12d). Allowing for sample withdrawal, the yield was 97.4% based on diphosphonate adduct.

Diethyl bornyl-2-phosphonate (10b): d^{24} = 1.0346, $n^{20}D$ 1.4692, $\alpha^{25}D$ 18.6°; ir 3450, 2910, 1455, 1385, 1365, 1285, 1235, 1155, 1090, 1055, 1025, 949, 787, 748 cm^{-1}; nmr δ 0.87 (s, 6, $C_{8,9}$-CH_3), 1.02 (s, 3, C_{10}-CH_3), 1.32 (t, 6, J = 7 Hz, $C_{12,14}$-CH_3), and 4.12 ppm (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29, H, 9.92; P, 11.29. Found: C, 61.09; H, 10.11; P, 11.44.

Diethyl 1-*p*-menthenyl-9-phosphonate (11): d^{24} = 1.0076, $n^{20}D$ 1.4680, $\alpha^{26}D$ +11.7°; ir 3415, 2880, 1430, 1380, 1235, 1155, 1090, 1050, 1025, 952, 875, 829, 792, 714 cm^{-1}; nmr δ 1.03 (d, 3, J = 6.5 Hz, C_{10}-CH_3), 1.32 (t, 6, J = 7 Hz, $C_{12,14}$-CH_3), 1.64 (s, 3, C_7-CH_3), 4.09 (qn, 4, J = 7 Hz, $C_{11,13}$-CH_2).

Anal. Calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92; P, 11.29. Found: C, 61.43; H, 10.00; P, 11.17.

Diethyl *p*-methanyl-2,9-diphosphonate (12): glc 2.5% **12a**, 45.5% **12b**, 45.9% **12c**, 6% **12d**; d^{24} = 1.0894, $n^{25}D$ 1.4676, $\alpha^{25}D$ +4.9°; ir 3440, 2890, 1430, 1380, 1230, 1155, 1090, 1045, 1020, 942, 823, 784 cm^{-1}; nmr δ 1.04 (d, 6, J = 6 Hz, $C_{7,10}$-CH_3), 1.34 (t, 12, J = 7 Hz, $C_{12,14,16,18}$-CH_3), 4.11 ppm (qn, 8, J = 7 Hz, $C_{11,13,15,17}$-CH_2).

Anal. Calcd for $C_{18}H_{38}O_6P_2$: C, 52.41; H, 9.29; P, 15.02. Found: C, 52.23; H, 9.41; P, 14.96.

When heated at 140–150° for 3.5 hr, 13.6 g of **5** and 60.1 g of DEHP yielded 3.04 g (11.1%) of crude product which had a composition similar to the run with the peroxide.

Hydrogenation of the Limonene Adducts. A 0.3 g sample of **10** was reduced in 10 ml of acetic acid using 29.5 mg of PtO_2 as catalyst. The sample absorbed only 2.45 ml (STP 13% of theory) of H_2 in 42 min. Glc of the 0.29 g recovered indicated that it was mostly starting material.

A 0.16 g sample of **11** and 26.2 $MgPtO_2$ in 5 ml of acetic acid absorbed 12.84 ml (STP, 98% of theory) of H_2 in 44 min. Glc of the recovered material (0.15 g, $[\alpha]^{25}D$ 0° (15% EtOH)) showed a peak at α (**11**) 0.731. Ir bands at 1250–970 cm^{-1} indicated the presence of the phosphonate structure.

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Registry No.—**1**, 18172-67-3; **2**, 7785-70-8; **3**, 79-92-5; **4**, 1195-31-9; **5**, 5989-27-5; **6**, 49830-14-0; **7**, 49830-15-1; *endo*-**8**, 49830-16-2; *exo*-**8**, 49830-17-3; **9a**, 49775-19-1; **9b**, 49775-20-4; **9c**, 49775-21-5; **9d**, 49775-22-6; **10b**, 49830-18-4; **11**, 49830-19-5; **12**, 49830-20-8.

References and Notes

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(16) This is in accord with J. H. Brewster's rules [*J. Amer. Chem. Soc.*, **81**, 5483 (1959)], which predict the same interrelationship for the isomeric phosphonates.
(17) Even with the OH group at least half has this conformation.[14,15]
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(20) The carvomethene was kindly supplied by Newport Industries, the α-pinene by Arizona Chemical Co., the β-pinene by Crosby Chemicals, Inc., and the diethyl hydrogen phosphite by Mobil Chemical. Use of a company and/or product name by the department is for the convenience of the reader and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Some Properties and Reactions of 1-Methyl-3-phospholanone 1-Oxide[1]

