M NaOH which had been thermostatted in an external water bath. This solution was immediately transferred to the second syringe of the stopped flow apparatus and the reaction trace was recorded. Imidatonium ions III were trapped into acid solutions by placing a small amount of amide acetal in a syringe needle and rapidly passing through this 2 mL of dilute phosphate buffer (pH 7.2) such that the resultant solution was immediately injected into an acidic buffer.

Rate constants were evaluated as slopes of plots of $\ln (A_\infty - A_t)$ vs. time. Excellent linearity was observed in all cases. All solutions in which rate constants were obtained were at ionic strength 0.1. For studies requiring buffered media, rate constants were obtained at three or four different total buffer concentrations maintaining the same buffer ratio and extrapolated to zero buffer concentration.

Product Analysis. The ratio of ester to amide was analyzed by dissolving substrate (0.1 g) in aqueous solution (100 mL), and after a time corresponding to ten half-lives of hydrolysis, the solution was extracted with ether. The ether was removed, and the products were analyzed by NMR spectroscopy.

The intermediate absorbances of Figures 1 and 2 were obtained using stopped-flow spectroscopy as previously described. These have been corrected for the partial hydrolysis of the amide acetal which occurs in the sodium hydroxide solution prior to mixing.

Acknowledgment. Financial support of the National Research Council of Canada is gratefully acknowledged.

Registry No.—Ethylene glycol, 107-21-1; *N,N*-dimethylbenzamide dimethyl acetal, 35452-04-1; *N,N*-dimethyl-*p*-methoxybenzamide dimethyl acetal, 66475-66-9; *N,N*-dimethyl-*p*-methylbenzamide dimethyl acetal, 66475-67-0; *N,N*-dimethyl-*p*-chlorobenzamide dimethyl acetal, 66475-65-8; *N,N*-dimethyl-*m*-chlorobenzamide dimethyl acetal, 66475-64-7.

References and Notes

(1) R. A. McClelland, *J. Am. Chem. Soc.*, **100**, 1844 (1978).
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(3) M. Ahmad, R. G. Bergstrom, M. J. Cashen, A. J. Kresge, R. A. McClelland, and M. F. Powell, *J. Am. Chem. Soc.*, in press.
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(6) This is a case where the equilibrium assumption and the steady-state assumption are equivalent.
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(9) Y. Chiang, A. J. Kresge, and C. I. Young, *Finn. Chem. Lett.*, 13 (1978).
(10) Unfortunately, a direct comparison of k_3 (or k_3/K_{SH^+}) for cyclic vs. acyclic amide acetals is not possible at present, since the acyclic systems were of necessity studied in mixed solvents.[1]
(11) This assumes that the value of k_5 for the ring-opened imidatonium ion is the same as the value for an *O*-ethyl imidatonium ion (see ref 5).
(12) R. A. McClelland, M. Ahmad, and G. Mandrapilias, *J. Am. Chem. Soc.*, **101**, 970 (1979).
(13) Although this may not be apparent from Figure 2 the term in k_8 is statistically valid.
(14) There might be a question as to whether the base-catalyzed limb of F3 actually refers to hydrogen ortho ester decomposition, since the evidence associated with the similarity of rate constants for amide acetal and ortho ester is lacking here. We suggest firstly that there is no other interpretation for this process consistent with any simple mechanisms that can be pictured for this system. Secondly, and more importantly, in a separate paper[3] a set of experiments is described starting directly with a 1,3-dioxolenium ion in which all three kinetic processes for decomposition of the hydrogen ortho ester are observed. Although these data refer to 50% acetonitrile (of necessity) their feature is that the hydroxide ion catalysis (k_7) is extremely efficient, and the actual value of k_7 is of the same order of magnitude as that obtained with the amide acetal in water alone.
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Sequential Protonation and Dealkylation Modes of Monocyclic Phosphite Esters

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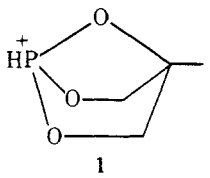
Protonated forms of monocyclic phosphites of the type $MeOP\overline{(OC_nO)}$ in $HFSO_3$ at −50 °C exhibit $^1J_{PH}$ couplings which decrease in the order five membered > six membered > seven membered for the same degree of methyl substitution on the ring. Within a ring of given size, this coupling also decreases with increased methyl substitution. In highly methyl-substituted esters, a ring-opening dealkylation by solvolysis readily takes place near −50 °C, resulting in the formation of $MeO(H)P^+(OH)OC_nOSO_2F$ ions. In dilute acid at room temperature, dealkylation occurs on the MeOP group. NMR data from the only other reported attempt to protonate a monocyclic phosphite ester (ref 3) are inconsistent with the present study and probably represent a dealkylated acyclic product.

