-7.6 ($J_{HF\text{-}gem}$), $+17.7$ ($J_{HF\text{-}cis}$), and $+5.4$ ($J_{HF\text{-}trans}$) Hz were calculated. An equally good fit of the spectra was found if all signs were negative, but not for $-, +, -$ or $-, -, +$. As indicated above[26] we favor the $-, +, +$ combination of signs.[46]

Anal. Calcd for $C_{15}H_{12}ClF$: C, 73.03; H, 4.90. Found: C, 72.89; H, 5.10.

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[46] S. Terabe and W. Funasaka have independently arrived at the same conclusion regarding this compound (private communication from S. Terabe).

Acknowledgments. The hospitality of Cornell University during the tenure of a visiting professorship is gratefully acknowledged. We wish to thank the Cornell and University of Massachusetts Computation Centers for the use of CDC 1604 and 3600 computers and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Public Health Service (Grant GM 10224) for financial support.

Pseudorotation in Trigonal-Bipyramidal Molecules

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Abstract: A systematic geometrical analysis of isomerizations of trigonal-bipyramidal molecules by pseudorotation is presented. The consequences of introducing several types of constraints upon the processes are discussed.

Isomerization about 5-coordinated atoms has been discussed by a number of workers.[1-5a] In particular, Berry[5] and Muetterties[1] have called attention to the existence of an intramolecular bond-bending process which can result in positional exchange of the groups attached to a 5-coordinated atom such as phosphorus. This process has been called "pseudorotation"[5] or "polyhedral rearrangement."[1] The recent literature contains several examples of isomerizations in the halophosphoranes,[1,2] the arylphosphoranes,[6] and the oxyphosphoranes.[7-9]

We present here a systematic geometrical analysis of isomerizations by pseudorotation in trigonal bipyramidal molecules which provides a useful classification and permits straightforward analyses of the consequences of various constraints upon the process. We identify some specific cases in which stereomutations and racemizations of certain phosphoranes by pseudorotation may be inhibited or altogether prevented.

Notation and Derivation of Isomers

A phosphorane derivative with five different but symmetrical substituents may be labeled as shown in formula a of Figure 1.

The bonds terminated by substituents 1 and 2 will be called *apical;* those by substituents 3, 4, 5, *equatorial.* Our notation will describe this isomer as (1,2)(3,4,5). The first parentheses contain the apical substituents in numerical order. The second parentheses contain the equatorial substituents in a clockwise order, starting with the smallest number, as viewed from the side of the bipyramid that has the lower numbered apical substituent. A process geometrically equivalent to pseudorotation[1,5] is carried out as follows (the actual process is, of course, a *concerted* one).

The bipyramid a is grasped by the "pivot" group 3, and the apical groups 1 and 2 are pushed back to close the angle $<$1P2 from 180 to 120°; this gives a *tetragonal pyramid* with substituents 1, 2, 4, and 5 in the same square plane. The groups 4 and 5 are now pulled forward to open the angle $<$4P5 from 120 to 180°; this gives a new trigonal bipyramid which will be denoted as (4,5)(1,3,2) and identified by the symbol $\bar{j}$, as defined below. This type of pseudorotation will be called an "E process" (to distinguish it from other less probable ones) and symbolized by

$$(1,2)(3,4,5) \xrightarrow{E_3} (4,5)(1,3,2)$$

or a(3)$\bar{j}$. The subscript in E_3, or the parentheses in the shorter notation, refers to the substituent formally undisturbed during the isomerization, *i.e.*, to the "pivot." The pseudorotation moves *two* equatorial groups into apical positions.

There are ten different trigonal bipyramids corresponding to formula P(1.2.3.4.5); these will be designated by the letters a, b, ...j. Each of these structures has an enantiomer $\bar{a}$, $\bar{b}$, ...$\bar{j}$. The notations for these 20 stereoisomers are given in Table I.

Since the trigonal bipyramid has three equatorial substituents, there will be three possible "E isomerizations." These processes, applied to isomer a, are shown in Figure 2. The corresponding notations

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[1] (a) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[2] R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

[3] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

[4] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965.

[5] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

[5a] Note Added in Proof. For recent important contributions to this subject see: E. L. Muetterties *J. Am. Chem. Soc.*, **90**, 5097 (1968); R. R. Holmes and R. M. Deiters, *ibid.*, **90**, 5021 (1968).

