Quantum Yield of Formation of Diaminofumaronitrile (2) from Diaminomaleonitrile (1) and of 4-Amino-5-cyanoimidazole (3) from the 1:2 Photostationary Ratio. A 3.0-ml sample of 1.4×10^{-3} M **1** was prepared, degassed, and irradiated in the wheel for 60 min. The light intensity during the irradiation averaged 2.7×10^{15} quanta/sec as measured by potassium ferrioxalate actinometry. Uv analysis indicated that the concentration of **2** was 1.9×10^{-4} M, a 14% conversion. This gave a quantum yield of cis–trans isomerization of 0.045 after correction for back reaction[11] and after

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correction for the difference in the amount of light absorbed by the actinometer and the amount of light absorbed by **1**. Of the light absorbed by the actinometer, 84% was absorbed by **1**. This percentage was calculated from the uv absorption for the Pyrex glass of the samples tubes, the uv absorption of **1**, the uv absorption of the actinometer, and the lamp emission intensity as a function of wavelength available from the Southern New England Ultraviolet Co., Middletown, Conn. A 3.0-ml solution of 1.1×10^{-3} M **2** and 0.3×10^{-3} M **1** was similarly irradiated for 476 min. This yielded a concentration of **3** of 1.2×10^{-4} M (a 9% conversion) and gave a corrected quantum yield of **3** formation equal to 0.0034.

Monomeric Methyl Metaphosphate[1]

Charles H. Clapp and F. H. Westheimer*

Contribution from the James Bryant Conant Laboratories, Harvard University, Cambridge, Massachusetts 02138. Received January 12, 1974

Abstract: Monomeric metaphosphates have been implicated in phosphorylation reactions and in the solvolysis of phosphate esters but none had previously been prepared. In this article, we present evidence that monomeric metaphosphate has been produced in the gas phase by the pyrolysis of methyl 2-butenylphostonate and trapped by N-methylaniline: methyl 2-butenylphostonate $\rightarrow$ $H_2C{=}CH{-}CH{=}CH_2$ + CH_3OPO_2; CH_3OPO_2 + $2C_6H_5$-$NHCH_3$ $\rightarrow$ $CH_3OP(N(CH_3)C_6H_5)O_2^-$ + $C_6H_5N^+H_2CH_3$.

Monomeric metaphosphate ion, PO_3^-, and esters of monomeric metaphosphoric acid have been postulated as intermediates in numerous phosphorylation reactions,[2-4] in the hydrolysis of monoesters of phosphoric acid,[5-7] and in the hydrolysis of various esters of pyrophosphoric acid.[8] But although trimeric and polymeric metaphosphates are well known,[9] no salts or esters of monomeric metaphosphoric acid, HPO_3, have previously been reported. In the present paper, we present experimental evidence for the preparation of monomeric methyl metaphosphate and for trapping it as its methylanilide.

The chemistry of phosphate esters can be compared to that of carboxylic esters. Most reactions occur by nucleophilic attack on the central atom, to form a tetrahedral intermediate from carboxylic esters or a

pentacovalent intermediate from phosphate esters;[10-12] the stereochemistry and ligand reorganization[10,11] of the latter intermediates have proved complex and these complexities have helped elucidate the detailed mechanism of some of these hydrolytic processes.[13] But just as carboxylic esters can undergo hydrolysis through acylonium ions, where the ligand number at carbon is reduced from three to two, so some phosphates are presumed to react by way of monomeric metaphosphates, where the ligand number at phosphorus is reduced from four to three. But since monomeric metaphosphate ion is isoelectronic with SO_3, it might reasonably function as a strong electrophile and therefore be difficult to prepare in solution. (The resonance stabilization that characterizes NO_3^- will be expected to be less prominent in compounds of second-row elements, where double bonding is poorer than with first-row elements.)