Because phosphite esters are easily solvolyzed in acidic media, systematic studies of these compounds in protonated form have until recently[1] been restricted to acyclic systems[2,3] such as $P(OR)_3$ and $P(OAr)_3$, which are strain-free and hence relatively unreactive. Prior to our report of the P–H coupling constants of **1–4**[1] (Table I), there has appeared only a single disclosure of a $^1J_{PH}$ value for a cyclic phosphite ester, namely, **5**.[3]

In this paper we describe our low temperature ^{31}P NMR investigations of **5–11** dissolved in $HFSO_3$. Evidence is presented which indicates the following: (1) the $^1J_{PH}$ and δ ^{31}P data reported for **5** are incorrect, (2) $^1J_{PH}$ values are a function of ring substitution as well as ring size, (3) the appearance of a new protonated species with time or with a moderate in-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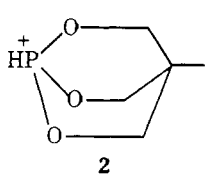
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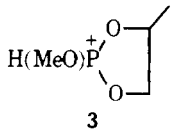
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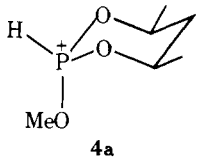
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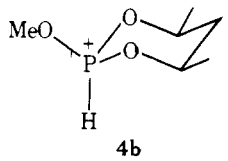
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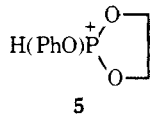
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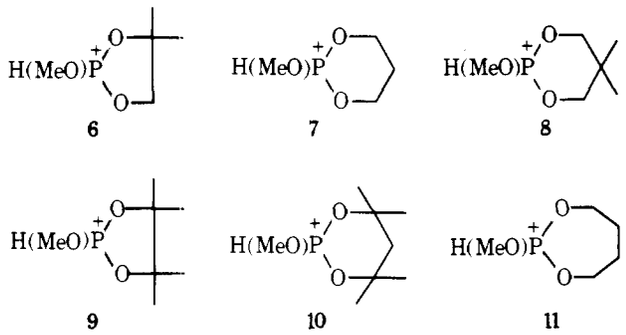
Table I. ^{31}P NMR Parameters for Protonated Cyclic Phosphite Ester [a]

	$^1J_{PH}$ [b] (±1 Hz)	$^3J_{PH}$ [c] (±1 Hz)	$\delta^{31}P$ [d] (±0.5 ppm)	ref
1	929	*e*	46.1	1
2	899	4.5 (sept)	32.2	1
3	890	12.8 (sept)[f]	44.7	1
4a	865	12.8 (q)[g]	17.3	1
4b	850	12.8 (q)[g]	18.2	1
5	913	8.9	43.9	present work
	822 (±2)	*h*	16	3[i]
6	882	12.2 (sext)[j]	44.8	present work[k]
7	870	*l*	18.2	present work
8	861	11.1	17.1	present work
9	856	13.4 (q)	40.2 (q)	present work
10	851	12.8	15.7	present work
11	844	*m*	28.7	present work

[a] Data taken at −50 °C in $HFSO_3$ unless otherwise indicated. [b] Doublet in all cases. [c] q = quartet, sept = septet, sext = sextet. [d] Downfield chemical shifts relative to 85% H_3PO_4 (external) are positive. [e] Insufficient fine structure to resolve this coupling. [f] $^3J_{POCH_3} = {}^3J_{POCH_2} = {}^3J_{POCH}$. [g] $^3J_{POCH}$. [h] Not reported. [i] Data taken in 100% H_2SO_4 at ambient probe temperature. [j] Outer four peaks of sextet were shoulders. [k] Data taken at −60 °C. [l] Insufficient resolution for determination. [m] The symmetrical pattern of 16 peaks for each half of the P–H doublet which became resolved at −20 °C was not analyzed.