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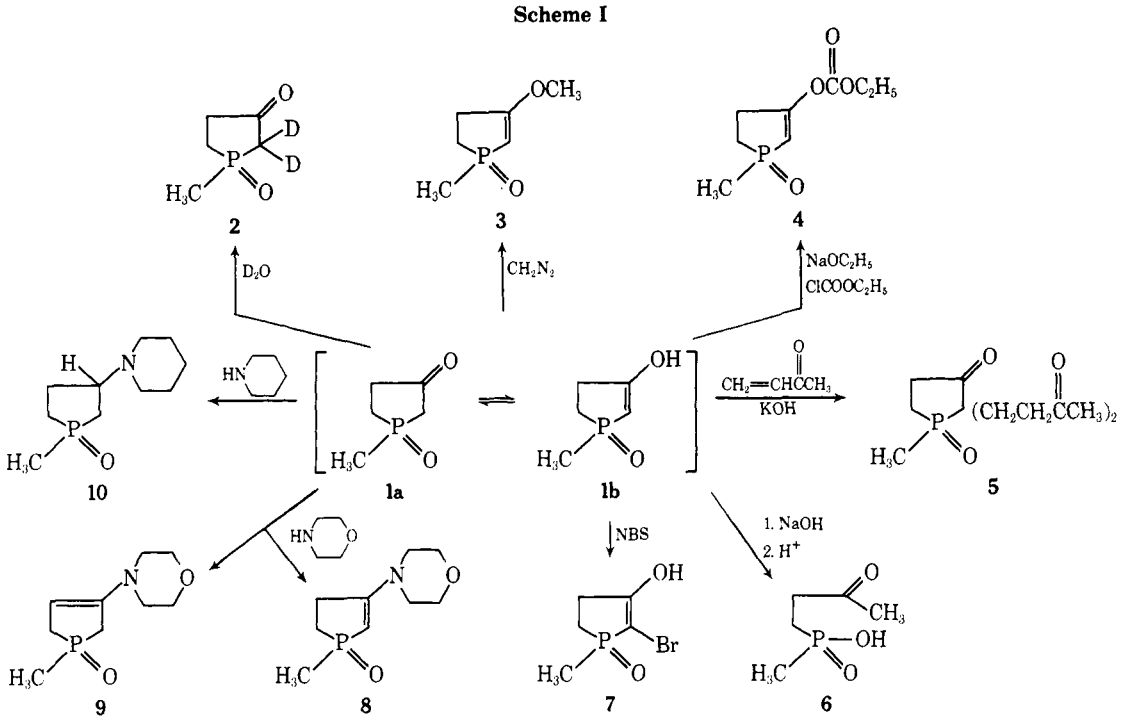
1-Methyl-3-phospholanone 1-oxide (**1**) is in tautomeric equilibrium with 1-methyl-3-hydroxy-2-phospholene 1-oxide, permitting uncatalyzed rapid exchange with D_2O at the 2 position. In appropriate media, the ^{13}C nmr spectra of both keto and enol forms can be observed, giving conclusive assignment of the enol structure. Reactions of **1** can occur at oxygen (with diazomethane or ethyl chloroformate), at C-2 (with *N*-bromosuccinimide or Michael addition to 2-butenone), at C-3 (enamine formation), or at phosphorus (ring opening with base). Some of the functionally substituted phosphine oxides so obtained were reduced to the phosphines with trichlorosilane. Of particular importance was the reduction of **1** itself which gave 1-methyl-3-phospholanone, the first known ketophospholane.

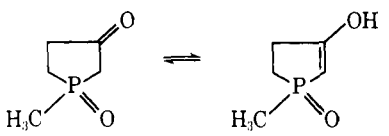
In 1968,[2] we reported the synthesis of the first keto derivative of the phospholane oxide system,[3] 1-methyl-3-phospholanone oxide (**1**). The compound was found to have considerable enolic character; depending on the medium, as much as 20–25% could be present as the enol **1b**. Conditions favoring the enol form were those where intermolecular hydrogen bonding was enhanced (high concentrations in aprotic solvents, or the solid state). The tautomeric forms were easily recognizable in admixture by substantial differences in their ir and nmr (^1H and ^{31}P) spectra.

In the present paper, we report further on the tautomeric character of this compound, particularly as it influences other properties. The compound has been demonstrated to

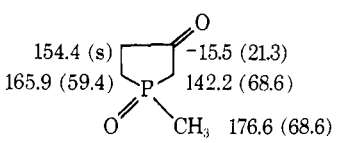
Scheme I



have utility as a precursor of a variety of functionally substituted phospholane derivatives.