A preparation of monomeric methyl metaphosphate from methyl 2-butenylphostonate by pyrolysis in the gas phase is outlined below.
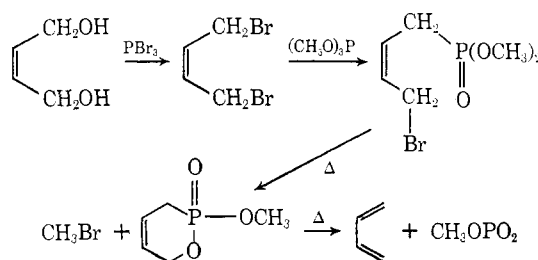
(1) (a) Presented as the Remsen Lecture, The Johns Hopkins University, May 23, 1973; (b) preliminary communication, *Pure Appl. Chem.*, in press.

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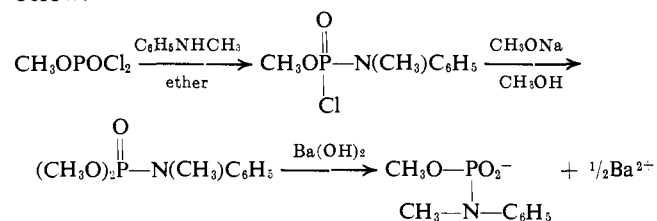
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cis-1,4-Dibromobutene-2 reacts smoothly with trimethyl phosphite in an Arbuzov reaction to yield dimethyl 4-bromo-2-butenylphosphonate, and this in turn cyclizes to the required methyl 2-butenylphostonate. Its pyrolysis was carried out in a vertically mounted furnace that is shown schematically in Figure 1 and described in detail in the Experimental Section. The phostonate was distilled through the quartz reaction tube in a stream of nitrogen at a total pressure of around 200 μ and a ratio, N_2 to phostonate, ranging from 15–50 to 1; the compound was decomposed at about 600° with a residence time of about 0.02 sec.

The product obtained in the pyrolysis trap was identified as methyl polyphosphate. When N-methylaniline, or better when a stirred solution of N-methylaniline in n-propylbenzene, was present in the pyrolysis trap, the N-methylanilinium salt of methyl N-methyl-N-phenylphosphoramidate was obtained and identified by comparison with an authentic sample of the corresponding barium salt.

The latter was synthesized by the reaction sequence below.

$$CH_3OPOCl_2 \xrightarrow[\text{ether}]{C_6H_5NHCH_3} CH_3O\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{P}}-N(CH_3)C_6H_5 \xrightarrow[\text{CH}_3OH]{CH_3ONa}$$

$$(CH_3O)_2\overset{\overset{O}{\|}}{P}-N(CH_3)C_6H_5 \xrightarrow{Ba(OH)_2} CH_3O-\underset{\underset{CH_3-N-C_6H_5}{|}}{PO_2^-} + \tfrac{1}{2}Ba^{2+}$$

The evidence for the statements in this introductory section, and their consequences, are given in the Experimental Section and the Discussion.

Experimental Section

Materials. *cis*-2-Butene 1,4-Dibromide. This material was prepared from the corresponding diol (Aldrich Chemical Co. or K & K) by the procedure described by Valette.[14] The dibromide shows the strong out-of-plane bending frequency at 775 cm⁻¹ that is characteristic for *cis*-olefins,[15] together with a weak band at 965 cm⁻¹ that indicates small amounts of trans isomer. The *cis*-dibromide rearranges[14,16] to the trans; some preparations proved stable for months when stored in brown bottles in a freezer, while others isomerized almost immediately after work-up. The reasons for this variability have not been determined.

Reaction of *cis*-2-Butene 1,4-Dibromide with Trimethyl Phosphite. *cis*-2-Butene 1,4-dibromide (50.8 g, 0.238 mol) was introduced into a three-necked flask fitted with a nitrogen inlet tube, a dropping funnel, and a reflux condenser with a gas exit tube leading to a Nujol bubbler. After the system had been purged with nitrogen, the flask was heated to 80° and trimethyl phosphite (24.2 g, 0.195 mol) was added with magnetic stirring at 80–84° over 40 min. During this period nitrogen was passed through the reaction mixture and the condenser cooled with a stream of air, so as to facilitate removal of methyl bromide. The reaction was continued for an additional 20 min at 80°, when the excess dibromide was removed by vacuum distillation at a pressure of 1 mm or less, while the flask was maintained at 80°. On thin-layer chromatography of the slightly yellow residue on silica gel with acetone as eluent, almost all of the material showed an R_f 0.50. Its nmr spectrum was consistent with that expected for dimethyl 4-bromo-2-butenylphosphonate. The crude product was used without further purification for the next step.

