Substituted 1-Oxyphosphole 1-Oxides

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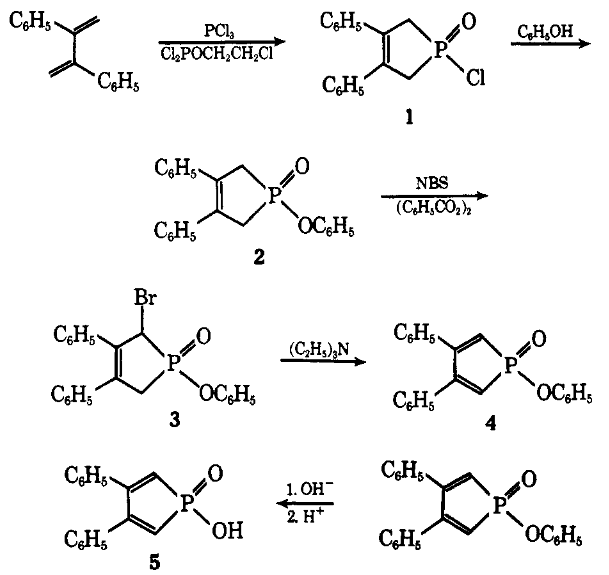
Abstract: 1-Phenoxy-3,4-diphenylphosphole 1-oxide and the corresponding phosphinic acid have been prepared as stable, crystalline compounds. Their properties and those of related oxyphosphole oxides have been surveyed and compared to those of thiophene dioxides and cyclopentadienones. The rate of saponification of 1-phenoxy-3,4-diphenylphosphole 1-oxide is comparable to those of related phospholenes and phospholanes.

Only two examples of 1-oxyphosphole 1-oxides have previously been reported. 1-Ethoxyphosphole 1-oxide has been prepared but rapidly dimerizes.[2] Although 1-ethoxy-3,4-dimethylphosphole 1-oxide[3] is more stable in solution, and dimerizes less rapidly, it has not yet been isolated. The present paper reports the preparation of the first pure 1-oxyphosphole 1-oxides; 1-phenoxy-3,4-diphenylphosphole 1-oxide and the corresponding phosphinic acid have been isolated as stable, crystalline compounds. Their properties are compared to those of other phospholes and of analogous five-membered cyclic compounds.

The general preparative plan is analogous to those previously employed,[2-4] and is illustrated in the equations of Scheme I.

Scheme I



Experimental Section

1-Phenoxy-3,4-diphenyl-3-phospholene 1-oxide (2) was prepared from the corresponding chloride that, in turn, was made according to the general method of Bliznyuk, *et al.*[5] Diphenylbutadiene[6] (0.15 mol, 30.9 g) and an equivalent amount of a 2-chloroethyl dichlorophosphinite–phosphorus trichloride mixture (prepared by dissolving 1 mol of ethylene oxide in 2 mol of phosphorus trichloride) were sealed in a Carius tube and held at 100° for 44 hr. The solid obtained on cooling the tube was triturated twice with 200 ml of hexane and then with 400 ml of hexane in a dry atmosphere, to yield about 36 g of a pale yellow solid melting in the range 135–140°. The crude material, presumably 1-chloro-3,4-diphenyl-3-phospholene 1-oxide (1), is not readily purified, but served for the preparation of esters.

A solution of phenol (0.050 mol, 4.71 g) and triethylamine (0.51 mol, 5.1 g) in 35 ml of benzene was added in an argon atmosphere to an ice-cold suspension of the phosphinic chloride (0.50 mol, 14.5 g) in 75 ml of benzene. The temperature was maintained below 10° during the addition; the resulting slurry was stirred for 2 hr at 0° and for an additional 4 hr at room temperature, and finally refluxed for 30 min. The reaction mixture was then cooled and filtered to remove triethylammonium chloride, and the filtrate was evaporated to dryness. The solid residue was crystallized from acetonitrile to yield 10.1 g (58%) of colorless needles, mp 138–140°. An analytical sample of 2, recrystallized once from methyl acetate and once from acetonitrile, melted at 140–141.5°. *Anal.* Calcd for $C_{22}H_{19}O_2P$: C, 76.29; H, 5.53; P, 8.94. Found: C, 75.98; H, 5.39; P, 8.90. The ^{31}P nmr spectrum shows a quintet at −60.8 ppm (relative to 85% phosphoric acid). The proton nmr spectrum shows a clean doublet at δ 3.20 (J_{H-P} = 12 Hz) and a multiplet centered at 7.2; the ratio of the intensities is 4:15.

