R = Et	33.3	66.6	63
1c, n = 4, R = Me	25.4	74.6	77
1d, n = 4, R = Et	95.6	4.4	5.1
2	99.5	0.5	0.56

[a] Determined by glpc analysis of phosphine oxide product mixtures. Retention times are in agreement with those for authentic compounds. [b] Average of three separate runs, except for **1b** for which only one run was made.

studies for several cyclic phosphonium salts of interest in this investigation. All decomposition reactions reported in this discussion, unless otherwise noted, were carried out in 70 mol % aqueous dimethyl sulfoxide at 60° using equimolar amounts of potassium hydroxide and phosphonium salt (0.633 *M*). Use of aqueous[8,9] or alcoholic[5] hydroxide results in prolonged reaction times for the cleavage of tetraalkylphosphonium salts, while sodium hydroxide fusion[9] suffers the disadvantage of possible dealkylation of the phosphine oxides formed.[10] Therefore, 70% aqueous dimethyl sulfoxide, a solvent which enhances the nucleophilic properties of hydroxide ion, was chosen because it afforded rapid conversion of tetraalkylphosphonium salts to the phosphine oxides without complication.

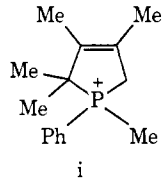
Even with favorable leaving groups at phosphorus, the phosphetane ring structure has been reported in some cases to give rise to ring opening[1f,2,3] and ring expansion[1e,2,11] upon treatment with hydroxide be-

(1) (a) For a summary of pertinent references, see K. L. Marsi, *J. Amer. Chem. Soc.*, **92**, 3791 (1970), ref 1; also see (b) K. L. Marsi, *ibid.*, **93**, 6341 (1971); (c) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970); (d) K. L. Marsi, F. B. Burns, and R. T. Clark, *J. Org. Chem.*, **37**, 238 (1972); (e) W. Hawes and S. Trippett, *J. Chem. Soc. C*, 1465 (1969); (f) J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *ibid.*, 1855 (1970); (g) K. F. DeBruin and M. J. Jacobs, *Chem. Commun.*, 59 (1971).

(2) S. E. Cremer, B. C. Trivedi, and F. L. Weitl, *J. Org. Chem.*, **36**, 3226 (1971), and references cited therein.

(3) S. E. Fishwick and J. A. Flint, *Chem. Commun.*, 182 (1968); S. E. Cremer and C. H. Chang, *ibid.*, 1456 (1969).

(4) (a) J. R. Corfield, N. J. De'Ath, and S. Trippett, *J. Chem. Soc. C*, 1930 (1971), report 14% ring cleavage of the phospholene i with aqueous sodium hydroxide. (b) H. M. Priestley and J. P. Snyder, *Tetrahedron Lett.*, 2433 (1971), have found compound ii and its Δ^2 isomer to lead



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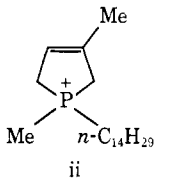

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to varying amounts of ring cleavage products depending upon solvents and reaction conditions. However, in these cases a resonance stabilized allyl carbanion is implicated in ring cleavage.

(5) During the course of this investigation, B. D. Cuddy, J. C. F. Murray, and B. J. Walker, *ibid.*, 2397 (1971), reported the alkaline cleavage of the iodide salt of **1d** under conditions different from our own and record slightly different results; *vide infra*.

(6) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

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

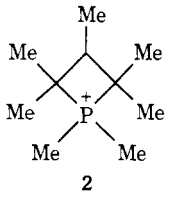
(8) K. L. Marsi, *J. Amer. Chem. Soc.*, **91**, 4724 (1969).

(9) H. R. Hays and R. G. Laughlin, *J. Org. Chem.*, **32**, 1060 (1967).

(10) (a) L. Horner, H. Hoffmann, and H. G. Wippell, *Chem. Ber.*, **91**, 64 (1958); (b) B. R. Ezzell, *J. Org. Chem.*, **35**, 2426 (1970); (c) B. R. Ezzell and L. D. Freedman, *ibid.*, **35**, 241 (1970); B. R. Ezzell and L. D. Freedman, *ibid.*, **34**, 1777 (1969).