[6] (a) G. Wittig, *Bull. Soc. Chim. France*, 1162 (1966); (b) D. Hellwinkel, *Chem. Ber.*, **99**, 3668 (1966).

[7] (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, **90**, 1275 (1968); (c) F. Ramirez, *Trans. N. Y. Acad. Sci.*, **30**, 410 (1968).

[8] (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) D. G. Gorenstein and F. H. Westheimer, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1747 (1967).

[9] M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. Chim. France*, 773 (1968).

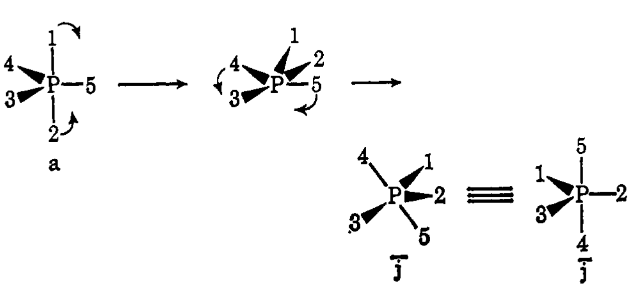


Figure 1.

(other than the one already given) are

$$(1,2)(3,4,5) \xrightarrow{E_4} (3,5)(1,2,4)$$

or a(4)i

$$(1,2)(3,4,5) \xrightarrow{E_5} (3,4)(1,5,2)$$

or a(5)$\bar{h}$.

Each of the new bipyramids, $\bar{j}$, i, and $\bar{h}$, still has two equatorial substituents *which have not been involved as pivots in pseudorotation.* Therefore, two additional "E isomerizations" can occur in each isomer, to produce a total of six new isomers. These pseudorotations are shown in Figure 3. The symbols for the new isomers are obtained from Table I.

Table I

a	(1,2)(3,4,5)	$\bar{a}$	(1,2)(3,5,4)
b	(1,3)(2,4,5)	$\bar{b}$	(1,3)(2,5,4)
c	(1,4)(2,3,5)	$\bar{c}$	(1,4)(2,5,3)
d	(1,5)(2,3,4)	$\bar{d}$	(1,5)(2,4,3)
e	(2,3)(1,4,5)	$\bar{e}$	(2,3)(1,5,4)
f	(2,4)(1,3,5)	$\bar{f}$	(2,4)(1,5,3)
g	(2,5)(1,3,4)	$\bar{g}$	(2,5)(1,4,3)
h	(3,4)(1,2,5)	$\bar{h}$	(3,4)(1,5,2)
i	(3,5)(1,2,4)	$\bar{i}$	(3,5)(1,4,2)
j	(4,5)(1,2,3)	$\bar{j}$	(4,5)(1,3,2)

Each of the new six isomers shown in Figure 3 has two equatorial substituents which have not been used as pivots *in a given sequence.* However, now only some of the pseudorotations give new isomers, while others result in isomers already derived. This situation is clearly depicted in Table II; the new isomers are d, $\bar{c}$, $\bar{g}$, f, b, and e. The structure of these isomers can be easily derived by reference to Table I.

One can still perform pseudorotations on the isomers shown in Table II, beginning with d, $\bar{c}$, etc., *without utilizing twice the same substituent as pivot within a given pseudorotation sequence.* For example, the equatorial substituent 2 in isomers d and $\bar{c}$ (see Table II) has not been used as pivot in the corresponding sequence; when this substituent is used the new isomers h and $\bar{i}$ are obtained. Likewise, the process b(2)j gives a new isomer, the 19th new structure. Other such pseudorotations simply lead to isomers identical with those already derived.

A final pseudorotation is possible without repeated use of a given substituent as pivot within a given sequence; this leads to the 20th isomer, a, the enantiomer of the original structure, a, selected for the particular set of pseudorotations illustrated in Table II. *Note that racemization of a can be achieved by five consecutive pseudorotations using different substituents as pivots,* and that there are, in this set, twelve different ways of racemizing a. One of these pathways can be represented by the notation a(3)$\bar{j}$(1)e(4)d(2)h(5)$\bar{a}$.

Simple inspection of Tables I and II reveals some important consequences resulting from the introduction

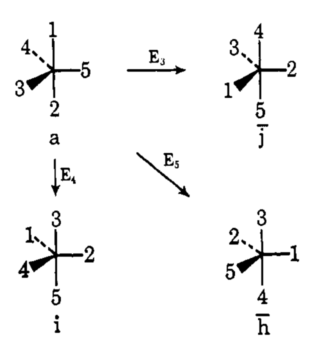


Figure 2.