1-Phenoxy-3,4-diphenylphosphole 1-Oxide (4). The phenylphospholene 2 (0.016 mol, 5.5 g) and freshly dried, recrystallized *N*-bromosuccinimide (0.016 mol, 2.85 g) were refluxed for 90 min with 10 mg of benzoyl peroxide under argon in 40 ml of dry carbon tetrachloride. The mixture initially darkened, but subsequently lightened to a lemon yellow. The cooled mixture was filtered to remove succinimide, and the solvent was removed by rotary evaporation. The residual oil (presumably 3) was taken up in 75 ml of dry ether, stirred with Norite (100 mg), and filtered through diatomaceous earth.

Triethylamine (2.0 g) was added to the pale yellow ethereal solution, and the mixture was allowed to stand at room temperature. After 18 hr, 2.1 g of amine salt was removed by filtration, and after another 24 hr, an additional 0.1 g of dark oily solid was removed. Evaporation of the supernatant then yielded a red mixture of solids. This material was transferred in minimum benzene to a 35-cm column containing 95 g of Florisil. Elution with 700 ml of benzene yielded traces of a yellow oil with an ir spectrum similar to that of starting material. Elution with 375 ml of 20% ether–80% benzene yielded the product 4, obtained (on evaporation of the solvent) as 1.6 g of long, colorless needles, mp 152–153°. One recrystallization from acetonitrile afforded an analytically pure sample of 4, mp 156.5–157°. *Anal.* Calcd for $C_{22}H_{17}O_2P$: C, 76.73; H, 4.98; P, 9.00. Found: C, 76.48; H, 5.27; P, 8.93.

The melting point of the phosphole 4 is not depressed by admixture with small amounts of the corresponding phospholene 2 (despite the lower melting point of the latter compound) nor can modest amounts of phospholene as impurity be detected by combustion analysis. The mass spectrum of the phosphole, however, showed that it was contaminated with less than 1% of the phospholene.

The 60-MHz nmr spectrum of 4 is shown in Figure 1. The relative intensity of the aromatic to vinyl protons is 15:2. The 40-MHz ^{31}P nmr spectrum shows a sharp triplet centered at −46.6 ppm (relative to 85% phosphoric acid) with J_{H-P} = 25 Hz.

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[1] National Science Foundation Predoctoral Fellow, 1966–1969.

[2] D. A. Usher and F. H. Westheimer, *J. Amer. Chem. Soc.*, **86**, 4732 (1964).

[3] R. Kluger, F. Kerst, D. G. Lee, and F. H. Westheimer, *ibid.*, **89**, 3919 (1967).

[4] R. Kluger and F. H. Westheimer, *ibid.*, **91**, 4143 (1969).

[5] N. Bliznyuk, Z. Kvasha, and A. Kolomiets, *J. Gen. Chem., USSR*, 37, 1726 (1967).

[6] K. Alder and J. Haydn, *Justus Liebigs Ann. Chem.*, **570**, 212 (1950).

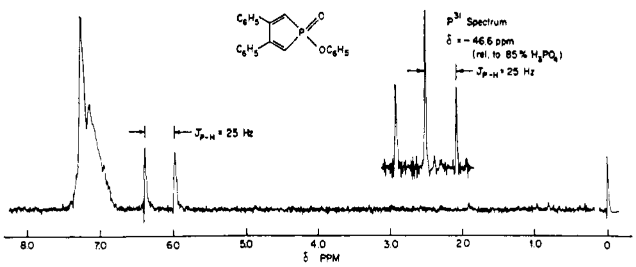

Figure 1. Nuclear magnetic resonance spectra of 1-phenoxy-3,4-diphenylphosphole 1-oxide. The abscissa shows chemical shifts for a 60-MHz spectrum in $CDCl_3$ against TMS as an internal standard. The insert triplet shows the 40.5-MHz ^{31}P nmr spectrum (in the same solvent); the chemical shift is −46.6 ppm relative to an external standard of 85% phosphoric acid.