(11) (a) S. E. Cremer, *Chem. Commun.*, 1132 (1968); (b) S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *ibid.*, 1113 (1967); (c) S. E. Cremer and R. J. Chorvat, *Tetrahedron Lett.*, 413 (1968).

cause of the reactivity of the four-membered ring itself. It is therefore of interest to note that survival of the ring for cleavage of **2**, although to a very small extent,



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does occur even with such an unfavorable departing group as methyl. However, ring strain, rather than carbanion stability, is apparently the overriding factor in controlling product formation in this case.

In order to explain the results of ring cleavage for five- and six-membered rings it is necessary to examine cleavage behavior for acyclic systems. Table II summarizes results appearing in the literature for hydroxide decomposition of several acyclic phosphonium salts. From the data presented it is seen that for normal alkyl groups greater than methyl, essentially no preference among alkyl substituents for displacement is evident, and the composition of hydrocarbon mixtures is statistical within the expected limits of experimental error. Under the conditions of cleavage employed by us, ethyl is found to be expelled in the presence of methyl (Table III). This is contrary to the findings of Fenton and Ingold shown in the first two entries in Table II. Hays and Laughlin[9] also report 0.5 and 12% dodecane formation for trimethyldodecylphosphonium iodide and methyltridodecylphosphonium bromide, respectively, when these salts are treated with sodium hydroxide. Taking into consideration the results in Table II, and assuming no special ring effects exist, approximately equal amounts of ring cleavage and exocyclic cleavage would be expected for **1b** and **1d**. However, it is seen from the data presented in Table I that ring opening for the six-membered ring compound (**1b**) is significantly less than expected, while for the five-membered ring salt (**1d**) almost complete ring opening is observed.

Table II. Cleavage of Some Acyclic Alkylphosphonium Salts[6]

$R_3'P^+R$		%	%
R′	R	R′H	RH
Me	Et	100	0
Et	Me	0	100
Et	*n*-Pr	73	27
Et	*n*-$C_{12}H_{25}$	75	25[a]
n-Pr	Et	77	23
n-Pr	*n*-Bu	76	24
n-Pr	*n*-Octyl	77	23

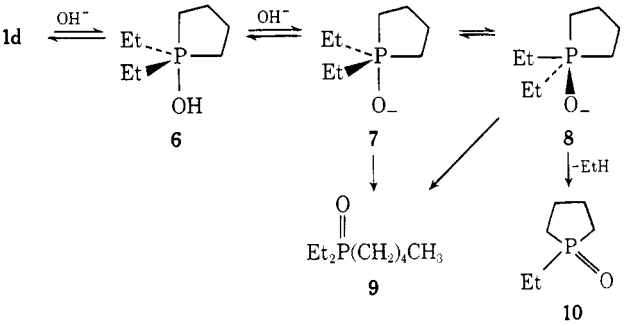
[a] Reference 9.

Table III. Cleavage Data for Methyl and Ethyl Tetraalkylphosphonium Salts

	$R'R_2P^+Me\ Br^-$		%	%	%	%
Compd	R	R′	EtH	MeH	MeRR′PO	$R_2R'PO$
3	Me	Me		100		100
4	Et	Me	0.6	99.4	0.6	99.4
5	Et	Et	3.8	96.2	4.4	95.6

The high degree of ring opening for **1d** can be explained by the formation of the intermediate **6** by apical introduction of hydroxide and in which apical-equatorial disposition of ring bonds is dictated by minimization of ring strain. The concept of apical-equatorial ring bond disposition in pentacovalent phosphorus compounds containing small rings incorporating phosphorus is well supported by X-ray, spectroscopic, reaction product, and stereochemical data.[12] Because the ring is strained in **6**, and also in the product (**10**), ring opening is presumably favored over loss of ethane by way of **7**, and also possibly *via* the pseudorotamer, **8**. Transformation of **7** to **8** or the conjugate bases of **11** and **12** to the conjugate base of **13** is not in conflict with the electronegativity rules[12a] governing pseudorotation, since the oxide substituent is regarded as electropositive.[10b] Scheme I depicts displacement at phosphorus from **7** and **8** *via* an apical position, presently thought to be the mode of departure of leaving groups from pentacovalent phosphorus.[12a,c] However, equatorial departure cannot be ruled out as a viable mechanistic alternative.[12c]

