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Experiments on the Generation of 2-Coordinate Phosphoryl Species by Fragmentation of 7-Phosphanorbornene and 3-Phospholene Derivatives

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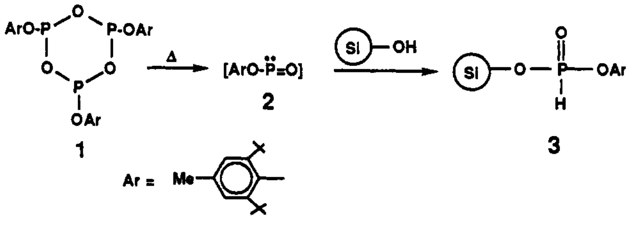
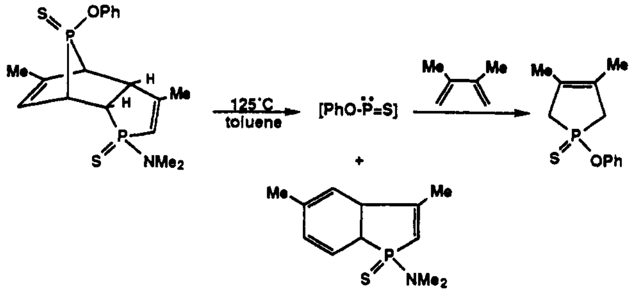
2,6-Di-*tert*-butyl-4-methylphenyl phosphenite (ArOP=O) was released into the gas phase on heating a neat sample of a 7-phosphanorbornene derivative **6** bearing this aryloxy substituent at 300 °C (0.01 mm). Attempts to prepare 1-adamantyl phosphenite similarly were not successful. Irradiation of **6** in 1,2-dichloroethane at 254 nm failed to cause release of the phosphenite, but when some alcohol was present fragmentation proceeded readily to give the H-phosphonate (ArOPH(O)OR). It was deduced that the species undergoing the fragmentation was a 5-coordinate adduct of **6** and the alcohol. Similar behavior was observed for the other esters and also for a *P*-phenyl oxide and a *P*-phenyl sulfide in the 7-phosphanorbornene series, as well as for a 3-phospholene oxide. Isotope exchange experiments with $^{18}OH_2$ proved the influence of the irradiation on the formation and fragmentation of the 5-coordinate adduct. Earlier literature reports that 2-coordinate species are released on irradiation of 7-phosphanorbornene and 3-phospholene derivatives therefore need reinterpretation.

Esters of phosphenous acid (HOP=O) have been frequently mentioned in the literature as transient reaction intermediates,[1] but only recently has such a compound been directly observed by spectral techniques.[2] The compound 2,6-di-*tert*-butyl-4-methylphenyl phosphenite (**2**) had been proposed[3,4] to result from the thermal cracking of an easily obtained cyclic trimer **1**. It was confirmed in this laboratory[5] that the monomer was present in the gas phase by reacting it with the OH groups on the surface of silica gel exposed directly to the gas in the cracking apparatus (an evacuated, heated Kugelrohr tube). The reaction produces an H-phosphonate group **3** on the surface, readily recognized by CP/MAS ^{31}P NMR (δ −4).



Also, deposition of the monomer **2** at 12 K on spectral plates allowed the recording of the IR ($\nu_{P=O}$ 1235 cm^{-1}) and UV (λ_{max} 271 and 278 nm) spectra; extraction of the condensate from a liquid nitrogen trap gave a sample whose ^{31}P NMR spectrum contained a small transient signal at δ 238, assigned to **2**, along with much dimer and trimer. While useful for generating phosphenite **2**, this cracking technique is of limited scope for the generation of other phosphenites, however, since very few of the stable trimeric forms are known[1] or likely to be synthesized as easily from phosphorodichloridites as is the sterically hindered **1**. A more versatile approach would employ the fragmentation of derivatives of the 7-phosphanorbornene (7-PNB) ring system; many such compounds are known,[6] and indeed the literature already contains examples of their fragmentation under conditions where the presumed released fragment is trapped immediately (usually by reaction with an alcohol or a diene).[1] An example is the generation and trapping of an aryl thiophosphenite:[7]



There has been no prior attempt to perform the fragmentation under conditions where the monomer can be preserved or observed spectrally. We now report on such experiments, which initially involved the thermal generation of the same phosphenite (**2**) as was characterized spectrally from the cracking of trimer **1**, and then were expanded to attempt the fragmentation under photochemical conditions. The latter approach would offer a significant feature; the irradiation can be performed at low temperatures, as we have recently done in the case of the generation of metaphosphoramides (R_2NPO_2, stabilized as a THF complex at −75 °C[8]), thus allowing

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[†] On leave from Technical University of Lodz, Poland.

