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

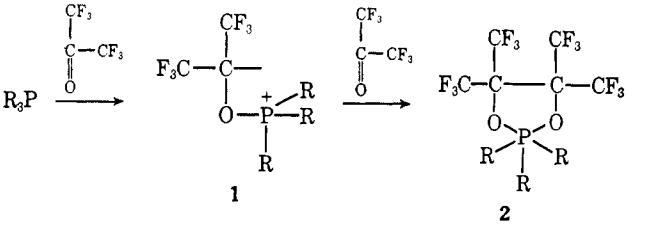
Fausto Ramirez,[1] C. P. Smith, and J. F. Pilot

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. *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 ^1H 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.



1 **2**

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

(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).

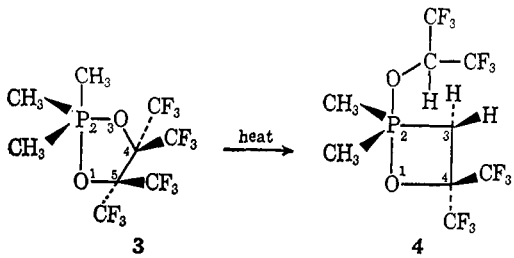
(3) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968).

Table I. Elemental Analyses and Main Infrared Bands[a] of 2,2-Dihydro-1,2-oxaphosphetane Derivatives Made from Tertiary Phosphines and Hexafluoroacetone

No.	—(X₂Y)P— X	Y	Bp (mm) or mp, °C	Mol formula	Calcd, % C	H	F	Found, % C	H	F	Ir bands,[a] μ
4	CH_3	CH_3	45[b]	$C_9H_9O_2F_{12}P$[c]	26.5	2.2	35.8	26.3	2.1	35.5	7.35, 7.48, 7.62, 7.75, 8.20, 8.35, 8.75, 9.05, 10.38
6	C_2H_5	C_2H_5	51–52 (0.1)	$C_{12}H_{15}O_2F_{12}P$[d]	32.0	3.3	50.7	32.2	3.4	50.8	6.85, 7.35, 7.85, 8.20, 8.36, 8.60, 8.90, 9.05, 10.60, 11.45
8-I **8-II**	C_2H_5	C_6H_5	74–76[e] (0.05)	$C_{16}H_{15}O_2F_{12}P$	38.6	3.0		38.7	3.0		6.90, 7.37, 7.48, 7.72, 8.25–8.45, 8.90, 9.15, 9.90, 10.68, 11.50
10	C_6H_5	C_2H_5	70[f]	$C_{20}H_{15}O_2F_{12}P$	44.0	2.8	41.8	44.1	2.7	41.6	6.95, 7.30, 7.48, 7.73, 8.25, 8.40, 8.82, 8.95, 9.10, 9.88, 10.65, 11.45

[a] In CH_2Cl_2 solution. [b] From hexane. Can be sublimed unchanged at *ca.* 60° (0.1 mm). [c] *Anal.* Calcd for $C_9H_9O_2F_{12}P$: P, 7.6; mol wt, 408. Found: P, 7.0; mol wt, 463, thermoelectric method in benzene. All the oxaphosphetanes were very sensitive to moisture. [d] *Anal.* Calcd for $C_{12}H_{15}O_2F_{12}P$: P, 6.9. Found: P, 7.0. [e] The *distilled* analytical sample was a mixture of two diastereomers, **8**-I ($\delta^{31}P$ +30.3 ppm) and **8**-II ($\delta^{31}P$ +21.7 ppm) in the proportion 1:1.5. [f] From hexane.

bond was formed, and a hydrogen atom was transferred from one carbon to another.



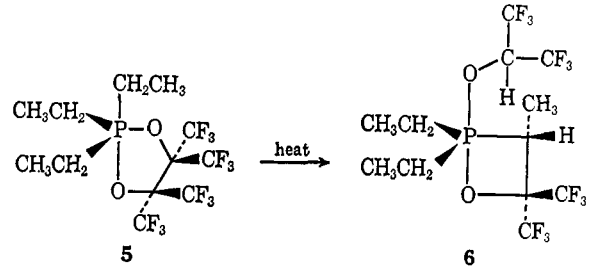
3 **4**

The phosphetane **4** is drawn with the phosphorus at the center of a trigonal bipyramid, and the ring in an apical–equatorial plane, from previous data on other oxyphosphoranes.[3] Structure **4** is one of four possible diastereomers, two of them are *meso* forms and two are *racemic* forms. The data of Table I showed that the elemental composition did not change during the conversion of **3** into **4**. The ^{31}P nmr data of Table II disclosed that the shift was displaced 27 ppm toward *higher magnetic field* as a result of the transformation **3** → **4**. This is strong evidence in favor of the oxaphosphetane structure with pentavalent phosphorus,[3] **4**. The ^{19}F nmr spectrum had a singlet due to the CF_3 groups on the ring, and a doublet due to the CF_3 groups on the alkoxy carbon (F–C–C–H coupling).