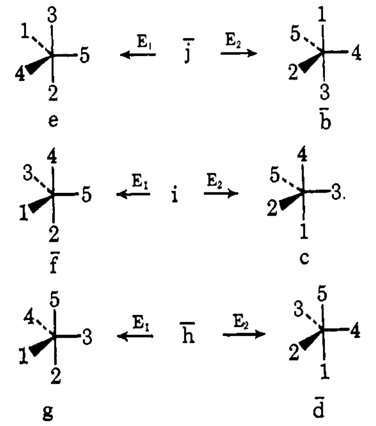
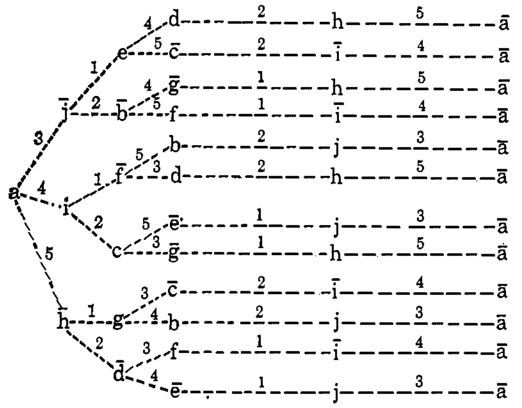


Figure 3.

Table II. Pathways for Isomerization of One of the Twenty Trigonal Bypyramids Having Substituents 1, 2, 3, 4, and 5 Attached to Phosphorus[a]



[a] The substituent used as pivot in each pseudorotation is indicated on dotted line. The ∠2P5 is 90° in a, $\bar{a}$; d, $\bar{d}$; e, $\bar{e}$; f, $\bar{f}$; i, $\bar{i}$; and j, $\bar{j}$. This angle is 120° in b, $\bar{b}$; c, $\bar{c}$; and h, $\bar{h}$. This angle is 180° in g, $\bar{g}$.

I, R = H
III, R = CH$_3$

II, R = H
IV, R = CH$_3$

Figure 4.

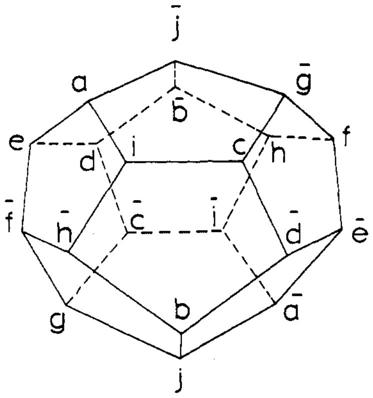


Figure 5.

of small rings into the trigonal bipyramid. Table I gives the notations which permit the construction of the 20 isomers. Table II gives a limited set of pseudorotation pathways. It can be seen, with reference to Figure 2, that the presence of a four-membered ring joining substituents 2 and 5 of a prevents the isomerization a(5)$\bar{h}$, because this requires the expansion of the $<$2P5 from 90° in a to 120° in $\bar{h}$. The ring does not prevent isomerizations a(3)$\bar{j}$ and a(4)i.

Another example is illustrated in Figure 4. When a four-membered ring is joining substituents 2 and 5, as in structure I, the $<$2P5 of a must be expanded to 120° in b, $\bar{b}$; c, $\bar{c}$; h and $\bar{h}$. It is, therefore, impossible to arrive at the enantiomer $\bar{a}$ by any path of Table II which requires the formation of any one of these isomers. Moreover, the $<$2P5 would have to be expanded to 180° in isomer g. Therefore, none of these pathways can achieve the conversion of I into its *enantiomer* II. Note that the same is true for the conversion of isomer III, having a *trans* relationship of substituents 3 and R, to diastereomer IV, having a *cis* relationship of 3 and R; *i.e., this stereomutation is not possible by these pseudorotation pathways.*[10]

General Geometrical Representation of Pseudorotation Pathways. The 20 isomers of the trigonal bipyramid may be represented by the 20 vertices of a regular pentagonal dodecahedron, as shown in Figure 5. Isomerizations may be represented by 30 connections between these vertices; each connection corresponds approximately to a square pyramidal form.