1-Hydroxy-3,4-diphenylphosphole 1-Oxide (5). The phenoxyphosphole 1-oxide (4) (450 mg, 0.0013 mol) was dissolved in 7 ml of acetone and 4 ml of 1 *M* sodium hydroxide solution. The solution was allowed to stand at room temperature for 5 min and then evaporated at 25° until the first crystals appeared. Cooling the solution in an ice bath afforded colorless plates (presumably the sodium salt of the phosphole dioxide **5**) which were recovered by filtration, washed with 25 ml of acetone, and then dissolved in a minimum amount of water. Addition of 3 ml of 1 *M* hydrochloric acid to the solution precipitated the free acid as a white solid, which was obtained, after filtration and drying, as a microcrystalline powder, mp 181–182°. Its nmr spectrum corresponds to that anticipated: a doublet, δ 6.15 (J_{H-P} = 23 Hz) and a broad peak at 7.08 in the intensity ratio of 2:10.

Attempts to recrystallize the compound from ethylene chloride led to chemical reaction (as shown by nmr spectroscopy); presumably one molecule of acid added to a β position of a second molecule. The precipitated and dried acid was therefore submitted directly for analysis and found to be the monohydrate. *Anal.* Calcd for $C_{16}H_{13}O_2P \cdot H_2O$: C, 67.13; H, 5.28; P, 10.52. Found: C, 66.84; H, 5.35; P, 10.73.

1-Phenoxy-3,4-dibromo-3,4-dimethylphospholane 1-Oxide (6). 1-Chloro-3,4-dimethyl-3-phospholene 1-oxide was prepared from dimethylbutadiene by the method of Bliznyuk, *et al.*[5] The material, obtained in 73% yield, boiled at 87–90° (0.3 mm).[7] A solution of phenol (0.0315 mol, 2.96 g) and triethylamine (0.0315 mol, 3.18 g) in 25 ml of benzene was added over 25 min to an ice-cooled, stirred solution of the chlorophosphinate (0.0315 mol, 5.18 g) in 25 ml of benzene. After the addition was complete, the slurry was stirred for 1.5 hr at room temperature. After salt and solvent had been removed, the oil was distilled at 135–136° (0.35 mm), and then melted at 39–41°. Arbuzov and Shapinskaya[8] previously prepared 1-phenoxy-2,3-dimethyl-3-phospholene from dimethylbutadiene and phenyl phosphorodichloridite, but reported it as an oil, bp 146° (2.5 mm). *Anal.* Calcd for $C_{12}H_{15}O_2P$: C, 64.85; H, 6.80; P, 13.94. Found: C, 64.47; H, 7.12; P, 13.94.

A solution of bromine (0.041 mol, 6.6 g) in 20 ml of methylene chloride was added drop by drop to an ice-cooled solution of the phospholene (0.041 mol, 9.1 g) in 50 ml of the same solvent. The reaction mixture was allowed to stand at room temperature under argon for 12 hr, and then subjected to evaporation. The residue, dissolved in a minimum quantity of ether–methyl acetate (1:1) was filtered under argon pressure through a 3.0-cm column containing 250 g of Woelm neutral alumina packed in the same solvent. The first 125 ml of effluent was evaporated to yield 9.3 g (59%) of the dibromide as colorless prisms, mp 82–84°. An analytical sample was prepared by recrystallization from ether–ligroin, mp 84–86°. *Anal.* Calcd for $C_{12}H_{15}Br_2O_2P$: C, 37.72; H, 3.96; Br, 41.84; P, 8.11. Found: C, 38.01; H, 4.03; Br, 41.67; P, 8.31.

1-Phenoxy-3,4-dimethylphosphole 1-Oxide (7). Solutions of the phosphole **7** were prepared by incubating the dibromide **6** (0.019 *M*) with a 50% excess (0.50 *M*) of 1,5-diazobicyclo[4.3.0]non-5-ene (DBN) at 25° for 1 hr. The resulting acetonitrile solutions were used directly in kinetic experiments.