Methyl 2-Butenylphostonate. Crude 4-bromo-2-butenylphosphonate (21.0 g) was heated under nitrogen to 135°, where gas was vigorously evolved.[17] The solution was stirred at 135–142° for

another 35 min, while the gas evolved escaped through a bubbler. In a typical preparation, the viscous yellow residue was molecularly distilled in two batches in a Hickman still at 10⁻⁴ Torr and a pot temperature of 50–60°. A total of 3.4 g of distillate was collected; a large amount of gummy residue remained in the still pot. Thin-layer chromatography (ethyl acetate on silica gel; visualization with iodine) revealed a strong spot (R_f 0.29) and a much weaker spot, which was sensitive to uv, with R_f 0.39.

The distillate (1 g) was purified by chromatography on a column (2.6 × 44 cm) containing 100 g of Florisil made up in ethyl acetate-hexane (7:3 by volume). The column was eluted with 1450 ml of this solvent mixture at a rate of 3.5 ml/min. After 1200 ml of solvent had been collected the more mobile component could no longer be detected. The column was finally eluted with 1000 ml of ethyl acetate, and this eluate was combined with the last 250 ml of the ethyl acetate–hexane mixture and evaporated to yield an almost colorless oil (664 mg) which gave satisfactory analytical and spectroscopic data for the pure phostonate. The very faint yellow color can be removed by molecular distillation: ir (thin film) C=C stretch, 1670 cm⁻¹; nmr δ 2.41 (broad doublet, J_{H-P} = 17 Hz, 2 H), 3.73 (d, J_{H-P} = 11 Hz, 3 H), 4.75 (broad doublet, J_{H-P} = 11 Hz), 5.70 (broad multiplet, 2 H); mass spectrum (mass number, intensity in parentheses) 149 (6, P + 1, calcd 5.7), 148 (84, P), 70 (100, P − CH₃PO₂), 54 (86, P − CH₃PO₃). *Anal.* Calcd for C₅H₉PO₃: C, 40.55; H, 6.13; P, 20.91. Found: C, 40.66; H, 6.14; P, 20.83. Preliminary tests (Leberco Laboratories, Roselle Park, N. J. 07204) indicate no lethal effects of this compound on mice at least at concentrations high compared to those effective for most anticholinesterases.

Barium Methyl N-Methyl-N-phenylphosphoramidate. N-Methylaniline (53.5 g, 0.50 mol) was added over 30 min at 0° to a stirred solution of methyl dichlorophosphate (37.2 g, 0.250 mol; Aldrich) in 150 ml of absolute ether. The reaction mixture was stirred for 40 min at 0° and for an additional 40 min after removal of the ice bath. The precipitated N-methylaniline hydrochloride was removed by filtration and the filtrate was washed with water (2 × 125 ml), dried over anhydrous magnesium sulfate, and concentrated to a slightly yellow oil. The nmr spectrum of this crude material is consistent with that expected for the intermediate phosphoramidic chloride.

The yellow oil was dissolved in 50 ml of methanol, and a solution of 13.8 g (0.260 mol) of sodium methoxide (Fisher) in 120 ml of methanol was added with cooling by tap water. The mixture was stirred for 19 hr at room temperature, the precipitated sodium chloride removed by filtration, and the solution concentrated. The residue was partitioned between equal volumes (100 ml) of water and ether. The ether layer was washed with water, dried with magnesium sulfate, and concentrated; the residue was distilled through a short-path condenser to yield 8.6 g (16%) of a colorless oil, bp 87.5–89° (0.1 mm). The nmr spectrum of this material was consistent with that expected for dimethyl N-methyl-N-phenylphosphoramidate: δ 3.2 (d, J = 9 Hz, 3 H), 3.7 (d, J = 11 Hz, 6 H), 7.2 (5 H).