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[•] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Quin, L. D.; Szewczyk, J. Oxo-, Thioxo- and Selenoxophosphines. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; Part D, Chapt. D-11.

(2) The positive ions derived from PhOP=O (Duddeck, H. *Phosphorus Sulfur* **1986**, *28*, 307) and compound **2**[4] have been detected in very small amounts in mass spectra.

(3) Chasar, D. W.; Fackler, J. P.; Mazany, A. M.; Komoroski, R. A.; Kroenke, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5956.

(4) Chasar, D. W.; Fackler, J. P., Jr.; Komoroski, R. A.; Kroenke, W. J.; Mazany, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 5690.

(5) Quin, L. D.; Jankowski, S.; Sommese, A. G.; Lahti, P. M.; Chesnut, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 11009.

(6) Quin, L. D. *Rev. Heteroat. Chem.* **1990**, *3*, 39.

(7) Quin, L. D.; Szewczyk, J. *J. Chem. Soc., Chem. Commun.* **1986**, 844.

(8) Quin, L. D.; Bourdieu, C.; Quin, G. S. *Tetrahedron Lett.* **1990**, *31*, 6473.

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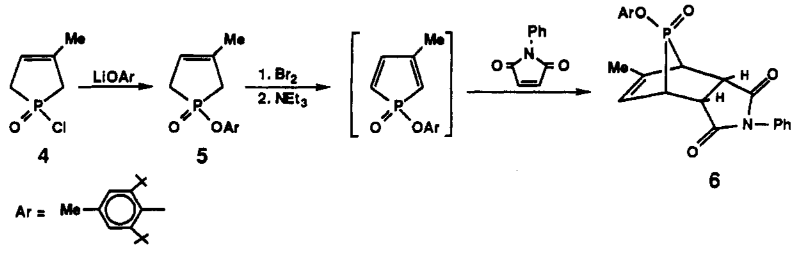
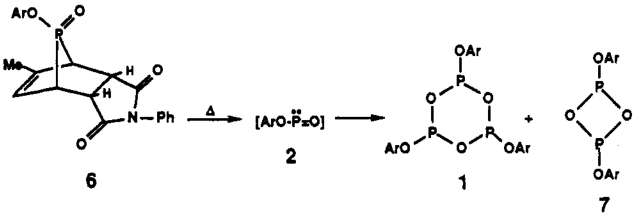
Scheme I



Scheme II

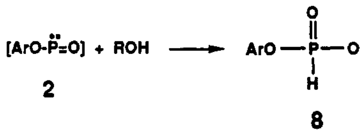


a better opportunity for the phosphenites to have a lifetime adequate for direct detection techniques. In these experiments we again employed a precursor of phosphenite **2**, since it can be expected, as in many other cases of low-coordination species,[9] that the sterically demanding substituent might add a significant degree of kinetic stabilization. When it was observed that no fragmentation occurred under these conditions, other compounds were examined. As will be seen, no photolysis was ever achieved in the absence of an alcohol trapping agent, and a reinterpretation of the observations in the literature became necessary.

Thermal Fragmentation of 7-PNB Derivatives. The synthesis of compound **6** was accomplished by adaptation of methods used in previous work[10] (Scheme I). The use of the very large aryl substituent caused no difficulty except in the displacement of chloride from **4**. Normally this is accomplished by reaction with the hydroxy compound in the presence of triethylamine, but for the synthesis of **5** it was necessary to preform the phenoxide ion using lithium hydride.

A neat sample of compound **6** was thermolyzed at 300 °C in a glass bulb attached to a vacuum line (0.01 mm); gaseous products were condensed in a liquid nitrogen trap. The contents of the trap were dissolved in 1,2-dichloroethane, and subjected to analysis by ^{31}P NMR. There was only a small signal for unreacted **6**; the major absorption consisted of a doublet at δ 120.0 (J = 10 Hz) and a triplet at δ 128.5 (J = 10 Hz). These signals match those originally reported by Chasar et al.[3] for the cyclic trimer **1**; the former arises from two P nuclei having *cis*-substituents and the latter from P with a *trans*-substituent. We have also observed the same spectrum in previous work.[5] In addition, there was a signal for the dimer **7** of the phosphenite at δ 177.0, also as reported.[4,5] The spectrum was basically the same as that obtained for the condensate from the thermolysis of the trimer **1**.