The ^1H nmr spectrum at −62° in $CDCl_3$ had a 1 H doublet, J_{HP} = 9.7 cps, of septets, J_{HF} = 5.5 cps, at τ 5.73 ppm (from TMS = 10), due to the alkoxy group. There was a 2 H doublet, J_{HP} = 20.7 cps, at τ 5.96, from the ring protons, and a 6 H doublet, J_{HP} = 15.0 cps, at τ 8.01, from the two methyls on phosphorus. The spectrum did not change significantly at +30°. The spectrum was similar at +30, +65, and +79° in *o*-dichlorobenzene. Irreversible changes occurred above 100°. *These data, taken together with other data presented below, suggested that there was no positional exchange of the groups attached to the phosphorus in the oxaphosphetane, i.e., that the trigonal bipyramid* **4** *was frozen in the time scale of the nmr phenomenon, in the entire temperature range.*[4] On the other hand, the three methyl groups of the phospholane **3** gave one doublet, J_{HP} = 9.4 cps, at τ 8.32, in solution in the range −62 to +80°. In that case[2] the data were compatible only with a rapid positional exchange of the groups attached to the phosphorus, in the same temperature range, since apical and equatorial methyl groups should have different absorptions, as has been demonstrated in other systems (*vide infra*).

It was possible to follow the conversion of the phospholane **3** into the phosphetane **4** in *o*-dichlorobenzene by ^1H nmr spectrometry. At about +80°, the signals of **3** began to be replaced by those of **4**, and at 93°, *ca.* 45% of **4** had formed. At +108°, no **3** was left, 95% of **4** was produced but new signals began to appear. The new signals were due to the thermal decomposition of the phosphetane **4** by a process which will be described in the next section.

The 1,3,2-dioxaphospholane[2] **5**, made from triethylphosphine, was significantly less stable than the methyl analog **3**. In fact, **5** was completely transformed into the phosphetane **6** within 48 hr at +30° in $CDCl_3$, and within 5 min at +80° in benzene (*cf.* Tables I and II).



5 **6**

As expected of structure **6**, *the two CF_3 groups on the ring were no longer equivalent;* each gave a quartet, and one of these showed additional splitting which was attributed to a long-range coupling of the fluorines with the hydrogen on the ring. The two CF_3 groups on the alkoxy groups were not equivalent either, but their signals were very close to each other.

The most interesting situation was encountered during the rearrangement of the phospholane[2] **7** made from diethylphenylphosphine. *This reaction gave two diastereomeric oxaphosphetanes in unequal proportion.*

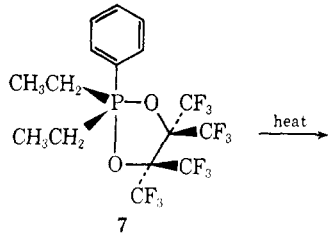
(4) (a) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966), and references therein.

Table II. ^{31}P and ^{19}F Nmr Signals[a] of Tertiary Phosphines and of Derivatives of 2,2-Dihydro-1,3,2-dioxaphospholanes and 2,2-Dihydro-1,2-oxaphosphetanes Made from the Phosphines and Hexafluoroacetone

Oxaphosphetane no.	(X₂Y)P X	Y	δ³¹P of (X₂Y)P	δ³¹P of phospholane	δ¹⁹F of phospholane	δ³¹P of phosphetane	δ¹⁹F of phosphetane[b] A	A′	B	B′	J values of phosphetane $J_{FF}^{AA'}$	$J_{FF}^{BB'}$	J_{FH}^{A}	J_{FH}^{B}
3, 4	CH_3	CH_3	+62.0	−3.2	−9.3	+23.7	+0.4	None	−3.9	None	None	None	*c*	5.5
5, 6	C_2H_5	C_2H_5	+19.1	−11.7		+15.7	−0.9	−5.3	−4.2	−4.0	10.2	7.2	2.3	7.2[d]
7, 8-I						+30.3[e]	−0.3	−6.0	−4.4	−3.7	9.6	8.5	2	5
	C_2H_5	C_6H_5	+17.0	−1.1	−9.8									
7, 8-II						+21.0[e]	−1.4	−5.2	−3.7	−3.4	9.6	*f*	*f*	*f*
9, 10	C_6H_5	C_2H_5	+12.1	+4.0	−10.4	+32.1	−2.0	−7.4	−5.0	−4.2	10.8	9.1	3.0	6

[a] $\delta^{31}P$ in parts per million *vs.* H_3PO_4 as 0, at 40.5 Mcps, 25°, in CH_2Cl_2. $\delta^{19}F$ in parts per million *vs.* CF_3COOH as 0, at 94.1 Mcps, at 25°, in $CDCl_3$. *J* in cycles per second. [b] A = fluorines of CF_3 on C_4 of ring, *cis* to CH_3 on C_3 of ring, when applicable. A′ = fluorines of CF_3 on C_4 of ring, *trans* to CH_3 on C_3 of ring, when applicable. B and B′ = fluorines on $(CF_3)_2CHO$. [c] No F(A)–H coupling observed. No (F(A′)–H coupling observed in any case. [d] The F(B′)–H couplings were very close to the F(B)–H couplings and are omitted. [e] Two stereomers at P; isomer **8**-I assumed to have *trans*-C_2H_5/CH_3; isomer **8**-II assumed to have *cis*-C_2H_5/CH_3. [f] Could not be resolved.