The crude diester (1.211 g, 5.64 mmol) was refluxed for 4 hr in 15 ml of saturated barium hydroxide solution (*ca.* 7.5 mequiv). Subsequently, after carbon dioxide had been bubbled through the solution until the pH fell to about 7, the resulting barium carbonate was removed by centrifugation. The supernatant was evaporated to dryness and the residue crystallized from methanol/acetone to yield 590 mg (39%) of a flocculent white precipitate: nmr (in D₂O) δ 3.1 (d, J = 8 Hz, 3 H, CH₃NP), 3.5 (d, 12 Hz, 3 H, CH₃OP), 7.3 Hz (5 H, aromatic protons). *Anal.* Calcd for C₁₆H₂₂P₂O₆Ba: C, 35.74; H, 4.31; P, 11.52; N, 5.21; Ba, 25.54. Found: C, 35.63; H, 4.09; P, 11.61; N, 5.17; Ba, 25.37.

The salt is moderately stable when stored at room temperature but very sensitive to acid hydrolysis.

Methods. General. The nmr spectra were obtained with Varian A 60, T 60, and XL 100 spectrometers. The latter is equipped for Fourier transform spectroscopy and has a phosphorus probe at 40.5 MHz. Ir spectra were obtained with a Perkin-Elmer Infracord and mass spectra with an MS-9 instrument. Vpc analyses were conducted with a Hewlett-Packard 5750 research chromatograph with thermal conductivity detector. A Cary 15 spectrophotometer was used for uv measurements.

The Pyrolysis Furnace. The furnace (Figure 1) was constructed from a brass cylinder 8 in. long and 2.25 in. i.d. with ⅛ in. walls, with broad ⅜ in. thick flanges at both ends. The cylinder was mounted vertically and wound with 11 turns of 0.25 in. copper tubing for water cooling. A glass well, 9 cm deep and 4.8 cm i.d., was clamped to the bottom flange with a Vitron O-ring vacuum

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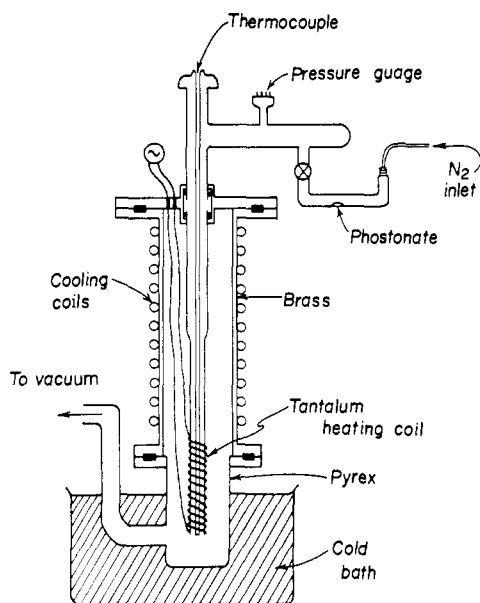
Figure 1. Schematic diagram of the pyrolysis apparatus. Tap water was circulated through the cooling coils, and the cold bath was maintained with Dry Ice slushes or liquid nitrogen, as described in the Experimental Section. In some of the trapping experiments, the bath was maintained in a Nalgene pan and the methylaniline solutions in the cold trap were stirred magnetically.

seal. This glass well, referred to as the pyrolysis trap, had a flat bottom and a side arm leading to a vacuum manifold and pumping system. A flat brass plate with Cajon O-ring connectors in the center of each face was bolted to the top flange and vacuum sealed with an O-ring. The upper connector supported a small manifold from which the phostonate was distilled into the system, while the lower connector supported the quartz reaction tube (10 mm i.d.) which extended to a level about 2 cm above the bottom surface of the pyrolysis trap. The lower 8 cm of the tube was wound with 60 turns (80 in.) of tantalum wire, 0.01 in. diameter. The lead wires for this winding were attached to porcelain-insulated through connectors in the top end plate. Temperatures were measured with a chromel-alumel thermocouple in a quartz thermocouple well (5 mm o.d.) mounted in the center of the reaction tube.