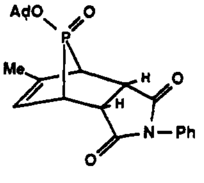
These results were consistent, then, with the release of the monomeric phosphenite **2** from **6** into the gas phase; formation of the dimer and trimer could occur after condensation in the cold trap, since in our earlier study[5] of the thermal cracking of trimer **1** it was shown that the gas when allowed to impinge on a plate at the much lower temperature of 12 K consisted primarily of the monomer. This study had also revealed that the deposited monomer condensed to dimer or trimer as the temperature was raised, but that a very small amount of monomer (about 3–5% of total ^{31}P NMR signal area) with ^{31}P NMR δ 238 remained detectable for a brief period at room temperature. This signal was also present in the condensate from the thermolysis of **6** and similarly disappeared on standing. The signal was quenched on addition of ethanol; the solution had a new signal consistent with formation of an H-phosphonate (**8**, R = Et; δ 5.6, $^1J_{PH}$ = 720 Hz).



$$[\mathrm{ArO{-}\ddot{P}{=}O}] + \mathrm{ROH} \longrightarrow \mathrm{ArO{-}P(=O)(H){-}OR}$$

2 8

We have therefore established that the thermal fragmentation of the 7-PNB derivative **6** does indeed release the phosphenite **2**. Initial experiments aimed at extending the method to the generation of other phosphenites have so far not been successful, however. Thus, the condensate from the attempted fragmentation of the 1-adamantyl ester **9** at 330 °C (100 mm) contained no ^{31}P NMR signals that would correspond to the phosphenite monomer, dimer or trimer. At lower pressure, much of the phosphinate simply sublimed.



9, Ad = 1-adamantyl

Photochemical Studies on Esters in the 7-PNB Family. Irradiation (254 nm) for 3 h of a solution of 7-PNB ester **6** in 1,2-dichloroethane (DCE) containing 5–10 equiv of ethanol resulted in the formation of H-phosphonate **8** (R = Et) as the sole product; none of the starting ester **6** remained. The phosphonate was easily recognized by its characteristic ^{31}P NMR spectrum (δ 4.1, d of t, $^1J_{PH}$ = 704, $^3J_{PH}$ = 8.6 Hz). However, when ethanol was omitted from the DCE solution, there was no change in the concentration of the starting ester **6** as determined by ^{31}P NMR, and no new signals that would arise from the trimer or dimer of phosphenite **2**, if released, were present. The irradiation was performed for an extended period of time without effect. This experiment has been repeated several times, with the same observation. Changing the solvent to acetonitrile was without effect. The conclusion is inescapable that the starting phosphinate **6** is unaffected by irradiation at 254 nm, and that it is fragmented only when an alcohol (or water) is present as a coreactant. The

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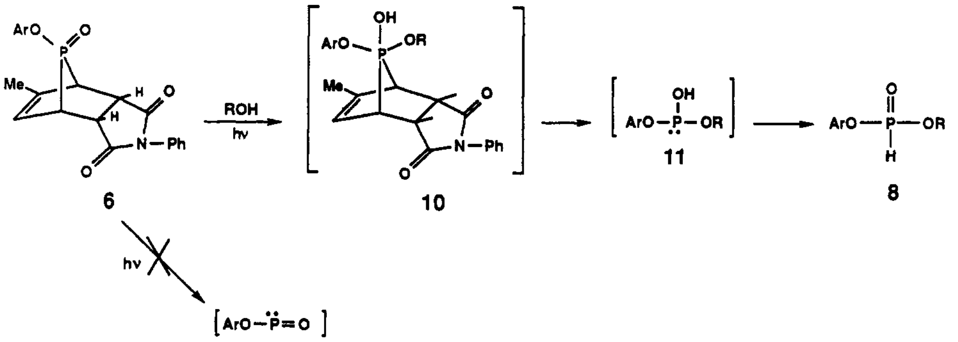
[9] Regitz, M.; Scherer, O. J., Eds. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; George Thieme Verlag: Stuttgart, Germany, 1990.

[10] Quin, L. D.; Marsi, B. G. *J. Am. Chem. Soc.* 1985, *107*, 3389.

