Substituted 1-Chlorophosphetanium Salts. Synthesis, Stereochemistry, and Reactions[1a]

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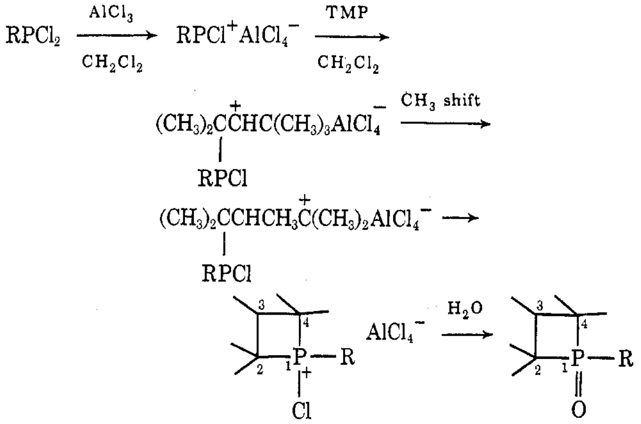
The phosphetanium tetrachloroaluminates **1b** and **1c** derived from $PhPCl_2$–$AlCl_3$ or CH_3PCl_2–$AlCl_3$, and 2,4,4-trimethyl-2-pentene have been isolated and fully characterized. The cis–trans isomer distribution in these salts has been correlated with the isomer ratio of the oxides **2b** and **2c** when the former are quenched with water. The experimental mode of water addition is critical and determines the isomeric composition; an explanation consistent with these observations is advanced. The three chlorinated adducts **11**, **10**, and **6** derived from 1-methyl-, 1-phenyl-, and 1-*tert*-butyl-2,2,3,4,4-pentamethylphosphetane have been prepared. The cis–trans isomers of these chlorides undergo interconversion in solution; the rate of stereomutation follows the order **10** faster than **11** faster than **6** at 35°. Trigonal bipyramidal intermediates (or transition states) are invoked to account for the isomer crossover. Interconversion can be frozen by addition of aluminum chloride to give **1b**, **1c**, or **7**. Thermolysis of the phosphetanium chlorides leads to ring-opened and ring-expanded products. Hydrogen bromide "adducts" of several phosphetane oxides have been synthesized, and the nature of their structure is discussed.

There are only a limited number of reports which have described the successful synthesis of the phosphetane ring system.[2] Of these, the addition of PCl_3–$AlCl_3$ to 2,4,4-trimethyl-2-pentene (TMP) to give **1a**[2c] (Scheme I) and its subsequent generalization[2f] have led to substituted phosphetanes which have been widely employed for stereochemical,[2f,g,3] kinetic,[3l,n] ^{13}C nmr,[3h–j,m] and other studies.[3k]

The mechanism suggested by McBride[2c] for the formation of **2a** (Scheme I) implied that **1a** was formed as an intermediate; however, the latter was not characterized at the time. Our initial observation[2f] that the cis:trans ratio of the products **2b** or **2c**[4] was dramatically dependent upon the mode of addition of water to **1b** or **1c** (see Table I) prompted us to isolate **1b**[5] and **1c** and to relate the stereochemistry of these intermediates to the corresponding oxides. The results of these and related experiments form the basis of the present investigation.

SCHEME I



1a, R = Cl
b, R = Ph
c, R = CH_3

2a, R = Cl
b, R = Ph
c, R = CH_3

Results and Discussion

Isolation of the Tetrachloroaluminate Salts.—Treatment of CH_3PCl_2– or $PhCl_2$–$AlCl_3$ in methylene chloride with TMP was carried out in the usual manner[2f] except that the intermediate salts were isolated prior to the addition of water. The reactivity of these compounds required the rigorous exclusion of atmospheric moisture and manipulation in dry solvents. The nmr of the crude reaction products **1b** or **1c** indicated the presence of two isomers in each case. The ^1H nmr of **1a** *in situ* showed a single isomer as anticipated from its structure. Isolation of the crystalline intermediates **1b** and **1c** followed by redissolution in CH_2Cl_2 did not change the original isomer ratio. The ^1H nmr spectra were similar to other phosphetanium salts[2f] and the low field ^{31}P shifts were in accord with values of chloro-substituted phosphonium salts;[6] addi-

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[1] (a) This work was partially supported by Public Health Service Grant CA 11631, National Cancer Institute, and a grant from the Marquette University Committee on Research. (b) Alfred P. Sloan Research Fellow, 1971–1973.

[2] (a) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957); (b) M. Green, *ibid.*, 541 (1965); (c) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962); (d) D. Berglund and D. W. Meek, *J. Amer. Chem. Soc.*, **90**, 518 (1968); (e) T. A. Zyablikova, A. P. Panteleeva, and I. M. Shermergorn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 373 (1969); (f) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967); (g) G. Zon and K. Mislow, *Fortschr. Chem. Forsch.*, **19**, 88 (1971); (h) R. I. Wagner, U. S. Patent 3,086,053 (1963); *Chem. Abstr.*, **59**, 10124 (1963); (i) B. A. Arbuzov, L. A. Shapshinskaya, and V. M. Erokhina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1820 (1965).

[3] (a) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970), and references cited therein; (b) R. F. Hudson and C. Brown, *ibid.*, **5**, 204 (1972); (c) D. Gorenstein, *J. Amer. Chem. Soc.*, **94**, 2808 (1972); (d) J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 713 (1972); (e) R. K. Oram and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 554 (1972); (f) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, **94**, 245 (1972); (g) N. J. De'ath, D. Z. Denney, and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 272 (1972); (h) G. A. Gray and S. E. Cremer, *Tetrahedron Lett.*, 3061 (1971); (i) G. A. Gray and S. E. Cremer, *J. Chem. Soc., Chem. Commun.*, 367 (1972); (j) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972); (k) see appropriate chapters in Specialist Periodical Reports, "Organophosphorus Chemistry," Vol. 1–3, S. Trippett, Ed., The Chemical Society, London, 1970–1972; (l) S. E. Cremer, B. C. Trivedi, and F. L. Weitl, *J. Org. Chem.*, **36**, 3226 (1971); (m) G. A. Gray and S. E. Cremer, *ibid.*, **37**, 3470 (1972); (n) P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwarz, and D. A. Tyssee, *J. Amer. Chem. Soc.*, **92**, 3828 (1970).

[4] An initial report[2f] indicated that the stereochemistry of **2c** was invariant with the mode of quench; a subsequent publication[3j] showed this to be incorrect. Also, the isomer ratios of **2b** in the earlier report[2f] were determined after recrystallization of the product; since fractionation occurs, these ratios differ from those in the present paper which records the ratios prior to recrystallization.

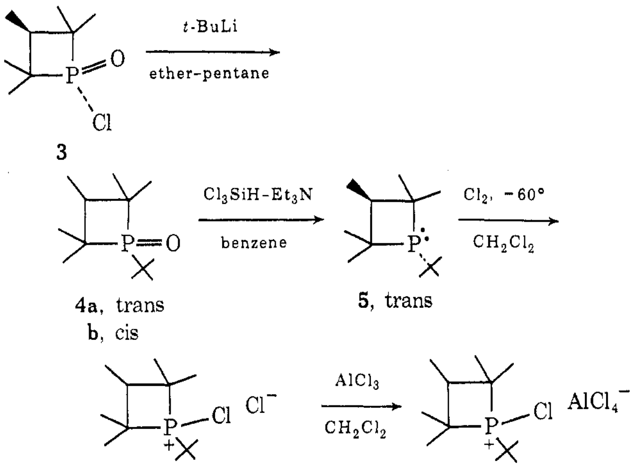
[5] A preliminary report on the isolation of **1b** has appeared: 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract ORGN 62.

[6] A. J. Kirby and S. G. Warren in "The Organic Chemistry of Phosphorus," C. Eaborn and N. B. Chapman, Ed., Elsevier, Amsterdam, 1967, pp 26–27, 194; (b) J. R. Van Wazer, *et al.*, in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Wiley-Interscience, New York, N. Y., 1967, Chapters 3 and 4.

tional structural support comes from ^{13}C nmr[3m] and satisfactory elemental combustion analysis.

A single attempt was made to prepare **7** from *tert*-butylphosphonous dichloride–aluminum chloride and TMP; the liquid product (after H_2O quench) did not show the characteristic nmr features[2f] of a phosphetane oxide. An alternate route for the preparation of **7** was achieved following Scheme II.

SCHEME II



3

4a, trans
b, cis

5, trans

6a, *t*-Bu and 3-CH_3, trans
b, *t*-Bu and 3-CH_3, cis

7a, trans
b, cis

The trans acid chloride **3**[7] was treated with *tert*-butyllithium to give **4a**; retention of configuration about phosphorus was expected from analogy to similar systems.[3d,8] The ^{13}C nmr spectrum supported[3j] the trans assignment. Reduction of **4a** to give **5** should also go with retention;[2f,3a] the ^{31}P shifts[8a] are consistent with this assignment. The phosphetane **5** was converted to **6a** with chlorine, and the latter gave **7a** with $AlCl_3$; the stereochemistry of **5** → **7a** is discussed under Chorination of the Phosphetanes.

