computer program provided a rate constant with standard error based on one standard deviation. In each case, at least six points were used to determine the pseudo-first-order rate constant, and no deviation from the first-order kinetics was observed.

Run 54. The general procedure of run 47 was utilized with 149.1 mg of (±)-**2**-*d*, 0.3 ml of DBN, and 19.7 ml of *tert*-butyl alcohol.

Run 55. The general procedure of run 39 was followed utilizing 16.6 mg of (+)-**2**-*d*, 0.015 ml of PMG, and 2 ml of *tert*-butyl alcohol. The initial observed rotation was α^{25}_{obsd} +0.195° and the final was α^{25}_{obsd} +0.071° at 436 nm.

Run 61. To a solution of 110 mg of (±)-**2** in 10 ml of *tert*-butyl alcohol was added 0.04 ml of PMG. The solution was mixed thoroughly and placed in a thermostated bath at 49.8°. Aliquots were withdrawn at appropriate times and shaken with 2 *N* hydrochloric acid, ether, and a trace of methanol. Subsequent procedures followed the pattern of run 47.

Run 60. To a solution of 22.1 mg of (+)-**2**-*d* in 2 ml of *tert*-butyl alcohol was added 0.003 ml of PMG. The solution was mixed thoroughly, and a portion was transferred to a 1-dm polarimeter cell which was thermostated by water circulating from a 51.1° bath. The temperature of the water was measured immediately after leaving the polarimeter cell at 50.9°. The initial observed rotation was $\alpha^{50.9}_{obsd}$ +0.198°, and the final observed rotation was $\alpha^{50.9}_{obsd}$ +0.029° at 436 nm. Subsequent procedures for recording data and determining base concentration were patterned after run 39.

Run 49. The procedure of run 60 was applied to 22.0 mg of (−)-**1**-*d* in 2 ml of *tert*-butyl alcohol followed by 0.012 ml of PMG. The initial observed rotation was $\alpha^{49.4}_{obsd}$ −0.490°, and the final observed rotation was $\alpha^{49.4}_{obsd}$ −0.092° at 436 nm.

Kinetic Components of Isotopic Exchange–Racemization Reactions by the Reresolution Technique. Run 66. The procedure as applied to (+)-**1**-*d* reactions in methanol–potassium methoxide has been detailed elsewhere.[4c] Only an outline is given here. A solution of 320.1 mg of (−)-**1**-*d* ($[\alpha]^{25}_{546}$ −32.7° (*c* 1.3, dioxane), containing 0.96 atom of excess deuterium per molecule) in 25 ml of *tert*-butyl alcohol was thermostated at 25.0°. By a graduated syringe, 0.4 ml of PMG was added and the solution was mixed thoroughly. A portion of the solution was transferred to a thermostated polarimeter cell. When the rotation decreased to α^{25}_{obsd} −0.292° from an initial rotation of α^{25}_{obsd} −0.579° at 546 nm the solution was quenched with hydrochloric acid. Aliquots from the polarimeter cell were titrated with standard hydrochloric acid to a phenolphthalein end point to give a base concentration of 0.105 *M*. The quenched mixture was extracted with ether. The combined ether solutions were washed with water, dried (Na_2SO_4), and concentrated to 275 mg of a dry, white solid A. An ir spectrum of solid A showed the typical absorption spectrum of **1** and no spurious absorptions. This material was subjected to fractional crystallizations in reagent grade acetone. Rotations were taken in dioxane at 546 nm and 25.0°. Recrystallization of solid A gave 50 mg of solid B having $[\alpha]^{25}_{546}$ +0.53° (*c* 1.1, dioxane), mp 132–133° (racemic **1**, lit.[4b] mp 133–134°). From the mother liquors of B, 150 mg of solid C was recovered. Solid C contained two distinct types of crystal structures. These structures were separated manually into prisms D having $[\alpha]^{25}_{546}$ − 16.1° (*c* 1.12, dioxane) and plates E having $[\alpha]^{25}_{546}$ −31.3° (*c* 1.6, dioxane). Recrystallization of the plates E gave solid F having $[\alpha]^{25}_{546}$ −31.4° (*c* 1.65, dioxane) (95% optically pure), mp 126–128° (optically pure **1**, lit.[4b] mp 127–128°, $[\alpha]^{25}_{546}$ +33.7°, *c* 1.1, dioxane). Solids B and F contained 0.76 and 0.88 atom of excess deuterium per molecule, respectively, by mass spectrometry using the direct insertion technique. The values of k_1, k_2, and k_3 were calculated from the above data with the method detailed previously,[4c] and they are recorded in Table VII.

Kinetic Runs of Table VI. Runs 62–65 were identical with runs 39, 44, 51, and 55, respectively, except the former runs involved many more data points.

Base-Catalyzed Nucleophilic Substitutions at Pentacoordinated Phosphorus

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Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. *Received July 30, 1971*

Abstract: The alkoxy groups that occupy the equatorial positions in the trigonal-bipyramidal pentacoordinated phosphorus atom of four-membered cyclic tetraoxyalkylphosphoranes are replaced by the alkoxy groups of alcohols, under base catalysis. Analogous base-catalyzed nucleophilic substitutions are reported for five-membered cyclic unsaturated pentaoxyphosphoranes. The rings are preserved in these substitutions. The relative rates of (a) the substitution reactions and (b) the permutational isomerizations of the trigonal-bipyramidal oxyphosphoranes determine the course of the substitutions. The reactions of phosphonites, $RCH_2P(OCH_3)_2$, of phospinites, $(RCH_2)_2P(OCH_3)$, and of tertiary phosphines, $(RCH_2)_3P$, with highly electrophilic carbonyl compounds, *e.g.*, hexafluoroacetone, constitute a general synthesis of 1,2-oxaphosphetanes with pentacoordinated phosphorus.