The side arm of the pyrolysis trap was attached to an auxiliary trap to collect volatile products. The pumping system comprised a Consolidated Vacuum Corp. VMF-20 oil diffusion pump and a Welch 1402 high capacity mechanical pump. Pressures were measured with a Consolidated Vacuum Corp. CTC-100 thermocouple vacuum gauge, attached to the manifold at the top of the furnace.

Procedures. The starting material was introduced by a micropipet into a U tube that was wrapped with heating tape and attached to the manifold at the top of the furnace. The sample of phostonate was warmed and distilled into the reaction tube with a stream of nitrogen, regulated by a Nupro Type S valve, 0.031 in. orifice. The ratio of carrier to phostonate was estimated from the flow rate for nitrogen and the time required to distil a known weight of starting material.

Experiments where no trapping agent was used were conducted by pumping out the system overnight and then introducing about 60 mg of phostonate into the U tube. The pyrolysis trap was immersed to a depth of about 1 in. in liquid nitrogen, the reaction tube heated to 600°, and the sample tube heated to about 35–40°. In some experiments the nitrogen flow (about 3 mmol/hr) was adjusted to yield a pressure in the system of about 200 μ. Under these conditions all of the phostonate distilled in about 2 hr and its residence time in the heated zone of the reaction tube was estimated at about 0.02 sec. After the furnace had cooled to room temperature, the volatile materials were distilled into the auxiliary trap. The residual film was extracted with 0.5 ml of deuteriochloroform (which dissolved some but not all of the product) or extracted (essentially completely) with a solution of sodium bicarbonate in D_2O. Proton and ^{31}P nmr spectra were obtained for these solutions.

The proton nmr spectrum in $CDCl_3$ of the polymer consists of doublets in the region from 3.6 to 4.0 ppm downfield from TMA, with coupling constants of 10–12 Hz. Similar spectra[18] have been obtained for methyl polyphosphate obtained from P_2O_5 and dimethyl ether. The multiplicity of doublets results from the slightly different chemical shifts for the methoxyl groups bonded to terminal, penultimate, and interior phosphorus atoms in chains of various lengths. A broad signal at δ 7.8 is presumably due to water in exchange with the acidic protons in the polymeric mixture. A fundamentally similar spectrum was obtained for the sodium salt in D_2O.

A ^{31}P nmr spectrum was also obtained in water for the sodium salt mentioned above. The spectrum showed broad signals centered at -3.36 and $+9.50$ ppm relative to 85% phosphoric acid, with relative intensities of 1:10. An additional barely visible signal appears at $+23.0$ ppm. The intensities of these peaks differ considerably from one preparation to the next. These matters require further consideration. Van Wazer and his collaborators[19] have reported signals at $+14$, $+29$, and $+41$ ppm for a solution of the acidic form of ethyl polyphosphate in chloroform and have assigned these signals to terminal, interior, and branching phosphorus atoms. A large difference between the spectrum of the anion in water and that of the acid in chloroform is expected. Our material is not sufficiently soluble in chloroform to allow us to obtain a spectrum under the conditions which Van Wazer employed.

In other experiments, methyl 2-butenylphostonate was pyrolyzed using a greater flow rate of nitrogen, so that the ratio of nitrogen to phostonate approximated 50:1. The oily residue which remained in the pyrolysis trap after distillation of volatiles was almost completely insoluble in chloroform but soluble in 0.1 N sodium bicarbonate solution. The proton nmr spectrum of this solution showed only a cluster of doublets in the region from δ 3.4 to 3.9.

Identification of Butadiene. As stated above, after pyrolysis the volatile products were distilled from the pyrolysis trap into an auxiliary trap. The volatiles were then analyzed by vpc at 25° at flow rate (helium) of 42 ml/min on $^1/_8$ in. $\times$ 12 ft columns of (a) 10% dinonyl phthalate on Chromosorb P (60–80) and (b) 15% β,-β'-oxydipropionitrile on Chromosorb P (80–100). These analyses revealed only one detectable component, which had the same retention time as does butadiene. The effluent from this peak was passed through 5 ml of ethanol; the ultraviolet spectrum of this solution, after dilution, was identical with that of butadiene in ethanol, with λ_{max} at 218 nm.