Carbon-13 Nmr Spectra. The spectrum of a dilute chloroform solution of compound 1 was clearly that of the keto form (**1a**). The carbonyl group absorbed at δ −15.5, which is in its characteristic region, and no olefinic carbon signals were present. Other assignments are shown below; δ values are relative to CS_2 = 0, and J_{PC} values are in parentheses.



The large coupling of P with adjacent C in cyclic phosphine oxides[4,5] was helpful in assigning these carbons; the deshielding effect of C=O[6a] allowed ready recognition of the carbon α to it and to P=O. Upon increasing the concentration of the solution, additional signals due to the enol form appeared. Those at δ 16.6 (45) and 102.1 (115) are assignable to olefinic carbons, the former being that bearing hydroxy.[7] Similar wide differences, explainable by resonance, are also known among enol ethers[6b] and indeed are seen in 1-methyl-3-methoxy-2-phospholene[8] (**11**, δ 23.6 and 100.1).

The ^{13}C studies provide unequivocal proof that the enol does indeed have the double bond in the 2,3 position, as postulated previously,[2] and not in the 3,4 position.

In water solution, only the keto form was detected, regardless of concentration. This would suggest that water is competing with the enolic OH in forming a hydrogen bond to phosphoryl, thus eliminating this source of stabilization of the enol. That hydrogen bonding by water is present is clearly revealed by the significant differences between the ^{13}C values for **1a** in $CHCl_3$ and in water (CH_3, δ 172.1; C-2, 145.5; C=O, −6.7; C-4, 148.6; C-5, 160.1).

The tautomeric equilibrium provides a vehicle for rapid exchange of the protons at C-2 with deuterium. Dideuterio derivative **2** was obtained simply on several exposures of **1** to fresh D_2O, in the absence of base. The location of the deuterium was revealed by the ^{13}C spectrum in D_2O solution; the doublet for C-2, seen at δ 145.5 in H_2O, was virtually eliminated, while no other changes occurred. Such simplification of ^{13}C spectra by exchanging H for D has been reported elsewhere,[10] and is a consequence of the splitting of the carbon signal by the (undecoupled) deuterium, and of the weakening of the signal relative to the other carbons by the diminished nuclear Overhauser effect. In our case, the signal simply vanished into the base line.

Reactions at the Keto-Enol Site. Reactions of compound **1** that gave definite products are shown in Scheme I. It is seen that products can be derived from attack on oxygen, C-2, or C-3. Enol ether **3** was formed with diazomethane, while enol carbonate **4** was formed with ethyl chloroformate. The latter reaction, conducted on the enolate ion, could have been accompanied by C-acylation, but none was observed. Indeed, in only one of several other attempts to effect attack at C-2 was the desired result obtained; twofold Michael addition of the enolate to methyl vinyl ketone occurred in dilute aqueous base to form a product lacking the enolic properties of the 3-phospholanone oxide system yet showing ir absorption for a ring carbonyl (1725 cm^{-1}; exocyclic $\nu_{C=O}$ occurred at 1710 cm^{-1}). The structure proposed is **5**, and this was supported by the presence of a 6 H singlet for the two CH_3CO groups.

In some other attempts to effect condensations in aqueous base, a product was obtained that appeared to be noncyclic. An intentional attempt to effect ring opening of **1** with hot sodium hydroxide proved successful, and a compound identified as methyl(3-oxobutyl)phosphinic acid (**6**) was obtained in high yield. This sensitivity of the keto phosphine oxide to base parallels that known also in cyclic β-diketones.[11]

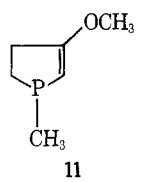
Oxide **1** absorbed 2 mol of bromine in water-methanol at titration rate. Since the oxide is spectroscopically seen as the keto form **1a** in this medium, the conversion of keto to the reactive enol form must be very rapid. Attempts to

isolate a product gave only oils. However, a crystalline monobromo derivative (7) was obtained in 38% yield with *N*-bromosuccinimide in hot chloroform, a procedure useful for the bromination of cyclic β-diketones.[12] This bromo compound was seen from its ir spectrum to be entirely in the enol form; no C=O absorption was present. Location of the bromine at the 2 position, as expected from the β-diketone reaction,[12] was suggested from titration with bromine, since only 1 mol was consumed. The compound had low solubility in organic solvents and attempts at performing some typical α-halo ketone reactions so far have been unsuccessful.