6 7 8

9 10 11

crease in temperature is due to a species arising from an S_N1 dealkylation involving ring opening by the solvent, and (4) dealkylation of **9** under certain conditions takes place on the POMe group (presumably by an S_N2 mechanism) instead of in the ring system.

The dealkylation of acyclic phosphite esters, illustrated in eq 1, has been extensively studied for hydrohalic acids.[2-6] In

$$P(OR)_3 + HX \rightleftarrows HP^+(OR)_3 + X^- \rightarrow H(O)P(OR)_2 + RX$$

R = alkyl, aryl; X - halogen, SO_3F, CF_3CO_2, HSO_4, SO_3CF_3 (1)

a strongly acid medium such as HSO_3F[1,2] or HCl–ether,[6] complete protonation and slow proton exchange on the NMR time scale can be achieved and dealkylation can be inhibited below −50 °C. The generality of this reaction and its similarity to the widely applied Michaelis–Arbuzov reaction of phosphite esters with alkyl halides have led several investigators to explore the mechanism of reaction 1.[2,6-12] When R is an unhindered straight chain or secondary alkyl, dealkylation appears to occur by an S_N 2 mechanism,[7] while concurrent S_N1 and S_N2 mechanisms are implicated for more sterically bulky groups.[8,9] Qualitative and quantitative rate studies which have been carried out[2,6,10-12] lead to the following conclusions. (1) The ease of O–C bond cleavage increases in the order $(n\text{-BuO})_3P < (i\text{-PrO})_3P < (t\text{-BuO})_3P$, which follows the order of increasing stability of the carbonium ion. Here an S_N1 mechanism is implied. (2) The first dealkylation proceeds at a much faster rate than the second and third. (3) Dealkylation is rapid above −50 °C for sterically unhindered phosphite esters. (4) The reaction of $(n\text{-BuO})_3P$ with HCl is first order in phosphite and second order in HCl, implying initial protonation followed by nucleophilic S_N2 displacement of alkyl by HCl or HCl_2^-.

Experimental Section

Undecoupled ^{31}P resonances were recorded with a Bruker HX-90 spectrometer operating at 36.44 mHz in the Fourier mode. The $HFSO_3$ solution provided the ^{19}F signal required for lock stabilization. Samples of protonated phosphites were prepared by cooling 2 mL of $HFSO_3$ to −78 °C in a 10-mm (o.d.) NMR tube and allowing the phosphite (liquid, solid, or frozen) to flow down the side of the tube in small amounts (~20 mg per addition) until about 200 mg of solute had been added. Vigorous shaking along with alternate warming (−40 °C) and cooling (−78 °C) served to effect solution. *Severe decomposition or small explosions occurred if localized areas of heating were allowed to intensify around undissolved phosphite.* The ^{31}P signal of 85% H_3PO_4 was used as the external standard, even though slight broadening occurs at low temperature.

Routine ^1H NMR spectra were obtained on either a Varian A-60 or a Hitachi Perkin-Elmer R20-B spectrometer operating at 50 mHz. An Atlas CH-4 mass spectrometer provided the low-resolution mass spectra. Infrared spectra were obtained on a Beckman IR-4250 spectrometer using the 2851.5-cm^{-1} band of polystyrene as a calibration.

Fluorosulfonic acid was obtained from Aldrich Chemical Co. and distilled before use. Compounds **5**,[13] **6**,[14] **7**,[15] **8**,[15] **9**,[14] and $CH_3OP(O)(OCH_2CH_2OH)H$ (**12**)[16] were prepared by literature procedures.