Careful quantitative measurements of the yield of butadiene have not yet been made. Crude determinations, however, were based on the volume of the gas sampling system and the heights of the vpc peaks; the maximum yield so far recorded is 83%. Somewhat lower yields were calculated from the uv spectrum in ethanol.

Trapping Experiments. Although trapping experiments with methanol were probably successful, the results are potentially ambiguous. First, dimethyl phosphate could be detected, although in minute yield, when no trapping agent was present. Second, although the yield of dimethyl ester obtained in trapping experiments exceeded that in control experiments, the known[20,21] reactivity of polyphosphates with alcohols introduces uncertainty into the conclusions. Finally, the volatility of methanol raises difficult questions in interpreting the data. Results with higher alcohols were similarly promising but potentially ambiguous.

Trapping with N-methylaniline was conducted in two ways. (a) Trapping with N-methylaniline alone. N-Methylaniline (2.5 ml; Eastman, redistilled) was introduced into the pyrolysis trap, the system evacuated, and the trapping agent degassed by repeated freezing and thawing. The furnace was heated to 600° and the pyrolysis trap cooled with Dry Ice/acetone slush. A 90-mg sample of phostonate was distilled through the furnace at a nitrogen pressure of 200 μ and a nitrogen:phostonate ratio of 18. After termination of the pyrolysis, the trap was warmed to 25° and the volatile products (butadiene, excess methylaniline) were removed *in vacuo*. The residual product was dissolved in deuteriochloroform; the proton nmr spectrum of the solution is shown in Figure 2. The most important feature of this spectrum is the presence of a doublet centered on δ 3.2, ascribed to the N-methyl doublet of the phos-

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(19) J. R. Van Wazer, C. R. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, **78**, 5715 (1956).

(20) K. Langheld, *Chem. Ber.*, **43**, 1857 (1910); **44**, 2076 (1911); **45**, 3753 (1912).

(21) H. Berger, *Z. Naturforsch. B*, **26**, 694 (1971).

phoramidate, with J_{H-P} of 7 Hz. This signal is then present in the crude product, before work-up.

The chloroform solution was also analyzed by thin-layer chromatography on cellulose strips (Eastman, with fluorescence indicator), with n-propyl alcohol/3% aqueous ammonia (7:3) as eluent. Irradiation of the chromatogram at 254 nm revealed a spot with the same mobility (R_f 0.80) as that of authentic barium methyl N-methyl-N-phenylphosphoramidate. In addition, a small still unidentified spot at R_f 0.71, a diffuse spot for methylaniline near the solvent front, and a weak spot at the origin were observed.

The sodium salt of the product was isolated as follows. The pyrolysis trap from the previous experiment was washed with 10 ml of 0.1 N sodium bicarbonate solution and 7 ml of chloroform, and these washings were combined with the nmr solution described above. The aqueous layer was separated, washed with a second 7-ml portion of chloroform, and treated with 2.5 ml of Amberlite IR 50 (carboxylate) exchange resin, 3.5 mequiv/cm³, in the acid form. The resulting solution, pH 6.4, was evaporated to dryness. The nmr spectrum of the residue in D_2O showed only signals for aromatic protons, methoxyl protons, and CH_3NP protons. Thin-layer chromatography revealed that the two components mentioned above were still present. These materials were separated and the phosphoramidate isolated by thin-layer preparative chromatography on silica gel with n-propyl alcohol/3% aqueous NH_3 (7:3) as developing solvent.

The more mobile component was eluted with water. From the optical density of the solution the yield of product was calculated as 6%; a higher yield of crude product is evidenced by the spectrum of the crude product mixture described above. A small amount of salt crystallized from methanol/acetone and showed an nmr spectrum identical with that of synthetic barium methyl N-methyl-N-phenylphosphoramidate.

