

Synthesis and Reactions of Some Tetraalkoxyphosphonium Salts¹

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Abstract: Several relatively stable tetraalkoxyphosphonium salts were synthesized by reactions involving phosphates and trialkyloxonium fluoroborates. Their proton and ³¹P nmr spectra were studied. The acyclic salts underwent slow decomposition at room temperature to give alkyl fluorides and boron trifluoride complexes of the parent phosphates. With certain five-membered tetraalkoxyphosphonium fluoroborates facile ring-opening reactions were observed which gave carbonyl compounds by typical Wagner-Meerwein shifts. Studies on the reactivity of the acyclic salts showed that they are strong alkylating reagents. For example, tetraethoxyphosphonium fluoroborate (**1**) underwent quantitative reactions with some strong nucleophiles to give typical Arbusov products. In addition, **1** was found to participate in exchange reactions with methanol or sodium methoxide.

Alkoxyphosphonium salts are important intermediates in many reactions of organophosphorus chemistry; for example, they form as transient intermediates in the Arbusov² and Perkow³ reactions.

Isolation of alkoxyphosphonium salts has been difficult because of their rapid decomposition by nucleophiles. Formation of alkoxyphosphonium salts as intermediates in the reaction of phosphines with *t*-alkyl hypochlorites was demonstrated by Denney and Di Leone,⁴ who obtained bicyclo[2.2.1]-1-heptyloxyphosphonium chloride from triphenylphosphine and bicyclo[2.2.1]-1-heptyl hypochlorite. Its isolation was possible because nucleophilic attack by chloride at a bridghead carbon is prohibited and S_N1 decomposition is quite slow. Tetraneopentylphosphonium chloride was formed as an intermediate when trineopentyl phosphite was oxidized with neopentyl hypochlorite.⁵ It decomposed with a half-life of *ca.* 3 min at room temperature to neopentyl chloride and trineopentyl phosphate. Isolation of tetramethoxyphosphonium hexachloroantimonate was reported by Cohen.^{6,7} In this case the intermediate phosphonium salt formed by reaction of trimethyl phosphite and methyl hypochlorite was intercepted with antimony pentachloride. Similar attempts by Cohen to trap the intermediate phosphonium salt in a Perkow reaction were not successful.

Teichmann⁸ and Nesterev⁹ studied reactions of various phosphates and phosphonates with trialkyloxonium salts and obtained evidence for formation of relatively stable alkoxyphosphonium salts.

The present work was directed toward the synthesis of relatively stable tetraalkoxyphosphonium salts. An investigation of reactions of these salts with nucleophilic reagents, which has received little attention in the past, was also carried out. Studies of their properties both chemical and physical have been conducted. In

particular their proton and phosphorus (³¹P) nmr spectra have received considerable study.

Results and Discussion

(a) **Tetraethoxyphosphonium Fluoroborate (1).** When equimolar quantities of triethylphosphate and triethyloxonium fluoroborate were allowed to react either in methylene chloride or without solvent, tetraethoxyphosphonium fluoroborate (**1**) was formed in quantitative yields. Completeness of the reaction was shown by the absence of methylene absorptions for triethyl phosphate and triethyloxonium fluoroborate at 4.06 and 4.78 ppm, respectively, in the proton nmr after 20 hr. The proton nmr spectrum of **1** consists of a methyl triplet (*J* = 7 Hz) which is further split by weak coupling with phosphorus (*J* = 2 Hz) at 1.48 ppm and a distorted quintet at 4.65 ppm. The quintet arises because of strong coupling of the methylene hydrogens with both phosphorus and the methyl protons. By comparison with the position of the methylene absorption for triethyl phosphate at 4.06 ppm (Table I), the

Table I. Proton and ³¹P nmr Spectral Data of Phosphorus Species in Methylene Chloride

Compound	δ (ppm) ^a for α protons	<i>J</i> , Hz	³¹ P absorption (ppm) <i>vs.</i> H ₃ PO ₄
Triethyl phosphate	4.06 (m)		+1.0
Tetraethoxyphosphonium fluoroborate	4.65 (m)		+2.4
Triethyl phosphate-BF ₃ complex	4.32 (m)		+7.8
Trimethyl phosphate	3.75 (d)	11.5	-5.2
Tetramethoxyphosphonium fluoroborate	4.37 (d)	11.5	-1.9
Trimethyl phosphate-BF ₃ complex	4.00 (d)	11.5	+1.6

^a TMS used as internal standard.

downfield shift of *ca.* 0.6 ppm found in **1** is consistent with less shielding of the α-protons in the positively charged salt. Further evidence for alkylation of triethyl phosphate by the oxonium salt was supplied by the infrared spectrum of **1** which showed that the phosphoryl absorption of the starting material had virtually disappeared. Hydrolysis of **1** in methylene chloride

(1) This research has been supported by the National Science Foundation under NSF GP 4997X and by the National Institutes of Health under GM 12625.

(2) A. Michaelis and R. Kaehne, *Chem. Ber.*, **31**, 1048 (1898); (b) A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

(3) W. Perkow, K. Ullerich, and F. Meyer, *Naturwissenschaften*, **39**, 353 (1952).

(4) D. B. Denney and R. R. Di Leone, *J. Am. Chem. Soc.*, **84**, 4737 (1962).

(5) D. B. Denney and H. Relles, *Tetrahedron Lett.*, 573 (1964).

(6) J. S. Cohen, *ibid.*, 3491 (1965).

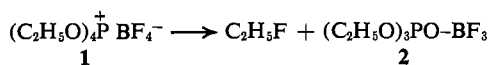
(7) J. S. Cohen, *J. Am. Chem. Soc.*, **89**, 2543 (1967).

(8) H. Teichmann, M. Jatkowski, and G. Hilgetag, *Angew. Chem. Intern. Ed. Engl.*, **6**, 372 (1967).

