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A Phosphorus Analogue of α-Pyrone and Evidence for Monomeric Mesitylmetaphosphonate

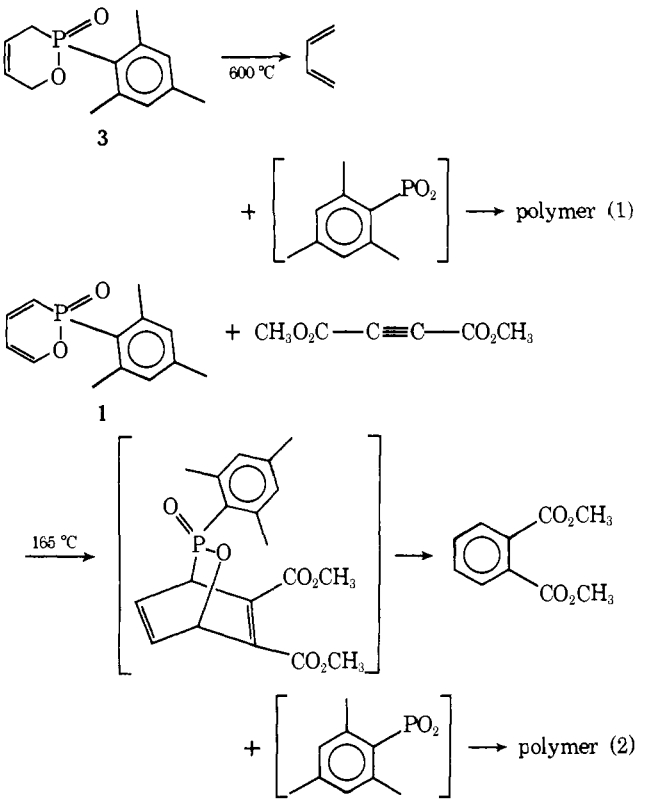
Irving Sigal*[1] and Leslie Loew

Contribution from the James Bryant Conant Laboratory of Harvard University, Cambridge, Massachusetts 02138. *Received April 11, 1978*

Abstract: A phosphorus analogue of α-pyrone, **1**, has been prepared by the addition of bromine to mesityl-2-butenylphostinate, followed by dehydrobromination. The compound undergoes Diels–Alder addition with maleic anhydride or dimethyl acetylenedicarboxylate, but only at temperatures above 140 °C; the postulated adducts apparently decompose at that temperature to yield the expected dihydroaromatic or aromatic compound, plus a polymer of mesitylmetaphosphonate. The latter has also been obtained by the pyrolysis of mesityl-2-butenylphostinate, **3**. These latter findings help illuminate the chemistry of monomeric metaphosphonates. Furthermore, both the polymerization and other data suggest that steric hindrance is not important for reactions at the phosphorus atom of mesitylphosphonate.

In pursuing investigations carried out in these laboratories,[2,3] on the chemistry of monomeric metaphosphates, we have attempted to prepare monomeric mesitylmetaphosphonate, $(CH_3)_3C_6H_2PO_2$. Evidence has been obtained that this compound can be produced by either of two methods: (1) pyrolysis of mesityl-2-butenylphostinate (**3**) according to eq 1, or (2) by the reaction of mesityl-2,4-butadienylphostinate[4] (**1**) with dienophiles. Presumably the Diels–Alder reaction with dimethyl acetylenedicarboxylate proceeds as shown in eq 2, and the reaction with maleic anhydride as shown in eq 3. In neither case, however, was either the initial adduct or the monomeric mesitylmetaphosphonate isolated; their formation has been inferred from the isolation of polymeric mesitylmetaphosphonate from both reactions, and from the isolation of dimethyl phthalate and of *cis*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, respectively, from the processes shown in eq 2 and 3. The stereochemistry of the Diels–Alder adducts is entirely conjectural, since neither was isolated.

Mesityl-2,4-butadienylphostinate (the phosphorus analogue of α-pyrone) was prepared as shown in eq 4. Evidence for these statements and the validity of these equations and a discussion of the polymerization of the postulated monomeric mesitylmetaphosphonate are presented below.