This investigation is concerned with the mechanism of nucleophilic substitutions at the pentacoordinated phosphorus of the 1,2-oxaphosphetane ring system,[2] *e.g.*, **1** + $R^{V}OH$ → **2** + $R'''OH$; see Chart I.

We are also concerned with substitutions at the pentacoordinated phosphorus of the 1,3,2-dioxaphospholene ring system,[3] *e.g.*, **3** + $R'''OH$ → **4** + $R''OH$; see Chart II.

The four-membered cyclic oxyphosphoranes required in this research have four or three oxygen atoms attached to the phosphorus, **1**, **2**, or **5**, respectively. Previous work from this laboratory[2] has shown that the reaction of tertiary phosphines, *e.g.*, **6** (Chart III), with hexafluoroacetone (**7**) gives derivatives of the 1,3,2-dioxaphospholane ring system, **8** (Chart IV), which can be transformed into oxaphosphetanes with two oxygen atoms attached to the phosphorus, **9** (Chart I). The overall reaction **6** + **7** → **8** → **9** proceeds in excellent yields, and the dioxyphosphetanes **9** are remarkably stable. The cyclic intermediates in the usual variation of the Wittig olefin synthesis[4] are

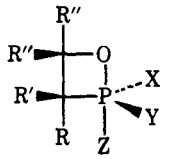
(1) This research was supported by grants from the National Cancer Institute of the NIH (CA-04769) and from the National Science Foundation (GP-6690).

(2) (a) F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968); (b) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, **90**, 6726 (1968).

(3) F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, *ibid.*, **90**, 751 (1968).

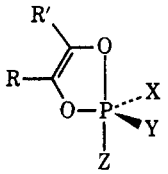
(4) (a) G. Wittig and U. Schollkopff, *Chem. Ber.*, **87**, 1318 (1954);

Chart I



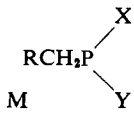
No.	X	Y	Z	R	R′	R″
1	R‴O	R‴O	R^{IV}O	H	H	H
2	R‴O	R^{V}O	R^{IV}O	H	H	H
5	R‴O	RCH_2	R^{IV}O	H	H	H
9	C_2H_5	C_2H_5	$(CF_3)_2CHO$	CH_3	H	CF_3
10	C_6H_5	C_6H_5	C_6H_5	H	H	H
16	CH_3O	CH_3O	$(CF_3)_2CHO$	H	H	CF_3
17	CH_3O	CH_3O	$(CF_3)_2CHO$	CH_3	H	CF_3
22	CH_3O	C_2H_5	$(CF_3)_2CHO$	CH_3	H	CF_3
23	C_2H_5	CH_3O	$(CF_3)_2CHO$	CH_3	H	CF_3
24	C_6H_5	C_2H_5	$(CF_3)_2CHO$	CH_3	H	CF_3
25	C_2H_5	C_6H_5	$(CF_3)_2CHO$	CH_3	H	CF_3
26	$(CF_3)_2CHO$	CH_3O	CH_3O	H	H	CF_3
29	CH_3O	CD_3O	$(CF_3)_2CHO$	H	H	CF_3
30	CH_3O	CD_3O	CH_3O	H	H	CF_3

Chart II



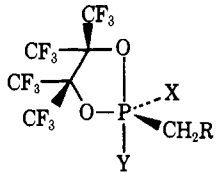
No.	X	Y	Z	R	R′
3	R″O	R″O	R″O	H	H
4	R″O	R‴O	R″O	H	H
31	CH_3O	CH_3O	CH_3O	CH_3	CH_3
32	CH_3O	C_6H_5-CH_2O	CH_3O	CH_3	CH_3
33	C_6H_5-CH_2O	C_6H_5-CH_2O	C_6H_5-CH_2O	CH_3	CH_3
34	C_6H_5-CH_2O	CH_3O	C_6H_5-CH_2O	CH_3	CH_3

Chart III



No.	X	Y	R
6	C_2H_5	C_2H_5	CH_3
12	CH_3O	CH_3O	H
13	CH_3O	CH_3O	CH_3
20	CH_3O	C_2H_5	CH_3

Chart IV



No.	X	Y	R
8	C_2H_5	C_2H_5	CH_3
14	CH_3O	CH_3O	H
15	CH_3O	CH_3O	CH_3
21	C_2H_5	CH_3O	CH_3

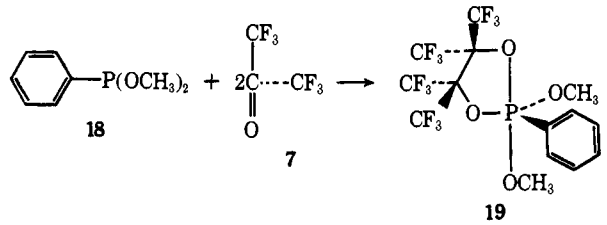
phosphetanes with only one oxygen atom attached to phosphorus, *e.g.*, **10** (Chart I), and are quite unstable. This difference is the result of the marked decrease in the stability of oxyphosphoranes as the number of highly electronegative ligands decreases.[2] While the Wittig intermediates **10** are seldom isolable,[5] the dioxyphosphetanes **9** require relatively drastic conditions for their transformation into olefin, $RR'C{=}C(R'')_2$, and phosphinate, **11**, (XYZ)PO.