(9) L. V. Nesterev and R. I. Mutalopova, *Tetrahedron Lett.*, 51 (1968).

was followed by proton nmr and required several hours. Absorptions for **1** were gradually replaced during this period by new absorptions corresponding to triethyl phosphate. In a separate experiment, formation of ethanol was confirmed by glpc. Further reactions of tetraethoxyphosphonium fluoroborate with nucleophilic reagents gave the expected alkylation products (see section d).

Tetraethoxyphosphonium fluoroborate undergoes complete decomposition when it is heated at 100° for 10 min. On storage at room temperature under anhydrous conditions, its half-life is 20 days. At refrigeration (10°) temperature, **1** was found to be 22% decomposed after 1 month. The major decomposition products in all cases were ethyl fluoride and the boron trifluoride complex of triethyl phosphate (**2**). The complex **2**, which



was also prepared by reaction of triethyl phosphate and boron trifluoride etherate, showed a methylene quintet centered at 4.32 ppm in the proton nmr spectrum. An undetermined quantity of diethyl ether was also formed during decomposition of **1**. Hydrolysis of **1** yields ethanol which is alkylated by **1** to give ether.

The ³¹P nmr spectrum (Table I) of **1** showed that it absorbs in a region between that of parent phosphate and the complex **2**. This trend of increasing upfield absorptions in the order phosphate, tetraalkoxyphosphonium salt, boron trifluoride complex was also observed in several other acyclic systems. These results also support other work by Teichmann⁶ and coworkers who found that tetraalkoxyphosphonium salts absorb in the same region of the ³¹P nmr spectrum as their parent phosphates. It is also interesting to note that the value of +2.4 ppm for the ³¹P nmr absorption of **1** lies between the chemical shifts reported for triethyl phosphite (-138 ppm) and pentaethoxyphosphorane (+70.9 ppm).¹⁰ The upfield shifts illustrate that phosphorus is more highly shielded by successive addition of ethoxy groups.

(b) Tetramethoxyphosphonium Fluoroborate (3). Attempted synthesis of tetramethoxyphosphonium fluoroborate (**3**) from equimolar quantities of trimethyl phosphate and trimethyloxonium fluoroborate in methylene chloride, in which the oxonium salt is sparingly soluble, gave low yields of **3**. The reaction was next allowed to proceed in liquid sulfur dioxide at 0° in a sealed tube. In this media both of the reactants and the product **3** were soluble. However, after *ca.* 2 days, during which time the proton nmr spectrum was scanned periodically, it was apparent that no further reaction was taking place. Integration of the nmr peaks showed that *ca.* 39% of the phosphate was converted to **3**. A doublet (*J* = 11.5 Hz) at 4.25 ppm was observed for **3** in sulfur dioxide. Another doublet (*J* = 11.5 Hz) at 3.77 ppm indicated unreacted trimethyl phosphate and possibly small amounts of its boron trifluoride complex (**4**). Singlet absorptions for dimethyl ether and unreacted trimethyloxonium fluoroborate were also found in the spectrum at 3.2 and 4.5 ppm, respectively.

(10) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, **86**, 3897 (1964).

It was noted that proton nmr spectra of mixtures containing both the complex **4** and trimethyl phosphate gave only one doublet absorption, indicating that rapid exchange of boron trifluoride with trimethyl phosphate takes place at room temperature. The position of the doublet can be shifted upfield or downfield from *ca.* 3.7–4.0 ppm by addition of trimethyl phosphate or **4**. The complex, prepared independently from boron trifluoride etherate and trimethyl phosphate, exhibited a doublet absorption at 4.0 ppm. It is therefore possible that small quantities of the complex **4** which may have been building up in the sulfur dioxide solution could not be detected by proton nmr and could reduce the nucleophilicity of trimethyl phosphate sufficiently to inhibit further reaction after 2 days at 0°. Alternatively, in the closed system an equilibrium may have been reached. In any case, when the mixture was allowed to stand at room temperature, the upfield doublet

$$\text{(CH}_3\text{O)}_3\text{P}=\text{O} + \text{(CH}_3\text{)}_3\text{O}^+\text{BF}_4^- \rightleftharpoons \text{(CH}_3\text{O)}_4\text{P}^+\text{BF}_4^- + \text{CH}_3\text{OCH}_3$$

3

shifted from 3.77 to 3.9 ppm after 1 more day. A concomitant decrease in the area of the 4.25 ppm doublet indicated that **3** was rapidly decomposing to the complex **4** at room temperature.

Tetramethoxyphosphonium fluoroborate **3** was obtained in 88% yield by allowing trimethyloxonium fluoroborate to react at room temperature with a fivefold excess of trimethyl phosphate without solvent. After 3.5 hr, the phosphonium salt could be precipitated as a white solid by adding dry ether. The proton nmr spectrum of **3** in methylene chloride, in which it was highly soluble, consisted of a doublet (*J* = 11.5 Hz) at 4.37 ppm. A smaller doublet (*ca.* 5%) at 4.0 ppm is attributed to the complex **4**.

At high resolution, the ³¹P nmr spectrum of freshly prepared **3** showed a seven-line pattern (*J* = 11.5 Hz) centered at -1.9 ppm (Table I). This multiplet contains a large center band indicating that phosphorus is coupled with an even number of protons. The position of the ³¹P nmr absorption is not in agreement with Cohen's reported value of -51.5 ppm for the tetramethoxyphosphonium hexachloroantimonate.^{6,7} The ¹H nmr spectrum reported by Cohen is in agreement with that found in this work. It is not possible at this time to explain the discrepancy between the ³¹P nmr spectra (private communication from Dr. Cohen).