Experimental Section

Methods. ^1H NMR spectra were obtained with a Varian A-60, T-60, or CFT-80 spectrometer, and the data are quoted in parts per million downfield from Me_4Si. ^1H noise-decoupled ^{31}P NMR spectra

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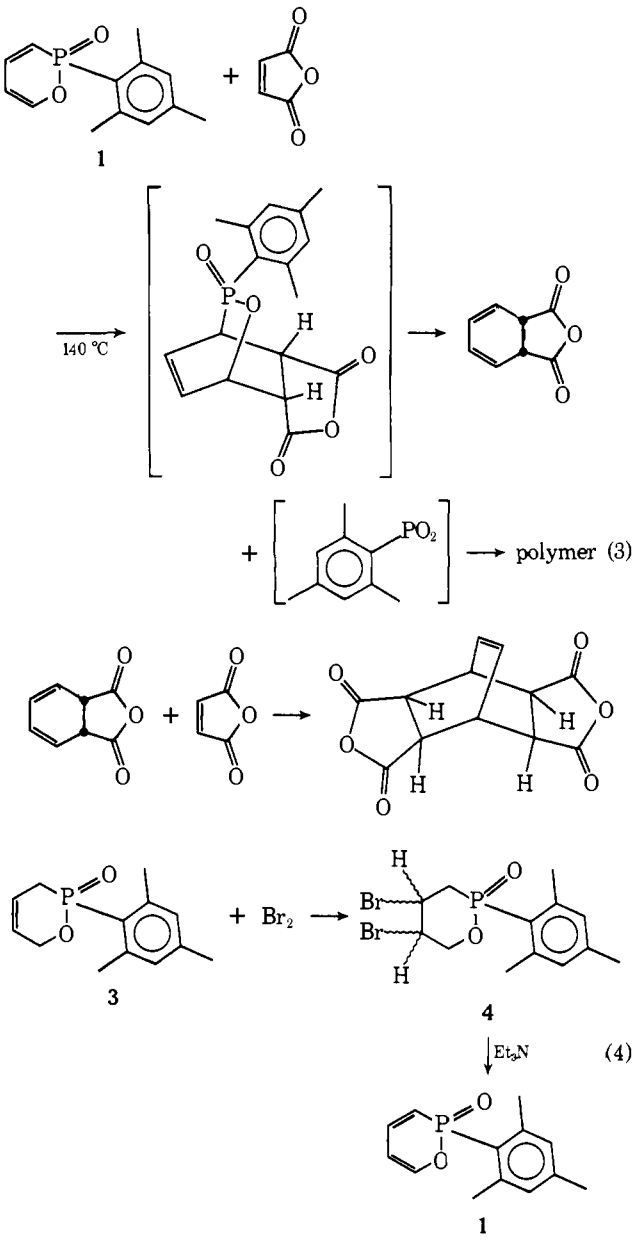

were determined at 40.5 MHz with a Varian XL 100 spectrometer, equipped for Fourier transform, and are quoted in parts per million relative to 85% phosphoric acid; downfield displacements are given a positive sign. Mass spectra were determined with an MS-9 high-resolution spectrometer. Infrared spectra were taken with an Infracord.

Materials. Dimethyl Mesitylphosphonite (2). A Grignard reagent, prepared in ether (150 mL) from 59.7 g (0.3 mol) of bromomesitylene, was introduced over 45 min under nitrogen to a solution of 37 g (0.3 mol) of freshly distilled trimethyl phosphite in 150 mL of dry benzene. The reaction mixture was stirred under reflux for 15 h, and then quenched with 120 mL of 40% ammonium chloride solution. The organic phase was separated, and the aqueous phase, together with a suspended white solid, was extracted with 3 × 100 mL of benzene. The combined organic solutions were dried over magnesium sulfate, and concentrated to an oil that was distilled (73–74 °C (0.1 mm)) through a 22-cm Vigreux column to yield 24.2 g (38% yield) of the phosphonite. Anal. Calcd for $C_{11}H_{17}O_2P$: C, 62.25; H, 8.07; P, 14.59. Found: C, 62.18; H, 8.05; P, 14.32. ^1H NMR ($CDCl_3$): δ 2.25 (s, 3 H), 2.59 (d, J_{HP} = 1.5 Hz, 6 H), 3.68 (d, J_{HP} = 13 Hz, 6 H), 6.82 ppm (d, J_{HP} = 2 Hz, 2 H). IR (film): 2900, 1605, 1445, 1178, 1050, 1020, 852, 735, and 718 cm^{-1}.