Another typical carbonyl reaction given by 1 is enamine formation with morpholine. The product was a mixture of two position isomers, 8 (85%) and 9 (15%). The predominance of the oxide with the 2-phospholene ring is consistent with other observations of greater stability for this ring system than for the 3-phospholene system,[13] and is suggestive of some stabilization of the double bond by conjugation with the phosphoryl group. Another indication of some interaction between these groups was the lack of reactivity of the 2 position to alkylating or acylating reagents. Normally, this carbon is a reactive site in enamines, and such reactions occur with ease. However, conjugation with a carbonyl group is known to deactivate this position, and enamino ketones undergo alkylation on oxygen.[14] Acylic phosphorylenamines have recently become available,[15] but so far no information has been published on the reactivity of the corresponding enamine carbon in these compounds.

When piperidine was used for enamine formation, the major product was a saturated amine (10), formed by reduction of initially formed 1-methyl-3-piperidino-2-phospholene 1-oxide. Such reduced products have been obtained by others when excess piperidine is used, but in the presence of added acid.[16] The present result would suggest that the enolic character of 1 provides sufficient acidity for the reaction to proceed.

Reduction of the Phosphine Oxide Function. Several years ago, silanes were introduced as reagents for reducing phosphine oxides to phosphines,[17] and the method has since found wide use. Some of the oxides prepared in the present study were unique in containing functional groups, and offered the possibility of serving as precursors to the corresponding phosphines. We have found that these oxides react with trichlorosilane in a normal manner, and functionally substituted phosphines **11**, **12**, and a mixture of 13 (85%) and 14 (15%) were prepared. Phospholenes **11** and **13** were of special interest spectroscopically, as they provided further examples of exceptionally large coupling of phosphorus with the 2 proton[18] (38 and 40 Hz, respectively). The ^{31}P nmr shifts for these vinyl phosphines were similar (+14.4 and +18.1 ppm, respectively) and like that of 1,3-dimethyl-3-phospholene (+15.2[18]), indicating little transmission through the double bond of the electronic character of the substituent.



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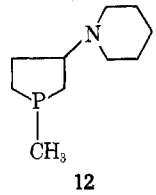

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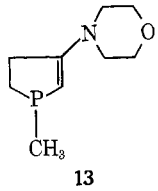

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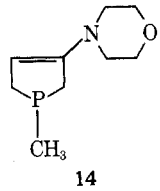

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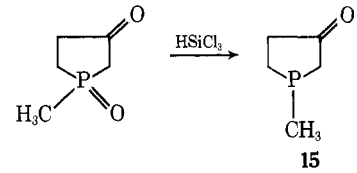
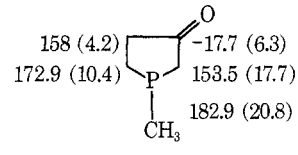
Synthesis of 1-Methyl-3-phospholanone. By applying the trichlorosilane reduction directly to phosphine oxide 1, we have prepared the first keto derivative (15) in the phospholane series. No interference by the carbonyl group[19] was evident in this reaction. While the yield was only 21%, the product was obtained in good purity. This ketone does not show the tendency to exist in the enol form as exhibited by the phosphoryl derivative (1).



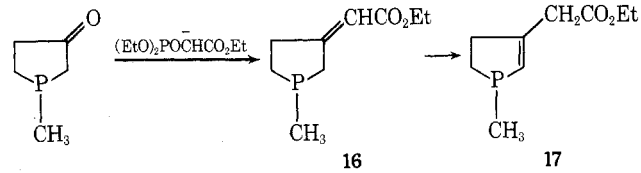
15

Attempts to prepare ketone 15 by acid hydrolysis of enol ether 11 or enamine 13 were not very successful. These compounds showed unusual reluctance to undergo hydrolysis. In the acid medium, they probably would exist in phosphonium salt form, which would impede the further protonation required for carbonyl formation.

Ketone 15 was easily characterized by its spectral properties. Its ^{13}C spectrum (in $CHCl_3$), compared with that of **1a**, exemplifies quite well the considerable differences in J_{PC} between a phosphine and its oxides, and at the same time the similarity in chemical shifts. As for **1a**, carbons α to phosphorus have the larger coupling constant, and the deshielding effect of C=O assists in locating C-2.



Availability of ketone 15 prompted examination of an anomalous property observed for a derivative of the homologous ketone 1-methyl-4-phosphorinanone. The carbethoxymethylene derivative of the latter was found to be prone to rearrange to the endocyclic olefinic structure.[20] When 15 was subjected to the Wadsworth–Emmons olefination to produce ester **16**, the product was found to consist chiefly (60–65%) of the rearranged form (17). The 2-phospholene structure was easily recognized from the characteristically large (41 Hz) coupling of the olefinic proton with phosphorus. Even greater propensity for rearrangement is therefore present in this ring system; the six-membered ring required base catalysis for rearrangement to the endocyclic structure.