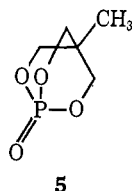
Decomposition of *ca.* 90% pure **3**, containing about 10% **4** at room temperature for several days, gave **4**. The vapor phase above the decomposing mixture was found to contain both methyl fluoride and dimethyl ether. The latter can arise by reactions of **3** with moisture. In addition, a small quantity of trimethyloxonium fluoroborate was precipitated from the reaction mixture by addition of methylene chloride. That this material was formed during storage of **3** at room temperature is best explained by a reaction of **3** with dimethyl ether. Although more complicated pathways involving pyrophosphates or phosphorofluoridates can be postulated as intermediates in oxonium salt formation from **3**, no evidence for these species was found by careful examination of the proton and ³¹P nmr spectra.

In another study, tetramethoxyphosphonium fluoroborate was found to be 47% (by weight) decomposed

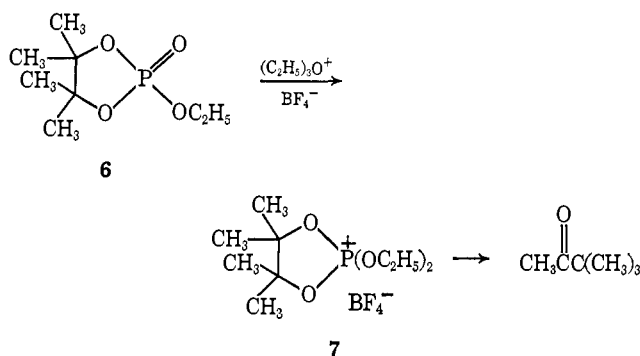
after storage at 10° for 1 month under anhydrous conditions.

(c) **Alkylation of Other Phosphates.** No detectable quantities of phosphonium salts were formed in reactions involving triphenyl phosphate and either triethyl or trimethyloxonium fluoroborate when they were allowed to react at room temperature. Triphenyl phosphate is alkylated by triethyloxonium fluoroborate in refluxing methylene chloride.¹¹

The bicyclic phosphate **5** also failed to react with triethyloxonium fluoroborate in sulfur dioxide solution. This was indicated by the proton nmr spectrum of the mixture after 3 days which contained absorptions corresponding only to starting materials.

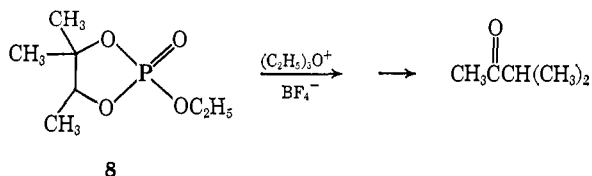


Reaction of the cyclic phosphate **6** with triethyloxonium fluoroborate appears to give the tetraalkoxyphosphonium salt **7**. The parent phosphate shows two CCH₃ absorptions at 1.37 and 1.41 ppm; these disappear when the oxonium salt is added and a new singlet appears at 1.51 ppm. It is believed that this absorption is due to the *gem*-dimethyl groups of **7**. The lifetime of **7** is quite short at room temperature and it undergoes an interesting decomposition to give a high yield of pinacolone and uncharacterized phosphorus containing products. The mechanism of this reaction may well be complex; however, it most surely includes as one of its steps a typical Wagner–Meerwein rearrangement in



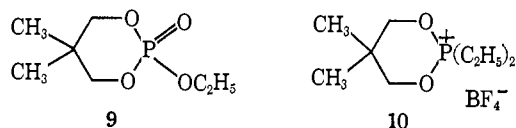
which a methyl group migrates.

In a similar manner the cyclic phosphate **8** gave high yields of methyl isopropyl ketone *via* a hydride migration when it underwent reaction with triethyloxonium fluoroborate.¹²



The phosphate **9** reacted with triethyloxonium fluoroborate to give a phosphonium salt **10** which was stable

for at least 4 days and which did not undergo ring opening. The nmr spectrum of **9** in methylene chloride contains two singlets at 0.89 and 1.20 ppm for the *gem*-dimethyls. It cannot be stated whether the large differ-



ence in the methyl absorptions indicates that the molecule is frozen in one conformation or is mobile because the two methyl groups cannot become magnetically equivalent in either case. The *gem*-dimethyl groups become equivalent in the phosphonium salt **10** as evidenced by the fact that the absorptions collapse to give a single sharp peak at 1.18 ppm when triethyloxonium fluoroborate is allowed to react with **9**. Its area is twice as large as that for either of the peaks for the starting material. The ³¹P nmr spectrum of **10** contained a major peak at +4.3 ppm and a smaller absorption at +8.8 ppm; the latter absorption may be due to either the phosphate **9** or its boron trifluoride complex since authentic samples of both materials absorb in the same region of the ³¹P nmr spectrum. Hydrolysis of **10** in methylene chloride slowly gave back the phosphate **9**. This was shown by the fact that the absorption at +4.3 ppm in the ³¹P nmr was gradually replaced by another peak at +8.8 ppm. The proton nmr spectrum of the hydrolyzed material was also consistent with that of the phosphate **9**.

When **10** was pyrolyzed at 100°, its weight decrease corresponded to that expected for loss of ethyl fluoride. The complex contained proton nmr absorptions for the *gem*-dimethyl groups at 1.09 and 1.16 ppm which were in agreement with those found for the authentic complex. The equivalency of the *gem*-dimethyls of **10** strongly suggests that this is a conformationally mobile substance.

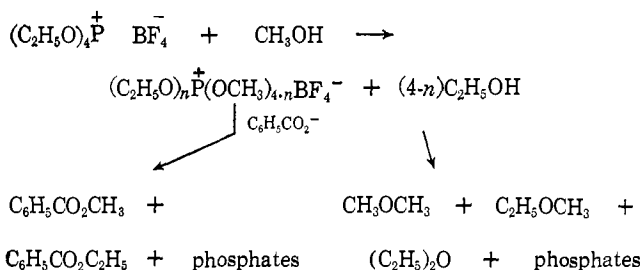
(d) **Reactions of Tetraalkoxyphosphonium Salts.** Both tetraethoxyphosphonium fluoroborate (**1**) and tetramethoxyphosphonium fluoroborate (**3**) react rapidly and quantitatively with sodium benzoate at room temperature to give esters and trialkyl phosphates. These reactions provide a convenient method for determining the extent of decomposition of **1** and **3** *vs.* time.