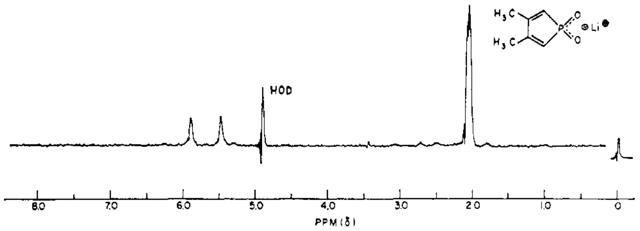

Figure 2. 60-MHz nuclear magnetic resonance spectrum of the lithium salt of 1,1-dioxy-3,4-dimethylphosphole in D_2O, with TMS as an external standard.

1,1-Dioxy-3,4-dimethylphosphole, Lithium Salt (8). A solution of 0.016 mol of the dibromide **7** and 0.048 mol of DBN in 20 ml of acetonitrile was incubated for 5 min at room temperature, and then added to 100 ml of water containing 0.07 mol (1.7 g) of lithium hydroxide. The mixture was stirred for 10 min at 25°, and then washed with 50 ml of methylene chloride. The aqueous solution was concentrated to 60 ml and washed with two more portions of methylene chloride. A 30-ml portion was neutralized with 2 *N* hydrochloric acid, extracted again with methylene chloride, and evaporated to dryness. The residue was suspended in 100 ml of methanol and filtered to remove lithium sulfate. The filtrate was evaporated to dryness, and the resulting solid was suspended in 100 ml of isopropyl alcohol, filtered to remove lithium chloride, and resuspended in 75 ml of ethanol, and the filtration was repeated. This procedure yielded 1.2 g of a finely divided colorless solid. *Anal.* Calcd for $C_6H_8LiO_2P$: C, 48.03; H, 5.37; Li, 4.63; P, 20.64. Found: C, 47.61; H, 5.45; Li, 4.68; P, 20.40. The nmr spectrum of the salt in D_2O (Figure 2) showed (in addition to a peak for adventitious water) a broadened doublet at δ 5.65 (J_{H-P} = 24 Hz) and a multiplet at 2.01 in an intensity ratio of 2:6. Irradiation of the doublet reduced the upfield signal to a doublet with J_{H-P} = 2 Hz. Irradiation of the upfield multiplet converted the signals from the vinyl protons to a sharp doublet; the original signal then is presumably a doublet of quartets with J_{H-H} around 1 Hz. The ^{31}P nmr spectrum of the salt showed a chemical shift of −45.0 ppm relative to 85% phosphoric acid.

1-Ethoxy-3,4-dimethyl-3-phospholene 1-Oxide. The compound, prepared by the method of Korte, *et al.*[7] (who reported it as an oil), crystallized from pentane as long, hygroscopic needles, mp 41.8–43.5°. *Anal.* Calcd for $C_8H_{15}O_2P$: C, 55.16; H, 8.68; P, 17.78. Found: C, 55.19; H, 8.41; P, 18.11.

1-Methoxy-3,4-dimethyl-3-phospholene 1-oxide (9) was similarly prepared, and boiled at 74–79° (0.3 mm) (lit.[7] 76–90° (0.9 mm)); mp about 10°. *Anal.* Calcd for $C_7H_{13}O_2P$: C, 52.49; H, 8.17; P, 19.34. Found: C, 52.75; H, 8.21; P, 20.00. The ir and nmr showed no trace of the 2 isomer, and no isomerization could be detected by nmr after the product had been refluxed for 24 hr in 5% methanolic hydrochloric acid.

1-Methoxy-3,4-dibromo-3,4-dimethylphospholene 1-Oxide (10). A 1 *M* solution of bromine (63 ml) in carbon tetrachloride was added drop by drop at room temperature under argon to a solution of 0.0625 mol (10.0 g) of the phospholene in 75 ml of carbon tetrachloride. A small amount (1.0 g) of yellow oil separated, and crystallized when the mixture was allowed to stand overnight; it was removed by filtration, and identified by mixture melting point with an authentic sample as 1-hydroxy-3,4-dibromo-3,4-dimethylphospholane 1-oxide.[7] The clear supernatant was evaporated and the residue crystallized from methylcyclohexane–benzene to give the dibromide as 12.8 g (62%) of colorless needles that are sensitive to air and moisture. An analytical sample was prepared by digesting the material in dry ether and filtering and evaporating the filtrate. *Anal.* Calcd for $C_7H_{13}Br_2O_2P$: C, 26.48; H, 4.10; Br, 49.95; P, 9.68. Found: C, 26.26; H, 4.10; Br, 49.94; P, 9.96.