Mesityl-2-butenylphostinate (3). *cis*-1,4-Dibromo-2-butene[5] (10 g, 0.047 mol) was added at 80 °C over 30 min to the phosphonite **2** (10 g, 0.047 mol). A stream of nitrogen was passed through the reaction mixture to facilitate removal of methyl bromide produced in the Arbuzov reaction.[2,6] After 45 min, a short distilling head was attached, the system evacuated, and the temperature increased over 2 h to 118 °C and held there for an additional 1 h. During the heating, a gas (presumably again methyl bromide) was evolved. The contents of the flask was molecularly distilled at 10^{-4} Torr to give a forerun of 1.2 g at a pot temperature of 80 °C and a main fraction of 4.4 g of clear, viscous oil at a pot temperature of 110 °C; the distillation took 16 h. The oil was then chromatographed in 1-g portions over a 1.5 × 48.5 cm column containing 40 g of Florisil packed in ethyl acetate; it was eluted with ethyl acetate, at a flow rate of 2 mL/min. The compound appeared in the 200 mL of eluent following a 110-mL forerun. A final purification was effected by another molecular distillation of 3.2 g (pooled from four chromatographs) at 3 μ and a pot temperature of 105 °C to give 2.9 g (26% yield) of a clear, viscous oil. Anal. Calcd for $C_{13}H_{17}O_2P$: C, 66.09; H, 7.25; P, 13.11. Found: C, 66.16; H, 7.26; P, 13.09. ^1H NMR ($CDCl_3$): δ 2.28 (s, 3 H), 2.61 (d, J_{HP} = 1 Hz superimposed on a multiplet, 8 H in total), 4.27–5.08 (m, 2 H), 5.40–6.12 (m, 2 H), and 6.9 (d, J_{HP} = 4 Hz, 2 H). ^{31}P NMR ($CDCl_3$): δ 35.6. IR (film): 3000–2850, 1645, 1605, 1205, 1060, 1005, and 855 cm^{-1}.

Mesityl-2,3-dibromobutanylphostinate (4). Mesityl-2-butenylphostinate (**3**, 1.95 g, 8.35 mmol) in 5 mL of chloroform was treated in the dark with stirring with bromine (1.44 g, 9.0 mmol) in 5 mL of chloroform over a period of 90 min at room temperature. The reaction mixture was washed with 3 mL of 10% aqueous bisulfite and with saturated brine, and then dried over magnesium sulfate. After the solid was removed by filtration, the solvent was distilled in vacuo, and residual chloroform "chased" with dichloromethane; the residue was evacuated at 0.03 mm. The product (3.16 g of a white foam) gave two spots on thin layer chromatography (3:1 ether–hexane on silica gel with fluorescent indicator). When the foam (2.75 g) was triturated with 6 mL of ether, 1.64 g (57% yield) of a crystalline product was obtained that gave only one spot on TLC. This material recrystallized as colorless prisms from a minimal amount of dimethoxyethane and four volumes of hexane, and then melted at 115.5–117 °C. Anal. Calcd for $C_{13}H_{17}Br_2O_2P$: C, 39.42; H, 4.32; P, 7.81; Br, 40.32. Found: C, 39.57; H, 4.33; P, 7.89; Br, 40.10. ^1H NMR ($CDCl_3$): δ 2.28 (s, 3 H), 2.68 (d, J_{HP} = 1 Hz, superimposed on a multiplet, 8 H in total), 4.48–4.53 (m, 3 H), 5.32–5.42 (m, 1 H), 6.91 (d, J_{HP} = 4.2 Hz, 2 H). IR (KBr): 2950, 1605, 1450, 1215, 1200, 1100, 1000, 940, 840, 805, 765, and 735 cm^{-1}.

Mesitylbutadienylphostinate (1). Dry triethylamine (0.1 mL, 0.72 mmol) and dry dimethylformamide (1 mL) were added by syringe to mesityl-2,3-dibromobutanylphostinate (124.5 mg, 0.32 mmol) in a 5-mL round-bottom flask equipped with magnetic stirrer and reflux condenser, and protected from moisture by an argon-filled balloon. The reaction mixture was heated to 140 °C over 30 min, and maintained at that temperature for 45 min more. After addition of ether (4 mL) to the cooled solution, triethylammonium bromide was removed by filtration, and solvent evaporated under vacuum. The resulting crude product, in ether solution, was spotted on 0.25-mm preparatory silica gel plates containing fluorescent indicator, and developed with ethyl acetate. The major band, R_f 0.3, was extracted with 4 drops of methanol in 10 mL of dichloromethane; after removal of solvent, 27 mg (36% yield) of a light green oil was obtained. A colorless oil could be obtained by treating the product with 100 mg of Norit in 5 mL of chloroform, or by molecular distillation at 110 °C (0.05 mm). For a preparation with about twice these amounts, chromatography on a 1.5 × 13.5 cm column over 5 g of Florisil was substituted for the preparative thick layer separation. Anal. Calcd for $C_{13}H_{15}O_2P$: C, 66.66; H, 6.45; P, 13.22. Found: C, 66.37; H, 6.50; P, 13.17. Exact mass, calcd 234.0894; found 234.0836. ^1H NMR ($CDCl_3$): δ 2.29 (s, 3 H), 2.47 (d, J_{HP} = 1 Hz, 6 H), 6.89–6.95 (d, J_{HP} = 4.5 Hz, superimposed on a multiplet, 5.79–7.10, 6 H in total). IR (film on NaCl): 2850, 1630, 1605, 1550, 1450, 1250, 1080, 1060, 910, 775, and 725 cm^{-1}.