Further reactions of **1** with nucleophilic reagents at room temperature gave typical Arbusov products by displacement at carbon. The rate of reaction of **1** parallels the nucleophilicity of the attacking species. For example, aniline reacted quantitatively with **1** to give a 79:21 mixture of *N*-ethylaniline and *N,N*-diethylaniline in *ca.* 5 min. By contrast, phenol gave only a 29% yield of phenetole after 1 day and ethyl benzoate was formed in only 16% yield from benzoic acid and **1** after 12 hr. Similarly, tetramethoxyphosphonium fluoroborate reacted with benzoic acid to give a 32% yield of methyl benzoate after 2 days.

Reaction of **1** with methanol at room temperature occurs rapidly and gives products which indicate that both alkylation and exchange take place. This was shown by the fact that after allowing a dilute solution of **1** to react with methanol for 3 min, addition of excess sodium benzoate gave both methyl and ethyl benzoate. After 100 min no more esters were formed on adding

(11) J. E. Baldwin, private communication, Pennsylvania State University.

(12) This experiment was conducted by Dr. G. Chen.



the mixture to sodium benzoate. The formation of the three ethers was confirmed by glpc. However, since diethyl ether may have been formed by the previously cited reaction of **1** with moisture, its role as an exchange product is not established. No attempt was made to characterize the phosphates in this study.

Exchange reactions were also observed when **1** was allowed to react with sodium methoxide at -78° . In this case the presence of both trimethyl and triethyl phosphate was established by glpc. In addition two other glpc peaks, which undoubtedly correspond to the two mixed phosphates, were found. No evidence for formation of pentaalkoxyphosphoranes was obtained in reactions involving sodium alkoxides and **1** at 0 or -78° .

Experimental Section¹³

Triethyloxonium Fluoroborate. The procedure used for the synthesis of this salt was described by Meerwein.¹⁴ A 50% solution of the salt in methylene chloride, overlaid with ether, could be stored under refrigeration conditions for at least 6 months with little decomposition.

Table II. Gas Chromatographic Columns and Instruments

Column	Instrument
A	10% Carbowax 20M, 6 ft \times $\frac{1}{4}$ in., Perkin-Elmer 801
B	Hi Pak SE-30, 50 ft \times $\frac{1}{8}$ in., F & M 700
C	Si-1 cyanosilicone, 16 ft \times $\frac{1}{8}$ in., F & M 700
D	10% SE-30, 6 ft \times $\frac{1}{8}$ in., F & M 700
E	14% Carbowax 20M, 12 ft \times $\frac{1}{8}$ in., F & M 700
F	10% UC-W98, 6 ft \times $\frac{1}{8}$ in., F & M 700
G	1.5% SE-30, 12 ft \times $\frac{1}{8}$ in., Perkin-Elmer 801

Tetraethoxyphosphonium Fluoroborate (1). Methylene chloride solvent was removed from a portion of the triethyloxonium fluoroborate solution under reduced pressure (*ca.* 75 mm). The residue was washed with dry ether several times and dried under high vacuum. To the dried oxonium salt, an equimolar quantity of triethyl phosphate was added. The reaction mixture was allowed to stand overnight at room temperature. After 20 hr ether was removed under high vacuum. The loss in weight of the residue after removal of ether indicated that the reaction was 91% complete. The proton nmr spectrum of the residue exhibited a triplet ($J = 7$ Hz) and a distorted quintet at 1.48 and 4.65 ppm, respectively, for the methyls and methylenes of **1**. Its infrared spectrum (4% in CH_2Cl_2) showed a weak band at 7.8μ . By contrast, triethyl phosphate showed a strong phosphoryl stretching vibration at 7.8μ . Hydrolysis of a methylene chloride solution of **1** could be followed by proton nmr over several hours. Two quintets at 4.65 and 4.06 ppm which corresponded to **1**

(13) Proton nuclear magnetic resonance (nmr) spectra were recorded on a Varian Model A-60 spectrometer. Values are reported in parts per million (ppm) relative to tetramethylsilane. Phosphorus spectra (^{31}P nmr) were recorded on a Varian Model HA-100 spectrometer with 85% phosphoric acid as the external standard. Infrared spectra were obtained on a Perkin-Elmer Model 137 (Infracord) spectrometer. Values are reported in microns (μ). Gas chromatographic columns, designated by capital letters, are appended in Table II. Methylene chloride was distilled from phosphorus pentoxide and stored over potassium carbonate. Diethyl ether was dried over sodium ribbon. Trialkyl phosphates were commercial materials.

(14) H. Meerwein, *J. Prakt. Chem.*, **147**, 257 (1937).

and triethyl phosphate were found. In another experiment in which **1** was hydrolyzed, ethanol was shown to be formed by glpc (column A, 30°). Its retention time, 4.6 min, was confirmed with authentic ethanol. Hydrolysis of **1** also produced fluoroboric acid. This could be determined by back-titration of a measured excess of sodium hydroxide used to hydrolyze **1**, with standard hydrochloric acid to the phenolphthalein end point. A neutralization equivalent of 287 (theory = 298) was obtained in one experiment in which freshly prepared **1** was hydrolyzed.