Solutions of 1-Alkoxy-3,4-dimethylphosphole 1-Oxide (11). When dilute (*e.g.*, 0.002 *M*) alcoholic solutions of one of the dibromides (*e.g.*, **10**) are dehydrohalogenated with an excess of base (alkoxide or DBN) the OD at 296 nm rises to a maximum and then undergoes decay, first order in phosphole, with *k* about 2×10^{-3} min^{-1}. The extinction coefficient of **11** (710) can be obtained by extrapolation to zero time.

A relatively pure solution of **11** in ether can be prepared by passing a 1 *M* solution of a dibromide in ether through a 6-in. column of dry powdered sodium hydroxide suspended in ether.

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[7] U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

[8] B. A. Arbuzov and L. A. Shapinskaya, *Chem. Abstr.*, **57**, 1379 (1962).

(The powdered base was made by grinding dry reagent grade pellets in a Waring blender.) Neither the methyl nor the ethyl ester has been isolated, but the nmr spectrum of a solution of the ethyl ester in carbon tetrachloride is shown in Figure 3.

1,8-Phospha(oxomethoxy)-3,3a,5,6-tetramethyl-4,7,7a-trihydromethanoindene. Methoxydibromide **10** (0.0100 mol, 3.20 g) and triethylamine (0.0400 mol, 4.04 g) were refluxed in 75 ml of dry tetrahydrofuran for 30 hr. Filtration of the cooled mixture removed 3.4 g of the amine salt. Rotary evaporation then yielded 1.7 g of a tarry brown residue, which was taken up in carbon tetrachloride, filtered, and diluted with petroleum ether. The product (0.7 g, 39%, mp 146–148°) crystallized overnight at −20°. An analytical sample, twice recrystallized from ethyl acetate, melted at 147–148°. *Anal.* Calcd for $C_{14}H_{22}O_4P_2$: C, 53.15; H, 7.01; P, 19.58. Found: C, 52.80; H, 6.92; P, 19.50. Exact mass: calcd 316.0992; found 316.0996. The nmr spectrum is consistent with that expected for a Diels–Alder dimer, but the stereochemistry of the ring junction has not yet been determined.

Other chemicals were generally reagent or spectroscopic grade. Dioxane, used as part of the mixed solvent for some of the kinetics, was purified by distillation from sodium in an argon atmosphere.

Other Diels–Alder Reactions. 1-Ethoxy-3,4-diphenylphosphole 1-oxide (0.05 g) was allowed to react in 0.5 ml of carbon tetrachloride with 0.1 g of dimethyl acetylenedicarboxylate over a period of 48 hr at room temperature. The reaction, followed by nmr, showed the shrinkage of the signal from the vinyl protons at δ 6.0 ppm, and the growth of a singlet at 7.6 ppm (corresponding to two aromatic protons of the central ring of the product, dimethyl 4,5-diphenylphthalate). The isolated ester melted at 120°.

An authentic sample of this ester was prepared by refluxing 1.03 g (0.005 mol) of 2,3-diphenylbutadiene with 0.71 g (0.005 mol) of dimethyl acetylenedicarboxylate in 5 ml of benzene for 12 hr. The resulting product was aromatized by refluxing for 1 hr a 0.759-g portion with 0.380 g of NBS in 10 ml of carbon tetrachloride containing 10 mg of benzoyl peroxide. The product was purified by recrystallization from methanol, followed by filtration of a benzene solution of it through 3 g of Woelm neutral alumina. A mixture of this material and that obtained from the phosphole melted without depression at 121°. The dimethyl ester of 4,5-diphenylphthalic acid has previously been prepared by Alder and Haydn[6] from the same Diels–Alder intermediate as above, using sulfur as dehydrogenating agent, and is reported to melt at 122°.

The reaction of 1-ethoxy-3,4-dimethylphosphole 1-oxide with maleic anhydride has been reported previously.[3] The bicyclic phosphinic acid (presumably obtained by hydrolysis of the original Diels–Alder adduct with fortuitous moisture) is best prepared in ether as solvent.