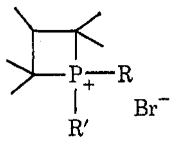
Chlorination of the Phosphetanes.—Our initial efforts were directed toward a stereospecific synthesis of the pure cis or trans isomers of **1b** and **1c** by an independent route. The availability of a predominance[2f] of *cis-* and *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane (**8**) and 1,2,2,3,4,4-hexamethylphosphetane (**9**) suggested that **1b** and **1c** could be prepared by low-temperature chlorination and subsequent treatment with aluminum chloride as in the conversion of **5** to **7**. However, chlorination of a predominance of *either* the cis or trans isomers of **8** led to the same chlorinated product, **10**, which showed a remarkably simple nmr pattern of two overlapping doublets corresponding to the four C–CH_3 groups at carbons 2 and 4, a double doublet due to the C–CH_3 at carbon 3, a multiplet due to the hydrogen at carbon 3, and five aromatic protons. Likewise, chlorination of a predominance of the cis or trans isomers of **9** led to the same product whose nmr spectrum was considerably broadened but interpretable on the basis of the presence of two isomeric phosphetanium chlorides **11a**(**b**). The nmr spectrum of **10** is readily understood if the 1-phenylphosphetanium salts undergo rapid interconversion on the nmr time scale to give a simple, time-averaged spectum. In **11** the interconversion is slower, and the individual isomers are discernible, but as broadened peaks. Low-temperature nmr experiments support this explanation. At about −20° sharp nmr signals due to the separate isomers are observed in **10** as well as in **11**. Treatment of **10** and **11** in methylene chloride with anhydrous aluminum chloride converted them to their respective $AlCl_4^-$ derivatives, **1b** and **1c**. The former showed a 2:1 (cis:trans, refers to 1-Ph *vs.* 3-CH_3) mixture of isomers and the latter a 3:2 mixture (trans:cis 1-CH_3 and 3-CH_3 relationship).

As anticipated, low-temperature chlorination of a cis–trans mixture of 1-chloro-2,2,3,4,4-pentamethylphosphetane (**12**) followed by the addition of $AlCl_3$ gave **1a** which was identical with that prepared through addition of TMP to PCl_3-$AlCl_3$.

The low-temperature chlorination of the *trans-tert*-butylphosphetane (**5**) gave only the *trans*-phosphetanium chloride (**6a**), provided that the nmr spectrum of **6a** was taken immediately after chlorination. Similarly, chlorination of a 1:1 cis:trans mixture rendered a 1:1 ratio of **6a**:**6b**. On standing pure **6a** isomerized; for example, after 1.5 hr at 35° a 1:1 composition was observed, and on standing about 1 day a 3:1 (**6b**:**6a**) equilibrium mixture was reached. The same equilibrium ratio prevailed by starting from a 9:1 mixture of **6b**:**6a**. The equilibration could be stopped by adding dry $AlCl_3$.

Isomer Assignments.—The isomer assignments in **1c** have previously been made on the basis of empirical correlations using ^{13}C nmr.[9] The assignment in the *tert*-butylphosphetanium chloride is made on the same basis; for a 3:1 mixture of **6b**:**6a** the ^{13}C nmr spectrum ($CDCl_3$, shifts relative to TMS-^{13}C) gave a peak at δ 47.86 (J_{PCC} = 8.2 Hz) for ring C-3, corresponding to the major component *vs.* 42.68 (J_{PCC} = 11.3 Hz) for the minor isomer. The relative shifts and coupling constants are parallel to those in **1c**.

In compounds **6** and **10** the equilibrium distribution[10] favors the isomer in which the larger group[11] on phosphorus is pseudoequatorial and is cis to the pseudoequatorial 3-CH_3.[7b,12] This is consistent with the base catalyzed equilibration of **13a–c**; in chloroform



13a, R = Ph; R′ = Bz
b, R = Bz; R′ = CH_3
c, R = Ph; R′ = CH_3

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[7] (a) S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, **91**, 7200 (1969); (b) M. Haque, *J. Chem. Soc. B*, 934 (1970).

[8] (a) S. E. Cremer, *Chem. Commun.*, 616 (1970); (b) W. Hawes and S. Trippett, *J. Chem. Soc. C*, 1465 (1969).

[9] The relative chemical shifts of C-3 and the J_{PCC} couplings have been diagnostically used to distinguish between cis and trans isomers.[3m]

[10] In cases **10** and **11** it is assumed that the isomer composition of the tetrachloroaluminate salts produced by $AlCl_3$ treatment reflects the composition in the rapidly equilibrated chlorides.

[11] The relative *A* values for the substituents are *t*-Bu > Ph > CH_3 > Cl; see E. L. Eliel, N. L. Allinger, S. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 44.

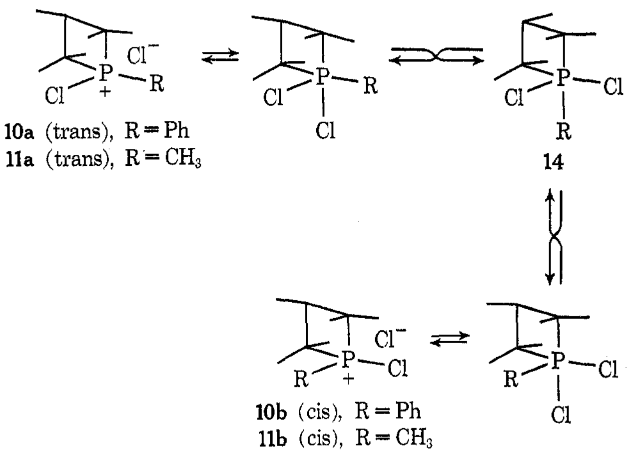
[12] X-Ray data is in accord with placement of the 3-CH_3 in a pseudoequatorial position in 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide (both cis and trans) and in 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide, personal communications from M. Haque and L. M. Trefonas; see also M. Haque, *J. Chem. Soc. B*, 117 (1971); M. Haque, *ibid.*, 938 (1970); C. Moret and L. M. Trefonas, *J. Amer. Chem. Soc.*, **91**, 2255 (1969).

or water the predominant isomer (2:1 to 4:1, dependent on R and R′) had the bulkier substituent R cis to the 3-CH_3 group.[13] In compound **11**, however, it is noted that the trans isomer is favored (a 3:2 ratio corresponds to a free energy difference of 0.24 kcal/mol at 25°). Hence, the relative stability of isomers cannot always be predicted on the basis of simple steric considerations, especially when the energy difference is small.

The resultant stereochemistry of the oxides derived from **1b**, **1c**, and **7** on treatment with water provides indirect evidence that the above cis–trans assignments are reasonable (*vide infra*).

Mechanism of Isomerization.—One pathway for isomer interconversion involves a manifold of pentacovalent phosphorus intermediates (Scheme III).

SCHEME III



10a (trans), R = Ph

11a (trans), R = CH_3

14

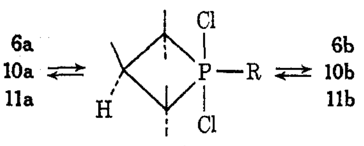
10b (cis), R = Ph

11b (cis), R = CH_3

Ample precedent for pseudorotation in similar systems is available.[3a,14] The four-membered ring is best accommodated in the equatorial–apical positions of a trigonal bipyramid because of angle constraint.[3a,15] The intermediate **14**, however, is of high energy, especially if R = *tert*-butyl; the two chlorine atoms are also in the unfavored equatorial positions.[16] A case in point is *cis*- and *trans*-1-*tert*-butyl-1,2,2,3,4,4-hexamethylphosphetanium iodide which do not interconvert on heating with 1 *N* NaOH.[17]

An alternate pathway for stereomutation is shown in Scheme IV; Quin first proposed a similar scheme to explain cis–trans interconversion (rapid on the nmr time scale) in phospholenium salts.[18] The ring spans the two equatorial positions in the trigonal bipyramid **15** (intermediate or transition state); previous stereochemical[3d,19] and nmr data[3g] suggest this geometry especially when other balancing, stereoelectronic factors[16a] are present. In an idealized trigonal bipyramid the two equatorial positions are 120° apart; however, it is possible that the four-membered ring spans these positions in an unsymmetrical trigonal bipyramid with one of the basal angles <120°. The relative rates (in the nmr at 35°) of interconversion (Ph > CH_3 > *t*-Bu) in **10**, **11**, and **6** are consistent with Scheme IV. An inductive effect (*t*-Bu > CH_3 > Ph) would slow down the rate of Cl^- attack[20] at P^+; moreover, a steric effect may be present in the *t*-Bu derivative.

SCHEME IV



6a **10a** **11a**

6b **10b** **11b**

15

R = CH_3, *t*-Bu, Ph

As a test of Quin's[18] suggestion of rapid interconversion of the isomers of 1-chloro-1,2,5-trimethyl-3-phospholenium chloride (**16**), we have treated this salt with dry $AlCl_3$ in both $CDCl_3$ and nitrobenzene. This froze the equilibration and gave nmr signals for the separate isomers (ratio ~ 5:1).

It should be noted that the ^{31}P shifts in **6**, **10**, and **11** are virtually identical with their $AlCl_4^-$ derivatives and range from −110 to −138 ppm. Thus, the concentration of pentacovalent intermediates must be small in Scheme III or IV; it is assumed that the ^{31}P values for **14**, **15**, etc., would be at least 0–10 ppm.[20b] Likewise, if **15** is a transition state, the ^{31}P shifts are also understandable.

Water Quench of Intermediates.—Table I summarizes the stereochemical relation of the phosphetane oxides to the salt precursors. The salts in CH_2Cl_2 were quenched with water by two methods: (a) water was added dropwise to a cold solution of the intermediate; (b) the intermediate was added dropwise to cold water. The data for **1b** and **1c** suggest that the latter quenching method gives a mixture of oxides whose

TABLE I

H_2O QUENCH OF THE INTERMEDIATE SALTS

Compound	Isomer ratio[a] of salts (c:t)	Mode of quench	Isomer ratio[a] of oxides (c:t)
1b	2:1	H_2O to salt	1:3
		Salt to H_2O	2:1
1c	7:3	H_2O to salt	1:3
		Salt to H_2O	7:3
	2:3	H_2O to salt	1:4
		Salt to H_2O	3:7
1a		H_2O to salt	>95% trans
		Salt to H_2O	>95% trans
6a	Pure trans	NaOH[b]	Pure trans
6b:**6a**	3:1	NaOH[b]	3:1
16	~5:1[c]	H_2O to salt	~3:2
		Salt to H_2O	~7:1

[a] The ratios are approximate in some cases due to integration of partially overlapping peaks; the error is estimated at ±10%. In the case of **1b** and **1c**, the ratios are the average of three separate runs. [b] The mode of quench was immaterial in this case, since the salt did not react with H_2O in the cold. Sodium hydroxide was used for the conversion—see Discussion and Experimental Section. [c] The ratio obtained by treatment of **16** with $AlCl_3$ is assumed to reflect the ratio in **16**.