16 17

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Proton nmr spectra were taken on a Varian A-60 spectrometer; chemical shifts are relative to external TMS. Phosphorus nmr spectra were obtained with a Varian V-4300B spectrometer at 19.3 MHz or a Bruker HFX-10 system at 36.43 MHz, and are referenced to 85% H_3PO_4. Proton noise-decoupled Fourier transform ^{13}C spectra were obtained on the Bruker system at 22.62 MHz utilizing C_6H_6 in a 3-mm coaxial capillary as an external heteronuclear lock; chemical shifts are referenced to CS_2. Gas chromatography (gc) was performed with a Varian Aerograph 202-B chromatograph on a 150-cm column of OV-17 (4%) on Chromosorb G at 60 ml/min

of helium. Chloroprene (50% in xylene) was generously provided by the Du Pont Co. Analyses were performed by the Galbraith (Knoxville, Tenn.) or Schwarzkopf (Woodside, N. Y.) Laboratories. All reactions or transfers of phosphines were conducted in a nitrogen atmosphere in a glove bag.

1-Methyl-3-phospholanone 1-Oxide (1). A mixture of $\Delta^{2,3}$ (90%) and $\Delta^{3,4}$ (10%) 1-methyl-3-chlorophospholene oxides was obtained[2] by slow addition of the chloroprene–methylphosphonous dichloride adduct[21] to ice water. After 12 hr, the mixture was neutralized with K_2CO_3. The solution was extracted continuously with chloroform; from the extract was obtained a colorless oil which solidified on standing, mp 58–62°, bp 87–90° (0.1 mm).

A solution of 85.3 g (0.586 mol) of the above oxide in 100 ml of methanol was added to 400 ml of methanol treated previously with 13.5 g (0.586 mol) of sodium. The mixture was stirred at room temperature for 1 hr and then refluxed for 6 hr, during which time sodium chloride precipitated. After being cooled, the mixture was acidified with 6 *N* HCl and then stripped to dryness. Extraction of the residue with benzene provided crude 1-methyl-3-methoxy-2-phospholene oxide[2] (**3**). Distillation of a small sample gave bp 116–120° (0.15 mm), correcting a value [90° (0.15 mm)] previously reported.[2] The ir and nmr properties agreed with those already published.[2]

Anal. Calcd for $C_6H_{11}O_2P$: C, 49.31; H, 7.59; P, 21.20. Found: C, 49.17; H, 7.47; P, 21.38.

The crude **3** was placed in a solution of 100 ml of water and 1 ml of 6 *N* HCl. The solution was heated on a steam bath for 6 hr and then extracted with two 50-ml portions of methylene chloride. The aqueous layer was further extracted continuously with methylene chloride for 3 days. The combined extracts were dried ($MgSO_4$) and then concentrated on a rotary evaporator. The residue was taken up in a minimal amount of hot benzene and placed in the refrigerator. After a few days, the white solid that had precipitated (39% from the mixed chlorophospholene oxides) was removed by filtration. Recrystallization from benzene gave a solid: mp 89–91°; nmr (concentrated $CDCl_3$ solution) δ 2.12 (doublet, $^2J_{PH}$ = 13.2 Hz, PCH_3), 2.27 (doublet, $^2J_{PH}$ = 13.5 Hz, PCH_3), 2.51–3.63 (complex, $-CH_2-$), 5.41 (doublet, $^2J_{PCH}$ = 20.5 Hz, C=CH) (on dilution of the sample, the doublets at δ 2.12 and 5.41 due to **1b** disappeared): ir spectrum ($CHCl_3$, concentrated) 3450 (-OH), 1740 (C=O), 1590 cm^{-1} (C=C) (dilution of the sample significantly decreased the **1b** peaks at 3450 and 1590 cm^{-1}); ^{31}P nmr ($CHCl_3$, concentrated) δ −51.0 (**1a**) and −60.5 (**1b**).

Anal. Calcd for $C_5H_9O_2P$: C, 45.46; H, 6.87; P, 23.45. Found: C, 45.50; H, 7.03; P, 23.47.

The 2,4-dinitrophenylhydrazone, recrystallized from methanol, had mp 207–207.5°.

Anal. Calcd for $C_{11}H_{13}N_4O_5P$: C, 42.31; H, 4.20; N, 17.95; P, 9.92. Found: C, 42.51; H, 4.50; N, 18.05; P, 9.64.

A solution of 0.175 g (1.33 mmol) of **1** in 10 ml of water–methanol (1:1) was titrated with bromine. A total of 0.15 ml (0.44 g, 2.7 mmol) of bromine was decolorized at a titratable rate. The addition of one additional drop gave a deep bromine color which persisted for several minutes.