Dimethyl Mesitylphosphonate (5). Goldman's activated manganese dioxide[7] (150 g of wet preparation) was dried (102 g of water was removed over 10 h by azeotropic distillation with benzene) and added as a slurry in 500 mL of benzene to 10 g (0.047 mol) of dimethyl mesitylphosphonite. After 15 min of stirring, no phosphonite could be detected by TLC. The reaction mixture was filtered through Celite, and the filtrate concentrated; distillation at 92–94 °C (0.05 mm) gave 9.1 g (85% yield) of a clear oil. Anal. Calcd for $C_{11}H_{17}O_3P$: C, 57.89; H, 7.51; P, 13.57. Found: C, 58.01; H, 7.61; P, 13.48. ^1H NMR ($CDCl_3$): δ 2.26 (s, 3 H), 2.58 (d, J_{HP} = 1 Hz, 6 H), 3.67 (d, J_{HP} =

11 Hz, 6 H), and 6.87 (d, J_{HP} = 4.5 Hz, 2 H). IR (film): 2880, 1610, 1460, 1265, 1190, 1030, 830, and 785 cm^{-1}.

Hydrogen Methyl Mesitylphosphonate (6). The diester **5** (1 g, 4.4 mmol) and sodium iodide (1 g, 6.7 mmol) were dissolved in 30 mL of dry acetonitrile and the solution refluxed for 16 h. The white powder that had then deposited was filtered, washed with solvent, and added to a slurry of 50 mL of Amberlite IR 120 resin (Mallinckrodt, acid form) in 75 mL of absolute ethanol. The resin was decanted and washed five times with 75 mL of ethanol. The combined solutions were concentrated to give 0.8 g of a yellow oil. Molecular distillation at 160 °C (0.001 mm) gave 0.6 g (64% yield) of almost colorless oil. Anal. Calcd for $C_{10}H_{15}O_3P$: C, 56.08; H, 7.06; P, 14.46. Found: C, 55.87; H, 7.13; P, 14.56. ^1H NMR ($CDCl_3$): δ 2.25 (s, 3 H), 2.54 (d, J_{HP} = 1.5 Hz, 6 H), 3.66 (d, J_{HP} = 12 Hz, 3 H), 6.88 (d, J_{HP} = 5 Hz, 2 H), 11.83 (s, 1 H). ^{31}P ($CDCl_3$): δ 25.4. IR (film): 2890, 2270, (broad), 1610, 1445, 1400, 1195, 1090, 1045, 980, 855, and 800 cm^{-1}.

Mesitylphosphonic Acid (7). A solution of monester **6** (0.5 g, 2.3 mmol) and sodium iodide (1 g, 6.7 mmol) in 25 mL of dry acetonitrile was refluxed under nitrogen for 48 h. The white precipitate that formed (360 mg) was washed with solvent; its NMR spectrum in D_2O showed no methyl ester protons. Treatment of 250 mg of this sodium salt with Amberlite IR 120 in absolute ethanol as described above afforded 210 mg of a white solid, which was recrystallized from chloroform to give 130 mg (41% yield) of a white powder, mp 177 °C. Anal. Calcd for $C_9H_{13}O_3P$: C, 54.00; H, 6.55; P, 15.47. Found: C, 53.90; H, 6.52; P, 15.28. ^1H NMR (Me_2SO-d_6): δ 2.23 (s, 3 H), 2.54 (d, J_{HP} = 1 Hz, 6 H), 6.85 (d, J_{HP} = 4 Hz, 2 H), 9.27 (s, 2 H). ^{31}P ($CDCl_3$): δ 27.5. IR (film): 2980 (b), 2280, 1610, 1195, 1175, 1090, 1045, 985, 920, 850, and 770 cm^{-1}.