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(13) B. C. Trivedi, Ph.D. Dissertation, Illinois Institute of Technology, Chicago, Ill., 1970.

(14) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969).

(15) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(16) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963). (b) The energy barrier associated with placing an alkyl or aryl group in an apical position has been reported: D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970).

(17) S. E. Cremer and C. H. Chang, *Chem. Commun.*, 1156 (1969).

(18) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, 4303 (1970).

(19) D. J. H. Smith and S. Trippett, *Chem. Commun.*, 855 (1969).

(20) (a) This is consistent with the relative ease of dissociation of a series of phenyl- and chloro-substituted phosphoranes;[20b] (b) D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, **90**, 6332 (1968).

composition correlates with that of the salts. That is, with an excess of water present a given isomer is rapidly converted to its oxide with retention of configuration about phosphorus.[21] In the reverse mode of quench, in which water is the limiting reagent, chloride ions are formed after the first drop of water has been added; the chloride ion then allows equilibration between the cis and trans tetrachloroaluminate salts. Subsequently, the cis *vs.* trans intermediates are bled off to the oxides at different rates; the predominant isomer is derived from the salt which reacts fastest. Thus either a 7:3 or 2:3 (cis:trans) mixture of **1c** leads to an isomer mixture which contains 75–80% of the trans oxide.[22] To support the assumption that the isomers of **1c** interconvert in the presence of Cl^-, a nonequilibrium composition, 4:1 (cis:trans) was treated with lithium chloride; a 3:2 (cis:trans) ratio was observed shortly after the addition. Trace amounts of water also induced interconversion. When **1c** was heated at 80° in acetonitrile with a trace of water, the equilibrium composition (2:3, cis:trans) was observed; this ratio was identical with that from treatment of **11** with $AlCl_3$.

Since **1a** is not associated with cis–trans isomerism, the mode of quench has no effect on the stereochemical outcome of the acid chloride **3**. It is curious that the reaction gives nearly one pure isomer.[23]

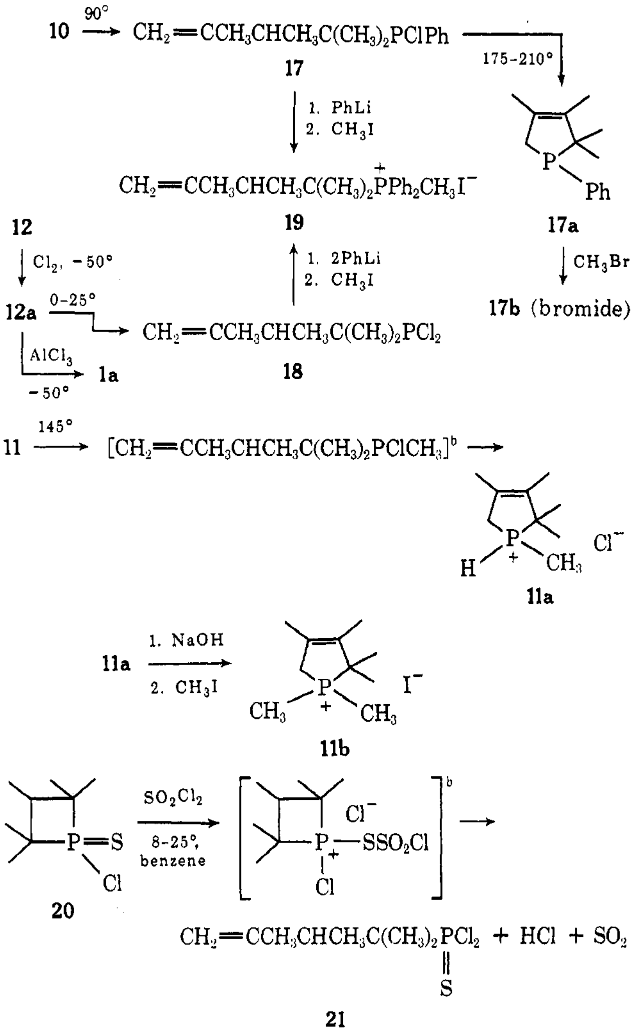
Treatment of **7a** with water by either mode of quench gave unexpected results. Examination of the methylene chloride layer revealed only about one-quarter of the expected amount of oxide; inspection of the aqueous layer showed the presence of a compound whose nmr spectrum was identical with that of **6a**. In a subsequent experiment it was found that solid **6a** (or **6b**) could be dissolved in water and then recovered unchanged after removal of the solvent. The *tert*-butyl substituent apparently makes attack at P^+ quite slow; this same effect was previously noted on the rate of isomerization of **6** by chloride ion.

On heating a sample of **6a** in H_2O at steam bath temperatures it was transformed into pure trans **4a** in about 45 min. Likewise a 9:1 mixture of **6b**:**6a** gave a 3:1 (cis:trans) composition of **4b**:**4a** under identical conditions, but required ~45 hr; a control experiment showed that **4b** does not give **4a** in aqueous HCl at 100° for 56 hr. These results are readily understood if one assumes that the equilibration **6a** $\rightleftarrows$ **6b** is quite slow[24] in water relative to the rate of conversion to oxide. In **6a** the transformation to **4a** is faster than its interconversion to **6b**. However, since the rate of **6b** → **4b** is about 60 times slower, some competitive isomerization occurs, but a predominance of the cis oxide is still obtained. Aqueous sodium hydroxide treatment of **6a** and **6b** gives the respective oxides **4a** and **4b** without concomitant isomerization.

Quin[18] had earlier observed difficulty in obtaining a reproducible isomeric composition of 1,2-dimethyl-3-phospholene oxide on hydrolysis of the intermediate salt. That the stereochemistry of a similar system is dependent on the mode of quench was shown by hydrolysis of 1,2,5-trimethyl-3-phospholenium chloride (**16**),[18] Table I. The isomer assignments in **16** are tentative; it is assumed that the addition of **16** to H_2O reflects the cis–trans composition at equilibrium. The isomer assignments in 1,2,5-trimethyl-3-phospholene oxide have already been established.[18,25]

Thermal Decomposition of the Phosphetanium Chlorides.—In an attempt to dry (for analysis) the phosphetanium chlorides **10** and **11** at elevated temperatures under vacuum, the salts decomposed. On purification of one of the products, **17**, by distillation, ring closure occurred to give **17a**. Scheme V summarizes the results of these and other reactions, including characterization of liquid products by conversion to crystalline derivatives. During the course

SCHEME V[a]



[a] Structure proof for these compounds is contained in the Experimental Section. [b] The compounds in brackets are postulated, unisolated intermediates.

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[21] Ample precedent for retention of configuration about phosphorus is available: see ref 2g, 3a,d, and 7a.

[22] In the hydroxide decomposition of other phosphetanium salts, a preference for the trans oxide has been observed.[14]

[23] A 2:1 cis:trans mixture of the acid chlorides[7a] in methylene chloride does not change composition when stirred with water (treated with $AlCl_3$) at 0° for 3 hr. Hence, it is assumed that, if the cis isomer had been present, it would have survived in the work-up process.

[24] In studies on isomerization of phosphetanium salts in base,[14] we have qualitatively observed slower stereomutation in H_2O than $CHCl_3$. Increased solvent polarity would stabilize the salts relative to the pentacovalent intermediate. Likewise, **6a** → **6b** and **6b** → **6a** is found to be faster in CH_2Cl_2 than in H_2O.

[25] A. Bond, M. Green, and S. C. Pearson, *J. Chem. Soc. B*, 929 (1968). Total nmr analysis of the phospholene (and oxide) supports the stereochemical assignments; J. P. Albrand and J. B. Robert, personal communication.

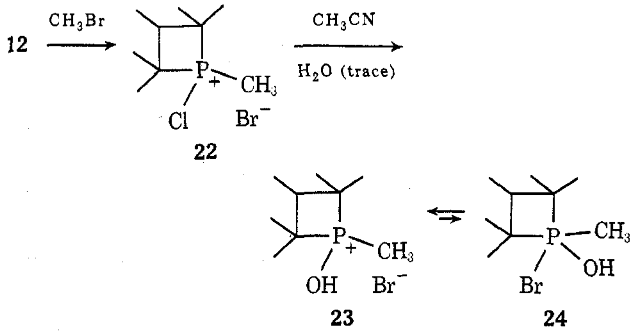
of this work,[26] Trippett[27] reported on the preparation of **17a** and **18** by similar reactions.