Deuteration of **1** was accomplished by allowing a solution of 1.0 g in 5 ml of D_2O to stand for 30 min and then removing the solvent by a rotary evaporator *in vacuo*. This procedure was repeated three times. The residual solid was recrystallized from benzene to give **2**. Integration of the ^1H nmr spectrum showed that 2 H had been eliminated from the 6 H complex methylene region of **1a**.

The ^{13}C nmr spectra of **1** and **2** are reported in the discussion.

1-Methyl-3-methoxy-2-phospholene 1-Oxide (3) from 1 and Diazomethane. A mixture of 5.0 g (0.038 mol) of phospholanone **1** in 300 ml of benzene containing 1 ml of boron trifluoride etherate was treated with excess diazomethane. After standing overnight, the solution was freed of a small amount of solid by decantation and then concentrated *in vacuo* to a small volume. On pouring into ether, there was precipitated 2.4 g of unreacted **1**. From this filtrate was recovered 0.7 g (13%) of enol ether **3**, identified by comparison of its nmr spectrum with that of a known sample.[2]

1-Methyl-3-methoxy-2-phospholene (11). A solution of 4.6 g (32 mmol) of 1-methyl-3-methoxy-2-phospholene oxide (**3**) in 200 ml of benzene was freed of traces of water by distilling off some of the benzene. While at 0°, the solution was treated with 3.24 g (32.1 mmol) of triethylamine and then over 30 min with 4.13 g (31.5 mmol) of trichlorosilane in 30 ml of benzene. The mixture was then refluxed for 2 hr. Hydrolysis with 10 *N* NaOH was performed slowly with ice-bath cooling, giving a clear solution. The benzene layer was removed, and the aqueous layer was extracted with 100 ml of benzene. After drying ($MgSO_4$), distillation was performed to give 1.82 g (45.2%): bp 63.5–65° (16 mm); nmr ($CDCl_3$) δ 1.45 (doublet, $^2J_{PH}$ = 3.0 Hz, PCH_3), 1.60–3.80 (complex signals), 4.01 (s, OCH_3), 5.04 (doublet, $^2J_{PH}$ = 38 Hz, C=CH); ^{31}P nmr ($CDCl_3$) +14.4; ir (neat) $\nu_{C=C}$ 1585 cm^{-1}. The compound was analyzed as the benzyl bromide salt, recrystallized from methanol–ethyl acetate, mp 181–182°.

Anal. Calcd for $C_{13}H_{18}BrOP$: C, 51.82; H, 6.03; P, 10.29. Found: C, 52.18; H, 6.10; P, 10.77.

Reaction of 1-Methyl-3-phospholanone 1-Oxide with Ethyl Chloroformate. A mixture of 30 ml of dimethylformamide, 1.0 g (7.6 mmol) of **1**, and 0.43 g (8.0 mmol) of sodium methoxide was stirred at room temperature for 10 hr, during which time a tan solid formed. The solid was removed by filtration, placed in a small flask, and treated directly with ethyl chloroformate (15 ml) in one portion. After overnight stirring, water (30 ml) was added to the mixture and stirring was continued for 1 hr. The acid solution was neutralized with sodium carbonate and then continuously extracted with chloroform overnight. The extract was dried ($MgSO_4$) and concentrated on a rotary evaporator to give a yellow oil. The product (**4**) had nmr (neat) δ 2.04 (doublet, $^2J_{PH}$ = 13 Hz, PCH_3), 6.50 (doublet of triplets, $^2J_{PH}$ = 18 Hz, $J_{allylic}$ = 1.5 Hz, =CH); ir (neat) 1770 cm^{-1} (C=O of enol ester). Attempts to purify the oil by distillation failed owing to decomposition.

1-Methyl-2,2-bis(3-oxobutyl)phospholan-3-one Oxide (5). A mixture of 1.0 g (7.58 mmol) of **1**, 30 ml of water, 5 ml of 95% ethanol, 0.86 g (12.3 mmol) of 2-butenone, and a drop of concentrated potassium hydroxide was stirred at room temperature for 4 hr and then refluxed for 4 hr. It was then cooled, acidified with dilute hydrochloric acid, and extracted with methylene chloride overnight. The methylene chloride extract was dried ($MgSO_4$) and then concentrated on a rotary evaporator to give a yellow oil. Addition of warm benzene to the residue precipitated 0.74 g (36%) of a white solid which was removed by filtration: nmr (D_2O) δ 1.85 (singlet, 2 H), 2.06 (doublet, $^2J_{PH}$ = 12.5 Hz, PCH_3, 3 H), 2.25–3.50 (complex, $-CH_2-$), 2.70 (singlet, CH_3CO, 6 H); ir (Nujol) 1725 (ring C=O), 1710 cm^{-1} (chain C=O). A sample recrystallized from methanol–ether had mp 210–211.5°. The sample failed to decolorize bromine.