Diels–Alder Reactions. Dimethyl acetylenedicarboxylate (0.1 mL, 0.82 mmol) and mesitylbutadienylphostinate (**1**, 100 mg, 0.43 mmol) were heated in a sealed NMR tube; reaction was observed (by diminution of the signal from the vinylic hydrogen atoms) when the temperature was raised to 165 °C. After 1.5 h at that temperature, the tube was cooled; an NMR spectrum of the product in $CDCl_3$ showed a ratio of aromatic ring hydrogen atoms for the phthalyl group to those of the mesityl group of 3:2 (75% yield). After the $CDCl_3$ had been removed in vacuo, the residue was stirred for 20 min with a mixture of THF (0.3 mL) and a saturated aqueous solution of sodium bicarbonate (0.5 mL). The solution was then extracted with ether (6 mL) and the ether back-extracted with three 1-mL portions of the bicarbonate solution. The product from the ether was purified by TLC on silica gel with ether–hexane (7:10) and then identified by IR and NMR spectroscopy as dimethyl phthalate.

Large needles (22 mg) separated from the aqueous phase. The presumed salt, dissolved in 6 mL of ethanol, was converted to the corresponding acid by treatment with 3 g of Amberlite IR 120 resin that had been soaked in ethanol. Evaporation of the alcohol left a crystalline, white powder (compound **8**) with an IR spectrum almost identical with that obtained in the pyrolysis experiments discussed later but distinct from that for authentic mesitylphosphonic acid. Compound **8** is later assigned the structure of the pyrophosphonate from mesitylphosphonic acid. Since the same material was obtained from the Diels–Alder synthesis and from pyrolysis, experiments were performed on either material, depending on which was available; the results obviously apply to compound **8**, regardless of its source.

Compound **8** (~8 mg) was dissolved in 3 mL of 1 N NaOH in 50% D_2O–H_2O. The major peak in ^{31}P NMR spectroscopy was found at δ 10.8, the same shift as for the dianion of authentic mesitylphosphonic acid. The solution was acidified with concentrated hydrochloric acid and extracted three times with one-half volumes of ether. After the ether had been removed, the resulting white crystals (6 mg, mp 177–178 °C) were washed with hot chloroform. This material gave identical IR and ^1H NMR spectra with those of authentic mesitylphosphonic acid. A mixture of this material with authentic mesitylphosphonic acid, in 50% D_2O–H_2O at pH 10, showed a single ^{31}P NMR signal at δ 10.80.

Maleic anhydride (235 mg, 2.4 mmol) and mesitylbutadienylphostinate (**1**, 94 mg, 0.40 mmol) were heated in a sealed tube at 140 °C for 1.5 h. The white crystals (which had appeared after 0.5 h) were filtered and washed with 1 mL of THF. Their IR spectrum was identical with that of authentic *cis*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic anhydride.[8] An NMR spectrum in D_2O of material that had been hydrolyzed in D_2O at 100 °C for 20 min was identical with that of a solution of the authentic[8] tetraacid.

Other attempted Diels–Alder reactions, under milder conditions, were followed by NMR spectroscopy, but showed no reaction. These included attempts to carry out such reactions at room temperature with diethyl azodicarboxylate and dicyanoacetylene, with TCNE at 115 °C, and with dimethyl acetylenedicarboxylate at temperatures below 165 °C.

Table I. Kinetics of Saponification of $RPO(OCH_3)_2$

R	temp, °C	NaOH, M	k, 10^4 s^{-1}	k_2, 10^4 s^{-1} M^{-1}
mesityl	50	0.431	3.85 ± 0.17[a]	8.9 ± 0.4
	50	0.173	1.9 ± 0.1[a]	11 ± 0.6
	60	0.431	18.5 ± 0.2[b]	43 ± 0.5
p-tolyl	50	0.431	11.7 ± 0.9[a]	27 ± 2
	50	0.173	5.63 ± 0.45[a]	33 ± 3

[a] Average of four determinations. [b] Average of two determinations.

Pyrolysis. Mesityl-2-butenylphostinate was pyrolyzed in an apparatus modified from that used earlier in these laboratories[2] by shortening the inlet manifold and installing the pressure gauge in the lower rather than the upper part of the oven. During the reactions, the sample tube was maintained at a temperature of 100 °C, the inlet manifold at a temperature of 150 °C, and the heating coil at a maximum temperature of 600 °C, with a flow rate of nitrogen of about 4 mmol/h and a pressure of 80 μ. Usually about 100–150 mg of phostinate was pyrolyzed over 5 h with a nitrogen to phostinate ratio of 30:1.