Kinetics of Saponification. The saponification of the phenyl esters was monitored by observing the appearance of the absorption band for phenoxide ion at 285 nm with a Cary 15 spectrophotometer. A concentrated stock solution of a compound (*e.g.*, **4**) was made up in acetonitrile or dioxane, and 2–20 μl were injected into 2.0 ml (water or 40% dioxane) of alkaline solution in a quartz cuvette thermostatted at 30°.

The kinetics for the saponification of methyl and ethyl esters was more difficult and less precise. The reactions were followed by scanning the spectra from 360 to 250 nm. The λ_{max} for the ester at 298 nm gradually shifted to that at 292 nm for the salt, with a concomitant rise of about 20% in OD_{max}. Although these changes are small, they permit determination of the rate constant.

Other Methods. Proton magnetic resonance spectra were obtained either with a Varian A-60, T-60, or Varian HR-100 nmr spectrometer. Decoupling was performed with a T-6059 decoupler attached to the T-60 spectrometer. Phosphorus spectra were obtained on the HR-100 spectrometer, equipped with phosphorus probe at 40.5 MHz.

Mass spectra were obtained using an MS-9 high resolution mass spectrometer.

Results

The ^{31}P nmr absorption for 1-phenoxy-3,4-diphenylphosphole 1-oxide is compared with those of related compounds in Table I. Ultraviolet spectra, obtained with a Cary 15 recording spectrophotometer, are reported in Table II.

The rate constants for the saponification of the esters of the 1-oxyphosphole 1-oxides, and of related compounds, are listed in Table III.

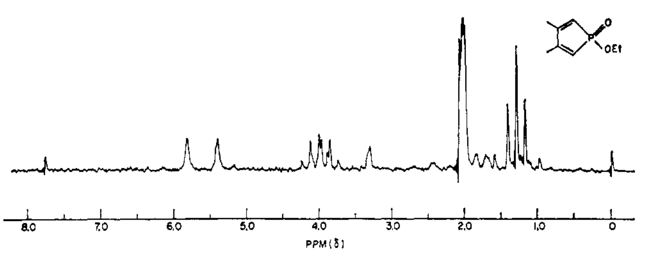
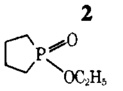
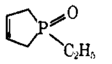
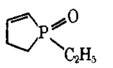
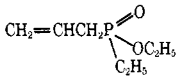
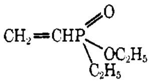


Figure 3. 60-MHz nuclear magnetic resonance spectrum of 1-ethoxy-3,4-dimethylphosphole 1-oxide in carbon tetrachloride, with TMS as internal standard. The material was prepared from the corresponding dibromide **10** by passing the latter through a column of powdered NaOH in ether. The small peaks at 0.95, 1.5–1.8, 2.4, 3.3, and 7.7 ppm are due to uncharacterized impurities.

Table I. ^{31}P Nmr Chemical Shifts

Compd	Chem shift rel to 85% phosphoric acid
4	−46.6
2	−60.8[a]
	−76.7[a]
	−71.3[a]
	−72.5[a]
$(C_2H_5)_2P(=O)OC_2H_5$	−56.4[a]
 $CH_2{=}CHCH_2P(=O)(OC_2H_5)C_2H_5$	−51.7[a]
 $CH_2{=}CHP(=O)(OC_2H_5)C_2H_5$	−40.6[a,b]

[a] E. A. Dennis, Ph.D. Thesis, Harvard University, 1967; *Diss. Abstr. B*, **29**, 1301 (1968). [b] In carbon tetrachloride solution.

Table II. Longest Wavelength Absorption of 1,1-Dioxyphospholes and of Related Compounds

Compd	λ_{max}, nm	ϵ	Solvent
1-Phenoxy-3,4-diphenylphosphole 1-oxide	293	5600	CH_3CN
1-Ethoxy-3,4-dimethylphosphole 1-oxide	298	720	C_2H_5OH
1-Ethoxyphosphole 1-oxide	293	1050	C_2H_5OH
trans-2-Styrenephosphonic acid[a]	293	1300	CH_3OH
2,4-Di-*tert*-butylcyclopentadienone[b]	395	230	C_2H_5OH
Styrene[c]	291	570	C_6H_{12}

[a] Sample of G. L. Kenyon: G. L. Kenyon and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3557 (1966). [b] E. W. Garbisch, Jr., and R. F. Sprecher, *ibid.*, **91**, 6785 (1969). [c] "UV Atlas of Organic Compounds," Vol. II, Plenum Press, New York, N. Y., 1966.