Decomposition of Tetraethoxyphosphonium Fluoroborate. On heating to 100° , **1** was completely decomposed in about 10 min. The oily residue showed a proton nmr triplet ($J = 7$ Hz) and quintet at 1.38 and 4.35 ppm. These absorptions are assigned to methyls and methylenes of the complex, $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{O}-\text{BF}_2$ (**2**). Authentic **2** was prepared by allowing 5.3 g (0.037 mol) of freshly distilled boron trifluoride etherate to react with 6.8 g (0.037 mol) of triethyl phosphate. After removal of 2.1 g (0.028 mol) of ether by distillation, **2** was obtained in 76% yield. Its proton nmr spectrum was identical with that of the decomposition product of **1**. A portion of **1** was decomposed at 100° and the effluent gas was collected in a sampling bulb. The presence of ethyl fluoride in the gas was confirmed by mass spectral data, which contained peaks with *m/e* values of 48 and 47 (relative ratio 1:10).¹⁵

In addition to ethyl fluoride, the presence of diethyl ether in decomposed **1** was indicated by the mass spectral analysis. To determine whether ether was formed during thermal decomposition or was left over from the alkylation of triethyl phosphate by triethyloxonium fluoroborate, 0.1866 g (6.3×10^{-4} mol) of **1** was degassed at 0.2 mm (room temperature) for 1 hr to remove any residual ether. The sample was then decomposed in methylene chloride at 100° in a sealed tube. Glpc analysis of the pyrolysate (column B, 30°) showed three components at 10.0, 10.4, and 12.9 min. Comparison with authentic material showed that the peak at 12.9 min corresponded to an undetermined quantity of diethyl ether.

The stability of **1** on storage at room temperature and at 10° , under anhydrous conditions, was determined by periodically allowing weighed portions to react with excess sodium benzoate. Ethyl benzoate which is formed in quantitative yields from **1** was determined by glpc. The proton nmr spectrum of **1** after 20 days storage at room temperature exhibited absorptions corresponding to **1** and the complex **2**. These consisted of two distinct quintets, centered at 4.61 and 4.35 ppm.

The ^{31}P nmr spectra for the species triethyl phosphate, tetraethoxyphosphonium fluoroborate (**1**), and the complex **2**, formed by thermal decomposition of **1**, were recorded in methylene chloride (Table I). The phosphonium salt used in this study exhibited the proton nmr absorptions previously cited for **1**. It also was allowed to react with sodium benzoate to give ethyl benzoate. The complex was prepared by thermal decomposition of **1**. It exhibited proton nmr absorptions corresponding to authentic **2**.

Trimethyloxonium Fluoroborate. The procedure has been described by Meerwein.¹⁶ The salt was obtained in 87% yield. Its neutralization equivalent, determined by titration of the fluoroboric acid formed by hydrolysis, was 145 (theory 147.8). The solid oxonium salt could be stored indefinitely in a refrigerator freezer if precautions were taken to exclude moisture. Trimethyloxonium fluoroborate was found to be very insoluble in methylene chloride and many other low-boiling organic solvents.

Tetramethoxyphosphonium Fluoroborate (3). Equimolar quantities (0.037 mol) of trimethyl phosphate and trimethyloxonium fluoroborate were allowed to react at 0° in a sealed tube. Sulfur dioxide was used as solvent. A portion of the reaction mixture was transferred to an nmr tube which was sealed and stored at 0° . The progress of the reaction was followed by periodically scanning the nmr spectrum. Singlets at 4.51 and 3.21 ppm were assigned to trimethyloxonium fluoroborate and dimethyl ether. Two doublets ($J = 11.5$ Hz) at 4.23 and 3.78 ppm were assigned to **3** and unreacted phosphate. It is also possible that a small quantity of complex **4** was formed since this could not be detected by nmr. It was found that the proton nmr spectrum of the mixture stored at 0° did not change after 2 days. After 4 days the reaction mixture was kept at room temperature. The doublet, originally at 3.78 ppm, had shifted downfield to 3.9 ppm after 1 day and had increased in intensity relative to the 4.23-ppm doublet.

Pure tetramethoxyphosphonium fluoroborate (**3**) was prepared

(15) These values are in agreement with those reported by the American Petroleum Institute Project 44.

(16) H. Meerwein in Houben Weyl's "Methoden der organischen Chemie," VI/2, Georg Thieme Verlag, Stuttgart, 1964, p 340.

by allowing 5.5 g (0.037 mol) of trimethyloxonium fluoroborate to react with a fivefold excess (26.1 g, 0.186 mol) of trimethyl phosphate. The oxonium salt was completely dissolved in *ca.* 10 min. Methyl ether was periodically removed by evaporation at *ca.* 75 mm under anhydrous conditions. After 3.5 hr, the theoretical weight of dimethyl ether was lost. Addition of cold dry diethyl ether to the reaction mixture resulted in formation of a white crystalline solid. This was removed by filtration and washed several times with ether. On drying under vacuum 7.9 g (88% yield) of **3** was obtained. The solubility of tetramethoxyphosphonium fluoroborate in methylene chloride was *ca.* 0.6 g/ml. Its proton nmr spectrum exhibited a doublet ($J = 11.5$ Hz) at 4.37 ppm. A smaller doublet (*ca.* 5%) at 4.0 ppm was attributed to the complex of trimethyl phosphate and boron trifluoride (**4**). The ^{31}P nmr spectrum showed an absorption at -1.9 ppm. This could be resolved to a seven- to nine-line pattern ($J = 11.5$ Hz) with a large center line, flanked by two smaller lines of equal intensity. Further proof for the structure of **3** was supplied by its reaction with sodium benzoate in methylene chloride. That methyl benzoate and trimethyl phosphate were formed, was shown by glpc (columns A and C). Augmentation of the reaction mixture with authentic trimethyl phosphate and methyl benzoate gave no new glpc peaks.

Decomposition of Tetramethoxyphosphonium Fluoroborate.