The isomer that was initially formed in higher amounts and that had the ^{31}P nmr shift at the higher magnetic field was tentatively assigned configuration **8**-I (*trans*-C_2H_5/CH_3). The other isomer, **8**-II, was assigned the *cis*-C_2H_5/CH_3 configuration. The ^{19}F signals due to the two CF_3 groups on C-4 of the major isomer **8**-I were at −6.0 and −0.3 ppm *vs.* CF_3COOH, while the corresponding signals of the minor isomer **8**-II were at −5.2 and −1.4 ppm. Note that the front CF_3 group in **8**-I is *cis* to both H and C_2H_5, while the front CF_3 group in **8**-II is *cis* to both H and phenyl. We assume, therefore, that phenyl shielding is responsible for the displacement of −6.0 to −5.2. Likewise, note that the back CF_3 group in **8**-I is *cis* to both CH_3 and phenyl, while the back CF_3 group in **8**-II is *cis* to both CH_3 and C_2H_5. Again, we assume that phenyl shielding is responsible for the difference in these signals (−0.3 in **8**-I and −1.4 in **8**-II.



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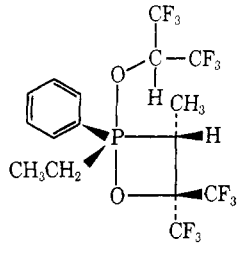
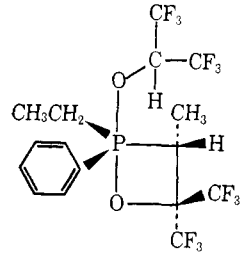


8-I, *trans*-C_2H_5/CH_3

+

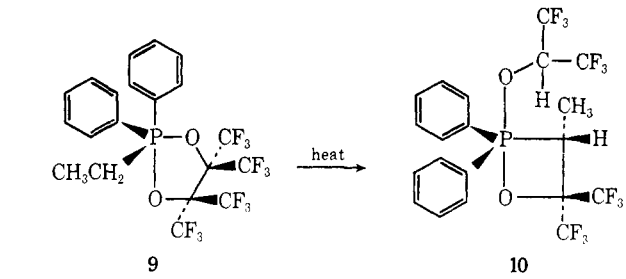


8-II, *cis*-C_2H_5/CH_3

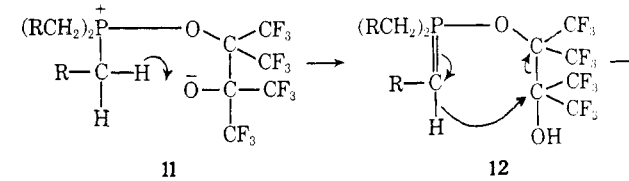
The proportion of isomers **8**-I and **8**-II, determined by ^{31}P nmr spectrometry, varied with the history of the sample due to stereomutation of the isomers. This important point will be discussed below.

As expected, only one oxaphosphetane, **10**, was obtained in the rearrangement of the phospholane[2] **9** made from ethyldiphenylphosphine (*cf.* Tables I and II).

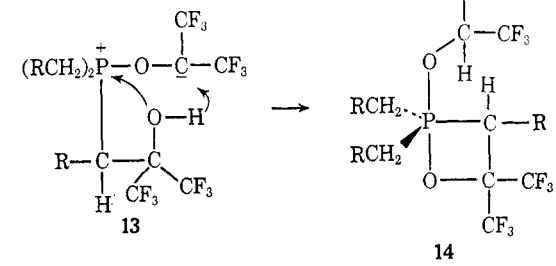
The data of Table III showed that the dioxaphospholanes derived from various phosphines rearranged to the oxaphosphetanes in the decreasing order $(C_2H_5)_3P \backsim (C_2H_5)_2PC_6H_5 > C_2H_5P(C_6H_5)_2 > (CH_3)_3P$. A possible mechanism for the rearrangement involves the rupture of a ring P–O to give **11**, which then undergoes proton transfer to the ylide **12**. An intramolecular step **12** → **13**, followed by another proton transfer and recyclization, leads to the oxaphosphetane **14**.