$CH_3OPOC(CH_3)_2CH_2C(CH_3)_2O$ (10). To a mechanically stirred solution of 27.5 g (200 mmol) of PCl_3 in 200 mL of ether at 0–5 °C was slowly added a solution of 24.6 g (200 mmol) of diol and 35 g (440 mmol) of pyridine in 50 mL of ether. After addition was complete, stirring was continued for about 1 h before a solution of 6.4 g (200 mmol) of methanol and 16 g of pyridine (200 mmol) in 50 mL of ether was slowly added. After this addition the ice bath was removed and stirring was continued overnight. With the use of a Schlenk apparatus, the ethereal solution was filtered from the pyridine salt and the solid was further washed with ether. Removal of the ether and distillation of the residue gave 21.5 g of the phosphite (56% yield; bp_{21} 82–83 °C). The ^1H NMR spectrum of the neat liquid showed a slightly broadened resonance at 1.34 ppm for the two pairs of chemically inequivalent methyl protons on the ring, a doublet ($^3J_{POCH}$ = 12.1 Hz) at 3.36 ppm for the methoxy protons, and an AB pattern of an ABX system for the methylene protons centered at 2.04 ppm with the correct integration of 12:3:2, respectively, for the three types of protons. In the ABX system where X is phosphorus, J_{AB} = 14.2 Hz, J_{AX} = 3.1 Hz, J_{BX} = 0.0 Hz, and $\delta_B - \delta_A$ = 0.56 ppm. The ^{31}P NMR spectrum consisted of a doublet at 128.9 ppm relative to 85% H_3PO_4 with $^3J_{POCH}$ = 12.1 Hz. A mass spectrum revealed a parent peak at *m/e* 192 corresponding to the molecular weight.

$H(O)POC(CH_3)_2CH_2C(CH_3)_2O$. This compound was isolated from the attempt to prepare compound **10** via transesterification. Equimolar amounts of $P(OCH_3)_3$ and the diol were mixed and slowly heated to 110–120 °C; CH_3OH and $P(OCH_3)_3$ were evolved. Vacuum distillation of the remaining liquid yielded a mixture of $OP(OCH_3)_3$ and $H(O)P(OCH_3)_2$. The residue left in the reaction vessel, which solidified upon cooling, proved to be $H(O)POC(CH_3)_2CH_2C(CH_3)_2O$. After recrystallization from ether (mp 61 °C), a mass spectrum revealed a parent peak at *m/e* 178 corresponding to the molecular weight. A ^1H NMR spectrum ($CDCl_3$) revealed resonances for the two different sets of methyl protons at 1.49 and 1.53 ppm, a doublet at 6.98 ppm with $^1J_{PH}$ = 694.0 Hz for the proton directly bonded to phosphorus, and a broadened resonance for the methylene protons at 2.04 ppm, all in the correct integration ratios for this hydrogen phosphonate. A ^{31}P NMR spectrum revealed a doublet at −6.2 ppm relative to 85% H_3PO_4 with $^1J_{PH}$ = 693 Hz. When dissolved in CCl_4, an infrared spectrum revealed a phosphoryl resonance at 1281 cm^{-1} with a shoulder at 1287 cm^{-1} and a P–H stretch at 2408 cm^{-1} with a shoulder at 2429 cm^{-1}.

$CH_3OPOCH_2CH_2CH_2CH_2O$ (11). To about 200 mL of benzene was added 30 g (330 mmol) of 1,4-butanediol. Some of the benzene and any benzene–water azeotrope were then distilled away from this heterogeneous mixture to ensure the absence of water. The mixture was then cooled to 40 °C, after which 47 g (380 mmol) of $P(OCH_3)_3$ and 0.1 g of $NaOCH_3$ were added. By vigorously stirring the mixture and slowly heating from 40 to 110 °C, the methanol–benzene azeo-

Table II. ^{31}P NMR Data for Time/Temperature Dependent Protonation [a]

initial species	second species $^1J_{PH}$ (±1 Hz)	$^3J_{PH}$ (±1 Hz)	$\delta^{31}P$ (±0.5 ppm)
6	848[c]	12.8 (q)[b] 6.4	20.8
9	831[d]	12.2	20.4
10	833[e]	12.6 (q)	20.5

[a] See text for conditions. [b] Quartet of triplets with some coincidence of peaks. Resonance appears as nine peaks. [c] Registry no., 69576-74-5. [d] Registry no., 69576-75-6. [e] Registry no., 69576-76-7.