The particular assignment of the isomers to vertices shown in Figure 5 was designed to give a set of connections all lying along edges or within the faces of the dodecahedron. The edges in Figure 5 do *not* all represent possible interconversions. The shortest closed cycle of isomerizations includes six isomers, and it is therefore impossible to map the pathways in any very simple way along the edges of the pentagonal faces.

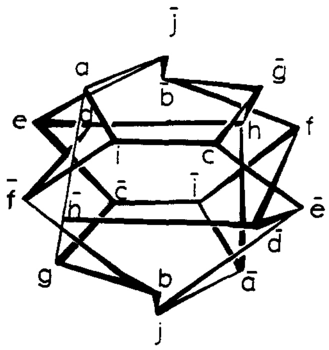


Figure 6.

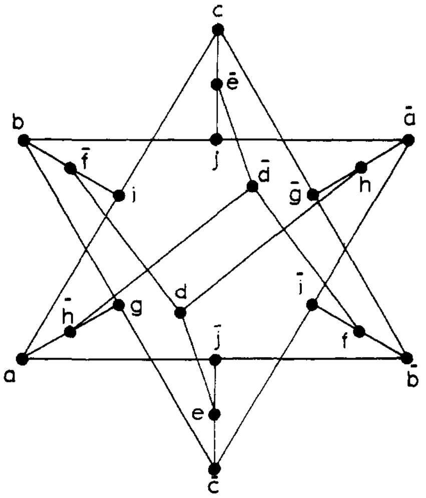


Figure 7.

An isomerization diagram for trigonal bipyramids undergoing *unrestricted type E processes* based on the assignments of Figure 5 is shown in Figure 6. Note that each vertex is connected to three others, and each connection represents a reversible process. The minimum number of isomers framing a closed path is six, as noted above, and all vertices are connected; *i.e.*, any isomer is accessible from any other by type E processes. Evidently, the simplified scheme given in Table I was constructed by omitting several connections, for example d(3)$\bar{f}$ and similar ones, and h(1)$\bar{g}$ and related ones. The omitted connections represented pseudorotations in which the *same substituent* was utilized more than once in a given sequence. Many representations based on the dodecahedron and equivalent to Figure 6 can be drawn. All are confusing and give ugly two-dimensional projections, although they have the merit of being based on a three-dimensional figure for which all 20 vertices are equivalent by symmetry (enantiomers are related by the center of symmetry). The possibility that a representation based on hexagonal symmetry might be useful is suggested by the occurrence of six-membered rings as pathways in Figure 6. This is indeed the case, and Figure 7 gives the projection of one of these hexagonal representations which maintains the center of symmetry. It can be visualized as a three-dimen-

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(10) Note Added in Proof. Stereoisomers at phosphorus, as in structures III and IV, have recently been synthesized; *cf.* F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Am. Chem. Soc.*, **90**, 6726 (1968).

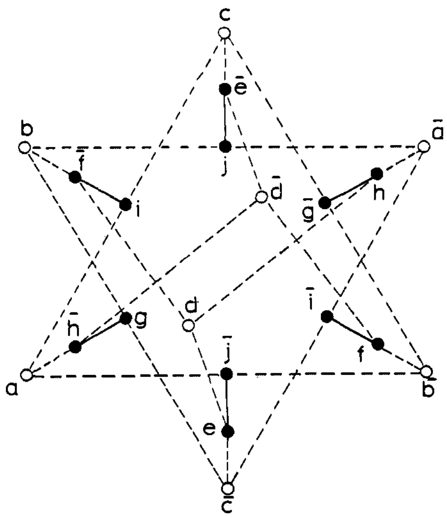

Figure 8.

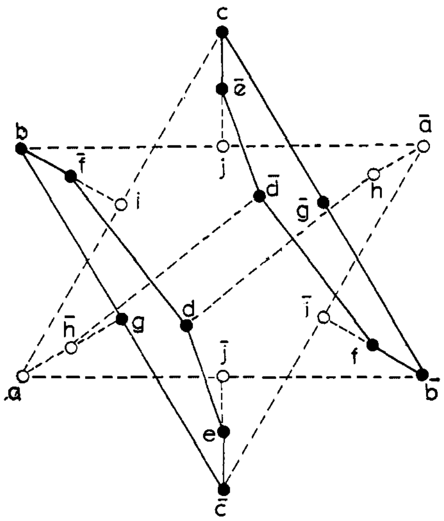

Figure 10.