Scheme I



Compound **1c** manifests more than 40 times the ring cleavage expected when compared to its acyclic counterpart **4**. When the cleavage of **1c** was carried out in aqueous 2 *M* sodium hydroxide[8] very similar results were observed indicating the course of the reaction to be particularly insensitive to solvent effects. In a recent communication[5] the iodide salt of **1d** was reported to produce **9** as the exclusive product when cleaved with 4 *M* potassium hydroxide in 95% ethanol. However, the authors state that the presence of small amounts of ring-retained product **10** might not have been detected by their analytical procedures.

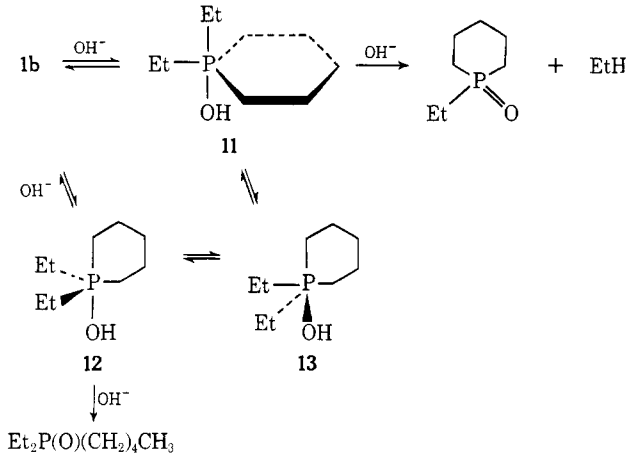
We have recently shown that inversion of configuration at phosphorus in phosphorinanium salts[1a] may be reasonably explained[1b] by displacement of the leaving group from an apical position in an intermediate phosphorane in which the CPC ring bonds of the six-membered ring are diequatorially disposed. Additional evidence for diequatorial orientation of CPC ring bonds of six-membered-ring containing phosphoranes in solution is found in the work of Muetterties[13] and Denney.[14] Thus, structure **11** (Scheme II) might very well be of importance in product determination. In fact, a significantly greater than statistical amount of ethyl cleavage over ring cleavage (2:1 as compared to

(12) For a summary of evidence see (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) F. Ramirez, *ibid.*, **1**, 168 (1968); (c) K. Mislow, *ibid.*, **3**, 321 (1970).

(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(14) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, **94**, 245 (1972).

Scheme II



the statistical 1:1) is observed which may indicate a higher concentration of structure **11** in an equilibrium mixture of pseudorotating structures.[15]

The 1,1-dimethylphosphorinanium salt (**1a**) displays virtually no ring opening in contrast to **1c**, and **1a** resembles its acyclic analog **4** in that the P–Me bond is the one almost exclusively cleaved.

Rate Studies. Half-lives for methyl and ethyl cleavage for compounds discussed previously are listed in Table IV and were determined by measuring gas volumes as a function of time.

Table IV. Half-Lives for Methyl and Ethyl Cleavage of Various Phosphonium Bromide Salts

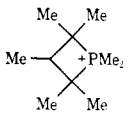
Compd	Half-life, min[a]	Rel rates
Me_4P^+ (**3**)	16	1.0
$Me_2P^+Et_2$ (**4**)	25	0.64
MeP^+Et_3 (**5**)	18	0.89
(**2**)	4	4.0
$(CH_2)_4P^+Me_2$ (**1c**)	6	2.7
$(CH_2)_4P^+Et_2$ (**1d**)	<2[b]	>8.0
$(CH_2)_5P^+Me_2$ (**1a**)	14	1.1
$(CH_2)_5P^+Et_2$ (**1b**)	104	0.15

[a] An average of three runs, except for **1b** for which one run was made. [b] This is a maximum value since the rapid evolution of ethane prevented very careful measurement of volume *vs.* time.