9 **10**



11 **12**



13 **14**

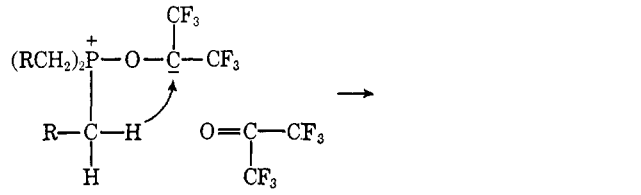
In this picture, the gaseous hexafluoroacetone is not liberated at any stage of the rearrangement, which is consistent with the facts. An alternate mechanism assumes rupture of a C–C bond in the original intermediate **11** to give **15**, and then the ylide **16** and the final product **14**. Intermediate **15** is simply the 1:1 adduct **1** from phosphine and hexafluoroacetone. Although the reactions were carried out in an open system and hexafluoroacetone was not lost, the available evidence does not distinguish between these alternatives. It should be emphasized that the reactions of phosphines with certain perfluoro ketones may simply produce the 1:1 adducts analogous to **15** which then proceed directly to the oxaphosphetane by

Table III. Rearrangement of 2,2-Dihydro-1,3,2-dioxaphospholane Derivatives into 2,2-Dihydro-1,2-oxaphosphetane Derivatives in Benzene Solution[a] at 80°

No.	(X₂Y)P[b] X	Y	% after 0.5 hr Phospholane	% after 0.5 hr Phosphetane	After 1 hr Phospholane	After 1 hr Phosphetane	% after other times Phospholane	% after other times Phosphetane
3, 4	CH_3	CH_3	50	50	26	74	2	98[c]
5, 6	C_2H_5	C_2H_5[d]	0	100	0	100		
8-I				71[f]		73[g]		67[h]
	C_2H_5	C_6H_5[d,e]	0		0		0	
8-II				29		27		33
9, 10	C_6H_5	C_2H_5	0	91	0	100	0	100[i]

[a] The 0.5 *M* solution was kept at reflux as specified. The solvent was removed under vacuum. The residue was analyzed by ^{31}P nmr in CH_2Cl_2 solution. [b] Parent phosphine from which the phosphoranes were made. [c] After 3 hr at reflux; the product was analyzed also by ^1H nmr. [d] No phospholane left, 100% phosphetane formed, after 5 min at 80°. [e] The isomeric phosphetanes **8-I** and **8-II** were formed in the proportion 3.1:1 within 5 min. [f] Isomers I:II as 2.5:1. [g] Isomers I:II as 2.7:1. [h] After 25 hr at reflux; isomers I:II as 2.0:1. [i] After 24 hr at reflux.

mechanism **15** → **16** without the formation of a 1,3,2-dioxaphospholane at all.



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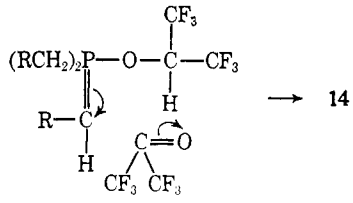
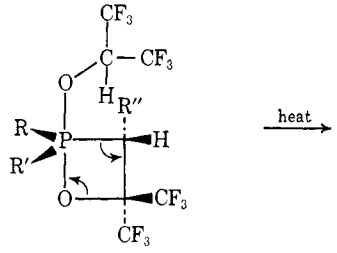
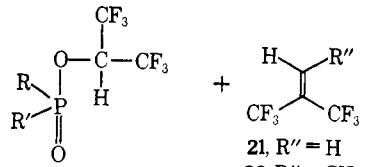


16

Pyrolysis of Four-Membered Cyclic Oxyphosphoranes to Olefins and Phosphinate Esters. The oxaphosphetane **4**, derived from trimethylphosphine, was converted into 1,1-bis(trifluoromethyl)ethylene[5] (**21**) and bis(trifluoromethyl)methyl dimethylphosphinate (**17**) within 8 hr at 120°. Other conditions used to effect this pyrolysis are summarized in Table IV.



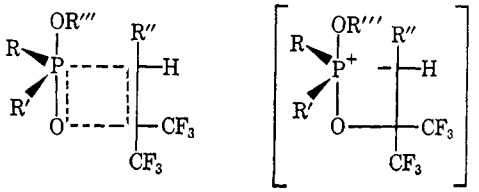
4, R = R′ = CH_3; R″ = H
6, R = R′ = C_2H_5; R″ = CH_3
8-I, R = C_6H_5; R′ = C_2H_5; R″ = CH_3
8-II, R = C_2H_5; R′ = C_6H_5; R″ = CH_3
10, R = R′ = C_6H_5; R″ = CH_3



17, R = R′ = CH_3
18, R = R′ = C_2H_5
19, R = C_6H_5; R′ = C_2H_5
20, R = R′ = C_6H_5

The oxaphosphetanes **6**, **8-I**, **8-II**, and **10** derived from other phosphines underwent analogous pyrolyses, as shown in Table IV. The properties of the resulting olefins, **21** and **22**, and of the phosphinate esters,[6] **17–20** are listed in Table V. With these data, it was possible to follow the course of the decomposition of the oxaphosphetanes in *o*-dichlorobenzene by means of ^1H nmr spectrometry. In fact, the sequence of steps which led from the dioxaphospholanes to the phosphinates and the olefins *via* the oxaphosphetanes was clearly delineated in the variable-temperature ^1H nmr spectra in this solvent. Both diastereomers **8-I** and **8-II**, in the diethylphenylphosphine series gave the same olefin **22** and phosphinate, **19**, as expected.