The products of pyrolysis were trapped at the temperature of an isopropyl alcohol–dry ice bath or at liquid nitrogen temperature. Butadiene was identified by VPC as before.[2] The nonvolatile residue was transferred to an NMR tube, and the ^{31}P spectrum determined, without allowing the material to warm from dry ice temperature. In order to accomplish this transfer, the following protocol was observed: at the conclusion of a pyrolysis, with the trap still immersed in a dry ice–isopropyl alcohol bath, and the pressure in the apparatus around 0.03 mm, 4 g of toluene-d_9 was distilled onto the pyrolysate. The apparatus was tipped, so that the toluene solution was transferred to an NMR tube that had previously been sealed to the trap at right angles, and which was also immersed in a dry ice–isopropyl alcohol bath. After the transfer, the tube was sealed and rapidly inserted into the ^{31}P NMR probe at a temperature of −80 °C. The ^{31}P spectrum always consisted of a complex pattern of singlets and multiplets, the relative proportions of which varied from one experiment to the next. When the sample was warmed to room temperature and the deuteriotoluene replaced by deuteriochloroform, all of these signals were replaced by a singlet at δ 12.4.

When this final product was treated with strong alkali (as was the similar material from the Diels–Alder reaction), and the mixture subsequently acidified, mesitylphosphonic acid was isolated. When the pyrolysis was conducted with rigorous exclusion of moisture, and the residue treated with methanol, the major ^{31}P signal corresponded to that for monomethyl hydrogen mesitylphosphonate. The monomethyl ester was isolated as follows. The pyrolysis residue was treated with methanol, excess methanol removed by evaporation, and the product extracted with benzene. Removal of the benzene left an oil with IR and ^1H and ^{31}P NMR spectra identical with those of the monomethyl ester of mesitylphosphonic acid.

Kinetics. The rates of saponification of dimethyl mesitylphosphonate and of dimethyl *p*-tolylphosphonate were determined spectrophotometrically at 50 °C, using a Gilford spectrophotometer, in 50% aqueous dioxane; the latter had been distilled from sodium benzophenone. For the mesityl compound, the absorption peak at 284 nm was monitored; for the *p*-tolyl compound, 273 nm was followed. The samples were placed in Teflon-capped 1-cm cuvettes, and the spectrophotomeric data analyzed by the method of Guggenheim. The data are shown in Table I. Dimethyl *p*-tolylphosphonate, prepared by the method of Tavs and Korte,[9] was prepared by Dr. Lorna Williamson.[10]

Oxygen Exchange. Dimethyl mesitylphosphonate (5×10^{-4} mol), NaOH (4×10^{-3} mol), and 10 mL of water enriched to 1.7% with ^{18}O were heated in a sealed test tube with stirring at 55 °C until all the phosphonate "dissolved" (0.5 h). The contents of the tube was then distilled, and the first drop of distillate collected for mass spectral analysis. Control experiments were conducted with ordinary instead

of ^{18}O-enriched water, and with methanol (0.6×10^{-3} mol) instead of the phosphonate. The distillate was analyzed in a high-resolution mass spectrometer at *m/e* 33.0218, corresponding to $H_3{}^{12}C^{18}O^+$ (calcd 33.0226), and *m/e* 33.0311, corresponding to $H_4{}^{13}C^{16}O^+$ (calcd 33.029 56). No difference in the ratio of peak heights was observed for the three samples.

Results and Discussion

The synthesis of mesitylbutadienylphostinate is straightforward. The addition of bromine to mesityl-2-butenylphostinate might be expected to lead to two different diastereomeric trans dibromides (and conceivably could lead to cis dibromides as well). In fact, two compounds were produced on bromination, and were detected chromatographically. The one formed in higher concentration, which was purified by recrystallization, led to the desired diene. Since, however, a parallel sequence of reactions failed, in our hands, to provide the corresponding diene from methyl 2-butenylphostonate, the method may not prove to be general. The structure of the product, mesityl-2,4-butadienylphostinate (**1**), is clearly defined by its analysis, high-resolution mass spectrum, and both IR and ^1H spectra. The compound, as a phosphorus analogue of α-pyrone, offers interesting possibilities for future exploitation.[11] For example, a more extensive examination of its physical properties might reveal the extent, if any, of "aromaticity", while photolysis could reveal interesting chemistry.

In the present paper, the Diels–Alder reactions of this compound have been explored, with the objective of preparing and then decomposing bicyclic derivatives that would lead to the preparation of monomeric mesitylmetaphosphonate. The mesityl derivative was selected in preference to the corresponding monomeric phenylmetaphosphonate (which should result from the pyrolysis of phenyl-2-butenylphostinate[12]) because we hoped that the mesityl compound would be sterically hindered, and so react less rapidly than does monomeric methylmetaphosphate; had this proved to be the case, it might have been isolable.

The Diels–Alder reaction requires elevated temperatures for many dienes, so perhaps it is not too surprising that the reaction with mesitylbutadienylphostinate only occurred at temperatures high enough to bring about the decomposition of the presumed bicyclic adduct. In any event, the reaction of mesitylbutadienylphostinate with dimethyl acetylenedicarboxylate gave dimethyl phthalate as one product, whereas the reaction of maleic anhydride gave (after hydrolysis) *cis*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid.