The results clearly show that the strained four- and five-membered ring systems react the most rapidly in exocyclic cleavage, even though the ring survives the cleavage process. This may be ascribed to a higher phosphorane concentration in the preequilibrium state as a result of relief of angle strain at phosphorus in passing from sp^3 hybridization in the phosphonium salt to dsp^3 hybridization in the intermediate phosphorane (see Scheme I, for example).[16] The more rapid cleavage observed for ethyl in **1d** as compared to methyl in **1c**, although experimentally reproducible, cannot be confidently explained at present and is the subject of further work.

Nucleophilic Attack at Carbon. In the course of this work the formation of alcohols was noted, presumably as a result of nucleophilic attack at the carbon α to phosphorus in the substrate phosphonium salts. We are not aware that alcohol formation has previously been reported to accompany hydroxide decomposition of phosphonium salts. However, the formation of SN2 products from attack on the α carbons of phosphonium salts by other nucleophiles such as carboxylate ions[17] and halide ions[18] has been observed. There is an excellent inverse correlation (Table V) between the amount of alcohol produced and expected steric accessibility to phosphorus by hydroxide ion.

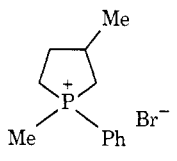
Table V. Alcohol By-Product Accompanying Phosphonium Salt Decomposition

Bromide salt	% total alcohol[a,b]
Me_4P^+	0.05
$(CH_2)_5P^+Me_2$	0.13
$(CH_2)_4P^+Me_2$	0.28
$Et_2P^+Me_2$	0.39 (MeOH only)
$(CH_2)_4P^+Et_2$	0.46
Et_3P^+Me	0.66 (0.57% MeOH, 0.09% EtOH)
	1.8
$(CH_2)_5P^+Et_2$	2.6
$n\text{-}Bu_2Et_2P^+$	5.63 (5.53% EtOH, 0.10% *n*-BuOH)

[a] Detected by glpc. [b] Alcohol production from cyclic phosphonium salts does not reflect attack at the ring carbon since the phosphines formed would not have been detected with column conditions used.

Miscellaneous Observations. In no case were Hofmann elimination products detected. For example, the gas resulting from decomposition of dimethyldiethylphosphonium bromide (**4**) and methyltriethylphosphonium bromide (**5**) gave no indication of the presence of ethylene by either gas chromatographic or infrared analysis. Formation of methane or ethane in part by base cleavage of the product phosphine oxides[10,19] (eq 2) was shown not to occur by subjecting the authentic

(15) It has been demonstrated (ref 1d) that pure cis and trans isomers of iii interconvert in the presence of hydroxide ion. By analogy it seems



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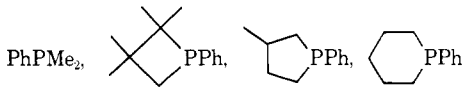
likely that **1b**, where the leaving groups are poorer than phenyl, would also be expected to form an equilibrating mixture of intermediate phosphoranes, **11**, **12**, and **13**.

(16) The relative rates observed for **3**, **2**, **1c**, and **1a** (1.0, 4.0, 2.7, and 1.1, respectively) show a remarkable resemblance to the relative rates of reaction of diethyl peroxide with the following phosphines



(1.0, 3.8, 2.0, and 1.3, respectively) (ref 14). These phosphines have been demonstrated to be converted to stable phosphoranes, $R_3P(OEt)_2$. The similarity in relative rates would therefore appear to provide good evidence for the intermediacy of a phosphorane in base-induced phosphonium salt hydrolysis. Such intermediates have not as yet been isolated or directly detected.