trope and finally the remaining benzene were distilled away. Distillation was then continued under vacuum, and a 13% yield of colorless liquid product was realized (bp_{8-9} 56–57 °C). This preparation therefore seems superior to the literature preparation from CH_3OPCl_2 and 1,4-butanediol, which results in only a 3% yield.[17]

$(CH_3O)P(O)(H)(OCH_2CH_2OH)$ (12). This compound was prepared strictly according to the literature preparation.[16] Equimolar (113.3 mmol) amounts of $(CH_3O)_2P(O)H$ and $HOCH_2CH_2OH$ were heated at 118–120 °C for 2.5 h under an N_2 atmosphere, allowing CH_3OH to distill off as it was formed. However, ^1H and ^{31}P NMR analyses of the reaction mixture after this time period revealed that the reaction was neither quantitative (as claimed in the literature) nor specific since a secondary product was also formed in the reaction in about one-third the yield of the primary product. Since purification procedures result in further side reactions of the product,[16] the protonation experiment was performed on the crude product mixture which was approximately 65–75% pure.

Discussion

In accord with our earlier observation that $^1J_{PH}$ decreases in the series bicyclic > monocyclic > acyclic protonated phosphites, this coupling is also found to decrease in the monocyclic ring series five membered > six membered > seven membered (Table I) for the same degree of methyl ring substitution. Extensive ring methylation reverses this trend as in the case of **9 < 4, 7, 8.** This apparent inductive effect (as well as that of an OC_6H_5 group on phosphorus in **5**), which can lower the positive charge on phosphorus and thereby reduce $^1J_{PH}$, can be seen within the five- and six-membered ring systems in that $^1J_{PH}$ decreases in the orders **5 > 3 > 6 > 9** and **7 > 4a,b, 8 > 10**,[18] respectively. A similar inductive effect is seen in the 5-Hz decrease in $^1J_{PH}$ from $HP^+(OCH_2)_3CH$ (904 Hz[19]) to **2**. This diminution is consistent with the 9-Hz decrease in this coupling when two methyl groups are introduced in the 5 position of **7** (i.e., **8**).

Although our low-temperature NMR data for **5** in $HFSO_3$ are very different from those reported by others in 100% H_2SO_4 at room temperature[3] (Table I), the previously recorded values for $^1J_{PH}$ and $\delta^{31}P$[3] are unexpected for the following reasons. (1) The relationship between constraint and $^1J_{PH}$ just discussed strongly suggests that this coupling should be larger in **5** than in $HP(OMe)_3^+$ (827 Hz[2]), particularly since an electronegative POPh group is present in the former [e.g., the value for $HP^+(OMe)_3$ is less than that for $HP^+(OPh)_3$ (875 Hz[2])]. (2) Our $\delta^{31}P$ value is in better agreement with those of other protonated five-membered ring systems (Table I). (3) In view of the ease with which systems of this type undergo dealkylation with ring opening above −50 °C (vide infra), it would be very surprising if **5** remained intact in 100% H_2SO_4 at room temperature. In our experiments **5** decomposes in $HFSO_3$ at temperatures as low as −20 °C.

The methylated ring systems **6, 9,** and **10** displayed two sets of resonances in $HFSO_3$ at −50 °C, indicating the presence of a second protonated species in smaller concentration (Table II). These spectra changed with time until after about 2–3 h only the second species remained (Figure 1). Increasing the temperature to −20 °C effected this conversion in about 20 min. The near equivalence of the fine structure in each arm of the P–H doublets and the relative magnitudes of the $^1J_{PH}$ values are consistent with the presence of conformational changes of the type shown in eq 2 and 3. Thus, lower $^1J_{PH}$