The dioxaphospholenes **3** and **4** required in this study have been described,[3] and the problems associated with the permutational isomerizations of the oxyphosphoranes, in general, have been considered in detail elsewhere.[6-8]

Results

Reaction of Phosphonites and Phosphinites with Hexafluoroacetone. Dimethyl methylphosphonite (**12**) and dimethyl ethylphosphonite (**13**) (Chart III) react with hexafluoroacetone (**7**) at −70° to give mainly derivatives of the 1,3,2-dioxaphospholane ring system **14** and **15** (Chart IV). Small amounts (15% or less) of the 1,2-oxaphosphetanes **16** and **17** (Chart I) are also formed in these reactions. The oxaphosphetanes **16** and **17** produced in the low-temperature reactions of the trivalent phosphorus compounds with the ketone do not result from further transformations of the dioxaphospholanes **14** and **15**, as can be demonstrated in independent experiments. However, the pyrolyses of the phospholanes **14** and **15** at much higher temperatures, *ca.* 120–140°, also produce the phosphetanes **16** and **17**.

To support the structure assigned to the oxaphospholanes **14** and **15**, the reaction of dimethyl phenylphosphonite (**18**) with hexafluoroacetone (**7**) was also



18 **7** **19**

investigated. Now, the resulting phospholane **19** lacks the hydrogen atoms in the equatorial ligand that are required for the ring contraction to the phosphetane. The data given in the Experimental Section support structure **19**.

The reaction of methyl diethylphosphinite (**20**) (Chart III) with hexafluoroacetone at −70° gives *ca.* 85% of phospholane (**21**) (Chart IV), and 15% of a mixture of stereoisomeric phosphetanes **22** and **23** (Chart I). When this reaction is carried out at 20°, the products are the phospholane **21** and the phosphetanes **22** and **23** in *ca.* 42, 26, and 22%, respectively. The phosphetanes must have been formed from precursors of the phospholane, since the latter, **21**, is transformed into the former, **22** + **23**, quite slowly even at much higher temperatures (*ca.* 100°).

The stereoisomeric phosphetanes **22** and **23** are not interconverted at about 100°. A relatively slow stereomutation **22** ⇄ **23** is observable at *ca.* 120–140° in the

(b) S. Trippett, *Quart. Rev., Chem. Soc.*, **17**, 406 (1963); (c) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(5) (a) G. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967); (b) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **4**, 1023 (1965); (c) F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth," Wiley-Interscience, New York, N. Y., 1970.

(6) Possible mechanisms for these and related permutational isomerizations of the trigonal bipyramids will be discussed in subsequent communications. The literature on this subject was reviewed recently; see ref 7 and 8.

(7) F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970).

(8) F. Ramirez, I. Ugi, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, D. Marquarding, P. Gillespie, and P. Hoffmann, *Phosphorus*, **1**, 1 (1971); (b) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971).

presence of the acid hexafluoroisopropyl alcohol. In contrast, the stereomutation **24** ⇄ **25** of the dioxyphosphetanes is relatively fast at 100° in the presence of hexafluoroisopropyl alcohol. The isomerization occurs by a bond rupture–recombination mechanism,[8a] and the reluctance of the trioxyphosphetanes **22** and **23** to undergo the permutational isomerization is consistent with their enhanced stability due to the three highly electronegative oxygen ligands.

The trigonal-bipyramidal structure for the cyclic oxyphosphoranes, with the rings in the apicoequatorial skeletal position, is based on the results of X-ray analysis.[9,10] The placement of the alkyl and aryl groups in the equatorial position follows from the lower electronegativity of the carbon atom relative to oxygen.[11,12]

The ^1H nmr spectra of the phospholanes **14** and **15** in solution at 30° show one signal due to the two CH_3O groups. If these phospholanes were "frozen" in the time scale of nmr, one should observe two CH_3O signals, barring accidental degeneracy, since the CH_3O groups are magnetically nonequivalent.[6]

The ^1H nmr spectra of the oxaphosphetanes **16** and **17** in solution at 30° show, respectively, one CH_3O signal and two CH_3O signals. Now, the "frozen" phosphetane **16** has two magnetically equivalent CH_3O groups, while the "frozen" phosphetane **17** has two magnetically nonequivalent CH_3O groups. Moreover, as discussed elsewhere,[6–8] if these phosphetanes **16** and **17** undergo relatively rapid positional exchange of the ligands at 30°, the two CH_3O groups of **16** should give one ^1H signal, while the two CH_3O groups of **17** should still give two ^1H signals.

The ^{19}F nmr spectrum of the phospholane **21** (Chart IV) in solution at 30° shows only one fluorine signal.[6] The "frozen" structure **21** should give rise to two fluorine signals since in it there are two sets of magnetically nonequivalent CF_3 groups.

Base-Catalyzed Substitutions in 1,2-Oxaphosphetanes. The phosphetane **16** does not react with methanol under the conditions specified in the Experimental Section. The addition of acid does not promote the reaction; however, the addition of catalytic amounts of triethylamine results in the substitution of the hexafluoroisopropoxy group by the methoxy group to give a trimethoxyoxaphosphetane (**30**, *cf.* Scheme I).

The course of the substitution can be followed by ^1H nmr spectroscopy in $CDCl_3$ as solvent and with CD_3OD and pyridine as reagents; the results are shown in Figure 1. *The key observation is that CH_3OD appears ca. 30 sec after the addition of 1 molar equiv of CD_3OD to the phosphetane* **16**. The amount of CH_3OD increases in the early stages of the reaction and then decreases (note the signal at the highest magnetic field in curves II through VIII of Figure 1). As the reaction proceeds, the amount of $(CF_3)_2CHOD$ increases as this