A portion of the salt **3** was dissolved in sulfur dioxide and transferred to an nmr tube. The tube was sealed and allowed to stand at room temperature. Proton nmr spectra were periodically recorded over several days. In sulfur dioxide, **3** exhibited a doublet ($J = 11.5$ Hz) at 4.25 ppm. Absorptions for the complex were found at 3.92–4.0 ppm. Two small singlets at 4.55 and 3.38 ppm, which increased in intensity with time, indicated that trimethyloxonium fluoroborate and dimethyl ether were also being formed. In two separate experiments the identity of the 4.53-ppm peak was established unequivocally to be due to trimethyloxonium fluoroborate. In the first experiment a portion of the salt, stored for 26 days at 10° , exhibited a small singlet at 4.55 ppm corresponding to about 5–6 mol %, calculated as trimethyloxonium fluoroborate. It is noted that this absorption was not present when **3** was freshly prepared. Other absorptions showed that the aged sample also contained **3**, the complex **4**, and dimethyl ether. The spectrum was then run at 100-Hz full scale sweep (175 Hz offset) to amplify the region around 4.5 ppm. After addition of authentic trimethyloxonium fluoroborate the spectrum (run again on an expanded scale) showed no new peaks. However, the peak at 4.55 ppm was amplified, as was evident by comparison of the two spectra. In the second experiment, 6.6 g of **3**, previously stored for 1.5 months at 10° , was treated with 15 ml of methylene chloride. A small quantity of the oxonium salt was precipitated and was removed by filtration. After washing several times with methylene chloride, the salt (0.24 g) was allowed to react with excess sodium benzoate in liquid sulfur dioxide; glpc analysis (column D, 100°) gave only one peak at 5.3 min. It was shown that methyl benzoate had formed by separate injection of this ester and augmentation of the reaction mixture with methyl benzoate. On column E at 105° , methyl benzoate was eluted at 4.5 min and confirmed in a similar manner. Trimethyl phosphate (retention time 6.6 min) was shown by glpc to be absent, proving that trimethyloxonium fluoroborate and not **3** was the alkylating agent.

No methyl fluoride was detected by proton nmr when **3** was allowed to decompose in a sealed tube. In a control experiment, trimethyloxonium fluoroborate was also allowed to decompose in sulfur dioxide in a sealed tube. After 12 days, although the oxonium salt was 65% decomposed, as indicated by the peak areas for the remaining oxonium salt and the dimethyl ether–boron trifluoride complex at 3.7 ppm, no methyl fluoride was detected by nmr. The absence of methyl fluoride absorptions strongly suggests that it was present in the vapor phase above the solution. Proof that methyl fluoride and dimethyl ether was formed during decomposition of **3** was supplied by another experiment in which a sample of **3** was allowed to decompose for 2 days at room temperature. The flask was connected during this time to a partially evacuated gas sampling bulb. Mass spectrographic analysis of the effluent gas showed the presence of methyl fluoride (m/e values of 33, 34) and dimethyl ether (m/e 45, 46).

The trimethyl phosphate–boron trifluoride complex was independently synthesized by allowing 2.7 g (0.019 mol) of trimethyl phosphate to react with 3.1 g (0.019 mol) of freshly distilled boron trifluoride etherate. Diethyl ether (2.1 g) was removed by distillation. Proof that this complex was formed by decomposition of **3** was supplied by two experiments. In one, a sample of **3**, stored for 1 week at room temperature exhibited only one doublet ($J =$

11.5 Hz) at 4.0 in the proton nmr. Augmentation with the authentic complex **4** gave no new peaks. It was noted that when trimethyl phosphate was added to the synthetically prepared complex **4** only one doublet was found. Its position in the region 3.7–4.0 ppm depended on the relative amounts of trimethyl phosphate and **4** present. In the ^{31}P nmr the decomposed phosphonium salt exhibited (possibly) what appeared to be two closely spaced peaks at $+1.14$ and $+1.58$ ppm. The downfield peak, which appeared as a shoulder, was poorly resolved; therefore assignment of two peaks is somewhat doubtful. However, addition of the authentic complex augmented the upfield peak and no new peaks were found in the spectrum. Except for the doubtful absorption at $+1.14$ ppm no other peaks were found in the ^{31}P nmr spectrum indicating that no phosphorus-containing species other than **4** were formed by decomposition of **3**.

In another experiment glpc analysis of decomposed **3** (column D, 98°) showed the presence of a small quantity of impurity (0.4 min) and trimethyl phosphate (1.0 min). No other peaks were found at longer retention times. The presence of trimethyl phosphate indicated that the complex **4** underwent decomposition at the glpc conditions. Hydrolysis of the complex formed by decomposed **3** also gave trimethyl phosphate. This was demonstrated by its glpc retention time (column F, 118°) of 1.5 min which corresponded to that of trimethyl phosphate. Addition of authentic phosphate augmented the peak at 1.5 min and gave no new peaks.

Reaction of 9 with Triethyloxonium Fluoroborate. To 6.75 g (0.035 mol) of **9** was added 6.6 g (0.035 mol) of triethyloxonium fluoroborate. The mixture was allowed to stand overnight in an evacuated desiccator over concentrated sulfuric acid. The ^{31}P spectrum of this material showed two absorptions, $+4.3$ and $+8.4$ ppm. After dilution with methylene chloride, the ^1H nmr spectrum was taken. There appeared in the methyl region one large single peak at 1.18 ppm, and rather complex triplets at 1.48 ppm as well as two small singlets at 0.90 and 1.21 ppm. In addition to methylene quartets, a downfield doublet at 4.65 ppm ($J = 12$ Hz) was found. Addition of authentic **9** led to augmentation of the 1.21- and 0.90-ppm absorptions.

In a similar experiment water was added to the methylene chloride reaction mixture. The ^{31}P spectrum showed a decrease in the $+4.3$ -ppm absorption with a comparable increase in the $+8.4$ -ppm peak. The ^1H spectrum had methyl absorptions at 0.90 and 1.21 ppm and a very small peak at 1.17 ppm.

After having been stored for 4 days in a vacuum desiccator the material showed no appreciable change in its ^{31}P spectrum. Six grams (0.0193 mol) of this material was heated for 75 min at *ca.* 100° . The loss in weight was 1.0 g (theory for ethyl fluoride is 0.95 g, 0.0193 mol). The residue solidified upon cooling. The ^{31}P spectrum showed an absorption at $+8.7$ ppm only. The ^1H spectrum showed *gem*-dimethyl hydrogens at 1.09 and 1.16 ppm.