The oxaphosphetanes derived from the various phosphines decomposed into olefins and phosphinates in the following decreasing order: $(CH_3)_3P > (C_2H_5)_2PC_6H_5 > (C_2H_5)_3P > C_2H_5P(C_6H_5)_2$. A possible mechanism for the pyrolysis involves the transition state **23**, if the breaking and making of bonds are synchronous processes. The dipolar structure **24** could make a contribution to the transition state, if the processes are not entirely synchronous. (In the extreme case of a stepwise decomposition, the intermediate would resemble **24**, with a tetrahedral phosphonium group.)



23 **24**

It is perhaps significant that the substitution of a hydrogen on C_3 of the ring (R″ = H) by an alkyl group (R″ = CH_3) decreased the tendency of the phosphetane to form olefin and phosphinate (compare the $(CH_3)_3P$ and $(C_2H_5)_3P$ derivatives in Table IV). This trend is reasonable if the alkyl group destabilizes a transition state with "carbanion character" at C_3, *i.e.*, if **24** contributes to the transition state (or if it is an intermediate, in the extreme case). The effect of a phenyl ring on phosphorus is difficult to assess because

(5) M. Kaufman and J. D. Braun, *J. Org. Chem.*, **31**, 3091 (1966).

(6) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3556 (1956) [$(CH_3)_2P(O)(OC_2H_5)$, $\delta^{31}P$ −50.3 ppm].

Table IV. Pyrolysis of 2,2-Dihydro-1,2-oxaphosphetane Derivatives to Phosphinite Esters and Olefins[a]

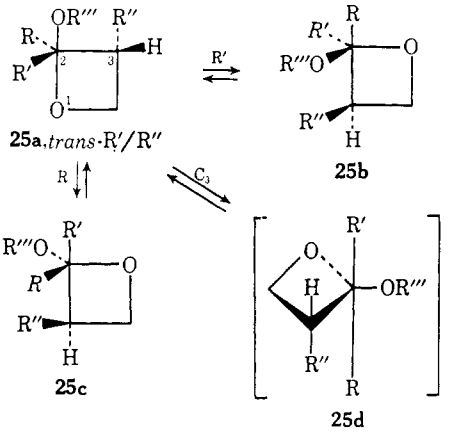
No.	(X₂Y)P[b] X	Y	% after 3 hr at 120° Phosphetane	Phosphinate	% after 1 hr at 150° Phosphetane	Phosphinate	% after other times at various temp Phosphetane	Phosphinate
4, 17	CH_3	CH_3	37	63	0	100	0	100[c]
6, 18	C_2H_5	C_2H_5	71	18[d]	44	56	0	100[e]
8-I			38[g]		5		0	
	C_2H_5	C_6H_5[f]		40		92		100[h]
8-II, 19			22		3		0	
10, 20	C_6H_5	C_2H_5	100	0	85	15	0	100[i]

[a] Samples (400 mg) were heated, as specified, in the absence of solvent. The product was analyzed by ^{31}P nmr in CH_2Cl_2. [b] Parent phosphine from which the phosphetane was derived. [c] After 8 hr at 120°. [d] There was a third product (11%), $\delta^{31}P$ −64 ppm. [e] After 8 hr at 160°. [f] Initial mixture of isomers I + II as 2.7:1. [g] Unreacted isomers I + II as 1.7:1. [h] After 8 hr at 160°. [i] After 15 hr at 150°.

it can affect both the ground state and the transition state of the pyrolysis to varying degrees, relative to an alkyl group. These questions are under further investigation.

The conversion of hexafluoroacetone into an olefin and a phosphinate can be effected by (a) combination of the ketone and the phosphine in hexane at −70°; (b) rearrangement of the phospholane to the phosphetane in benzene at 80°; (c) pyrolysis of the phosphetane in the absence of solvent at 120–150°. Evidently, these reactions are mechanistically related to the Wittig olefin synthesis.[7] Our observations strengthen the view that 1,2-oxaphosphetanes are *intermediates* in this reaction.[7-9] Birum and Matthews have reported the preparation of 4,4-bis(trifluoromethyl)-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-1,2-oxaphosphetane from the reaction of hexaphenylcarbodiphosphorane with hexafluoroacetone.[8] The oxaphosphetane was pyrolyzed to triphenylphosphine oxide and the olefin.

Stereochemistry of Four-Membered Cyclic Oxyphosphoranes. Previous data[3] suggested that trigonal bipyramid **25a** should be the most stable form of the oxaphosphetanes described in this paper. Placement of the two oxygens in apical positions conforms with the view that elements of high electronegativity (O = 3.5, C = 2.5) tend to occupy apical positions in trigonal bipyramidal phosphorus.[4] The inhibition of positional exchange[4] of groups attached to phosphorus in derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 ring system has been observed[3,10] during studies of their variable-temperature ^1H nmr spectra in solution. The results were interpreted[3,10] in terms of a pseudorotation mechanism[4,11] for the positional exchange.[11a] When applied to the oxaphosphetanes, pseudorotation gives rise to the bipyramids[12] **25b**, **25c**, and **25d**. The groups used as pivot in each pseudorotation are italicized in the new bipyramids.