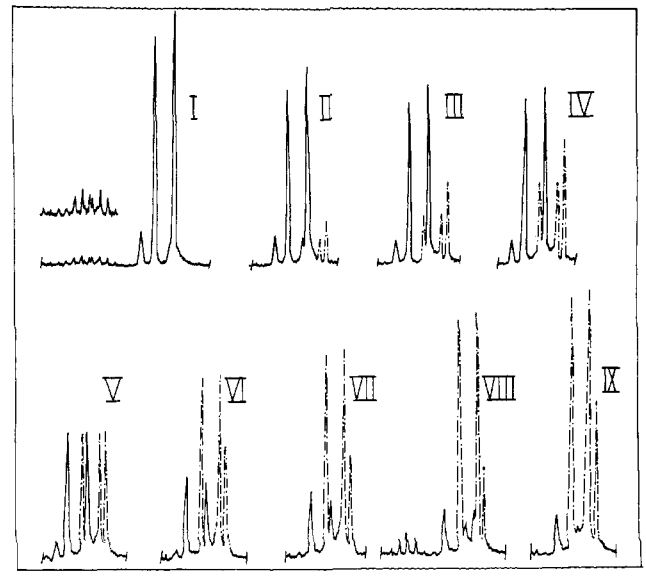
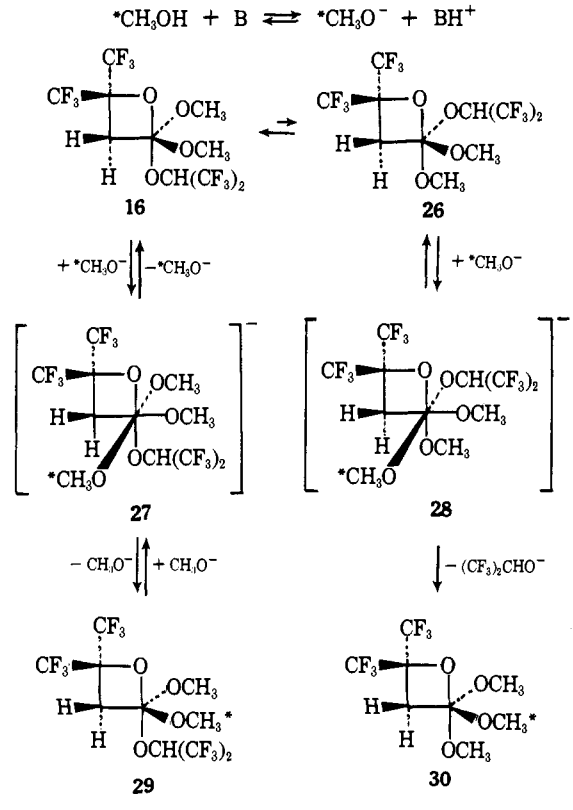


Figure 1. Pyridine-catalyzed reaction of 2,2-dimethoxy-2-hexafluoroisopropoxy-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (**16**) with 1 molar equiv of CD_3OD in $CDCl_3$ solution at 25°: (I) ^1H nmr spectrum, no CD_3OD added; (II–VIII) 1 molar equiv of CD_3OD added; (IX) 0.5 molar equiv of CH_3OH added to product of spectrum VIII. Times after addition of CD_3OD: (II) 2 min 30 sec; (III) 8 min 30 sec; (IV) 14 min; (V) 22 min 30 sec; (VI) 35 min 30 sec; (VII) 43 min; (VIII) 59 min. Each spectrum = 50 sec. The doublet of solid curve in II–VIII is due to $(CH_3O)_2[(CH_3)_2CHO]P<$ and $(CH_3O)(CD_3O)[(CF_3)_2CHO]P<$. The doublet of dashed curve is due to $(CH_3O)_2(CD_3O)P<$. The singlet of dashed curve at highest magnetic field is due to CH_3OD. The doublet of septets in I is due to $[(CF_3)_2CHO]P<$. The septet in VIII is due to $(CF_3)_2CHOD$. The ring CH_2P gives a doublet near CH_3OP.

ligand is displaced from **16**; the spectrum of the fluoro alcohol is shown in the insert of curve I and is omitted from the other curves. The increase in $(CF_3)_2CHOD$ is

Scheme I



(9) (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); (c) R. D. Spratley, W. C. Hamilton, and J. Ladel, *ibid.*, **89**, 2272 (1967).

(10) (a) M. U. Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *ibid.*, **93**, 5259 (1971).

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 90.

(12) (a) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc*, **11**, 339 (1957); (b) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970); (c) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963); (d) E. L. Muetterties, W. Mahler, K. F. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (e) W. Mahler and E. L. Muetterties, *ibid.*, **4**, 1520 (1965).

Table I. Reaction of Benzyl Alcohol (R'OH) (3 Molar Equiv) with 2,2,2-Trimethoxydioxaphospholene [>P(OR)$_3$], 1.5 *M* Benzene Solution at 25°

Catalyst, molar equiv	Time, hr	Composition of reaction mixture, mol % P(OR)$_3$	(P(OR)$_2$(OR')	P(OR)(OR')$_2$	P(OR')$_3$	ROH, molar equiv Obsd	Calcd
None	4	75	25	0	0	0.27	0.25
	33	52	38	10	0	0.47	0.58
Pyridine, 0.5	0.16	92	8	0	0		
	0.83	76	24	0	0		
	12.0	23	38	32	7	1.25	1.26
Pyridine, 1.0	0.25	78	22	0	0		
	0.50	64	29	7	0	0.42	0.43
	6.0	24	39	30	7	1.19	1.24
2,4,6-Trimethylpyridine, 1.0	0.25	74	26	0	0		
	0.50	60	32	8	0	0.82	0.80
	6.6	21	42	28	9	1.28	1.25

Table II. Reaction of Methanol (R'OH) (3 Molar Equiv) with 2,2,2-Tribenzoxydioxaphospholene [>P(OR)$_3$] in 1.5 *M* Benzene Solution at 25°

Catalyst, molar equiv	Time, hr	Composition of reaction mixture, mol % P(OR)$_3$	P(OR)$_2$(OR')	P(OR)(OR')$_2$	P(OR')$_3$	ROH molar equiv Obsd	Calcd
None	7	85					
	24	64	30	6	0	0.96	0.94
	42	42	44	12	2	1.44	1.48
Pyridine, 1.0	0.16	38	52	11	0		
	0.30	32	46	20	2		
	0.46	16	52	27	5	1.31	1.21
	0.80	7	40	41	12	1.66	1.68
	3	~2	32	44	22	2.00	1.90
	5		28	44	26	2.11	1.95

accompanied by an increase in the deuterated trimethoxyphosphetane **30**; note the signal associated with **30** shown by dashes and dots in curves III–VIII.