(17) D. B. Denney and L. C. Smith, *Chem. Ind. (London)*, 290 (1961); D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962); D. B. Denney and H. A. Kindsgrab, *ibid.*, **28**, 1133 (1963); K. L. Marsi and G. D. Homer, *ibid.*, **28**, 2150 (1963).

(18) G. F. Fenton, L. Hey, and C. K. Ingold, *J. Chem. Soc.*, 989 (1933); R. N. Haszeldine and B. O. West, *ibid.*, 3631 (1956).

(19) P. Haake and G. W. Allen, *Tetrahedron Lett.*, 3113 (1970).

$$R_3P{=}O + OH^- \longrightarrow R_2P(O)O^- + RH \qquad (2)$$

oxides to reaction conditions and noting the absence of any gas evolution.

Experimental Section

General. Alkaline decomposition of phosphonium salts, the results of which are reported in Tables I and III–V, was carried out in 70 mol % dimethyl sulfoxide–30 mol % water at an initial potassium hydroxide and phosphonium salt concentration of 0.633 *M* each. The dimethyl sulfoxide was distilled once under reduced pressure in a nitrogen atmosphere before use. Since the solution in the decomposition study is not homogeneous at room temperature, it was prepared by the addition of the required amounts of 6.45 *M* aqueous potassium hydroxide and dimethyl sulfoxide to the reaction flask. A preweighed quantity of the phosphonium salt was then added from an enclosed side arm of the flask to the stirred solution at 60 ± 2°. Prior to phosphonium salt addition, the system, which had been previously purged with nitrogen, was sealed. The volume of gas evolved was measured in a calibrated tube at atmospheric pressure by use of a mercury leveling bulb. After evolution of gas ceased, the reaction mixture was heated at 60 ± 2° for several half-lives to ensure completion of the reaction.

The purity and identity of all known phosphorus compounds used in this study were verified either by melting point or nmr spectroscopy. Previously unreported compounds and phosphonium salts of mp >300° were analyzed for carbon and hydrogen.[20] In all cases phosphine oxides, gases, and alcohols resulting from base decomposition were compared with authentic samples for verification by gas and vapor phase chromatography. In addition, gaseous products were examined by infrared spectroscopy. Melting and boiling points are uncorrected, and melting points of hygroscopic materials were taken in sealed tubes.

Nmr spectra were determined with a 60-MHz JEOLCO instrument, and gas and vapor phase chromatographic analyses were obtained from a Hewlett-Packard 700 laboratory chromatograph utilizing a thermal detector. A 6-ft Polypak 2 column was employed for purposes of determining gas composition (Table III) while a 6-ft SE-30 column was used for analysis of alcohols (Table IV). Phosphine oxides (Tables I and III) were determined by use of either a 6- or 20-ft OV-17 column. Both alcohols and phosphine oxides were determined by direct introduction of the reaction mixtures on the columns stated. Melting points were measured on a Thomas-Hoover 6406-K melting point apparatus.

Reactions involving trivalent phosphorus compounds were carried out in a dry-nitrogen atmosphere. Phosphines were quaternized by dissolving them in dry ether or dry benzene and treating the chilled solution with twice the molar quantity of alkyl halide. The elemental analyses of several new hygroscopic compounds show partial hydrate formation since transfers in the analytical weighing process were not conducted in a drybox. However, the pmr spectra are entirely consistent with assigned structures.

1,1-Dimethylphosphorinanium Bromide (1a). 1-Phenylphosphorinane (bp 135° (10 mm)[21] (lit.[22] bp1 19° (3 mm))) was quaternized with methyl iodide to give 86% 1-methyl-1-phenylphosphorinanium iodide (**14**), mp 175–176° (lit.[22] mp 176°). The salt (38 g) was dissolved in 300 ml of 2 *M* sodium hydroxide solution and refluxed for 24 hr; the solution was saturated with sodium chloride and then extracted four times with chloroform. The solvent was removed and the residue distilled to give 14.5 g of 1-methylphosphorinane 1-oxide (**15**), bp 143° (10 mm). Sublimation at 100° (20 mm) yielded an analytical sample, mp 120–122°.