Anal. Calcd for $C_{13}H_{21}O_4P$: C, 57.32; H, 7.79; P, 11.38. Found: C, 57.36; H, 7.86; P, 11.50.

Methyl(3-oxobutyl)phosphinic Acid (6). A solution of 4.0 g (30.3 mmol) of **1** in 50 ml of 2 *N* sodium hydroxide solution was refluxed overnight and then acidified with concentrated hydrochloric acid. The solution was evaporated to dryness on a rotary evaporator. Methanol (50 ml) was added to the solid residue and after 15 min of stirring a precipitate of NaCl was filtered off. The filtrate was evaporated to dryness on a rotary evaporator to give 3.82 g (84%) of **6**, a tan solid of indefinite melting point (with decomposition): nmr (D_2O) δ 1.74 (doublet, $^2J_{PH}$ = 13.5 Hz, PCH_3), 1.95–2.54 (complex, β CH_2–), 2.74 (singlet, $COCH_3$), 3.03–3.52 (complex, α CH_2–); ir (Nujol) 3230 and 2192 (OH), 1705 (C=O), ~1660 (OH, dimer), 1040 cm^{-1} (POH). The compound in water formed a bright orange precipitate of a 2,4-dinitrophenylhydrazone, which when recrystallized from ethanol had mp 204.5–206.5°.

Anal. Calcd for $C_{11}H_{15}N_4O_6P$: P, 9.38. Found: P, 9.32.

1-Methyl-2-bromo-3-phospholanone 1-Oxide (7). To 150 ml of chloroform was added 10.0 g (75.8 mmol) of **1** and 13.5 (75.8 mmol) of recrystallized *N*-bromosuccinimide. The mixture was stirred until homogeneous and then refluxed for 18 hr. A tan precipitate formed. The mixture was cooled and the solid (**7**) was removed by filtration. After washing with chloroform, there was obtained 6.07 g (38%): mp 153–154°; nmr (DMSO-d_6) δ 1.89 (doublet, $^2J_{PH}$ = 13.5 Hz, PCH_3), 2.10–3.32 (complex, $-CH_2-$), 3.70 (multiplet); ir (Nujol) 1637 cm^{-1} (C=C) with no $\nu_{C=O}$ signal

Anal. Calcd for $C_5H_8BrO_2P$: C, 28.46, H, 3.82; Br, 37.87; P, 14.66. Found: C, 28.23; H, 3.88; Br, 38.06; P, 14.69.

A sample of **7** (0.24 g, 1.14 mmol) dissolved in methanol–water (1:1) decolorized bromine at a titratable rate until 0.06 ml (0.18 g, 1.1 mmol) was added. The addition of one additional drop (0.01 ml) gave a deep bromine color which persisted for several minutes.

1-Methyl-3-piperidinophospholane (12) and Its Oxide (10). A solution of 2.0 g (17 mmol) of phospholanone oxide **1**, 3 ml of piperidine, and 100 ml of benzene was refluxed for 12 hr in a Dean-Stark apparatus to permit water removal. Solvent and excess piperidine were then removed and the residue of **10** was taken up in 200 ml of fresh benzene for reduction with trichlorosilane–triethylamine. The same procedure as for the preparation of **11** was fol-

lowed, except that the acidic solution from the hydrolysis was stirred for 20 hr before basification. This removed some (about 20%) enamine which accompanied the main product (**12**). Distillation gave 0.71 g (25.6%) of **12**: bp 71–71.5° (0.45 mm); nmr ($CDCl_3$) δ 1.55 (doublet, $^2J_{PH}$ = 3 Hz, PCH_3), 1.65–3.50 (complex absorption for ring protons); no absorption for olefinic protons was present, nor was $\nu_{C=O}$ observed in the ir spectrum; ^{31}P ($CDCl_3$) δ +39.2.

Anal. Calcd for $C_{10}H_{29}NP$: C, 64.82; H, 10.89; P, 16.73. Found: C, 64.92; H, 10.91; P, 16.65.