Base-Catalyzed Substitutions in Derivatives of the 1,3,2-Dioxaphospholene Ring System (Chart II). The reactions of the trimethoxyphospholene **31** with benzyl alcohol, and of the tribenzoxyphospholene **33** with methanol, are effectively catalyzed by tertiary amines. The results are summarized in Tables I and II, respectively. These substitutions are not catalyzed by acids.

The methanol reaction is significantly faster than the benzyl alcohol reaction. Both systems are reversible, and each one has three substitution stages whose rates are of comparable magnitudes; yet, the composition of the reaction mixtures are quite reproducible and surprisingly simple. *The amount of phosphate produced is negligible.* The amount of displaced alcohol, ROH, that is actually produced is quite close to the amount calculated from the distribution of alkoxide groups in the various dioxaphospholenes **31**, **32**, **33**, and **34**. Note, for example, the 6- and 5-hr runs in the presence of 1 molar equiv of pyridine in Tables I and II, respectively. Table I shows that the rate is roughly proportional to the concentration of the base. Blocking the nucleophilic site of the base, as in γ-collidine (2,4,6-trimethylpyridine), does not adversely affect its catalytic action.

Discussion

The results of this investigation are consistent with the mechanism shown in Scheme I. The nucleophile $^*CH_3O^-$ approaches the trigonal-bipyramidal five-coordinated phosphorus of **16** in the equatorial plane opposite the leaving equatorial group, CH_3O^-. The resulting transition state or intermediate **27** has six-coordinated phosphorus with octahedral skeletal symmetry,[3,13–18] and a collinear arrangement of the entering and leaving groups and the phosphorus. The collapse of **27** generates methanol, which is the first product observed in the experiments with CD_3OD; the other product is **29** with $C^*H_3O{=}CD_3O$.

The original dimethoxyphosphetane **16** undergoes permutational isomerization[6–8] to **26** with an equatorial hexafluoroisopropoxy ligand. Now, the attack by the nucleophile $C^*H_3O^-$ generates the six-coordinated transition state or intermediate **28** which collapses to the fluoro alcohol and the trimethoxyphosphetane **30** (or its deuterated analog).[19]

Hexafluoroisopropyl alcohol is much more acidic than methanol and, therefore, the anion of the former should be a much better leaving group than the anion of the latter. To account for the observations described in Figure 1 and in the Results section, we propose that

(13) It has been suggested (*cf.* ref 14) that a trigonal-bipyramidal intermediate with pentacoordinated cobalt is formed in the base-catalyzed hydrolysis of halogenoamminecobalt(IV) complexes. The addition of water to that intermediate in the second step of the hydrolysis is formally analogous to the addition of a nucleophile to the phosphorus of the oxyphosphorane.

(14) R. G. Pearson and F. Basolo, *Inorg. Chem.*, **4**, 1524 (1965).

(15) (a) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965; (b) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 7, 155 (1968).

(16) (a) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1962); (b) G. Wittig and A. Maercker, *Chem. Ber.*, **97**, 747 (1964); (c) D. Hellwinkel, *ibid.*, **99**, 3628, 3642, 3660 (1966); (d) D. Hellwinkel and H. J. Wilfinger, *Tetrahedron Lett.*, 3423 (1969).

(17) H. R. Allcock, *J. Amer. Chem. Soc.*, **86**, 2591 (1964).

(18) J. I. Muscher, *Angew. Chem.*, **81**, 68 (1969); (b) *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

(19) This picture is obviously highly simplified. For example, isomerization of phosphetane **29** moves the $(CF_3)_2CHO$–ligand to an equatorial position from which it can be eliminated by attack of CH_3O^- or of $^*CH_3O^-$. The phosphetanes with double labeling (*i.e.*, two $^*CH_3O$ groups) have been omitted.

(1) only groups in the equatorial positions of the trigonal bipyramid are displaceable, and (2) the rate of displacement **16** → **29** is faster, or at least of the same order of magnitude, as the rate of the particular process of permutational isomerization[6,8] that is capable of transforming oxaphosphetane **16** into **26**. These conclusions would explain why hexafluoroisopropoxide is not initially ejected from **16** or from **26**.

The same mechanism is applicable to the dioxaphospholenes **31** and **33**, but now the permutational isomerizations are quite rapid relative to the substitutions.[6-8,20]

Experimental Section

All nmr measurements are at 25°: ^1H at 60 Mcps, ^{31}P at 40.5 Mcps, and ^{19}F at 94.1 Mcps. Chemical shifts are given in ppm *vs* TMS = 10 (τ) for ^1H, *vs.* H_3PO_4 = 0 for ^{31}P, *vs.* CF_3COOH = 0 for ^{19}F. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Galbraith Laboratories, Knoxville, Tenn.

Reaction of Dimethyl Methylphosphonite (12) with Hexafluoroacetone (7). Note: In this, and in related syntheses, an excess of tertiary amine should be avoided, and the resulting amine hydrochloride should be thoroughly removed by filtration through a medium porosity sintered-glass funnel. These contaminants interfere with the rearrangement of the 1,3,2-dioxaphospholanes to the 1,2-oxaphosphetanes. If difficulties are encountered in these rearrangements, the crude dioxaphospholane should be kept 1 hr at 3 mm of pressure and 70° to remove volatile contaminants, prior to purification of the dioxaphospholane by distillation at lower pressures (0.1–0.5 mm).