(b) Trapping with a solution of N-methylaniline. A solution of 3.8 g of N-methylaniline and 7.7 g of n-propylbenzene was introduced into the pyrolysis trap, cooled with Dry Ice/acetone and stirred magnetically. After pyrolysis, the butadiene, propylbenzene, and excess N-methylaniline were removed in vacuo. The nmr spectrum of the remaining material corresponded to that obtained in the absence of propylbenzene. Thin-layer chromatography showed the same products.

Control Experiments. Phostonate (54 mg) was pyrolyzed in the absence of trapping agent, the nonvolatile residue, dissolved in N-methylaniline, and allowed to stand for 2 hr at room temperature; the amine was then removed by vacuum distillation. The nmr spectrum of the product did not show a CH_3NP doublet. The material was then treated with methylaniline for an additional 3.5 hr at room temperature and for 1 hr at 60°; no evidence (nmr or chromatography) for formation of phosphoramidate was observed. The methylanilinium ions were replaced by sodium ions according to the procedure already described; no N-methyl or aromatic protons could then be detected in the nmr spectrum. In further experiments when the polymer was allowed to stand with N-methylaniline at room temperature for 72 hr, sometimes but not always a small nmr signal suggested the formation of a low yield of N-methylanilide.

In another type of control, a sample of phostonate was pyrolyzed in the absence of trapping agent, with the trap at −78°. Subsequently, 2.5 g of N-methylaniline was introduced into the pyrolysis trap, the apparatus reevacuated, and the contents of the trap degassed by freezing and thawing. The trap was then immersed in Dry Ice/acetone; while the furnace was heated to 600°, nitrogen was allowed to flow through the system at 200 μ for 2 hr. The nmr spectrum of the product then obtained may have indicated an extremely weak signal, more or less at noise level, for a doublet at δ 3.2 expected for phosphoramidate but no phosphoramidate could be seen in thin-layer chromatography.

Discussion

The data presented in the Experimental Section leave little doubt that the pyrolysis of methyl 2-butenylphostonate leads to monomeric methyl metaphosphate and further that this compound can be trapped with N-methylaniline to yield methyl N-methyl-N-phenylphosphoramidate.

The identification of methyl polyphosphate as the major nonvolatile product from the pyrolysis of methyl 2-butenylphostonate in the absence of trapping agent
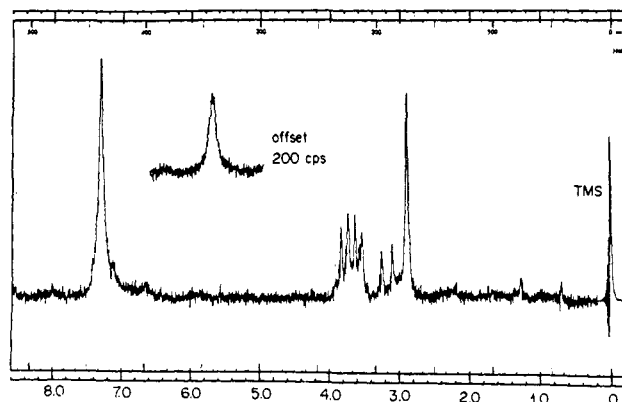
Figure 2. A 60-MHz spectrum in $CDCl_3$ of the crude reaction product from one of the trapping experiments, after excess methylaniline and other volatile materials had been removed by vacuum distillation at room temperature. The offset signal is that of the protons of the methylanilinium salt group. The signal at δ 7.3 is that of the aromatic protons and that at δ 3.7 the multiplet from the O-methyl groups of the methyl ester amide and the various polymeric methyl metaphosphates. The doublet at δ 3.2 and the singlet at δ 2.9 arise respectively from the $PNCH_3$ group of the ester amide (the trapped product) and from the NCH_3 group of the N-methylanilinium cation.