Discussion

Phospholes can be formulated as aromatic systems, where the unshared electron pair on phosphorus contributes to six π electrons in the ring. On the basis of

Table III. Rate Constants for the Saponification of Esters of 1,1-Dioxyphospholes and Analogs at 30°

Ester	Solvent	Rate constant, M^{-1} sec^{-1}
Phenoxy-3,4-diphenylphosphole 1-oxide	40% dioxane	4.0
Phenoxy-3,4-diphenyl-3-phospholene 1-oxide	40% dioxane	0.96
Phenoxy-3,4-dimethylphosphole 1-oxide	Water plus 1% acetonitrile	2.7
Methoxy-3,4-dimethylphosphole 1-oxide	50% methanol	0.008
Ethoxy-3-phospholene 1-oxide[a]	D_2O (25°)	0.012
Ethoxyphospholane 1-oxide[a]	D_2O (25°)	0.0002

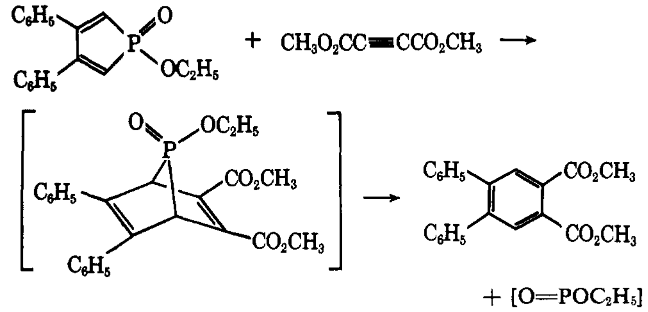
[a] E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3431 (1966).

nmr and other evidence,[9-11] phospholes are considered to have aromatic character. By contrast, no appropriate aromatic structure can be written for phosphole oxides. Structures that place a negative charge on the phosphoryl oxygen atom leave only four π electrons in the ring, and might be considered antiaromatic.[12] Experimentally, the chemical and spectroscopic properties of the alkoxy- and phenoxyphosphole 1-oxides reported here show relatively little interaction between the phosphorus atom and the ring.

Diels-Alder Reactions. 1-Ethoxyphosphole 1-oxide dimerizes with a rate constant of 0.55 M^{-1} sec^{-1} at 25°; it is considerably more reactive toward itself than thiophene dioxide,[13] but more stable than cyclopentadienone.[13-15] Like both of these compounds, 1-ethoxyphosphole 1-oxide acts as a dienophile with cyclopentadiene,[2] but it does not react as a diene with maleic anhydride.

1-Ethoxy-3,4-dimethylphosphole 1-oxide, as anticipated, is much more stable toward dimerization than its parent,[3] and the corresponding esters of 1-hydroxy-3,4-diphenylphosphole 1-oxide are even more stable. The predictions of greater stability toward dimerization and enhanced activity as a diene are made both on theoretical grounds and by analogy. Its behavior should parallel that of 2,3-dimethylbutadiene which is a much better diene than butadiene itself, presumably[16] because the electron-donating properties of the methyl groups stabilize a partial positive charge on the diene in the transition state. Simultaneously, each methyl group sterically hinders the adjacent double bond, and so makes the molecule less efficient as a dienophile. The stabilities of the less reactive substituted thiophene dioxides and the more reactive cyclopentadienones follow similar patterns.[17,18]

1-Alkoxy-3,4-dimethylphosphole 1-oxide reacts with maleic anhydride to give a Diels-Alder adduct, although as previously noted, the adduct has not been isolated directly, but only obtained as the corresponding acid, which readily crystallizes. Adducts of 1-ethoxy-3,4-dimethylphosphole 1-oxide have not been isolated so far with dienophiles other than maleic anhydride. 1-Alkoxy-3,4-diphenylphosphole 1-oxide does not readily react with most dienophiles, but it does react with dimethyl acetylenedicarboxylate, with loss of the elements of monomeric metaphosphite,[19] to yield dimethyl 4,5-diphenylphthalate, in accordance with the following equations.