A solution of methyldichlorophosphine, CH_3PCl_2 (8.21 g, 70 mmol), in hexane (100 ml) was added over a 1-hr period to a solution of methanol (5.63 ml, 140 mmol) and triethylamine (19.2 ml, 140 mmol) in hexane (200 ml) at 0°, with stirring. The mixture was kept 1 hr at 0° and 1 hr at 25° and was filtered (see above Note). The hexane filtrate containing $CH_3P(OCH_3)_2$ was treated with hexafluoroacetone (*ca.* 25 ml, an excess over 2 molar equiv) at −70° over a 1-hr period, with stirring. The solution was kept 1 hr at −70° and 2 hr at 0°, and was brought to 20° and evaporated at 20 mm. The residue contained *ca.* 85% of **2,2-dimethoxy-2-methyl-4,4,5,5-tetrakis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholane (14)** and *ca.* 15% of **2,2-dimethoxy-2-hexafluoroisopropoxy-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (16)**, from ^1H nmr spectrometry.

The 1,3,2-dioxaphospholane **14** was purified by short-path distillation, bp *ca.* 25° (0.1 mm, bath of *ca.* 40°). It was characterized by its spectral properties: $\delta^{31}P$ +15.6 ppm; τ_{CH_3O} 6.42 ppm, J_{HCOP} = 13.0 cps; τ_{CH_3P} 8.22 ppm, J_{HCP} = 17.2 cps (2:1 intensities).

The phospholane **14** was recovered unchanged after 12 hr at 55°, and after 5 hr at 90°. However, rearrangement to the phosphetane **16** was complete after 12 hr at 115°, or after 6 hr at 120° (in the absence of solvent, under N_2; see above Note). The phosphetane was purified by short-path distillation, bp *ca.* 30° (0.1 mm, bath at *ca.* 45°). It had the following spectral characteristics: $\delta^{31}P$ +35.7 ppm (neat or in C_6D_5Br); τ_{CH_3O} 6.25 ppm, J_{HCOP} = 14.6 cps; τ_{CH_2P} 6.17, J_{HCP} = 23.5 cps (3:1 intensities); $\tau_{(CF_3)_2CHO}$ 5.40 (multiplet).

Anal. Calcd for $C_9H_9O_4PF_{12}$: C, 24.6; H, 2.1; F, 51.8. Found: C, 24.7; H, 2.3; F, 51.6.

Base-Catalyzed Reaction of Methanol with 2,2-Dimethoxy-2-hexafluoroisopropoxy-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (16). (a) With CD_3OD–Pyridine. Pyridine (1 molar equiv, 80 μl) was added to a solution of the phosphetane **16** (440 mg) in $CDCl_3$ (0.5 ml) in an nmr sample tube. The ^1H nmr was recorded, and 1 molar equiv of CD_3OD (40 μl) was added. The first spectrum was recorded 30 sec after the addition of CD_3OD. Each measurement took 50 sec. Thirteen such measurements were made at *ca.* 3-min intervals; several of these are reproduced in Figure 1. Finally, 0.5 molar equiv of CH_3OH (20 μl) was added, and the spectrum was taken.

(b) With CH_3OH–Triethylamine. A solution containing the phosphetane **16** (5.5 mmol), methanol (5.5 mmol), triethylamine (0.55 mmol), and methylene chloride (10 ml) was kept 12 hr at 20° with stirring. The ^1H nmr spectrum of the solution revealed the formation of $(CF_3)_2CHOH$ and of the new **2,2,2-trimethoxy-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (30).** The solution was evaporated at 30° (20 mm) and the residue was distilled to give the phosphetane **30**, bp 35–36° (at 2.7 mm, bath at 60–75°). The spectral characteristics of **30** in $CDCl_3$ solution are as follows: $\delta^{31}P$ +32.4 ppm; τ_{CH_3O} 6.43 ppm, J_{HCOP} = 13.5 cps; τ_{CH_2} 6.30 ppm, J_{HCP} = 22.7 cps.

In the absence of triethylamine there was no noticeable substitution reaction after 20 hr at 20° under conditions analogous to those described above.

Reaction of Dimethyl Ethylphosphonite (13) with Hexafluoroacetone (7). Ethyldichlorophosphine, $C_2H_5PCl_2$, was converted into dimethyl ethylphosphonite (**13**), $\delta^{31}P$ −181.8 ppm (in $CDCl_3$), τ_{CH_3O} 6.47 ppm, J_{HCOP} = 11.0 cps (in $CDCl_3$), as described above for the methyl analog. The reaction of hexafluoroacetone was carried out in hexane solution at −70°, as before. The product consisted almost exclusively of **2,2-dimethoxy-2-ethyl-4,4,5,5-tetrakis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholane (15),** bp 25° (0.05 mm), in 90% of the theory. The spectral properties of **15** are $\delta^{31}P$ +14.9 ppm; τ_{CH_3O} 6.35 ppm, J_{HCOP} = 12.5 cps; $\tau_{CH_3CH_2}$ 8.78 ppm, J_{HCCP} = 26.0 cps, J_{HCCH} = 7.0 cps; $\tau_{CH_3CH_2}$ 7.80 ppm, J_{HCP} = 19.0 cps; all spectra in $CDCl_3$.