The ease of ring opening, **12a** > **10** > **11**, qualitatively parallels the combined electronegativity of the substituents on phosphorus. Phosphetanium salts which only have aryl and/or alkyl groups on phosphorus thermolyze at 200–350°.[28] In comparison, 1-benzyl-1,2,2-trimethylazetidinium perchlorate gives *N*-methyl-*N*-(3-methyl-3-buten-1-yl)benzylamine perchlorate on refluxing for 3 days in acetonitrile.[29]

Conversion of the phosphetanium chlorides to acyclic olefins bears analogy to a prior observation[13] in which **20** was converted to **21** by sulfuryl chloride.[30] In contrast **2a** did not react with sulfuryl chloride; this is reasonable in view of the greater nucleophilicity of sulfur (in P═S) *vs.* oxygen (in P═O).[31] The driving force for the formation of **17**, **18**, and **21** is attributed to angle strain in the four-membered ring.[31]

Hydrogen Bromide Adducts of Phosphetane Oxides.—In an earlier attempt to establish the stereochemistry of **1c**, we tried to convert a known[8a] isomeric mixture (2:1, trans:cis) of **12** with methyl bromide to the respective isomeric salts; isomer interconversion, at that time, had not been anticipated. The quaternization proceeded very slowly to give **22**, mp 176–179°. Recrystallization of this from acetonitrile (which was not rigorously dried) gave a different compound, mp 235–249° dec, which did not contain chlorine. The nmr spectrum and elemental analysis suggested isomeric (2:1) phosphetane oxide–HBr adducts shown as **23**. Treatment of *trans*-**2c** in chloroform or benzene with dry HBr gave a product which was identical with the major isomer of **23**; likewise *cis*-**2c** and HBr yielded the minor isomer. The ^{31}P chemical shifts of these adducts and that derived from **4a** were about 30 ppm downfield from the parent oxide; similar shifts have been reported for acyclic phosphine oxides.[32] The infrared of the HBr addition products showed the absence of P═O stretch (~1150–1200 cm^{-1}) and the presence of several new peaks in the region 1800–2700 (broad, PO–H stretch?) and 920–960 cm^{-1} (strong and broad, PO–H bending?). It was found that cis–trans interconversion of **23** at 100° in tetrachloroethane for 5 days does not occur. Moreover, these adducts are readily sublimed by heating under vacuum without apparent loss of HBr.

From the ^{31}P data it is unlikely that the structure of **23** can be written as **24**; however, an equilibrium, **23** ⇄ **24**, cannot be ruled out, especially if **23** is the predominant species. The absence of isomer interconversion is reasonable since Scheme IV does not apply (apical groups are not identical) and Scheme III would include high energy intermediates (*e.g.*, CH_3 apical, OH and Br equatorial). Hopefully, a definitive structure will be forthcoming from X-ray studies.[23]



Experimental Section

Nmr spectra were recorded on a Varian A-60A spectrometer; tetramethysilane was used as an internal standard. In those cases in which H_2O was employed as the solvent, Tier's salt [$(CH_3)_3Si(CH_2)_3SO_3Na \cdot H_2O$] was the reference standard. The ^{31}P–^{1}H decoupling experiments were performed with an NMR specialties Model HD-60A heteronuclear spin decoupler. Microanalyses were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany. All boiling and melting points (Thomas-Hoover apparatus) are uncorrected. All reactions were conducted under a nitrogen atmosphere; reaction work-up and isolation of moisture sensitive intermediates were conducted in a Labconco glove box in a dry, nitrogen atmosphere. The low temperature for the nmr studies was determined by methanol calibration.[34]

1-Chloro-1-phenyl-2,2,3,4,4-pentamethylphosphetanium Tetrachloroaluminate (1b).—To 40 g (0.30 mol) of anhydrous aluminum chloride (powder) suspended in 100 ml of methylene chloride was added 54 g (0.30 mol) of phenylphosphonous dichloride in 100 ml of methylene chloride. The mixture was briefly stirred until homogeneous and then cooled to 0–5° while 34 g (0.30 mol) of 2,4,4-trimethyl-2-pentene in 100 ml of methylene chloride was added dropwise over 2 hr. The solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed under vacuum (~20 mm) to give a crude, crystalline solid. The nmr spectrum ($CDCl_3$) of the crude product showed two isomers in a 2:1 ratio (estimated due to overlap of peaks). The tetrachloroaluminate was recrystallized twice from hot, dry acetonitrile (minimum) and dry ethyl acetate to give about 50 g of white, crystalline salt, mp 84–104° (sealed tube). The nmr spectrum ($CDCl_3$) of the major component showed peaks at τ 1.73–2.33 (m, 5 H), 6.67–7.20 (m, 1 H), 8.27 (d, 6 H, $J_{PCCH} \approx$ 24 Hz), 8.30 (d, 6 H, $J_{PCCH} = 25.5$ Hz), 8.80 (d d, 3 H, $J_{HCCH} =$ 7 Hz, $J_{PCCCH} \sim 1$ Hz). The minor isomer showed peaks at 8.28 (d, 6 H, $J \approx 24$ Hz), 8.39 (d, 6 H, $J = 25.5$ Hz), and 8.73 (d d, 3 H, $J_{HCCH} = 7$ Hz, $J_{PCCCH} \approx 1$ Hz); the aromatic and ring protons overlapped with those of the major isomer. A moderate concentration of tetrachloroaluminate formed two layers in chloroform. The upper layer contained most of the salt; the lower layer was about tenfold less concentrated in salt. In methylene chloride only one homogeneous phase was apparent. On ^{31}P–^{1}H decoupling all doublets due to ^{31}P coupling collapsed to singlets. From the frequency used to decouple this sample, the ^{31}P chemical shift was calculated[35] to be -111 ± 2 ppm (relative to 85% H_3PO_4); two standards (trimethyl phosphite and trimethyl phosphate in a sealed capillary tube) were employed as references for the calculation. Use of two references provided an internal check on the reliability of this method; the experimental difference (138 ± 1 ppm) in ^{31}P shift of the standards was in accord with literature values.[6b] This same technique was used for other ^{31}P shifts in this paper.

Anal. Calcd for $C_{14}H_{21}AlCl_5P$: C, 39.51; H, 5.21; Al, 6.34; Cl, 41.66; P, 7.28. Found: C, 39.25; H, 5.49; Al, 6.50; Cl, 41.39; P, 7.43.

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(26) The conversion of **10** → **17** and **20** → **21** was first reported at the Third Great Lakes Regional Meeting of the American Chemical Society, Northern Illinois University, DeKalb, Ill., June 5–6, 1969. Credit for the first observation of thermolysis of a phosphetanium chloride is due to M. Green, *Proc. Chem. Soc., London*, 177 (1963).

(27) J. R. Corfield, M. J. P. Harger, R. K. Oram, D. J. H. Smith, and S. Trippett, *Chem. Commun.*, 1350 (1970).

(28) S. E. Cremer and L. Wilkinson, unpublished work.

(29) N. J. Leonard and D. A. Durand, *J. Org. Chem.*, **33**, 1322 (1968).

(30) Sulfuryl chloride converts R_2PSCl to R_2POCl in acyclic systems; R. Cölln and G. Schrader, *Chem. Zentralbl.*, 17390 (1959).

(31) See ref 6a, p 230.

(32) See ref 6b, Chapter 4, pp 284–285.

(33) Several phosphetane–HBr adducts are under study by C. N. Caughlan, Montana State University. An X-ray of triphenylarsenic hydroxybromide [G. Ferguson and E. W. Macaulay, *Chem. Commun.*, 1288 (1968)] is suggestive of a structure $Ph_3As^{+}—O^{1/2-} \cdots H \cdots Br^{1/2-}$; the bonding in **23** may be similar.

(34) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1972).

(35) J. B. Stothers and J. R. Robinson, *Can. J. Chem.*, **42**, 967 (1964).

The quench of **1b** with H_2O followed the general procedure for that of **1c** (*vide infra*). The isomer ratio (Table I) in the oxide was determined (nmr, benzene) by integration of the $C-CH_3$ groups at the 2 and 4 positions.[2f]

1-Chloro-1,2,2,3,4,4-hexamethylphosphetanium Tetrachloroaluminate (1c).—This intermediate was prepared in 80–90% yield by the general method described for (**1b**).[2f] An nmr (CH_2Cl_2) spectrum of the crude reaction mixture (prior to evaporation) indicated an isomer ratio or ~4:1 (cis:trans).[36] The nmr spectrum (CH_2Cl_2) of the major component (cis isomer) showed absorption at τ 7.37 (d, 3 H, J_{PCH} = 11 Hz), ~8.41 (d, 6 H, J_{PCCH} ~ 26 Hz), ~8.43 (d, 6 H, J_{PCCH} ~ 24 Hz), 8.88 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). The minor component showed a peak at τ 7.32 (d, 3 H, J_{PCH} = 11 Hz); the upfield methyl absorption partially overlapped with that of the major component. The elemental combustion analysis and ^{13}C nmr spectrum have been reported.[3m] The cis and trans isomers showed ^{31}P shifts at −126 and −114 ppm, respectively.

Equilibration of the Isomeric Tetrachloroaluminate Salts (1c).—A sample of the salt (cis:trans, 4:1) in dry CH_3CN (dried over Linde Molecular Sieves 3A and then passed through Woelm neutral alumina) was heated in a sealed, degassed nmr tube at about 80°. The isomer ratio gradually changed: ~3:1 (2 hr), ~2:1 (4.5 hr), ~16:9 (7 hr), ~11:9 (11 hr), ~1:1 (19 hr), and ~9:11 (24 hr).

A sample of the salt (initially cis:trans, 4:1) was dissolved in dry acetonitrile and then solid LiCl (dried at 135°) was added to saturate the solution. An nmr spectrum this solution indicated that equilibration had already started (cis:trans, 3:2) at room temperature; heating the sealed, evacuated nmr tube for 1 hr at 80° was sufficient to reach the equilibrium composition (cis:trans, 2:3).

A solution of 8 g of the tetrachloroaluminate salt (cis:trans, 4:1) in 20 ml of dry CH_3CN in a flask was heated to about 80° for 13 hr to give a 3:2 (cis:trans) mixture; then, about 100 mg of D_2O was added; and the reaction was heated for 3 hr to give the equilibrium composition (cis:trans, 2:3).

H_2O Quench of 1c.—To 4.3 g of recrystallized tetrachloroaluminate salt (cis:trans, 2:3) in dry CH_2Cl_2 at 0°, 5 ml of water was added slowly and dropwise (*via* a medicine dropper) over 2 hr with stirring; then an additional 75 ml of water was added over 2 hr at 0°. The layers were separated, and the water layer was extracted three times with an equal volume of $CHCl_3$. The combined organic layers were dried and evaporated to give 2.1 g (95%) of **2c**; the isomer ratio 4:1 (trans:cis) was determined by relative integration of the characteristic $P-CH_3$ groups in the nmr (D_2O) spectrum.