Reaction of 9 with Boron Trifluoride Etherate. To 0.22 g (0.0011 mol) of **9** in 2 ml of methylene chloride was added 0.162 g (0.0011 mol) of freshly distilled boron trifluoride etherate. The ^1H spectrum showed methyl peaks at 1.07 and 1.16 ppm; addition of water to the solution caused them to shift to 0.93 and 1.18 ppm.

Reaction of 6 with Triethyloxonium Fluoroborate. To 0.8 g (0.0042 mol) of triethyloxonium fluoroborate was added 0.875 g (0.0042 mol) of the cyclic phosphate **6**. After 2 hr at room temperature some solid remained; 2 ml of methylene chloride was added. The nmr spectrum of a solution 2.5 hr after mixing showed a large singlet at 1.51 ppm as well as peaks at 1.37 and 1.41 ppm which are due to phosphate. There was also a peak at 1.11 ppm which was shown to be due to pinacolone. Other absorptions typical of ethyl groups were present. The spectrum obtained after 20 hr showed an increase in the 1.11-ppm absorption and a decrease in the 1.51-ppm absorption. It appears that after 24 hr at room temperature, the reaction is essentially complete.

After having been stored in a desiccator over phosphorus pentoxide for 6 days a similar reaction mixture (0.0060 mol of each reactant in 3 ml of methylene chloride) which had turned dark brown was further diluted with methylene chloride. The solution was washed with three 10-ml portions of water and dried with magnesium sulfate. After having concentrated this solution its infrared spectrum was compared to that of pinacolone. Every pinacolone absorption appeared in the spectrum of the residue plus peaks at 1270 – 1320 ($\text{P}=\text{O}$) and 1160 cm^{-1} ($\text{P}-\text{O}-\text{Et}$) and very strong absorptions in the 950 – 1150 - cm^{-1} range ($\text{P}-\text{O}-\text{C}$).

The nmr spectrum of this material confirmed the presence of pinacolone. There were also absorptions in the 4.1-ppm region (distorted quintet) and what appeared to be at least two different methyl absorptions at 1.45 and 1.33 ppm.

Reaction of 8 with Triethyloxonium Fluoroborate. A mixture of 4.815 g (0.0271 mol) of **8** and 5.354 g (0.0282 mol) of triethyloxonium fluoroborate were allowed to react for 1 hr at which time only one phase was present. Further stirring led to the formation of two phases. Evacuation of the reaction mixture at 0.2 mm and room temperature allowed condensation of a volatile fraction in a liquid nitrogen trap. Glpc showed one major component was present and the peak was augmented by the addition of authentic methyl isopropyl ketone. The 2,4-dinitrophenylhydrazone was prepared, mp 116–118°; there was no depression of melting point on admixture with an authentic sample.

Alkylation of Sodium Benzoate. In a typical experiment 0.786 g (0.0026 mol) of tetraethoxyphosphonium fluoroborate (**1**) was allowed to react with 0.823 g (0.006 mol) of sodium benzoate. After the exothermic reaction subsided, 0.438 g of methyl benzoate was added as an internal standard. After addition of about 3 ml of methylene chloride a portion of the reaction mixture was centrifuged and analyzed by glpc (column A, 100°). In addition to the solvent peak, methyl benzoate (retention time 15.5 min), ethyl benzoate (19.5 min), and triethyl phosphate (23.5 min) were eluted. Proof that these were the compounds formed was supplied by glpc analysis of authentic materials. The yield of ethyl benzoate, based on freshly prepared **1**, was 94%. Duplicate analyses agreed within 3%. This procedure was used to determine the purity of **1** or to follow its decomposition.

In one experiment, in which the internal standard was excluded, the infrared spectrum (liquid film) of the reaction mixture exhibited a strong carbonyl band (5.8 μ) corresponding to ethyl benzoate, and a strong phosphoryl absorption at 7.85 μ .

The decomposition of tetramethoxyphosphonium fluoroborate (**3**) was followed by allowing it to react with excess sodium benzoate. Ethyl benzoate was used as an internal standard in this case. The products, analyzed by glpc (column E, 92°), gave the following retention times: methyl benzoate 8.5 min, ethyl benzoate 9.7 min, and trimethyl phosphate 13.4 min. On column C at 88°, methyl benzoate and trimethyl phosphate were eluted at 5.0 and 6.7 min. Augmentation with authentic materials gave no new peaks.

Alkylation of Benzoic Acid. To 0.426 g (0.0035 mol) of benzoic acid in 2 ml of methylene chloride was added 1.0 g (0.0037 mol) of tetraethoxyphosphonium fluoroborate. Methyl benzoate (0.3845 g) was added as an internal standard. Periodically, a few drops of the reaction mixture were diluted with 2 ml of methylene chloride and shaken with 2 ml of 5% potassium carbonate solution. The organic phase was analyzed by glpc as described previously for sodium benzoate.

The reaction of benzoic acid with tetramethoxyphosphonium fluoroborate was carried out in a similar manner. The products were analyzed by glpc (column E, 92°).

Reaction of Tetraethoxyphosphonium Fluoroborate with Aniline. Aniline, 0.6972 g (0.0075 mol), and 2.3 g (0.0075 mol) of **1** reacted exothermically. *t*-Butylbenzene (0.1170 g) was added as an internal standard. About 6 drops of the reaction mixture in 2 ml of methylene chloride was then neutralized by shaking with 1 ml of 5% sodium hydroxide solution. The organic phase was analyzed by glpc (column A, 110°). Retention times, confirmed with authentic samples, were *t*-butyl benzene 2.0 min, N,N-diethylaniline 11.3 min, triethyl phosphate 16.2 min, N-ethylaniline 18.4 min, and aniline 22.3 min. On column G at 80°, the retention times were *t*-butyl benzene 2.2 min, aniline 4.0 min, N-ethylaniline 6.7 min, triethyl phosphate 9.3 min, and N,N-diethylaniline 10.0 min.