Anal. Calcd for $C_6H_{13}OP$: C, 54.54; H, 9.91. Found: C, 54.54; H, 10.10.

The oxide (**15**) (9.6 g) was added to 5.1 g of phenylsilane,[8,23] and the mixture heated to effect a homogeneous solution. The solution was allowed to stand for 45 min and then distilled to yield 8.0 g of 1-methylphosphorinane (**16**) of bp 146°. **16**, after quaternization with methyl bromide, yielded 7.9 g of hygroscopic crystals of 1,1-dimethylphosphorinanium bromide (**1a**), mp >300° (ethanol–ethyl acetate).

Anal. Calcd for $C_7H_{16}BrP$: C, 39.83; H, 7.64. Found: C, 39.85; H, 7.80.

Phosphine oxide cleavage products of **1a** in alkaline 70% dimethyl sulfoxide were demonstrated to be identical by glpc to **15** and dimethyl-*n*-pentylphosphine oxide (**17**). The latter compound was prepared by first quaternizing dimethylphenylphosphine, bp 70.5–71.5° (11.5 mm) (lit.[24] bp 83–84° (13.5 mm)), with *n*-pentyl bromide to give dimethyl-*n*-pentylphenylphosphonium bromide, mp 111–112°.

Anal. Calcd for $C_{13}H_{22}BrP$: C, 53.99; H, 7.67. Found: C, 53.97; H, 7.89.

The bromide salt was decomposed with 2 *M* sodium hydroxide to give **17**, bp 152° (30 mm), mp 56–57.5°.

Anal. Calcd for $C_7H_{17}PO \cdot {}^1/_3H_2O$: C, 54.23; H, 11.89. Found: C, 54.10; H, 11.82.

1,1-Diethylphosphorinanium Bromide (1b). 1,1-Diphenylphosphorinanium bromide[25] (16.8 g) was mixed with 50 ml of 2 *M* sodium hydroxide and refluxed overnight; the cooled solution was saturated with potassium hydroxide and then continuously extracted with chloroform. After removal of chloroform, the oxide was distilled to give 9.0 g of 1-phenylphosphorinane 1-oxide, bp 260° (65 mm), mp 127–129° (lit.[26] mp 128°). Phenylsilane reduction as described above for **15** yielded 7.8 g of 1-phenylphosphorinane which was quaternized with ethyl iodide to give 1-ethyl-1-phenylphosphorinanium iodide, mp 188–190° (lit.[21] mp 188°). Sodium hydroxide cleavage, as described for **14**, produced the hygroscopic oxide, 1-ethylphosphorinane 1-oxide (**18**), bp 120° (0.5 mm), mp 54–56°.

Anal. Calcd for $C_7H_{15}PO \cdot {}^2/_3H_2O$: C, 53.14; H, 10.40. Found: C, 53.35; H, 10.06.

Compound **18** was reduced in the same manner as **15** to give 1-ethylphosphorinane, bp 67° (24 mm) (lit.[22] bp 170°), which was quaternized with ethyl bromide to yield **1b**, mp 296–298° (ethanol–ethyl acetate).

Anal. Calcd for $C_9H_{20}PBr \cdot {}^1/_4H_2O$: C, 44.35; H, 8.48. Found: C, 44.31; H, 8.47.

Phosphine oxide products resulting from cleavage of **1b** in alkaline 70% dimethyl sulfoxide were found to be identical by glpc with **18** and diethyl-*n*-pentylphosphine oxide (**19**). **19** was prepared in a fashion similar to that of **17** by hydrolyzing the noncrystalline diethyl-*n*-pentylphenylphosphonium bromide intermediate resulting from quaternization of diethylphenylphosphine[27] with *n*-pentyl bromide in 2 *M* sodium hydroxide and isolating **19**, bp 120° (0.5 mm).

Anal. Calcd for $C_9H_{21}PO$: C, 61.32; H, 12.03. Found: C, 61.29; H, 11.87.