For the reverse mode of quenching, 4.6 g of intermediate (cis:trans, 2:3) in 100 ml of dry CH_2Cl_2 was added dropwise to 80 ml of water (maintained at 0–5° by external cooling) which was rapidly stirred. A nitrogen inlet tube was connected to the pressure equalized addition funnel to prevent water vapor from contacting the CH_2Cl_2 solution prior to its contact with the bulk sample of water. Work-up as described for the addition of H_2O to the tetrachloroaluminate salt gave a 92% yield of oxide, ~3:7 (cis:trans).

General Chlorination Procedure of Phosphetanes.—A solution of chlorine (0.015 mol) was prepared by passing dry chlorine into 10 ml of dry methylene chloride at about −30°; the flask and its contents were weighed to follow the amount of chlorine uptake. The solution was then transferred under nitrogen to an addition funnel and added slowly (15–30 min) to a stirred solution of phosphetane (0.015 mol) in 8 ml of methylene chloride. The temperature was maintained at −60 to −50° by external cooling. The solution was then placed in a drybox in order to fill nmr tubes or to add anhydrous aluminum chloride. The nmr spectra of the chlorinated solutions were "clean" which indicated that chlorination occurred in nearly quantitative yield.

H_2O Quench of 1-*tert*-Butyl-1-chloro-2,2,3,4,4-pentamethylphosphetanium Tetrachloroaluminate (7).—To **7a** (prepared from chlorination of 2 g of **5** followed by $AlCl_3$ addition) in 8 ml of dry CH_2Cl_2 at 0°, 8 ml of water was added dropwise over 3 hr. The layers were separated, and the water was extracted three times with 25 ml portions of chloroform. Evaporation of the $CH_2Cl_2-CHCl_3$ gave only ~25% of the expected amount of oxide; the nmr spectrum showed it to be pure trans. The aqueous solution contained the chloride analog of **7a** (namely, **6a**): the nmr spectrum (H_2O) showed peaks at τ 8.26 (d, 6 H, J_{PCCH} ~ 23 Hz), 8.33 (d, 9 H, J_{PCCH} = 19 Hz), and 8.43 (d, 6 H, J_{PCCH} = 21.5 Hz). The cold, water layer was brought to pH 9–10 with sodium hydroxide and extracted with chloroform. Evaporation of the chloroform and nmr examination of the solid in CH_2Cl_2 showed only trans oxide **4a**. The salt **7a** was also added slowly to an equal volume of water at 0°; the results were identical with those just described.

Similarly, a 3:1 mixture of **7b**:**7a** was treated with water by both methods of quench. In each case the aqueous layer contained a 3:1 mixture of **6b**:**6a**. Neutralization with sodium hydroxide gave a 3:1 mixture of the **4b**:**4a**. The nmr spectrum (H_2O) due to **6b** in a mixture showed peaks at τ 8.23 (d, 6 H, J_{PCCH} = 23.5 Hz), 8.41 (d, 9 H, J_{PCCH} = 19.3 Hz), 8.46 (d, 6 H, J_{PCCH} = 21.8 Hz), and 8.89 (d d 3 H, J_{HCCH} = 7 Hz; overlaps with **6a**).

1-Chloro-1,2,2,3,4,4-hexamethylphosphetanium Chloride (11).—Chlorination of either *trans*-1,2,2,3,4,4-hexamethylphosphetane (>95%) or a cis:trans (7:3) mixture of isomers using the general chlorination method gave the same nmr (CH_2Cl_2) pattern: τ 6.4–6.8 (very broad doublet, 3 H, J_{PCH} ~ 13 Hz), 8–8.8 (four broad peaks, 12 H), 8.95 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). As the sample was cooled from the normal probe temperature ~35° to lower temperatures the upfield methyl absorption (τ 8–8.8) became sharper and the low field doublet ($P-CH_3$) changed into two doublets. At −20° the major isomer showed peaks at τ 6.5 (d, J_{PCH} = 12.5 Hz), 8.32 (d, J_{PCCH} = 26.5 Hz), 8.59 (d, J_{PCCH} = 23.4 Hz); the minor isomer showed peaks at τ 6.6 (d, J_{PCH} = 12.5 Hz), 8.33 (d, shoulder, J_{PCCH} ~ 26 Hz), 8.48 (d, J_{PCCH} = 23.2 Hz). The C_3-CH_3 protons occurred at τ 8.95 for both isomers. The nmr spectrum reverted to its original pattern when the sample was allowed to warm to 35°. A $^{31}P-^{1}H$ decoupling experiment at 35° gave a ^{31}P value of approximately −121 ppm.

Addition of $AlCl_3$ to 11.—Samples of **11** derived from either the *trans*-phosphetane or a cis:trans (7:3) mixture were treated with an equivalent of $AlCl_3$ in CH_2Cl_2 solvent. In each case the nmr spectrum was the same. The ratio of isomers was about 3:2 (trans:cis); the nmr spectrum was also identical with the tetrachloroaluminate salt prepared from methylphosphonous dichloride–aluminum chloride and TMP followed by equilibration of the isomers.

1-Chloro-1-phenyl-2,2,3,4,4-pentamethylphosphetanium Chloride (10).—The general method of chlorination was applied to >95% *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane as well as to a cis:trans (7:3) mixture of the phosphetanes. In each case the same product was obtained. Rigorous exclusion of water was required since the phosphetanium chloride is very moisture sensitive. The nmr spectrum (CH_2Cl_2) showed absorption at τ 1.5–2.2 (m, 5 H), 6.6–7.1 (m, 1 H), 8.27 (apparent d, 12 H, J_{PCCH} = 24.5 Hz), 8.78 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). The ^{31}P shift was −110 ppm. When the anhydrous phosphetanium chloride partially hydrolyzed in the presence of trace amounts of water, additional peaks were observed in the nmr spectrum at τ −4 to −5 (s, function of the degree of hydrolysis), 8.20 (d, J_{PCCH} = 23.8 Hz), and 8.33 (d, J_{PCCH} = 25.8 Hz).

A sample for chlorine analysis was prepared by chlorination of distilled 1-phenylphosphetane; the white solid was washed in the glove box with anhydrous ether and then dried at 25° under vacuum (0.1 mm).

Anal. Calcd for $C_{14}H_{21}Cl_2P$: Cl, 24.35. Found: Cl, 24.74.

A sample of phosphetanium chloride in CH_2Cl_2 was treated with an equivalent of anhydrous $AlCl_3$; the $AlCl_3$ dissolved in this reaction. The nmr spectrum (CH_2Cl_2) showed the presence of two isomers in a ratio of 2:1 (cis:trans); the nmr spectrum (CH_2Cl_2) was identical with that of the phosphetanium tetrachloroaluminate salt prepared from 2,4,4-trimethyl-2-pentene and phenylphosphonous dichloride–aluminum chloride; moreover the chemical shifts and coupling constants in CH_2Cl_2 were similar to those in $CDCl_3$ (*vide supra*).

A low-temperature nmr study was run on **10**. As the sample was cooled the original doublet at τ 8.27 broadened at the base line; near 0°, additional peaks were observed which flanked this doublet. At −10 to −20° these peaks became sharp: τ 8.25 (d, J_{PCCH} = 24 Hz) and 8.35 (d, J_{PCCH} = 25.7 Hz). In addition, the upfield absorption at 8.78 changed to two broad doublets (J_{HCCH} ~ 7 Hz for each doublet). The isomer ratio at −20° was about 3:2. The low-temperature spectrum reverted to the original when allowed to warm to 35°.

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[36] The initial isomer ratio will sometimes vary and is probably dependent on the amount of water present in the reagents.

1-*tert*-Butyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide (4).—The synthesis of this compound has appeared elsewhere.[3j] The pure trans oxide, mp 149–151°, showed peaks in the nmr spectrum (CH_2Cl_2) at τ 8.0–8.4 (m, 1 H), 8.70 (d, 9 H, J_{PCCH} = 13.5 Hz), 8.73 (d, 6 H, J_{PCCH} = 17 Hz), 8.82 (d, 6 H, J_{PCCH} = 15.2 Hz), 9.15 (d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1.5 Hz).

The cis isomer was obtained by sodium hydroxide treatment of a 3:1 (cis:trans) mixture of **7b**:**7a**. Repeated recrystallization of the predominately cis isomer from cyclohexane followed by fractional sublimation gave a sample, mp 87–90.5°, which was ~90% cis oxide. The nmr spectrum (CH_2Cl_2) showed peaks at τ 7.7–8.1 (m, 1 H), 8.72 (d, 6 H, J_{PCCH} = 16.5 Hz), 8.80 (d, 9 H, J_{PCCH} = 13.5 Hz), 8.86 (d, 6 H, J_{PCCH} = 15.5 Hz), and 9.14 (d d, J_{HCCH} = 7 Hz, J_{PCCCH} = 1.3 Hz).

1-*tert*-Butyl-2,2,3,4,4-pentamethylphosphetane (5).—A solution of 26 g (0.12 mol) of the corresponding trans oxide in 200 ml of benzene was reduced with trichlorosilane–triethylamine by the usual method[2f] to give the phosphetane in 90% yield after distillation of the benzene at atmospheric pressure. Sublimation (~40°, 0.1 mm) gave a white, crystalline product, mp 66–67°. An nmr spectrum (benzene) showed peaks at τ 7.41 (q, 1 H, J_{HCCH} = 7.5 Hz); 8.72 (d, 6 H, J_{PCCH} = 19 Hz); 8.76 (d, 9 H, J_{PCCH} = 11.5 Hz); 8.82 (d, 6 H, J_{PCCH} = 5.5 Hz); 9.31 (d, 3 H, J_{HCCH} = 7.5 Hz). A 1:1 mixture of isomers was obtained by heating the trans isomer at 157°.[37] The nmr spectrum (benzene) of the cis isomer showed a characteristic peak at τ 7.99 (d q, 1 H, J_{HCCH} = 7.5 Hz; J_{PCCH} ~ 3.5 Hz); the ratio of cis:trans isomers was determined from this peak and τ 7.41 from the trans isomer. Treatment of the trans isomer with methyl iodide gave white needles, mp 323–326° dec, from acetonitrile–ethyl acetate.