has been presented in the Experimental Section. Pyrolysis in the presence of trapping agent gives rise to low yields of trapped product but that product has been unambiguously identified as a salt of methyl N-methyl-N-phenylphosphoramidate. Such salts are reasonably stable. Whereas phosphoramidates in general are sensitive to acid hydrolysis,[22] and phosphoramidates with one or more hydrogen atoms attached to nitrogen are sensitive to basic hydrolysis,[23] salts of the N-methylanilide here described can be handled relatively easily. Furthermore, control experiments make it unlikely that the phosphoramidate arose in some alternative, trivial manner. The polymer, although soluble in N-methylaniline, does not react with it under conditions far more severe than those used in the trapping experiments. One anticipated difficulty, which has now been eliminated, could have arisen if the heat radiated from the end of the furnace warmed the N-methylaniline in the pyrolysis trap despite the surrounding cooling bath. Such heating is, however, not reasonable for the stirred solution of methylaniline in n-propylbenzene; furthermore, in that instance, the pressure was measured in the system with the furnace turned on, but before pyrolysis; the pressure rise was small. Besides, a control experiment was carried out with methylaniline added to methyl polyphosphate while the furnace was turned on; phosphoramidate was formed, if at all, only in trace amounts. It may safely be concluded then that the phosphoramidate is formed directly in a trapping experiment, and not as a result of a secondary reaction.

The preparation of a monomeric metaphosphate provides considerable support to those mechanisms where such intermediates have been postulated. Obviously, in each specific study of the mechanism of a chemical or enzymic reaction, the intervention or absence of monomeric metaphosphates will have to be established by specific kinetic or trapping experiments,

(22) Reference 3, pp 71–84.
(23) (a) D. F. Heath, J. Chem. Soc., 3796, 3804 (1956); (b) F. H. Westheimer, Chem. Soc., Spec. Publ., No. 8, 181 (1957); (c) P. S. Traylor and F. H. Westheimer, J. Amer. Chem. Soc., 87, 553 (1965).

or the like. But just as carbonium ion mechanisms in general are strengthened by the isolation or spectroscopic evidence for the formation of carbonium ions,[24] so metaphosphate mechanisms are strengthened by the preparation of a monomeric metaphosphate.

Further studies directed to the preparation of phosphonobenzene and its homologs, and to the further determination of the properties of monomeric methyl metaphosphate, are under way.

Note Added in Proof

Recently the crude products of pyrolysis (prior to purification and without exposure to water) have been examined by Fourier transform ³¹P nmr spectroscopy. The presence of methyl N-methyl-N-phenylphosphoramidate in trapping experiments has been confirmed both by proton-decoupled spectra and by proton-coupled spectra; the signals obtained from crude reaction mixtures correspond with those from synthetic salt, both with respect to chemical shift (δ -3.5 in $CDCl_3$ relative to 85% phosphoric acid) and with respect to splitting pattern. In addition to polymeric methyl metaphosphate and to methyl N-methyl-N-phenylphosphoramidate, as reported in the body of this paper, an additional phosphorus-containing product was observed, with δ $+3.3$, again in $CDCl_3$. We have tentatively assigned this signal to one of the phosphorus atoms of a pyrophosphate salt with the structure $(C_6H_5NCH_3)PO(OCH_3)OP(OCH_3)O_2^-$. If this speculation is correct, the signal from the second phosphorus atom must be among the group otherwise assigned to the polymer.

Additional control experiments have also been conducted where the phostonate has been pyrolyzed, and the polymer so produced allowed to react, under a variety of conditions, with N-methylaniline. Some of the methylanilinium salt of methyl N-methyl-N-phenylphosphoramidate has definitely been formed under some conditions, but the amount was never more than a fourth of that formed in trapping experiments, and none of the second product (pyrophosphate?) was found. Other control experiments make it unlikely that the methyl N-methyl-N-phenylphosphoramidate was produced by reaction of the supposed pyrophosphate with N-methylaniline under the conditions of our experiments.

The formation of a pyrophosphate brings up the possibility that monomeric methyl metaphosphate was formed in the pyrolysis but then dimerized, that this dimer has been capture in the trapping experiments, and that the methyl N-methyl-N-phenylphosphoramidate we obtained is formed by degradation of the dimeric product. Although further control experiments are desirable, the evidence in hand makes this alternative explanation unlikely. But in any event, the data strongly support the contention that the pyrolysis of our phostonate has led to the formation, in the gas phase, of monomeric methyl metaphosphate.

(24) G. A. Olah, *Angew. Chem., Int. Ed. Eng.*, **12**, 173 (1973).