The formation of these products implies that the Diels–Alder reactions occurred as shown in eq 2 and 3, and that the bicyclic products then decomposed by reverse Diels–Alder reactions, presumably liberating monomeric mesitylmetaphosphonate along with the organic compounds identified above. The reaction conditions for the concurrent Diels–Alder reaction and the decomposition of the presumed adduct are comparable to, although perhaps somewhat milder than, those required to decompose the isolated adduct of maleic anhydride and α-pyrone.[8] This implies that the activation energy in a process that forms monomeric metaphosphonate is no greater than that of the corresponding process that releases carbon dioxide; in view of the instability of the monomeric metaphosphonate and the stability of CO_2, this finding was unexpected.

Monomeric methyl metaphosphate has previously been prepared by pyrolysis of methyl-2-butenylphostonate[2] and by the fragmentation of β-bromophosphonates,[3] and in each case identified by trapping. When the reactions are carried out in the absence of trapping agents, polymeric metaphosphates are formed. In the present case, trapping was only partially successful. Both methylaniline and methanol reacted with the product of gas-phase pyrolysis, but in neither case was a single product obtained in good yield. In the absence of trapping agent, polymer was formed. The polymer falls apart in the presence of water, presumably to a dimeric species, **8**, $^-O_2P(R)-O-P(R)O_2^-$, where R is mesityl. Larger moieties than the pyrophosphonate can readily be hydrolyzed, but the pyrophosphonate is protected against rapid nucleophilic attack by the negative charge on the molecule. This would explain why, even in the presence of bicarbonate, the pyrophosphonate rather than mesitylphosphonic acid was obtained. Strong alkali, however, cleaves the ion, and the product (after acidification) is mesitylphosphonic acid. A polymeric product that behaves in this fashion on hydrolysis is in fact what might be expected from the postulated monomeric mesitylmetaphosphonate. Further, the products of the pyrolysis (isolated before hydrolysis) vary with the experimental conditions under which the metaphosphonate was formed, as might be expected for a polymerization reaction. Presumably the length of the polymer varies with the amounts of adventitious moisture that had been present on the walls of the "dry" glassware.

Quite obviously, the hoped-for steric hindrance by the mesityl group to polymerization did not eventuate. Further investigation revealed that it might not have been anticipated. The rate constant of second-order hydrolysis for dimethyl *p*-tolylphosphonate is only about three times that for dimethyl mesitylphosphonate. Although the data, presented in Table I, are scanty, they leave no doubt as to the essential facts; steric hindrance cannot be important in these systems. The small rate difference that has been observed may even be (at least partly) caused by electron donation by the three methyl groups of the mesityl residue as contrasted to the single methyl group in the tolyl compound. It should further be noted that basic hydrolysis of dimethyl mesitylphosphonate does not involve S_N2 attack at a methyl group. This was shown by carrying out the saponification in water enriched in ^{18}O; no enrichment appeared in the methanol produced in hydrolysis. Apparently little or no steric hindrance obtains in the hydrolysis of an ester of mesitylphosphonic acid. This result contrasts strongly with the considerable steric effects noted, for example, in the hydrolysis of the esters of *tert*-butylphosphonic acid.[13] Presumably the *tert*-butyl group occupies a greater solid angle than does the mesityl group, and perhaps the only available direction for attack on the *tert*-butylphosphonate esters would force the *tert*-butyl group into an unfavorable apical position in a trigonal bipyramidal intermediate.

Alternatively, perhaps the difference between the phosphonic and the corresponding carboxylic acids lies in the difference in coordination number; the trigonal carboxyl group may be forced at right angles to the ring, whereas no conformation is especially favorable for the tetrahedral phosphorus atom in the phosphonate ester. But this explanation for the data of Table I may not help with respect to a monomeric metaphosphonate, which might well have a configuration similar to that of the carboxylic ester, where the phosphorus atom would be protected by the flanking methyl groups. Here, however, the difference may lie, at least in part, in the high energy of the monomeric metaphosphonate; the transition state may come early in the hydrolysis, when the attacking nucleophile—water or hydroxide ion—is still at a relatively long distance from the phosphorus atom. Alternatively, the increase in bond length for P–C as compared to C–C bonds may influence the extent of steric hindrance.

Still another possible explanation emerges from a theoretical molecular orbital treatment[14] of monomeric metaphosphate. Calculations suggest the involvement of a low-lying unoccupied σ* energy level that can contribute to the electrophilic reactivity of these systems; thus acceptor orbital density is available in the plane of the trigonal phosphorus atom, leading to softer potential surfaces than those available to 2p–2p π-bonded electrophiles.