Factors relating areas and weights of the internal standard and reaction products were obtained by chromatographing a synthetic mixture of these components. It was determined that 77% of the aniline reacted to give a 79:21 mixture of N-ethylaniline and N,N-diethylaniline.

Reaction of Tetraethoxyphosphonium Fluoroborate with Phenol. Phenol, 0.656 g (0.007 mol), 2.0 g (0.007 mol) of **1**, and 0.480 g of methyl benzoate were mixed. A portion of the reaction mixture was periodically added to 2 ml of methylene chloride and was neutralized with dilute potassium carbonate solution. The organic phase was analyzed by glpc (column A, 100°). Under these conditions, phenetole was eluted at 4.5 min. Methyl benzoate and triethyl phosphate had retention times of 15.5 and 23.5 min, respectively. The extent of reaction was determined by comparing the areas of the internal standard (methyl benzoate) and phenetole and applying a correction factor which was obtained with a synthetic standard.

Reaction of Tetraethoxyphosphonium Fluoroborate with Methanol. To a 10-ml volumetric flask was added 2.1128 g (0.007 mol) of

tetraethoxyphosphonium fluoroborate (91% pure) and 1.07 g (0.0034 mol) of methanol. The reaction mixture was quickly diluted to volume with methylene chloride. Three minutes after the reactants were mixed at room temperature, a 1-ml aliquot was withdrawn and allowed to react with excess sodium benzoate. A 1-ml aliquot of a phenetole solution (2.110 g/25 ml in methylene chloride) was added as an internal standard and glpc analysis (column A, 100°) showed the presence of four components with retention times of 4.5, 16.0, 20.0, and 23.5 min. These retention times corresponded to those for phenetole, methyl benzoate, ethyl benzoate, and triethyl phosphate, respectively. The identity of the esters in the 3-min experiment was confirmed by further glpc analysis (column F, 105°). Methyl and ethyl benzoate were eluted at 7.3 and 10.9 min on this column. These corresponded to the retention times found for the authentic esters. Augmentation of the reaction mixture with the authentic esters gave no new peaks. The yields of methyl benzoate and ethyl benzoate were 7.5 and 23.7% based on **1**. After 99 min another aliquot of the reaction mixture was added to excess sodium benzoate. Glpc analysis showed the presence of triethyl phosphate and two peaks at 17.8 and 20.5 min. That the two latter peaks in the 99-min experiment were not the esters was shown by glpc analysis on column G at 75°; authentic methyl and ethyl benzoate had retention times of 6.4 and 9.4 min, whereas the reaction mixture gave no peaks in this region.

The solution in the volumetric flask was analyzed for ethers on column B at room temperature. Three peaks were found at 5.6, 5.8, and 6.5 min. These corresponded to the retention times found for an authentic mixture of dimethyl ether, methyl ethyl ether, and diethyl ether. Assuming that the ethers are eluted in the order of their boiling points, it is presumed that the peak at 5.8 min corresponded to methyl ethyl ether. This peak constituted about 80–90% of the mixture, indicating that direct alkylation of methanol takes place more rapidly than exchange. Augmentation of the reaction mixture with the three ethers produced no new glpc peaks.

Reaction of Tetraethoxyphosphonium Fluoroborate with Sodium Methoxide. A slurry of 0.743 g (0.014 mol) of sodium methoxide in 5 ml of methylene chloride was cooled to –70° in a Dry Ice-acetone bath, and 4.7 g (0.014 mol) of **1** (87% pure) was added dropwise. No exotherm was observed until the reaction mixture was allowed to warm up slowly to ca. 0°. The nmr spectrum of the reaction mixture showed a variety of peaks including a doublet ($J = 11.5$ Hz) at 3.72 ppm. This indicated the presence of a methoxy group coupled with the phosphorus. Glpc analysis (column B, room temperature) showed the presence of the three ethers observed previously when methanol was allowed to react with **1**. The dimethyl ether peak comprised about 25% of the ether mixture indicating that exchange of **1** with methoxide at low temperatures is more extensive than with methanol at room temperature. Further glpc analysis (column C, 100°) showed four peaks at 8.2, 10.6, 13.1, and 15.0 min; the peak areas increased with longer retention time. The peaks at 8.2 and 15.0 min were shown to be trimethyl phosphate and triethyl phosphate, respectively, by separate injection of these phosphates and augmentation of the reaction mixture. The other two peaks are presumed to be dimethyl ethyl phosphate and methyl diethyl phosphate.

Reaction of Tetraethoxyphosphonium Fluoroborate with Sodium Ethoxide. A slurry, containing 1.200 g (0.02 mol) of sodium ethoxide in 5 ml of methylene chloride, was cooled to 0° and 6.0 g (0.02 mol) of tetraethoxyphosphonium fluoroborate was added dropwise. The temperature was kept below 17°. After addition was complete, the reaction mixture was allowed to reach room temperature. The proton nmr spectrum of the liquid phase (CH_2Cl_2) contained a triplet ($J = 7$ Hz) at 1.32 and a quintet ($J = 7$ Hz) at 4.1 ppm for triethyl phosphate. A triplet and quartet ($J = 7$ Hz) at 1.12 and 3.45 ppm were found for diethyl ether. Absorptions corresponding to pentaethoxyphosphorane¹⁰ at 3.82 ppm were absent. The infrared spectrum (liquid film) of the liquid phase, after allowing ether to evaporate, was consistent with that of triethyl phosphate.

The reaction was repeated at –58 to –70° to determine whether pentaethoxyphosphorane could be formed to the exclusion of Arbusov products. The solvent was removed *in vacuo* at room temperature under anhydrous conditions. The nmr and infrared spectral data on the residue were consistent with those of triethyl phosphate.

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