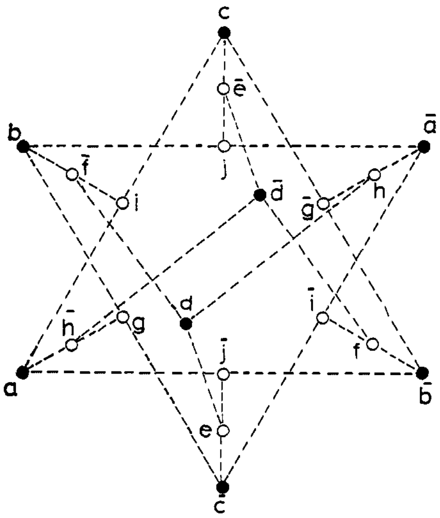

Figure 9.

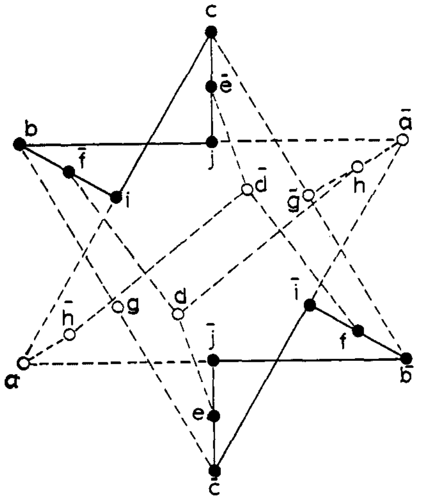

Figure 11.

sional figure by imagining $\bar{d}$ to be above the plane of the paper and in the center of the diagram, and d to be directly below it, and equal distance beneath the plane of the paper. *With the aid of Figure 7, one can easily deduce and display the subset of isomerizations generated by various restrictions which forbid the existence of certain isomers.* Several examples will now be given.

Example 1, Figure 8. Substituent 1 can be equatorial but not apical. Table I shows that isomers a, $\bar{a}$, b, $\bar{b}$, c, $\bar{c}$, d, $\bar{d}$ are precluded and the system becomes one in which only isolated pairs of isomers may interconvert, as shown by the solid lines between filled circles. In particular, *all racemizations are forbidden.*

Example 2, Figure 9. Substituent 1 can be apical but not equatorial. *Only* isomers a, $\bar{a}$, b, $\bar{b}$, c, $\bar{c}$, d, $\bar{d}$ are permitted, and *no isomerizations at all can occur.*

Example 3. Substituents 1 and 2 can not *both* be apical. This may result from the presence of a ring joining positions 1 and 2 and of such size as to be able to join groups occupying apical–equatorial and diequatorial but not diapical positions. Isomers a, $\bar{a}$ are forbidden but all others are allowed and may be interconverted.

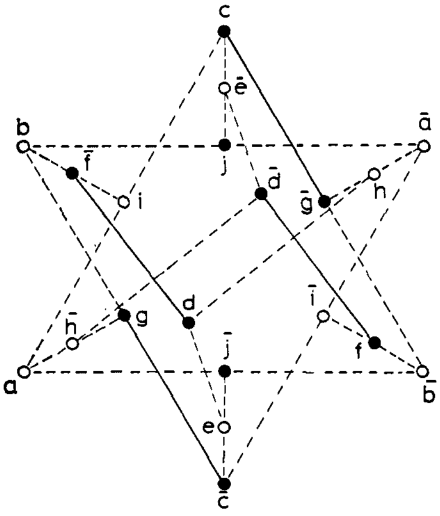

Figure 12.

Example 4. Neither 1 nor 2 can be apical. This may be the case if a ring joining these two positions can not accommodate angles of 90 or of 180°, but can accommodate a 120° angle. Only isomers h, $\bar{h}$, i, $\bar{i}$, j, $\bar{j}$ are permitted and all are isolated.

Example 5, Figure 10. Substituents 1 and 2 can not *both* be apical *or* equatorial. This is the case in which the substituents are in a four-membered ring where angles of 180 and 120° are excluded, but where a 90° angle is allowed.

Isomers a, $\bar{a}$, h, $\bar{h}$, i, $\bar{i}$, j, $\bar{j}$ are forbidden, and the remaining isomers form two distinct and unconnected sets. Interconversions are possible within each set, but *racemizations can not take place.* This case was already derived in an operational way in Table II and Figures 2, 3, and 4. It is desirable to provide examples of both types of approaches. The operational approach, although less rigorous than the geometrical one, lends itself to rapid analysis of particular situations.