At present, the cause of the easy hydrolysis of dimethyl mesitylphosphonate is unknown but worthy of further inves-

tigation. In any event, if monomeric mesitylmetaphosphonate, is formed both in pyrolysis and by decomposition of the Diels–Alder adducts, it polymerizes especially readily; if the polymerization is subject to any steric effect, that effect is quite insufficient to allow the easy isolation of the monomeric mesitylmetaphosphonate. Nevertheless the metaphosphonate presumably has been formed by the processes outlined in this paper.

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Free-Radical Reactions of Organophosphorus Compounds. 9.[1] The Question of Memory Effects in the Alkoxy-Radical Oxidations of Cyclic Trivalent Phosphorus Derivatives

Akira Nakanishi, Koichi Nishikida, and Wesley G. Bentrude*

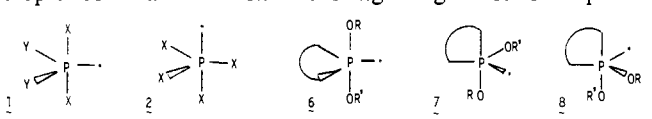
Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received February 2, 1978*

Abstract: Alkoxy-radical oxidations of a series of five- and six-membered ring phosphites and several five-membered ring phosphorodiamidites (1,3,2-diazaphospholanes) were studied. Determinations of product oxide ratios were made in reaction systems designed to generate a potentially common phosphoranyl radical intermediate by two different pathways. Both product studies (^{31}P or GLC) and product radical ratio determinations (ESR) were carried out on a given reaction system. In no case was a dependence of product oxide ratio on pathway of phosphoranyl radical generation noted. The lack of memory effect can be interpreted (1) in terms of initial formation of a common trigonal bipyramidal phosphoranyl radical with diequatorial ring attachment to phosphorus which then undergoes isomerization to permutamers with apical–equatorial ring prior to β-scission; or (2) by way of rapid equilibration of isomeric forms of the latter intermediate utilizing a rapid mode 4 permutation process. Such an equilibration is consistent with previous ESR measurements reported by another group.

Both ESR[2,3] and chemical[4] studies have implicated the probable intermediacy of phosphoranyl radicals, $X\dot{P}Z_3$, in reactions of free radicals with trivalent phosphorus compounds:

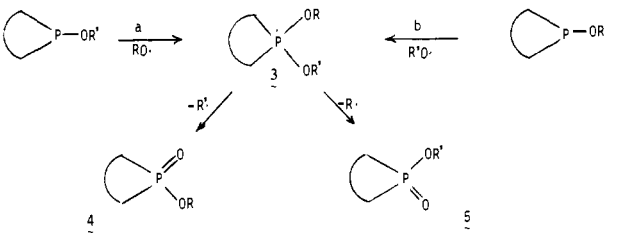
$$X\cdot + PZ_3 \rightarrow X\dot{P}Z_3 \rightarrow \text{products} \qquad (1)$$

These intermediates are generally assigned a local C_{2v}, near-trigonal-pyramidal (TBP) structure like **1**. (Exceptions occur when one or more phosphorus substituents are aryl.[3i,j,r,5]) Two substituents are equatorial in the TBP, while two are apical. MO treatments[6] of these species place the odd electron in an antibonding MO with spin density distributed between phosphorus and the apical ligands as do interpretations of anisotropic ESR data.[7] When discussing the geometries of phosphoranyl radicals, however, it is convenient to represent the nonsubstituted site as in **1**. The odd electron or vacant position thus becomes a phantom ligand and sterochemically significant as an equatorial substituent. No TBP C_{3v} species, **2**, have been identified by ESR in solution.[5]



One may generate a given cyclic phosphoranyl radical by more than one route as in Scheme I. The question then arises as to whether species **3** is a truly *common* intermediate or whether the observed ratio of product oxides (**4**/**5**) generated via β-scission may depend on the origin of **3**. TBP structures for **3** may be written with RO and R'O either configurationally equivalent (**6**) or nonequivalent (**7** and **8**). If the rate of β-scission were measurably different at the apical and equatorial sites of **7** and **8** and the latter were neither formed in the same proportions by routes a and b nor rapidly interconverted, then the system of Scheme I would exhibit a so-called *memory effect*. That is, the ratio **4**/**5** resulting from path a would be different from that formed via path b. We report here the study of several reactions of the type shown in Scheme I. Possible interpretations of the **4**/**5** ratios found in terms of the geometries of intermediates like **3** and probable permutational isomerization processes available to them are given.

Scheme I



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