Anal. Calcd for $C_{13}H_{28}IP$: C, 45.62; H, 8.25. Found: C, 45.57; H, 8.08.

1-Chloro-1-*tert*-butyl-2,2,3,4,4-pentamethylphosphetanium Chloride (6).—A solution of 2.0 g of the trans phosphetane **5** was chlorinated using the general procedure. The solution was transferred while still cold to a drybox. An aliquot was immediately examined in the nmr spectrophotometer. A similar aliquot was immediately treated with anhydrous $AlCl_3$ powder. The $AlCl_3$ rapidly dissolved in the solution; after 1 equiv had been added, the original pale yellow solution became light brown. Additional $AlCl_3$ was insoluble in the methylene chloride solution.

The nmr spectrum (CH_2Cl_2) of the phosphetanium chloride showed only one isomer, **6a**, to be present: τ 6.7–7.1 (m, 1 H), 8.15 (d, 6 H, J_{PCCH} = 23 Hz), 8.24 (d, 9 H, J_{PCCH} = 19 Hz), 8.37 (d, 6 H, J_{PCCH} = 21.5 Hz), and 8.80 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz).

The sample of pure *trans*-phosphetanium chloride showed about 10% of the cis isomer after spinning in the probe (about 35°) for 10–15 min. After 90 min in the probe the cis:trans isomer ratio was about 50:50. On prolonged standing at room temperature (58 hr) the cis:trans ratio was 3:1 which is the equilibrium distribution.

The nmr spectrum (CH_2Cl_2) of the *trans*-phosphetanium tetrachloroaluminate (**7a**) showed peaks at τ 6.8–7.4 (m, 1 H), 8.25 (d, 6 H, J_{PCCH} ~ 23 Hz), 8.30 (d, 9 H, J_{PCCH} = 19 Hz); 8.40 (d, 6 H, J_{PCCH} = 21.5 Hz), 8.84 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). Examination of this sample after 10 days at room temperature showed only trans isomer.

Chlorination of a 1:1 mixture of the *cis*- and *trans*-phosphetane gave a 1:1 mixture of **6a**:**6b**; the nmr spectrum was taken immediately after the completion of the reaction. The nmr spectrum (CH_2Cl_2) of the *cis*-phosphetanium chloride (**6b**) showed peaks at τ 6.8–7.3 (d q, 1 H, J_{HCCH} = 7 Hz, J_{PCCH} = 2.5 Hz), 8.10 (d, 6 H, J_{PCCH} = 23.4 Hz), 8.30 (d, 9 H, J_{PCCH} = 19.5 Hz), 8.37 (d, 6 H, J_{PCCH} ~ 21.5 Hz), and 8.85 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). The *cis*-phosphetanium tetrachloroaluminate (**7b**) had nmr (CH_2Cl_2) absorption at τ 6.8–7.3 (m, 1 H), 8.20 (d, 6 H, J_{PCCH} = 23.5 Hz), 8.38 (d, 9 H, J_{PCCH} = 19 Hz), 8.42 (d, 6 H, J_{PCCH} = 21.5 Hz), and 8.87 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} = 1 Hz). The ^{31}P shifts (relative to 85% H_3PO_4) of **6b** and **7b** (both in CH_2Cl_2) were −137 and −138 ppm, respectively.

A sample of the phosphetanium tetrachloraluminate in CH_2Cl_2 was treated with anhydrous ether to precipitate the solid salt. The solid was redissolved and reprecipitated several times to provide an analytical sample.

Anal. Calcd for $C_{12}H_{25}AlCl_5P$: Cl, 43.81. Found: Cl, 43.32.

The ^{13}C nmr spectrum ($CDCl_3$) of a 3:1 mixture of **6b**:**6a** showed peaks at δ 50.69 (J_{PC} = 66.8 Hz, C-2), 47.86 (J_{PCC} = 8.2 Hz, C-3), 17.21 (J_{PCC} < 1 Hz, C-5), 24.93 (J_{PCC} < 1 Hz, C-6), 5.78 (J_{PCCC} = 21.4 Hz, C-7), 50.41 [J_{PC} = 25.1 Hz, $C(CH_3)_3$], 24.93 [J_{PCC} < 1 Hz, $C(CH_3)_3$] for the major isomer. The minor isomer had peaks at δ 42.68 (J_{PCC} = 11.3 Hz, C-3), 19.70 (J_{PCC} = 5.8 Hz, C-5), 23.16 (J_{PCC} ~ 0 Hz, C-6), and 7.13 (J_{PCCC} = 21.4 Hz, C-7); the other peaks overlapped with the major component. The numbering of the carbons follows that in previous manuscripts; the chemical shifts were calculated relative to $(^{13}CH_3)_4Si$, and the instrumental methods were as previously described.[3j,m]

Treatment of 6 with H_2O.—Heating an aqueous solution of 3:1 (**6b**:**6a**) for 45 min at 100° converted all of the **6a** to **4a**, most of which could be extracted out of solution with several portions of CH_2Cl_2. The resultant aqueous solution of 90% pure **6b** was slowly converted to a mixture of cis:trans oxides (*ca.* 3:1) after 45 hr at 100°. Evaporation (under vacuum) of an aqueous solution of **6b** gave a solid which was redissolved in CH_2Cl_2; the nmr spectrum initially showed a 9:1 ratio of **6b**:**6a**. On standing for 24 hr, the equilibrium distribution (3:1) was obtained.

A solid sample of a **6b** and **6a** mixture which was isolated from aqueous solution was identical (infrared and nmr) with a sample of **6b** and **6a** which had never been in contact with water. For the infrared spectrum (Nujol mull) the samples were dried at 70° under vacuum to remove either H_2O or CH_2Cl_2 which form a solvate with **6**.

Chlorination of 1-Chloro-2,2,3,4,4-pentamethylphosphetane (12) and Conversion to 18.—To 1.0 g (5.7 mmol) of 1-chloro-2,2,3,4,4-pentamethylphosphetane[3m] in 10 ml of dry methylene chloride was added 0.40 g (5.7 mmol) of chlorine in 10 ml of dry methylene chloride; the temperature was maintained below −50° by external cooling. The addition required 5 min; a white precipitate was observed as the chlorine was added. Then 1.2 g (9.0 mmol) of anhydrous $AlCl_3$ was added at −50° and the reaction mixture allowed to warm to room temperature. The resultant solution showed the following absorption in the nmr spectrum: τ 7.02 (m, 1 H), 8.28 (d, 6 H, J_{PCCH} = 32 Hz), 8.30 (d, 6 H, J_{PCCH} = 32.5 Hz), 8.73 (d, 3 H, J_{HCCH} = 7 Hz). The nmr spectrum was identical with that of the tetrachloroaluminate salt **1a** prepared by treatment of TMP with PCl_3–$AlCl_3$.

In a second experiment, 2.0 g of the chlorophosphetane was treated with 0.8 g of Cl_2 in CH_2Cl_2 at −50°. The mixture was allowed to warm to room temperature; after stirring for about 1 hr all of the suspended, white solid went into solution. The nmr spectrum of the solution was consistent with ring-opened product, **18**: τ 5.0–5.3 (m, 2 H), 7.5 (m, 1 H), 8.4 (m, 3 H), 8.87 (d, 3 H, J_{PCCH} = 10.5 Hz), 8.92 (d, 3 H, J_{PCCH} = 13 Hz), 9.03 (d d, 3 H, J_{HCCH} = 7 Hz). Treatment of **18** with phenyllithium and then methyl iodide converted it into its corresponding phosphonium salt which was identical (infrared and nmr) with **19** (*vide infra*).

1-Chloro-1,2,5-trimethyl-3-phospholenium Tetrachloroaluminate.—A sample of the chloride **16** was prepared according to the procedure of Quin;[18] the nmr ($CDCl_3$) values were in agreement with those reported. To 497 mg of the chloride in ~3 ml of $CDCl_3$, 330 mg of anhydrous aluminum chloride was added; all of the $AlCl_3$ went into solution. An additional 50 mg of $AlCl_3$ was added whereupon the light, pale yellow solution turned yellow-brown. The nmr spectrum ($CDCl_3$) of the predominant isomer showed peaks at τ 3.80 (d, 2 H, J_{PCCH} = 35.5 Hz), 6.12 (m, 2 H), 7.30 (d, 3 H, J_{PCH} = 12.8 Hz), and 8.45 (d d, 6 H, J_{PCCH} = 21.5 Hz, J_{HCCH} = 7.3 Hz). The minor isomer showed peaks at τ 3.77 (d, J_{PCCH} = 35.5 Hz, partially obscured by the major isomer) and 7.41 (d, J_{PCH} = 12.5 Hz); the upfield methyl groups were partially obscured by the major isomer and appeared as shoulders. The isomer ratio was ~5:1.

The phospholenium chloride as a suspension in dry nitrobenzene was also treated with a slight excess of $AlCl_3$ whereupon the salt and $AlCl_3$ went into solution. The upfield C–CH_3 doublets of the minor isomer were now distinguishable from the major isomer.