The dioxaphospholane **15** was kept 1 hr at 140° in the absence of solvent, under N_2. The product was distilled giving **2,2-dimethoxy-2-hexafluoroisopropoxy-3-methyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (17),** bp 26° (0.1 mm), in about 70% of the theory. The phosphetane **17** had the following spectral characteristics in $CDCl_3$: $\delta^{31}P$ = +32.4 ppm, τ_{CH_3O} 6.20 ppm, J_{HCOP} = 14.6 cps; τ_{CH_3O} 6.23 ppm, J'_{HCOP} = 14.6 cps; τ_{C_3-H} 5.70 ppm, J_{HCP} = 29.5 cps, J_{HCH} = 8.0 cps; $\tau_{C_3-CH_3}$ 8.53 ppm, J_{HCCP} = 29.0 cps; J_{HCH} = 8.0 cps (the doublet of doublets shows fine structure due to long-range H–F coupling, probably with one of the two C_4CF_3 groups); $\tau_{(CF_3)_2CHO}$ 5.33 ppm (multiplet).

Anal. Calcd for $C_{10}H_{11}O_4PF_{12}$: C, 26.4; H, 2.4; P, 6.8; F, 50.2. Found: C, 26.5; H, 2.5; P, 6.9; F, 50.0

Reaction of Dimethyl Phenylphosphonite (18) with Hexafluoroacetone (7). Hexafluoroacetone (2 molar equiv) was added, over a 0.5-hr period, to a solution of the phosphonite **18** in hexane (20 ml) at −70°. After 1 hr at −70° and 1 hr at 20°, the mixture was diluted with 10 ml of hexane, warmed to achieve complete solution of the crystalline product, and cooled to 0° to obtain **2,2-dimethoxy-2-phenyl-4,4,5,5-tetrakis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholane (19),** mp 70–72° (70% of the theory). Spectral data in $CDCl_3$ exhibit $\delta^{31}P$ +30.8 ppm; τ_{CH_3O} 6.40 ppm, J_{HCOP} = 13 cps.

Reaction of Methyl Diethylphosphinite (20) with Hexafluoroacetone (7). Reaction at 20°. A solution of diethylchlorophosphine, $(C_2H_5)_2PCl$ (10 mmol), in heptane (20 ml) was added over a 45-min period to a solution of methanol (10 mmol) and triethylamine (10 mmol) in heptane (20 ml) at 25°. The mixture was kept 1 hr at 25°, filtered, and evaporated at 20 mm to yield methyl diethylphosphinite, $(C_2H_5)_2POCH_3$ (**20**), characterized by its nmr spectrum: τ_{CH_3O} 6.55 ppm, J_{HCOP} = 12.5 cps (heptane). Hexafluoroacetone (2 molar equiv) was added to the phosphinite **20** (5 mmol) in heptane (20 ml) at 20° over a 0.5 hr. The solution was evaporated at 30° (20 mm), and the noncrystalline residue was analyzed by nmr spectrometry in $CDCl_3$ which disclosed the following composition: 42% **2-methoxy-2,2-diethyl-4,4,5,5-tetrakis(trifluoromethyl)-2,2-dihydro-1,3,2-dioxaphospholane (21)** ($\delta^{31}P$ −13.5 ppm; τ_{CH_3O} 6.55 ppm, J_{HCOP} = 10.4 cps; $\delta^{19}F$ −9.4 ppm), 26% *anti*-C_2H_5/CH_3-**2-methoxy-2-hexafluoroisopropoxy-2-ethyl-3-methyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (22)** ($\delta^{31}P$ +7.5 ppm; τ_{CH_3O} 6.24 ppm, J_{HCOP} = 14.0 cps; $\delta^{19}F$ −4.2, −3.8, −0.3 ppm), 22% *syn*-C_2H_5/CH_3-**2-methoxy-2-hexafluoroisopropoxy-2-ethyl-3-methyl-4,4-bis(trifluoromethyl)-2,2-dihydro-1,2-oxaphosphetane (23)** ($\delta^{31}P$ +11.6 ppm; τ_{CH_3O} 6.15 ppm, J_{HCOP} = 14.0 cps; $\delta^{19}F$ −5.2, −3.0, +0.6 ppm). The oxyphosphoranes were purified as described below. The material balance in the product (10%) corresponded probably to methyl diethylphosphinate, $(C_2H_5)_2P(O)(OCH_3)$, $\delta^{31}P$ −61 ppm, which was not isolated.

Under the conditions of this experiment, the dioxaphospholane **21** is not converted into the oxaphosphetanes. **22** + **23** (see below).

Reaction at −70°. Diethylchlorophosphine (30 mmol) was combined with methanol and triethylamine in hexane solution (120

(20) NOTE ADDED IN PROOF. For a discussion of the permutational isomerization of these oxaphosphetanes by the *turnstile rotation* mechanism see (a) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem.*, **83**, 691 (1971); *Angew. Chem., Int. Ed. Engl.*, 10, 687 (1971); (b) F. Ramirez and I. Ugi, *Advan. Phys. Org. Chem.*, **9**, 25 (1971).

ml) at 20° as described above. The amine hydrochloride was filtered off, and the hexane filtrate containing methyl diethylphosphinite (**20**) was cooled to −70° and was treated with hexafluoroacetone (68 mmol) over a 1.5-hr period. The mixture was allowed to reach 20° in 2 hr and was evaporated at 30° (20 mm). The product consisted mainly (*ca.* 85%) of dioxaphospholane **21** (δ^{31}P −13), with some (*ca.* 15%) oxaphosphetanes **22** (δ^{31}P +7, *ca.* 9%) and **23** (δ^{31}P +11, *ca.* 6%).

The mixture of dioxaphospholane **21** (85%) and oxaphosphetanes **22** and **23** (15%) was kept 4.5 hr at 100° in the absence of solvent, under N_2. The product still had some phospholane **21** (*ca.* 10%), but consisted mainly of oxaphosphetanes *anti*-**22** (*ca.* 50%) and *syn*-**23** (*ca.* 40%). The proportion of oxyphosphoranes **21**, **22** and **23** was altered by fractional distillation, but no complete separation could be achieved. A sample of bp 25–26° (0.05 mm) obtained by distillation through an 8-in. spinning band column contained 28% of phospholane **21**, 44% of *anti*-phosphetane **22**, and 28% of *syn*-phosphetane **23**; it had the following analysis.