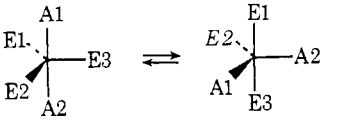


Bipyramid **25d** is impossible or improbable for steric reasons. Bipyramids **25b** and **25c** are of higher energy than **25a** because they have two carbon atoms in apical positions. The energy barriers for the corresponding pseudorotations should be relatively high, which accounts for the ^1H nmr data (R = R′ = CH_3, R″ = H, R‴ = $CH(CF_3)_2$ in formula **25a**) and for the existence of two diastereomers at phosphorus, **8-I** and **8-II**, in the oxaphosphetanes derived from $(C_2H_5)_2PC_6H_5$ (R = C_6H_5, R′ = C_2H_5 and R = C_2H_5, R′ = C_6H_5, with R″ = CH_3 and R‴ = $CH(CF_3)$ in formula **25a**).

Pseudorotations can be carried out in bipyramids **25b** and **25c**, to give the new diastereomers[12] **25e** and **25f**. Note that these have one carbon in an apical position, and should be more stable than their precursors. Other diastereomers[12] derived by pseudorotations of **25b** and **25c** are impossible for steric reasons.

One pseudorotation of **25e**, using as pivot the equatorial group R (which has not been previously used as pivot), gives **25g**, which has one apical carbon. Note that the only equatorial group of **25g** not used already as pivot is the ring O_1. If this group is used as

ferent groups as pivots transform a bipyramid into its *enantiomer* (identified by "primes"), for example, **1**(E2)**2**(A1)**5**(E1)**10**′(A2)**4**′(E3)**1**′.



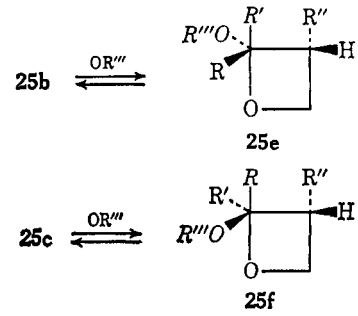
1 **2**

The presence of the four-membered ring joining groups A2 and E3 reduces the number of isomers because the A2–P–E3 angle that is part of the ring must be 120° in **4**, **6**, and **8**, and 180° in **9**.

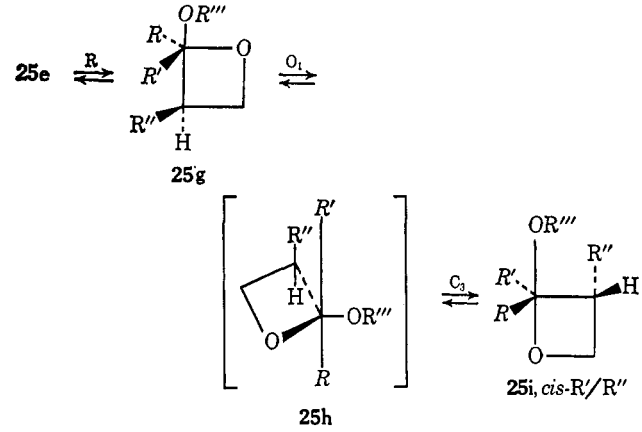
(7) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.
(8) G. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967).
(9) For four-membered cyclic phosphoranes, see (a) G. Märkl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1023 (1965); (b) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967), and references therein.
(10) F. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).
(11) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(11a) NOTE ADDED IN PROOF. For recent discussions of pseudorotation see R. R. Holmes and R. M. Deiters, *J. Am. Chem. Soc.*, 5021 (1968); E. L. Muetterties, *ibid.*, **90**, 5097 (1968).
(12) Ten *diastereomers*, all racemic, are possible for a trigonal bipyramid, P(A1,A2,E1,E2,E3), where the five groups are different but symmetrical. One pseudorotation of **1** using E2 as pivot gives **2**; *notation:* **1**(E2)**2**. To convert **1** into **2**, grasp E2 of **1**, push back A1 and A2 while pulling forward E1 and E3. This gives **2** *lying on its side;* rotate it 90° counterclockwise around the E2–P axis, and then turn it upside-down (*i.e.*, rotate 180° around the A2–P axis). The other diastereomers can be derived as **1**(E1)**3**, **1**(E3)**4**, **2**(A1)**5**, **2**(A2)**6**, **3**(A1)**7**, **3**(A2)**8**, **4**(A1)**9**, **4**(A2)**10**. Five *consecutive* pseudorotations using *dif-*

Table V. Elemental Analyses and Spectral Data of the Phosphinate Esters, RR'P(O)[OCH(CF$_3$)$_2$], and Olefins (CF$_3$)$_2$C=CHR'', Made by Pyrolysis of 2,2-Dihydro-1,2-oxaphosphetane Derivatives