H_2O Quench of 16.—To 3.5 g of the phospholenium salt in 50 ml of CH_2Cl_2 at 0°, 10 ml of water was added slowly. The water layer was saturated with NaCl and extracted repeatedly with CH_2Cl_2. Evaporation of the organic solvent gave 2.4 g 95% yield, of crude product. An nmr spectrum (benzene) indicated an isomer ratio of about 3:2 (cis:trans). The slow addition of 6.0 g of the salt in 50 ml of CH_2Cl_2 to an equal volume of ice water gave 4.2 g, 97% yield, of oxide. The isomer ratio

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[37] S. E. Cremer and C. H. Chang, *Tetrahedron Lett.*, 5799 (1968).

was ~7:1 (cis:trans).[18,25] The nmr spectrum (benzene) of the cis isomer showed peaks at τ 4.59 (d, 2 H, J_{PCCH} = 23.7 Hz), 7.27 (2 H, six-line pattern, J_{HCCH} = 7 Hz, J_{PCH} = 13 Hz), 8.87 (d, 3 H, J_{PCH} = 12 Hz), and 9.02 (d d, 6 H, J_{HCCH} = 7Hz, J_{PCCH} = 16 Hz). The trans isomer showed peaks at 4.40 (d, 2 H, J_{PCCH} = 26.5 Hz), 7.82 (2 H, apparent five-line pattern, J_{HCCH} = 7 Hz, J_{PCH} = 7 Hz), 8.72 (d, J_{PCH} ~ 12 Hz); the C-CH_3 groups were obscured by the cis isomer.

Thermal Decomposition of 1-Chloro-1-phenyl-2,2,3,4,4-pentamethylphosphetanium Chloride (10) to Chlorophenyl(1,1,2,3-tetramethyl-3-butenyl)phosphine (17).—A fresh sample of the salt **10** in a molecular still was heated at about 90° under vacuum (0.1 mm). A clear colorless liquid, bp 135–137° (1.6 mm), was obtained in 60% yield. The infrared spectrum (neat) showed absorption at 895 cm^{-1} (>C═CH_2) and at 695 and 742 cm^{-1} (monosubstituted phenyl). The nmr spectrum (neat) gave peaks at τ 2.2–3.0 (5 H, aromatic), 5.00–5.38 (2 H, m), 7.20–7.85 (1 H, m), 8.22 (3 H, m), and 8.7–9.4 (9 H, m); the ^{31}P decoupled spectrum was consistent with the assigned structure.

Anal. Calcd for $C_{14}H_{20}ClP$: C, 66.01; H, 7.91; Cl, 13.92; P, 12.16. Found: C, 65.52; H, 8.29; Cl, 14.05; P, 11.95.

The liquid phosphine **17** was characterized by conversion to a solid derivative. To 2g of the chlorophenylphosphine in 25 ml of ether at −30°, 12 ml of phenyllithium (0.7 *M*) was added. The mixture was then stirred at room temperature overnight. Water was added and the ether layer was dried and treated with an excess of methyl iodide. The resultant solid, **19**, was recrystallized twice from acetonitrile-ethyl acetate to give 1.7 g (50% yield), of salt, mp 181–188° dec. The nmr spectrum ($CDCl_3$) showed absorption at τ 1.6–2.4 (10 H, m), 5.0–5.47 (2 H, apparent doublet), 7.07 (d, 3 H, J_{PCH} = 12 Hz), 8.30 (3 H, broad s), 8.40 (d, 3 H, J_{PCCH} = 18 Hz), 8.46 (d, 3 H, J_{PCCH} ~ 20 Hz), 8.94 (d, 3 H, J_{HCCH} = 7 Hz); the single tertiary, allylic hydrogen was obscured by the doublet at τ 7.07.

Anal. Calcd for $C_{21}H_{28}IP$: C, 57.54; H, 6.44; I, 28.95; P, 7.07. Found: C, 57.53; H, 6.50; I, 29.12; P, 6.99.

1-Phenyl-2,2,3,4-tetramethyl-3-phospholene (17a).—The chlorophenylphosphine **17**, 7.7 g, was gradually heated and stirred under a nitrogen atmosphere. At about 175° a slow evolution of HCl gas was observed; at 200–210° the evolution was more vigorous. The liquid was heated at the latter range for 4 hr. On cooling two layers were observed, a viscous upper layer and a smaller bottom layer (about 1.5 g) which was hard. An nmr spectrum (neat) of the upper layer showed peaks at τ 2–3 (m, 5 H), 6.8–7.0 (m, 2 H), 8.28 (broad s, 3 H), 8.53 (broad s, 3 H), 8.77 (d, 3 H, J_{PCCH} = 20 Hz), and 9.28 (d, 3 H, J_{PCCH} = 9 Hz). The upper layer was dissolved in ether and treated with an excess of methyl bromide. The resultant precipitate, 6.9 g, was recrystallized from acetonitrile-ethyl acetate to give 5.3 g of the phospholenium salt **17b**, mp 159–161.5°. The nmr spectrum ($CDCl_3$) of the salt showed peaks at τ 1.6–2.5 (m, 5 H), 5.6–6.6 (m, 2 H), 7.2 (d, 3 H, J_{PCH} = 14 Hz), 8.0 (broad s, 3 H), 8.28 (broad s, 3 H), 8.39 (d, 3 H, J_{PCCH} = 17 Hz), and 8.86 (d, 3 H, J_{PCCH} = 17.5 Hz).

Anal. Calcd for $C_{15}H_{22}BrP$: C, 57.53; H, 7.08; Br, 25.51. Found: C, 57.51; H, 6.79; Br, 25.52.

Thermolysis of 1-Chloro-1,2,2,3,4,4-hexamethylphosphetanium Chloride (11).—The phosphetanium chloride did not show decomposition when dissolved in dry CH_2Cl_2 or $CHCl_3$ and heated at reflux for 24 hr. A 1-g sample was heated to 145° in a sublimation apparatus under vacuum (0.1 mm); a white solid (**11a**) gradually sublimed onto the cold finger. The solid had a distinct phosphine odor and was insoluble in dry benzene. The nmr spectrum ($CDCl_3$) showed resonances at τ 6.3–7.4 (m, 2 H), 7.78 (d, 3 H, J_{PCH} = 15.2 Hz), ~8.37 (broad s, 3 H), ~8.51 (d, 3 H, J_{PCCH} ~ 18 Hz), ~8.55 (broad s, 3 H), and ~8.64 (d, 3 H, J_{PCCH} ~ 16 Hz). The solid was treated with cold 10% NaOH and the liberated phosphine extracted with ether. The ether was dried and treated with methyl iodide to give the methiodide salt **11b**, mp 314–317° dec, and previous darkening at ~290°. The nmr spectrum (CF_3CO_2H) showed peaks at τ 6.88 (broad d, 2 H), 7.98 (6 H, d, J_{PCH} = 14 Hz), 8.14 (broad s), 8.24 (broad s), 8.58 (d, 6 H, J_{PCCH} = 17 Hz).

Anal. Calcd for $C_{10}H_{20}IP$: C, 40.28; H, 6.77; I, 42.57; P, 10.39. Found: C, 40.25, H, 6.56; I, 42.64; P, 10.25.

1,1,2,3-Tetramethyl-3-butenylthiophosphonyl Dichloride (21).—To 9.1 g (0.04 mol) of the sulfide **20**[3m] in 100 ml of benzene, 6.7 g (0.05 mol) of sulfuryl chloride in 50 ml of benzene was added over 20 min; the temperature was kept near 8° by ice bath cooling; considerable gas evolved on warming to room temperature. The mixture, which contained two phases, was stirred at ambient temperature for 24 hr. The solvent was evaporated and the product distilled to give 8.7 g of clear liquid, bp 67–68° (0.1 mm). The nmr spectrum ($CDCl_3$) showed absorption at τ 5.01 (m, 2 H, vinyl protons), 6.83 (six peaks observed, 1 H, J_{HCCH} = 7 Hz, J_{PCCH} ~ 14 Hz), 8.18 (m, 3 H, allylic CH_3), 8.49 (d, 3 H, J_{PCCH} ~ 28 Hz), 8.53 (d, 3 H, J_{PCCH} = 28 Hz), 8.68 (d, 3 H, J_{HCCH} = 7 Hz). A ^{31}P–^{1}H decoupling experiment was consistent with these assignments.

Anal. Calcd for $C_8H_{15}Cl_2PS$: C, 39.19; H, 6.17; P, 12.63; Cl, 28.92. Found: C, 39.23; H, 6.23; P, 12.49; Cl, 28.95.

1-Chloro-1,2,2,3,4,4-hexamethylphosphetanium Bromide (22) and Its Reaction with H_2O.—To 8 g of 1-chloro-2,2,3,4,4-pentamethylphosphetane (**12**) in 50 ml of dry ether in a thick-walled flask, an excess of methyl bromide was added; the flask was stoppered and allowed to stand at room temperature for 2 weeks. A white precipitate formed very slowly during this period. The solution was then filtered in the drybox to give 2.5 g of the phosphetanium bromide **22**. The filtrate contained unreacted **12**.

The phosphetanium bromide was nearly insoluble in $CHCl_3$ and CH_3CN. It was purified by trituration with hot CH_3CN to give a white solid, mp 176–179° dec (sealed tube under nitrogen). The ^{31}P shift (dilute solution in $CHCl_3$) was −116 ppm. The ^{1}H nmr spectrum (dilute CH_2Cl_2) showed peaks at τ 6.65 (broad d, 3 H, J_{PCH} = 11 Hz), 8.31 (broad d, J_{PCCH} ~ 25 Hz), 8.40 (d, J_{PCCH} ~ 21.5 Hz), 8.52 (d, J_{PCCH} = 21.5 Hz), 8.90 (3 H, d, J_{HCCH} = 7 Hz).

Anal. Calcd for $C_9H_{19}BrClP$: C, 39.51; H, 7.00; Br, 29.21; Cl, 12.96; P, 11.32. Found: C, 39.52; H, 7.03; Br, 29.06; Cl, 12.67; P, 11.34.