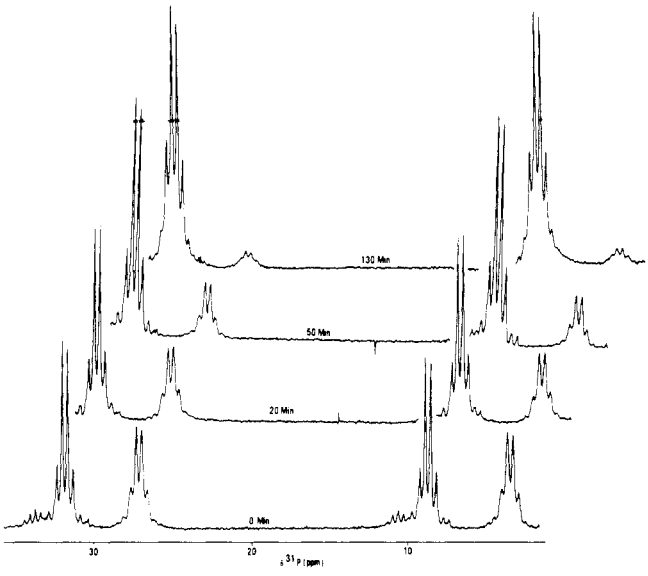
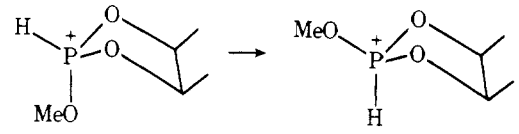


Figure 1. ^{31}P NMR spectra of **10** in $HFSO_3$ at −60 °C (upfield doublet of multiplets) showing its conversion to ring-opened product (downfield doublet of multiplets). At the time the first spectrum was obtained, partial conversion had already occurred.



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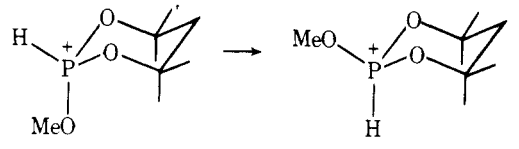


(3)

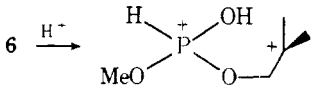
values are associated more with axial P–H bonds than with equatorial, as in isomeric **4a,b.**[1] The most compelling argument against this hypothesis, however, stems from the observation that the spectral change is irreversible upon cooling. For example, a sample of **10** containing only the second protonated species after being held at −78 °C for 5 days showed no trace of the initial protonated species in its NMR spectrum. Furthermore, the 20-ppm difference in chemical shift between the two species in each of the spectra of the five-membered ring systems (**6** and **9**) seems rather large to attribute to two envelope conformations. Such conformations are likely to be very similar in their electronic properties owing to ring strain, which is expected to flatten the rings considerably. It would also be surprising if such conformers did not rapidly interconvert on the NMR time scale.

The remarkable similarity in $^1J_{PH}$ values of the second species in these spectra to those of acyclic $HP^+(OR)_3$ systems[2] prompted an investigation of the possibility of a ring-opening dealkylation depicted for **9** in reaction 4. The fine structure

$$\mathbf{9} + HFSO_3 \rightarrow MeOP^+(H)(OH)(OCMe_2CMe_2OSO_2F) \quad (4)$$

on the arms of the ^{31}P doublet ($^1J_{PH}$), which arises from $^3J_{PH}$ couplings associated with the OCH_3 protons, is the same since ring opening is not expected to affect this coupling appreciably. The same reasoning applies to the spectrum of the ring-opened product of **10**, and hence the spectral parameters reported earlier for **5** are also consistent with a ring-opened solvolysis product. The preservation of both $^3J_{PH}$ couplings

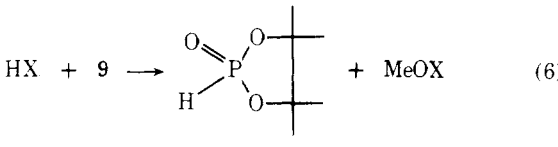
in **6** accords with ring opening at the substituted carbon in order to form an intermediate tertiary carbonium ion (eq 5).



$$\xrightarrow{SO_2F^-} MeO(H)\overset{+}{P}(OH)OCH_2CMe_2OSO_2F \quad (5)$$

This inference can be drawn from the increasing importance of an S_N1 solvolysis mechanism when bulky alkoxy groups are present in acyclic phosphite esters.[8,9] Further observations which are consistent with solvolysis with ring opening are the similar ^{31}P chemical shifts and $^1J_{PH}$ values for the second protonated species in Table II as well as the remarkably similar data for the protonated form of the model compound $MeO(H)P(O)OCH_2CH_2OH$[16] in $HFSO_3$ at −50 °C, which is presumably $MeO(H)P^+(OH)OCH_2CH_2OH$ [$\delta^{31}P$ 22.3 (d, $^1J_{PH}$ = 833 Hz)].[20]