1,1-Dimethylphospholanium Bromide (1c). For the preparation of **1c** and its phosphine oxide cleavage products, 1-methylphospholane 1-oxide and dimethyl-*n*-butylphosphine oxide, see ref 8. These two oxides were shown by glpc analysis to result from treatment of 1c with potassium hydroxide in 70% dimethyl sulfoxide.

1,1-Diethylphospholanium Bromide (1d). 1-Phenyl-2-phospholene 1-oxide[28] upon hydrogenation with platinum oxide catalyst in ethanol at 50 psi yielded 1-phenylphospholane 1-oxide (**20**), bp 141° (0.22 mm) (lit.[26] bp 176–180° (3 mm)). The oxide **20** was reduced with phenylsilane in the same manner described for **15** to give 1-phenylphospholane, bp 122–123° (13 mm) (lit.[29] bp 125° (14 mm)). Quaternization of 1-phenylphospholane with ethyl iodide yielded 1-ethyl-1-phenylphospholanium iodide, mp 120–122° (ethanol–ethyl acetate) (lit.[30] mp 122°). Cleavage of the iodide salt with 2 *M* sodium hydroxide produced 1-ethylphospholane 1-oxide (**21**), a hygroscopic compound of bp 167° (24 mm).

Anal. Calcd for $C_6H_{13}PO \cdot {}^1/_3H_2O$: C, 52.15; H, 9.95. Found: C, 52.34; H, 10.07.

Reduction of **21** with phenylsilane gave 1-ethylphospholane, bp

(20) Analyses were performed by G. I. Robertson, Jr., Florham Park, N. J.

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150° (lit.[22] by 145°), which was quaternized with ethyl bromide to yield **1d**, mp >300° (ethanol–ethyl acetate).

Anal. Calcd for $C_8H_{18}BrP$: C, 42.67; H, 8.07. Found: C, 42.67; H, 8.27.

Cleavage of **1d** with potassium hydroxide in 70% dimethyl sulfoxide was shown by glpc analysis to give two phosphine oxide products which were found to be identical with **21** and diethyl-*n*-butylphosphine oxide (**22**). Compound **22** was prepared by reaction of diethylphenylphosphine, bp 108° (13 mm) (lit.[27] bp 108–109° (20 mm)), with *n*-butyl bromide to give diethyl-*n*-butylphenylphosphonium bromide, an oil, which was cleaved with 2 *M* sodium hydroxide to yield diethyl-*n*-butylphosphine oxide, bp 160° (1 mm) (lit.[31] bp 85.5–86° (0.1 mm)).

1,1,2,2,3,4,4-Heptamethylphosphetanium Bromide (2). This compound was prepared with minor modification by literature methods,[32] mp >300°.

Anal. Calcd for $C_{10}H_{22}BrP$: C, 47.45; H, 8.75. Found: C, 47.28; H, 9.05.

Cleavage of **2** with potassium hydroxide in 70% dimethyl sulfoxide yielded phosphine oxides which were identical by glpc analysis with 1,2,2,3,4,4-hexamethylphosphetane 1-oxide, mp 120–130° (mixture of isomers) (lit.[1f] mp 170–171° for the cis isomer), and dimethyl(1,1,2,3-tetramethylbutyl)phosphine oxide,[1f] bp *ca.* 110° (0.1 mm) (kugelrohr).

Tetramethylphosphonium Bromide (3). To a rapidly stirred Grignard reagent prepared from 1.42 mol of methyl iodide and 2.00 g-atoms of magnesium turnings in 500 ml of ether and cooled to −78° was added 0.25 mol of phosphorus trichloride. After standing overnight the solution was distilled without prior hydrolysis and the distillate collected to 95°.[33] Treatment with methyl bromide yielded 8.4 g of **3**, mp >300°.

Anal. Calcd for $C_4H_{12}BrP$: C, 28.09; H, 7.07. Found: C, 28.17; H, 7.33.