Treatment of **22** with acetonitrile which had not been completely dried, followed by evaporation of the solvent gave white crystals, mp 235–249° dec. Traces of water added to a suspension of **22** in $CHCl_3$ led to the same product, **23**. Addition of excess H_2O or base to **22** gave **2c**, cis and trans. Compound **23** is soluble in $CHCl_3$ and can be sublimed at about 70° (0.1 mm). The nmr spectrum ($CDCl_3$) showed two isomers to be present.

The major component (trans) absorbed at τ −1.87 (s, 1 H), 7.82 (d, 3 H, J_{PCH} = 12.2 Hz), 8.57 (d, 6 H, J_{PCCH} = 18.0 Hz), 8.63 (d, 6 H, J_{PCCH} = 21.3 Hz), and 8.98 (d d, 3 H, J_{HCCH} = 7 Hz, J_{PCCCH} ~ 1 Hz). The minor component (cis) overlapped with the major isomer except for peaks at τ 8.52 (d, 6 H, J_{PCCH} = 18 Hz) and 8.67 (d, 6 H, J_{PCCH} = 22 Hz). The ratio of isomers was ~2:1 (trans:cis).

Anal. Calcd for $C_9H_{20}OBrP$: C, 42.36; H, 7.90; Br, 31.32; P, 12.14. Found: C, 42.53; H, 7.89; Br, 31.20; P, 12.12; Cl, 00.00.

1,2,2,3,4,4-Hexamethylphosphetane 1-Oxide HBr Adduct (23).—To 0.5 g of *trans*-1,2,2,3,4,4-hexamethylphosphetane 1-oxide in 5 ml of $CDCl_3$ a slow stream dry HBr gas was added for several minutes. An nmr spectrum matched the major isomer derived from the addition of H_2O to **22**. The solvent was evaporated and the product recrystallized from dry acetonitrile (sparingly soluble), mp 237–249° dec. The infrared spectrum (Nujol mull) showed strong peaks at 1800–2500 (broad), 990, 895, and 795 cm^{-1}.

The ^{31}P shift (in $CDCl_3$) of the *trans*-phosphetane 1-oxide was −63 ppm and its corresponding HBr adduct was −94.5 ppm.

Similarly, a 7:3 mixture (cis:trans) of oxides was converted to the respective adducts **23**. The cis isomer was identical (nmr) with the minor component derived from addition of H_2O to **22**.

Heating either isomer of **23** for 5 days at 100° in tetrachloroethane in sealed nmr tubes showed no isomer interconversion.

1-*tert*-Butyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide HBr adduct.—Into 5 g of **4a** in 25 ml of dry benzene, a slow stream of HBr gas was bubbled. The solvent was evaporated to give 6.7 g of white solid, mp 158–166°. The product was sublimed (80°, 0.1 mm) and recrystallized twice from dry acetonitrile. The infrared spectrum (Nujol mull) showed absorption at 2700–1800 (broad), 960, 810, 755, and 680 cm^{-1}. The nmr spectrum ($CDCl_3$) exhibited peaks at τ −2.38 (s, 1 H), 7.36–7.87 (m, 1 H), 8.41 (d, 9 H, J_{PCCH} = 15.5 Hz), 8.42 (d, 6 H, J_{PCCH} = 19 H*), 8.47 (d, 6 H, J_{PCCH} = 17 H*), 8.92 (dd, 3 H, J_{HCCH} = 7 H*, J_{PCCCH} = 1.5 H*). The ^{31}P shift (in $CDCl_3$) for **4a** was −72 ppm and the HBr adduct, −103 ppm.

Anal. Calcd for $C_{12}H_{26}OBrP$: C, 48.49; H, 8.82; Br, 26.89; P, 10.42. Found: C, 48.58; H, 8.93; Br, 27.11; P, 10.31.

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Registry No.—**1a**, 40084-63-7; *cis*-**1b**, 40084-64-8; *trans*-**1b**, 40084-65-9; *cis*-**1c**, 35616-95-6; *trans*-**1c**, 35616-97-8; **4a**, 35624-08-9; **4b**, 35624-09-0; **5**, 40085-35-6; **5** cis isomer, 22434-52-2; **5** methiodide, 26339-55-9; **6a**, 39990-53-9; **6b**, 39990-54-0; **6** phosphorane form, 39981-51-6; **7a**, 40084-68-2; **7b**, 40084-69-3; **10a**, 39990-55-1; **10b**, 39990-56-2; **10** phosphorane form, 39981-52-7; **11a**, 39990-57-3; **11b**, 39990-58-4; **11** phosphorane form, 39981-53-9; *cis*-**12**, 25145-23-7; *trans*-**12**, 25145-24-8; *cis*-**16**, 39990-60-8; *trans*-**16**, 39990-63-1; **16** phosphorane form, 20699-83-6; *cis*-**16** $AlCl_4$ derivative, 40084-70-6; *trans*-**16** oxide, 35623-32-6; **17**, 30092-42-3; **17a**, 30092-44-5; **17b**, 39981-57-2; **18**, 36044-91-4; **19**, 39981-59-4; **20**, 39981-60-7; **21**, 39981-61-8; **22**, 39990-66-4; **22** phosphorane form, 39981-62-9; *cis*-**23**, 39990-67-5; *trans*-**23**, 39990-68-6; **24**, 39981-63-0; phenyl phosphonous dichloride, 644-97-3; *cis*-1,2,2,3,4,4-hexamethylphosphetane, 35622-00-5; *trans*-1,2,2,3,4,4-hexamethylphosphetane, 35621-97-7; *cis*-1-phenyl-2,2,3,4,4-pentamethylphosphetane, 22434-51-1; *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane, 16083-95-7; 1-*tert*-butyl-2,2,3,4,4-pentamethylphosphetane 1-oxide HBr adduct, charged form, 40088-36-6; 1-*tert*-butyl-2,2,3,-4,4-pentamethylphosphetane 1-oxide HBr adduct, neutral form, 9981-10-0.

Stable Carbocations. CLI.[1] Protonation of Cyclic Carboxylic Acid Anhydrides in FSO_3H–SbF_5 ("Magic Acid")–SO_2 Solution

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Protonation of a series of cyclic carboxylic acid anhydrides (1–16) in SO_2 solutions containing varying amounts of 1:1 mol/mol FSO_3H–SbF_5 was studied by nmr spectroscopy. O-Protonated cyclic carboxylic acid anhydrides formed undergo rapid intermolecular hydrogen exchange with the acid solvent system or excess anhydride, even at the lowest accessible temperatures. Unsaturated cyclic carboxylic acid anhydrides (1–3), as well as cyclic aromatic carboxylic acid anhydrides (4–10), were not cleaved in magic acid solution up to 0°, in sharp contrast to the behavior of acyclic saturated cyclic carboxylic acid anhydrides.

Protonation of acyclic carboxylic acid anhydrides in superacids has been studied in our preceding work.[2] A preliminary study of protonation of cyclic anhydrides, including succinic and glutaric anhydrides, was also carried out in FSO_3H–SbF_5–SO_2 solution.[3,4] Protonated cyclic anhydrides such as succinic and glutaric anhydrides could not be observed even when the solutions were prepared and examined at $-80°$, as they were cleaved in "magic acid" giving the corresponding alkyleneoxocarbenium–carboxonium ions, $^+OC(CH_2)_n$-$COOH_2^+$ (n = 2 and 3, respectively).[5] On the other hand, succinic anhydride was reported to be only partially protonated in sulfuric acid.[6]

In continuation of our studies, we presently wish to report the results of protonation of a series of cyclic (both aliphatic and aromatic) carboxylic acid anhydrides (**1–16**) in SO_2 solutions containing varying amounts of 1:1 mol/mol FSO_3H–SbF_5.

Results and Discussion

The chemical behavior of cyclic carboxylic acid anhydrides in FSO_3H–SbF_5–SO_2 is different from that of acyclic anhydrides. In particular cyclic aromatic anhydrides **4–10** are not cleaved even with large excess of FSO_3H in SO_2 solution at 0°. They are protonated in the superacid and undergo rapid intermolecular hydrogen exchange with the solvent system. Intramolecular hydrogen exchange seems to be less feasible since the position of the two carbonyl groups are rigidly fixed and consequently their distance is too large. Intermolecular hydrogen exchange processes must be extremely rapid, since static mono- or diprotonated cyclic anhydrides were not observed even at the lowest possible temperature (*ca.* $-90°$) under the experimental conditions. Consequently, the proton chemical shifts of protonated cyclic anhydrides are dependent upon the concentration of both substrate and superacid used. Pmr parameters of cyclic carboxylic acid anhydrides protonated in SO_2 solutions containing varying amounts of magic acid and their precursors (in SO_2) are summarized in Table I (also showing the proportions of superacid and anhydride in the system).

Unsaturated cyclic carboxylic acid anhydrides including maleic (**1**), dimethylmaleic (**2**), and 3,4,5,6-tetrahydrophthalic anhydride (**3**) show similar behavior in FSO_3H–SbF_2–SO_2 solutions. When **maleic anhydride** (**1**) was protonated with 0.5 equimolar magic acid in SO_2 solution, the pmr absorption of the two vinylic protons was deshielded from δ 6.83 (s) to 7.21 (s). A very deshielded pmr singlet absorption ($\sim$0.5 proton intensity) is found at δ 14.5 and is assigned to the OH proton of protonated maleic anhydride, which undergoes intermolecular hydrogen exchange with **1**. The pmr singlet absorption of the two vinylic protons in protonated maleic anhydride **1a** was further deshielded at δ 7.63 when equimolar magic acid was used. The OH proton was slightly shielded to δ 13.5. These data suggest that another intermolecular H exchange process may occur (eq 1). When **1** was treated with a large excess of 1:1 mol/mol FSO_3H–SbF_5 in SO_2 or with neat magic acid solution, the pmr spectra of the resulting solution showed two more deshielded singlets at δ 8.09 and 8.30, respectively. The OH proton is not observed

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