Interestingly, $CDCl_3$ solutions of **9** treated with approximately equimolar quantities of CF_3COOH or $HFSO_3$ at room temperature exhibited ^{31}P NMR spectra indicative of the phosphite product in reaction 6 as shown by comparison under the same conditions with an authentic sample. It thus appears



that the dealkylation mechanism(s) is influenced by rather subtle kinetic and thermodynamic factors which can drastically alter the course of the reaction.

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Registry No.—**5**, 24151-47-1; **6**, 69576-69-8; **7**, 69576-70-1; **8**, 69610-98-6; **9**, 69576-71-2; **10**, 69576-72-3; **10** unprotonated form, 69576-77-8; **11**, 69576-73-4; **11** unprotonated form, 69576-78-9; **12**, 21941-55-9; **12** protonated form, 69576-79-0; phosphorus trichloride, 7719-12-2; 2,4-dimethyl-2,4-pentanediol, 24892-49-7; 4,4,6,6-tetramethyl-1,3,2-dioxaphosphorinane 2-oxide, 34883-00-6; trimethyl phosphite, 121-45-9; 1,4-butanediol, 110-63-4; dimethyl phosphonate, 868-85-9; ethylene glycol, 107-21-1; 2-methoxy-1,3,2-dioxaphospholane, 3741-36-4.

References and Notes

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(18) Although **3** is prepared as an isomeric mixture (Denny, D. Z.; Chen, G. Y.; Denney, D. B. *J. Am. Chem. Soc.* **1969**, *91*, 6838), only one protonated species is observed in the low-temperature $HFSO_3$ spectrum.[1] In contrast, the isomers of **4** give rise to isomeric protonated species with substantially different $^1J_{PH}$ values, which have been rationalized in terms of orbital repulsion effects.[1]
(19) We thank Mr. Phil Stricklen for this measurement.
(20) All attempts to protonate $MeOPOCH_2CH_2O$ failed owing to extensive decomposition. Among the many peaks present in the ^{31}P spectrum are two clusters of peaks separated by about 800 Hz whose chemical shift is approximately 25 ppm. This observation is reasonably consistent with the presence of $MeO(H)P^+(OH)(OCH_2CH_2OSO_2F)$ considering the similar data obtained for $MeO(H)P(O)(OCH_2CH_2OH)$ in $HFSO_3$.

Stabilities of Trivalent Carbon Species. 5. Equilibria of Excited Singlet Alcohols and Carbocations[1]

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Fluorescence titrations were carried out with four alcohols whose greatly enhanced reactivity to form carbocations in the excited singlet state is predicted by Förster cycle calculations. Analysis of the fluorescence titration of 5*H*-dibenzo[*a*,*d*]cycloheptatrien-5-ol indicates that the alcohol reacts with acid in the excited singlet state, but not the ground state, at H_R between +1 and −3. Formation of the cation at very low acid concentrations, as predicted by the Förster cycle, is precluded by the short lifetime of the excited singlet alcohol. The behavior of the fluorescence intensities of the alcohol and corresponding cation implies the involvement of another, nonfluorescing species in the excited-state reactions. Preparative photolyses of the cation indicate that its principal photoreactions are hydride transfer and ether formation.

In general, carbocations absorb light at lower energies than their covalent precursors, and consequently the dissociation constant for reaction 1 involving excited singlet species,

$$R\text{-}X = R^+ X^- \quad (1)$$

calculated from the Förster cycle,[3] is greater than that for the ground-state species (see Figure 1). However, Förster cycle calculations may not describe the actual behavior of the excited species if equilibrium is not established during their lifetimes.[4] We have examined the fluorescence spectra of several alcohols and their corresponding cations in aqueous sulfuric acid solution in order to establish the chemistry of these species in the first excited singlet state. Table I lists the alcohols which give rise to carbocations which display fluorescent emission, their pK_{R^+} values in the ground state, and pK_{R^+}* values calculated from the Förster cycle. Additionally,

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