Scheme III



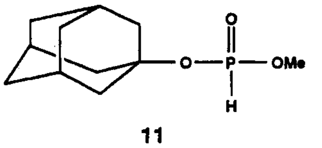
phosphinate therefore is *not* a precursor of a phosphenite under these conditions. A plausible role for the alcohol is that it adds to the phosphoryl group to form a 5-coordinate intermediate (**10**), which is the actual species undergoing the fragmentation.

It is well known in 7-PNB chemistry that there is a strong tendency for 5-coordinate species to form;[6] the contracted C–P–C bond angle in the 7-PNB structure (about 83° in phosphinates) is more compatible with the apical-equatorial angle (90°) of the trigonal bipyramidal 5-coordinate state than with the tetrahedral angle of phosphoryl compounds. It is also well known that 5-coordinate 7-PNB structures are prone to undergo elimination of the bridging phosphorus unit.[6] In the case of adduct **10**, the expelled unit would be the 3-coordinate **11**, which would immediately undergo tautomeric rearrangement to the more stable phosphoryl form **8**, the product observed in the photolyses in alcohol. A test of the involvement of a 5-coordinate intermediate in the photolyses is described in a later section.

The photochemical fragmentation of **6** also occurs in solutions of ethanol in other solvents (acetonitrile and tetrahydrofuran), as well as in DCE solutions of other alcohols (methyl, *i*-propyl, *tert*-butyl, and 1-adamantyl). The photolytic process is reasonably efficient; for a DCE solution containing ethanol, the quantum yield was 0.14.

The proton-coupled ^{31}P NMR spectra left little doubt that the products observed from the trapping reactions were indeed the H-phosphonates **8**. The doublet from one-bond coupling (700–710 Hz) was additionally split by three-bond coupling, giving a quartet for R = Me (12.2 Hz), a triplet for R = Et (8.6 Hz), and a doublet for R = *i*-Pr (8.3 Hz). Confirmation of the assignment was made in one case (**8**, R = Me) by adding an authentic sample to the reaction mixture, which intensified the signal for the reaction product.

The 1-adamantyl ester **9** gave similar results; it was stable on irradiation in DCE solution, but fragmented smoothly with the formation of the H-phosphonate **11** (δ ^{31}P 2.0, $^{1}J_{PH}$ = 687 Hz) when irradiated in the presence of methanol.



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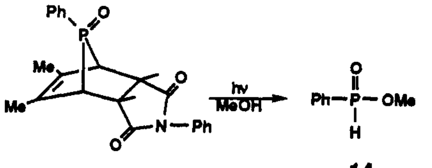
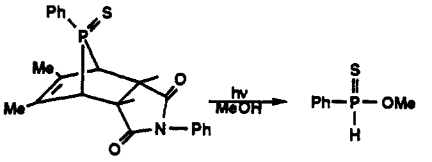
Photochemical Fragmentation of *P*-Phenyl Oxides and Sulfides with the 7-PNB Framework. The observation of the important role of alcohol in the photolysis of 7-PNB phosphinate derivatives prompted an examination of the behavior of phosphine oxides and sulfides with this structure, since the earlier literature[11-13] had proposed that such compounds underwent fragmentation in alcohol solution with the release of the two-coordinate unit (Ar or R)P=X, which then reacted with the alcohol. Phosphine oxide **12** and sulfide **13** were available to us from earlier work;[14] the latter had in fact been employed in one of the photochemical fragmentations purported to involve the release of free PhP=S[13] (in a review by one of the authors several years later,[15] it was noted that a 5-coordinate alcohol adduct could be involved; no experimental work was presented). The photolyses were performed in DCE solution containing a few equivalents of methanol as well as in neat methanol. The known H-phosphinates **14** and **15** were formed as expected, and were readily recognized from their ^{31}P spectra.



12 **14**



13 **15**

The critical experiment was then performed of irradiation in the absence of methanol. There was, in fact, no fragmentation of either oxide **12** or sulfide **13** in pure DCE, and therefore we have reproduced the effect seen for bicyclic phosphinates **6** and **9**. It must be concluded that the methanol is first involved in forming a 5-coordinate adduct which then fragments, and that irradiation of 7-PNB phosphine oxides and sulfides does not lead to release of 2-coordinate species as first thought.[11-13] This may be true also for selenides,[16] but we have not explored these compounds.

Influence of UV Radiation on the ^{16}O–^{18}O Equilibration at the Phosphoryl Group. An important conclusion from our studies is that a 5-coordinate intermediate plays a role in the photochemical fragmentation

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(11) Tomioka, H.; Hirano, Y.; Izawa, Y. *Tetrahedron Lett.* **1974**, 4477.