Formation and Reduction of Mixed Enamines from 1-Methyl-3-phospholanone 1-Oxide and Morpholine. A solution of 4.0 g (30.3 mmol) of **1** and 5 ml of morpholine in 200 ml of benzene was refluxed on a Dean-Stark apparatus overnight. Benzene was then distilled to leave about 20 ml of solution, and the remaining solvent was removed *in vacuo*. The residue was a yellow solid whose nmr spectrum (benzene) showed that **1** had been transformed to the enamine **8**: δ 1.27 (doublet, $^2J_{PH}$ = 13 Hz, PCH_3), 1.46–2.12 (complex multiplet, $-CH_2-$), 2.44 and 3.19 (unsymmetrical triplets, morpholine $-CH_2-$), 4.36 (doublet, J_{PCH} = 18.5 Hz,C=CH). The product also contained some of the $\Delta^{3,4}$ isomer (**9**), and was used directly in other studies.

Attempts to alkylate (methyl iodide or benzyl chloride) and acylate (benzoyl or acetyl chlorides, or ethyl chloroformate) were unsuccessful, resulting after hydrolysis in recovery of the original ketone **1**.

The enamine mixture from above was dissolved in 150 ml of benzene and reduced with trichlorosilane–triethylamine as in the preparation of **11**. Distillation of the product gave 3.58 g (64%) at 101–106° (1.05 mm), whose nmr spectrum (benzene) revealed that an isomer mixture was present. The major component (83.8%) was determined to be 1-methyl-3-morpholino-2-phospholene (**13**):[22] nmr δ 1.20 (doublet, $^2J_{PH}$ = 2.5 Hz, PCH_3), 4.71 (doublet, $^2J_{PH}$ = 40 Hz, C=CH); ^{31}P δ +18.1; ir (neat) $\nu_{C=C}$ 1565 cm^{-1}. The other component (16.2%) was the $\Delta^{3,4}$ isomer (**14**): nmr δ 1.18 (doublet, $^2J_{PH}$ = 3 Hz, PCH_3), 4.75 (doublet, $^3J_{PH}$ = 7.5 Hz, C=CH); ir $\nu_{C=C}$ 1630 cm^{-1}. Separation of the mixture was not performed.

1-Methyl-3-phospholanone (15). Using the previously described (for **11**) method, ketone **1** (4.0 g, 30 mmol) was reduced with 2 molar equiv of trichlorosilane–triethylamine to give 0.73 g (20.8%) of **15**: bp 73–74° (17 mm); nmr (benzene) δ 0.69 (doublet, $^2J_{PH}$ = 3.2 Hz, PCH_3), 0.99–2.48 (multiplet, ring CH_2); ^{31}P nmr (benzene) δ +45.7; ir (neat) $\nu_{C=O}$ 1720 cm^{-1}. The benzyl bromide salt, recrystallized from methanol–ethyl acetate, had mp 170.5–171.5°.

Anal. Calcd for $C_{12}H_{26}BrOP$: C, 50.17; H, 5.62; P, 10.79. Found: C, 49.93; H, 5.55; P, 10.77.

Reaction of 1-Methyl-3-phospholanone with Triethyl Phosphonoacetate. A slurry of 0.238 g (0.993 mmol) of sodium hydride in 50 ml of dimethoxyethane (DME) was treated with a solution of 2.22 g (0.993 mmol) of triethyl phosphonoacetate in 10 ml of DME over a period of 10 min. After 30 min of stirring, a solution of 1.15 g (0.993 mmol) of 1-methyl-3-phospholanone (**15**) in 10 ml of DME was added over a 30-min period. The mixture was stirred at room temperature for 20 hr. The liquid was then decanted from a viscous deposit on the walls of the flask into 150 ml of benzene. The mixture was extracted with three 70-ml portions of benzene. The extract was dried ($MgSO_4$) and distilled; product was collected at 78–131° (18 mm). Redistillation gave some **15** and a major fraction at 124–131° (18 mm). Gc revealed this fraction to be a mixture with the major component (62.8%) being the 2-phospholene derivative (**17**), as indicated from the nmr spectrum of the mixture (olefinic signal at δ 6.17, J_{PCH} = 41 Hz). Another component (28.8%) appeared to be the unrearranged product **16** from the nmr spectrum, which contained another olefinic signal (δ 6.16, broad s) in the proper ratio to **17**. The third component (8.4%) was not identified.

Registry No. **1**, 21229-61-8; **1** 2,4-dinitrophenylhydrazone, 49849-22-1; **2**, 49849-23-2; **3**, 21229-62-9; **4**, 49849-24-3; **5**, 49849-25-4; **6**, 49849-26-5; **6** 2,4-dinitrophenylhydrazone, 49849-27-6; **7**, 50599-76-3; **12**, 49849-32-3; **13**, 49849-33-4; **14**, 49849-34-5; **15**, 49849-35-6; **15** benzyl bromide salt, 50599-77-4; **17**, 49849-37-8; chloroprene–methylphosphonous dichloride, 49849-38-9.

References and Notes

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