The only cleavage product of **3** detected, other than methanol and methane, when **3** was treated with alkaline 70% dimethyl sulfoxide was trimethylphosphine oxide (**23**), identical with the product of 2 *M* sodium hydroxide decomposition of trimethylphenylphosphonium iodide, mp 234–235° (lit.[6] mp 236°), which melted at 139–141° (lit.[6] mp 140–141°).

Diethyldimethylphosphonium Bromide (4). The same general procedure was employed as for the preparation of **3** except for the use of ethyl iodide and methyldichlorophosphine and isolation of methyldiethylphosphine (**24**), bp 110°, by distillation. Quaternization of **24** with methyl bromide yielded 64% of **4**, mp >300°.

Anal. Calcd for $C_6H_{16}BrP$: C, 36.20; H, 8.10; Br, 40.14. Found: C, 36.50; H, 8.09; Br, 40.24.

Phosphine oxide products obtained by treatment of **4** with potassium hydroxide in 70% dimethyl sulfoxide were found to have the same retention times as methyldiethylphosphine oxide (**25**) and dimethylethylphosphine oxide (**26**). Compound **25**, bp 124–128° (16 mm) (lit.[24] by 230°), was prepared by oxidation of **24** with 70% *tert*-butyl hydroperoxide.[8] Dimethylphenylphosphine, when quaternized with ethyl bromide, yielded dimethylethylphenylphosphonium bromide (**27**), mp 200–201°.

Anal. Calcd for $C_{10}H_{16}BrP$: C, 48.60; H, 6.52. Found: C, 48.65; H, 6.66.

Cleavage of **27** with 2 *M* sodium hydroxide yielded **26**, bp 112° (14 mm), mp 76–77° (lit.[6] mp 73–75°).

Methyltriethylphosphonium Bromide (5). Methyldiethylphosphine (**24**) upon quaternization with ethyl bromide yielded **5**, mp >300°.

Anal. Calcd for $C_7H_{18}BrP$: C, 39.47; H, 8.46. Found: C, 39.28; H, 8.35.

Phosphine oxides resulting from treatment of **5** with potassium hydroxide in 70% dimethyl sulfoxide were demonstrated by glpc to be identical with methyldiethylphosphine oxide (**25**) and triethylphosphine oxide (**28**). Compound **28** was prepared by quaternizing diethylphenylphosphine, bp 108° (13 mm) (lit.[27] bp 108–109° (20 mm)), with ethyl bromide to give triethylphenylphosphonium bromide, mp 184–186° (lit.[24] mp 187–189°). Cleavage of the bromide salt with 2 *M* sodium hydroxide gave triethylphosphine oxide, bp 230° (lit.[34] bp 243°).

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Chemical Implications of Phosphorus Configuration in Isomeric 2-Substituted 2-Oxo-1,3,2-dioxaphosphorinanes

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Abstract: From the known configuration of the methoxy cyclic ester given in ref 11 and 12, the stereochemistry at phosphorus in isomers IIIa and IIIb was deduced from the stereospecific course of the Michaelis–Arbuzov-like reaction of the methoxy ester (IIa) with HBr. The isolable isomers equilibrate at higher temperatures and $\Delta H°$ for the conversion of IIIa to IIIb is 4.4 ± 1.5 kcal/mol. Comparison of the physical, chemical, and spectroscopic properties of VIIa and VIIb with those of IIIa and IIIb led us to conclude that a previous stereochemical assignment (ref 22) is incorrect. Under mild conditions, water destroys IIIb and VIIb, leaving the a isomers intact. Similarly, acetone at room temperature attacks only the b isomers to produce cyclic phosphonates which may well possess the stereochemistry shown in IX and X. Pmr chemical shift results of VIIa and VIIb in the presence of $Eu(fod)_3$ are also consistent with the stereochemical assignments.

The preferred stereochemical disposition of phosphorus substituents in 2-R-2-oxo-1,3,2-dioxaphosphorinanes (Ia, Ib) is still not known with certainty.[2] In the six solid-state structures reported in the literature, configuration Ia was observed when R = OPh,[3] OH,[4,5] Br,[6] Ph,[7] or Me[8] although configuration

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