Anal. Calcd for $C_{11}H_{13}O_3PF_{12}$: C, 29.2; H, 2.9; P, 6.8; F, 50.4. Found: C, 29.4; H, 3.0; P, 6.8; F, 50.5.

Attempts to Interconvert the *anti*-22 and *syn*-23 Oxaphosphetanes Derived from Methyl Diethylphosphinite and Hexafluoroacetone. Thermally. A mixture of *anti*-**22** and *syn*-**23** (2.3:1.0) was kept 12 hr at 100°, without significant change in the proportion of isomers. A new P-containing substance, probably due to the Wittig reaction, methyl hexafluoroisopropyl ethylphosphonate, $(C_2H_5)P(O)(OCH_3)[OCH(CF_3)_2]$, was observed at δ^{31}P *ca.* − 37 ppm, τ_{CH_3O} 6.22, J = 11 cps. After 1 hr at 150° and 1 hr at 180° the ratio of phosphetanes to phosphonate (Wittig reaction) was 1.3:1.0, but the proportion of the remaining stereoisomers *anti*-**22** to *syn*-**23** had not changed significantly.

Thermally, with Added Hexafluoroisopropyl Alcohol, $(CF_3)_2CH$-OH. This acidic alcohol (10 mol %) was added to mixtures of *anti*-**22** + *syn*-**23**, and the mixtures were kept 3 hr at 110°, with these results: initial mixture, 59% **22**:41% **23** → 55% **22**:45% **23**; initial mixture, 32% **22**:68% **23** → 32% **22**:68% **23**.

The acidic alcohol (50 mol %) was added to mixtures of *anti*-**22** + *syn*-**23** and the mixtures were kept 0.5 hr at 120° and 4.5 hr at 140°, with these results: initial mixture, 55% **22**:45% **23** → 40% **22**:60% **23**; initial mixture, 34% **22**:66% **23** → 40% **22**:60% **23**.

Reaction of Alcohols with 2,2,2-Trialkoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes. A given alcohol (3 molar equiv) was added to a 1.5 *M* solution of the indicated dioxaphospholene in benzene at 25°, in the absence of catalyst, and in the presence of various molar proportions of a tertiary amine (pyridine or 2,4,6-trimethylpyridine). The course of the reaction was followed by ^{1}H nmr spectrometry. The pure dioxaphospholenes corresponding to the formulas $>P(OR)_3$, $>P(OR)_2(OR')$, $>P(OR)(OR'_2)$, and $>P(OR')_3$ were available from previous work. The relative amounts of the four dioxaphospholenes present in a given reaction mixture were determined from the integration of the ^{1}H nmr signals of their RO and R′O groups and of their $CH_3C{=}CCH_3$ groups. The amounts of alcohol, ROH, produced were followed in the same manner. The results are given in Tables I and II. *p*-Toluenesulfonic acid had no noticeable effect on the substitution reaction of **31**.

Reactions of the Tri-*p*-anisylmethyl Carbonium Ion with Nucleophiles[1]

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Abstract: Kinetic salt effects upon the forward and back reaction of the tri-*p*-anisylmethyl carbonium ion with water have been measured. These salt effects and those upon the activity coefficient of the alcohol allow us to determine the relative stabilities of the hydronium and carbonium ions and the transition state, $X^{\pm}$. The salt order upon f_{H^+}/f_{R^+} is $LiClO_4 \sim NaClO_4 > NaBr > NaNO_3 > NaCl > LiCl >$ no salt $\sim CsCl > Me_4NCl \sim KCl$; upon $f_{H^+}/f_{X^{\pm}}$ it is $LiClO_4 \sim NaClO_4 > NaBr > NaNO_3 > NaCl \sim Me_4NCl \sim CsCl \sim$ no salt $> LiCl \sim KCl$; and upon $f_{R^+}/f_{X^{\pm}}$ it is $Me_4NCl >$ no salt $\sim CsCl > NaCl > KCl > NaBr \sim NaNO_3 > LiCl > NaClO_4 > LiClO_4$. These relative activity coefficients are considered in terms of direct and indirect interactions between the salts and the reacting species. The second-order rate constant for reaction of the carbonium and hydroxide ions is 8200 l. mol^{-1} sec^{-1}, and the kinetic salt order is no salt $> Me_4NCl > KCl \sim NaCl > NaBr > NaNO_3 > NaClO_4 > LiCl > LiClO_4$. The second-order rate constant for attack of azide ion is 5×10^6 l. mol^{-1} sec^{-1}, and the first-order rate constant for ionization of the alkyl azide is 75 sec^{-1} at 25.0° in water.

The stability of carbonium ions in aqueous solution is of considerable importance. Stable triarylmethyl carbonium ions, *e.g.*, Malachite Green and Crystal Violet, react relatively slowly with anionic and other nucleophiles,[2,3] but attack of water on the triphenylmethyl carbonium ion in acetonitrile is moderately fast on the nmr time scale[4] ($\tau \approx 10^{-2}$ sec), and allylic carbonium ions have half-lives of $<10^{-5}$ sec, in hydroxylic solvents.[5] Taft and his coworkers found that the reactivity of triarylmethyl carbonium ions toward water is related to their stability relative to the alcohol.[6]

Relatively short-lived carbonium ions can be trapped in aqueous solution, for example, by azide ion or by the common ion, showing that nucleophilic anions can compete with hydroxylic solvents for the carbonium ions or ion pairs.[7]

The rates of SN1 solvolyses of alkyl halides and related compounds are subject to positive salt effects.[7,8] The effects are large, and highly specific not only in

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