Example 6. Substituents 1 and 2 can not both be apical, and 3 and 4 cannot both be apical. This is the case of certain spiro compounds in which rings of suitable size join those positions. Isomers a, $\bar{a}$, h, $\bar{h}$ are not allowed, but all other isomers may interconvert.

Example 7, Figure 11. Substituents 1 and 2 cannot both be apical, and 3 and 4 cannot both be apical *or* equatorial. This case is analogous to example 6, but the ring joining 3 and 4 in the spiro compound cannot accommodate a 120° angle. The allowed isomers are b, c, e, f, i, j and their enantiomers. Now, there are two independent sets of isomers but no racemizations.

Example 8. Conditions similar to example 7, except that 3 and 4 *must* both be equatorial. Only isomers d, $\bar{d}$, g, $\bar{g}$ are allowed and *no pseudorotations can occur.*

Example 9. Substituent 5 in the spiro compound of example 6 must always be apical. This is equivalent to the requirement that *both* rings of the spiro compound cannot include an apical substituent. Only isomers d, g, i, j, and their enantiomers may exist but none can isomerize to another.

Example 10, Figure 12. Substituents 1 and 2 are not both apical and 3 is always equatorial. There are now four pairs of interconverting isomers and two isolated enantiomers.

Four-Membered Cyclic Oxyphosphoranes. Isolation of Stereoisomers at Phosphorus and Conversion into Olefins and Phosphinate Esters

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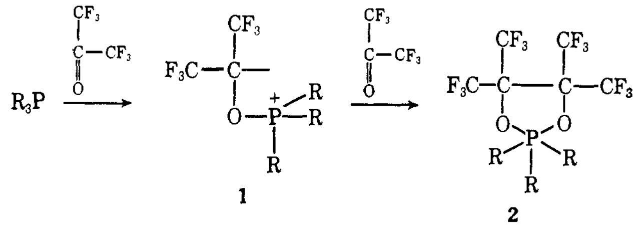
Received June 3, 1968

Abstract: The phosphorus of tertiary phosphines attacked the carbonyl oxygen of hexafluoroacetone. The 1:1 adducts reacted with more ketone and gave derivatives of the *2,2-dihydro-1,3,2-dioxaphospholane* ring system. The latter were quantitatively transformed into derivatives of the *2,2-dihydro-1,2-oxaphosphetane* ring system at approximately 80°. The phosphetanes had the four-membered ring in the apical–equatorial plane of a trigonal bipyramid and had the two oxygen atoms in apical positions. The ^{1}H nmr spectra did not vary in the range -70 to $+30°$. The phosphetane from $(C_2H_5)_2PC_6H_5$ was obtained as two diastereomers at phosphorus; stereomutation was observed under certain conditions. The oxaphosphetanes underwent decomposition to olefins and phosphinate esters at *ca.* 120°.

Tertiary phosphines, R_3P, reacted with hexafluoroacetone at approximately $-70°$ and gave derivatives of the *1,3,2-dioxaphospholane* ring system (**2**) having pentavalent phosphorus.[2] It was suggested that the phospholanes **2** were formed from intermediate 1:1 adducts (**1**), resulting from the addition of trivalent phosphorus to carbonyl oxygen.[2] This demonstrated the similarity of the reactions of tertiary phosphines, triaminophosphines, $(R_2N)_3P$, and trialkyl phosphites, $(RO)_3P$, with carbonyl functions which were activated by electron-withdrawing groups.[3]



This paper describes a new type of rearrangement of the five-membered cyclic oxyphosphoranes **2** into four-membered cyclic oxyphosphoranes, and the pyrolysis of the latter to olefins and phosphinate esters.

Results and Discussion

Rearrangement of Five-Membered Cyclic into Four-Membered Cyclic Oxyphosphoranes. The *1,3,2-dioxaphospholane*[2] **3**, made from hexafluoroacetone and trimethylphosphine, was converted into the *1,2-oxaphosphetane* **4** in benzene solution at 80°. In this rearrangement, a C–C bond was broken, a new C–C

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[1] John Simon Guggenheim Fellow, 1968. This work was supported by grants from the Public Health Service (CA-04769), the National Science Foundation (GP-6690), and the Petroleum Research Fund of the American Chemical Society (3082).

[2] F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, 33, 3787 (1968).

[3] F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968).