No.	R	R'	R''	Bp (mm) or mp, °C	Mol formula	Calcd, % C	Calcd, % H	Calcd, % F	Calcd, % P	Found, % C	Found, % H	Found, % F	Found, % P	$\delta^{31}P$	$\tau_H^{R''}$	τ_H^R	J_{HP}^R	$J_{HH}^{R''CH}$	τ_H^{OCH}	$\tau_H^{=CH}$	J_{HP}^{OCH}	Ir bands, μ
17	CH_3	CH_3		30 (0.2)	$C_6H_7O_2F_6P$	24.6	2.9	46.7	12.7	24.7	3.1	46.2	12.6	−62.0		8.36	14.4		4.62		13.0	8.15, 8.32, 8.90, 9.00, 10.65, 10.90, 11.35
18	C_2H_5	C_2H_5		47 33 (0.3)	$C_7H_{11}O_2F_6P$	30.9	4.0	41.9	11.4	30.8	4.1			−68.8		8.85, 8.20	18.8		4.08		12.0	6.89, 7.25, 7.75, 8.25, 8.95, 9.05, 9.70, 11.42, 11.82
19	C_2H_5	C_6H_5		68 (0.05)	$C_{11}H_{11}O_2F_6P$	41.3	3.4	35.6	9.7	41.3	3.4	35.4	9.4	−53.5		8.87, 8.08	20.0		4.58		11.9	6.25, 6.82, 7.00, 7.25, 7.78, 8.15, 8.32, 8.95, 9.70, 10.00, 11.10, 11.45
20	C_6H_5	C_6H_5		107 (0.03)	$C_{15}H_{11}O_2F_6P$	48.9	3.0	31.0	8.4	49.1	3.2	30.7	8.3	−39.2					4.36		12.1	6.25, 7.00, 7.25, 7.75
21			H	14	$C_4H_5F_6$	Ref 5												None	3.71			
22			CH_3	55	$C_5H_4F_6$	33.7	2.3	64.0		33.6	2.5	63.7			7.98			7.5	3.15			5.92, 6.90, 7.10, 7.60, 8.10, 9.20, 8.60, 9.10, 10.10, 10.55



pivot, the result is the impossible or improbable bipyramid **25h**. One pseudorotation of **25h** using the ring C_3 as pivot (not previously utilized) would have given **25i**, which differs from **25a** only in the relative positions of the equatorial groups *R* and *R'*. *In other words, a stereomutation* **25a** → **25i** *is impossible (or at least very improbable) by the series of pseudorotations shown because one step, the formation of* **25h**, *requires the expansion of the C–P–O angle in the four-membered ring from 90 to 120°*. It can be shown that all other conceivable pathways for the stereomutation **25a** → **25i** are blocked by similar or by more restrictive steric obstacles.[12a]



The data of Table VI showed that, in *spite of the restriction imposed by the four-membered ring on the stereomutation of isomers* **8-I** *and* **8-II** *by the pseudorotation mechanism,*[4,11] *such a stereomutation does, indeed, take place.*

The higher ratios of oxaphosphetane isomers **8-I**/**8-II** shown in Table VI were obtained when the dioxaphospholane **7** was heated for 5 min at 80° in benzene solution. However, note that the ratio **8-I**/**8-II** changed very slowly at 25° in CH_2Cl_2 solution, *without the appearance of the oxaphosphetane pyrolysis product, i.e., the phosphinate* **19**. In the absence of solvent, at 25°, the ratio **8-I**/**8-II** changed very little within a few days. The stereomutation **8-I** → **8-II** was much faster at higher temperatures, in solvents and in the absence of them. For example, after 10 min at 120° the **8-I**/**8-II** ratio had dropped from 2.8 to 1.1; however, as expected, pyrolysis to phosphinate and olefin began to compete with stereomutation at elevated temperatures. We conclude that either (1) bipyramids with a diequatorial ring (**25d, h**) are not entirely forbidden, which seems unlikely, or (2) stereomutation can occur by a mechanism other than exclusive pseudorotation. The

(12a) Note Added in Proof. P. C. Lauterbur and F. Ramirez, *J. Am. Chem Soc.*, **90**, 6722 (1968).

Table VI. Stereomutation at Phosphorus in 1,2-Oxaphosphetanes, 8-I and 8-II, from Hexafluoroacetone and Diethylphenylphosphine[a]

Initial Isomer I/isomer II	Reaction conditions: Solvent	Temp, °C	Time	Final: Isomer I/isomer II	Phosphinate[b]/isomer II
3.0	CH_2Cl_2	25	3 hr	2.8	0
2.8	CH_2Cl_2	25	6 hr	2.3	0
2.8	CH_2Cl_2	25	67 hr	1.5	0
2.8	CH_2Cl_2	25	10 days	0.7	0
2.6	Benzene[c]	80	10 hr	1.3	0.3
2.8	None	25	67 hr	2.6	0
2.5	None	25	5 weeks	2.0	0
2.8	None	110	10 min	1.9	0
2.8	None	120	10 min	1.1	0.1
2.7	None	120	3 hr	1.7	1.7
2.5	None	120	3 hr	1.6	1.6
3.0	None	125	20 min	1.0	0
2.8	None	130	10 min	1.0	0.2
2.7	None	150	1 hr	*d*	*e*