The 1-alkoxy- or aryloxyphosphole 1-oxides are considerably more reactive toward dimerization than the corresponding 1-alkyl- or 1-arylphospholes.[9,11,20] Moreover, the pronounced reactivity toward dimerization of 1-phenylphosphole oxide,[21] as contrasted to that for 1-phenylphosphole, suggests both that the phosphoryl oxygen atom destroys the aromatic stabilization of the phosphole ring and that it facilitates transfer of charge during the Diels-Alder reaction.

Spectra. The uv spectra of the esters of phosphole 1-oxides may give evidence for some interaction with or through a phosphorus atom. The relatively low extinction coefficients for the 1-ethoxyphosphole 1-oxide and 1-ethoxy-3,4-dimethylphosphole 1-oxide (see Table II) do not suggest a highly conjugated system, but the absorption is at a considerably longer wavelength than that of cyclopentadiene[22] (ϵ 2500 at 237 nm). By contrast, the uv absorption for 1-phenoxy-3,4-diphenylphosphole 1-oxide exhibits no bathochromic shift compared to that of *trans*-2-styrenephosphonic acid,[23] which in turn strongly resembles the uv spectrum of styrene.

Similar conclusions can be drawn from the nmr spectra. The chemical shifts of the vinyl protons in the substituted phenoxyphosphole 1-oxide and related compounds (Figures 1-3) suggest normal unsaturation as observed in other vinylphosphinates;[23] the strong deshielding that would be expected from a ring current is not observed. In particular, the signal from the vinyl protons of 1-ethoxy-3,4-dimethylphosphole 1-oxide shows the same chemical shift (δ 5.7) as does the vinyl proton of 1-ethoxy-3,4-dimethyl-2-phospholene 1-oxide.

The ^{31}P shift for 1-phenoxy-3,4-diphenylphosphole 1-oxide (see Table I) is a little less negative than those of related compounds, but the differences are not very

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large compared to the spread of values that has been observed for phosphorus compounds.[24]

Rates of Saponification. Finally, the rates of saponification (Table III) of phenoxy- and alkyloxy-substituted phosphole 1-oxides are about the same as those for the corresponding 3-phospholenes. In particular, the rate of saponification for phenoxy-3,4-diphenylphosphole 1-oxide is only four times that for phenoxy-3,4-diphenyl-3-phospholene 1-oxide, while the rate of saponification of methoxy-3,4-dimethylphosphole 1-oxide is actually less (although in a somewhat different solvent) than that of ethoxy-3-phospholene 1-oxide. The rates should also be compared to those of the corresponding 2-phospholenes, but unfortunately the esters related to the needed 2-phospholene 1-oxides have not yet been obtained. However, 1-ethoxy-3-phospholene 1-oxide saponifies 30–40 times faster than does 1-ethoxy-2-phospholene 1-oxide,[25,26] and one may tentatively assume a comparable rate ratio in analogous series. If this assumption is valid, then the phosphole esters saponify substantially faster than do those of the 2-phospholenes.

The cause of the various rate differences is not understood. First and foremost, the greater rate of hydrolysis of the esters of the 3-phospholene series, relative to those in the 2-phospholene series, has not been satisfactorily explained. Conjugation of a double bond with an ester group does not generally cause a large decrease in rate of saponification; ethyl hydrocinnamate saponifies only about three times as fast as does ethyl cinnamate.[27] Since conjugation with phosphorus (a second-row element) is unlikely to provide more stabilization than that with carbon (a first-row element), the relatively low rate of saponification of an ester in the 2-phospholene series is unlikely to be caused by resonance stabilization. (If such had been the case, the loss of such stabilization in the phosphole could then have been assigned to antiaromaticity.)

An alternative explanation for the greater rate of hydrolysis for an ester in the phosphole series relative to one in the 2-phospholene series is that the phosphole is presumably more highly strained, and strain usually causes an increase in the rate of hydrolysis.[28] This explanation, however, fails because of the comparison of esters of phospholes with those in the 3-phospholene series.

In any event, the rates of saponification of phenoxy-3,4-diphenylphosphole 1-oxide and of ethyl-3,4-dimethylphosphole 1-oxide are somewhat faster, rather than much slower than those of analogous phospholene esters; this fact again shows that, in these phosphole derivatives, the phosphoryl group does not interact strongly with the ring.

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