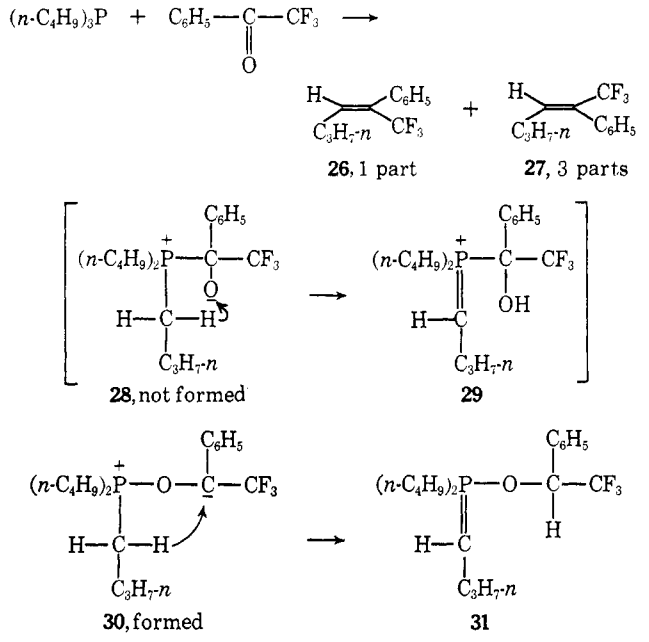
[a] The ratios of isomer **8**-I ($\delta^{31}P$ +30.3 ppm) to isomer **8**-II ($\delta^{31}P$ +21.0 ppm) were determined in a given sample by ^{31}P nmr spectrometry, before and after the treatment indicated. Measurements in CH_2Cl_2 solution and in the absence of solvent were reproducible to ±0.1. [b] The samples contained no phosphinate ester **19** before the thermal treatment. [c] Ratios of isomer I/isomer II fluctuating between 2.8 and 3.0 were observed when benzene solutions of 1,3,2-dioxaphospholane were kept 5 min at 80°; no phosphinate was formed. [d] About 8% of both isomers I + II was left while 92% of phosphinate was produced. [e] Mostly phosphonate.

nature of that mechanism[13] cannot be elucidated with the available data, but it may involve the rupture of a P–O bond at some stage of the stereomutation. The question is under further investigation.

Previous Work on the Reaction of Tributylphosphine with Trifluoroacetophenone. This reaction was said[14] to yield the two isomeric olefins **26** and **27**, when carried out in boiling hexane (Scheme I). The phosphorus-containing fragment was not characterized, but the reaction was said to have a 1:1 stoichiometry, and to involve a 1:1 adduct with P–C–O bond[14] **28** → **29**.

The formation of olefins **26** and **27** is adequately explained by *the formation of a 1:1 adduct with P–O–C bond* **30**, followed by a sequence of steps, **30** → **31** leading to two stereoisomeric oxaphosphetanes (isomers at carbon, not at phosphorus) as explained above. The reaction should involve 2 mol of ketone and one of phosphine, and should yield $(n\text{-}C_4H_9)_2P(O)[OCH(C_6H_5)(CF_3)]$ as the by-product.

Scheme I



Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Rearrangement of 2,2,2-Trialkyl- and 2,2,2-Alkylaryl-4,4,5,5-tetrakistrifluoromethyl-2,2-dihydro-1,3,2-dioxaphospholanes into 2,2-Dialkyl- and 2,2-Alkylaryl-2-(bis(trifluoromethyl))methoxy-3-alkyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetanes. The phospholanes **3**, **5**, **7**, and **9** were prepared from hexafluoroacetone and the phosphines at −70°, as described.[2] The conversion of the phospholanes into the phosphetanes **4**, **6**, **8**-I, **8**-II, and **10** was carried in boiling benzene (*ca.* 0.3 *M* solution; approximately 3 hr at reflux, or as indicated in Table IV). The solvent was removed at 30°, first at 20 mm, then at 0.1 mm. The crude, *fresh*, residues were analyzed by ^1H and ^{31}P nmr spectrometry. The phosphetanes were formed in nearly quantitative yields. They were purified as shown in Table I. The spectral data of analytical samples are given in Tables I and II. Moisture should be avoided at all times.

Pyrolysis of 2,2-Dialkyl- and 2,2-Alkylaryl-2-bis(trifluoromethyl)-methoxy-3-alkyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetanes into Bis(trifluoromethyl)methyl Dialkyl- and Alkylarylphosphinates Plus 1,1-Bis(trifluoromethyl)-2-alkylethylenes. The phosphetanes **4**, **6**, **8**-I, **8**-II, and **10** were heated in a flask connected to a receiver cooled in a Dry Ice–solvent bath. The volatile olefins, **21** and **22**, distilled into the receiver and the phosphinates, **17**–**20**, remained in the reaction flask. (At the end of the pyrolysis, the flask containing the phosphinate was evacuated to remove last traces of olefin.) The pyrolysis conditions are given in Table IV, and the properties of the phosphinates and olefins are listed in Table V.

(13) For discussions of the stereochemistry of phosphorus and related systems, see (a) W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 1–42; (b) L. A. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(14) D. J. Burton, F. E. Herkes, and K. J. Klabunde, *J. Am. Chem. Soc.*, **88**, 5042 (1966).