(12) Tomioka, H.; Miura, S.; Izawa, Y. *Tetrahedron Lett.* **1983**, *24*, 3353.

(13) Holand, S.; Mathey, F. *J. Org. Chem.* **1981**, *41*, 4386.

(14) Quin, L. D.; Wu, X.-P. *Heterat. Chem.* **1991**, *2*, 359.

(15) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

(16) Hussong, R.; Heydt, H.; Registz, M. *Phosphorus Sulfur* **1985**, *25*, 201.

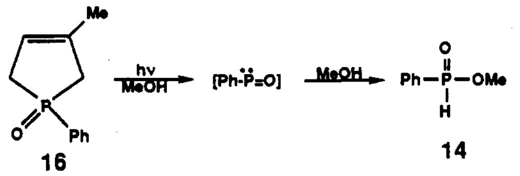
of 7-phosphanorbornene phosphinates and phosphine oxides in the presence of alcohols or water. The intermediate is not observable in the ^{31}P NMR spectra of the solutions used, however. It was nevertheless considered possible that the absorbed radiation acts to fragment the minute amount of the 5-coordinate intermediate that is present in equilibrium with the phosphoryl form, and that is continually replenished by the equilibrium process. Another possibility is that the radiation exerts an influence on the equilibrium process, by increasing the rate of the addition of the nucleophilic species to the phosphoryl group. We have probed these possibilities by examining the isotope equilibration that takes place at the P=O group when the starting material is exposed to water enriched in ^{18}O.

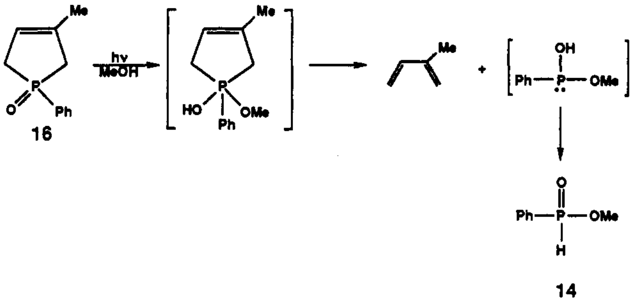
It is known[17] that *syn–anti* isomerization of phosphoryl groups in 7-PNB derivatives can be promoted by nucleophilic species, presumably by the creation of a 5-coordinate adduct. We first confirmed that isotope exchange could occur through such an adduct for a typical compound (12) of the present study. The compound was heated in an acetonitrile solution that contained 5 equiv of water with 74.8% enrichment of ^{18}O. Analysis of the solution by ^{31}P NMR showed that there was no decomposition of the starting material after 35 h at 100 °C. The starting material was recovered by chromatography and subjected to analysis by FAB mass spectrometry. The isotope exchange was determined by measuring the increase in the ratio of the peak intensity for *m/z* 380 ($M^+ + 3$) to *m/z* 378 ($M^+ + 1$), relative to a calibration value (0.0654 ± 0.0018) obtained for natural water at room temperature. The experimental value was 0.803 ± 0.0016, which after correction corresponded to 38% of the theoretically possible exchange. This experiment shows that the 5-coordinate adduct is indeed formed under thermal conditions, but is not decomposed by these conditions.

We then examined the influence of radiation on the exchange at room temperature of a similar solution of 12. When the solution was irradiated in the usual way at 254 nm, the ratio increased to 0.0856 ± 0.001 after 30 min, when 75% fragmentation had been achieved. The radiation has therefore clearly led to more extensive isotope exchange, presumably by increasing the rate of the exchange process that involves the 5-coordinate adduct in equilibrium with the phosphoryl form. Since the adduct was shown not to decompose thermally, the radiation must be responsible for its fragmentation. Further studies on mechanistic details of the photochemical process are planned.

Photochemical Fragmentation of 3-Phospholene Oxides. It has also been reported[18,19] that when 3-phospholene oxide 16 was irradiated in methanol a high yield of H-phosphinate 14 was obtained, and this was interpreted to mean that the free 2-coordinate species PhP=O was released and then reacted with the alcohol.

With our new results on the 7-PNB system clearly requiring a pre-association reaction, we felt it necessary to re-examine the photolysis of 3-phospholene oxides, under similar conditions to those used for the 7-PNB system. We first confirmed that oxide 16 indeed reacted smoothly when photolyzed in DCE solution containing a few equivalents of methanol. The process was complete in 4 h and gave the expected H-phosphinate 14 as the sole product. The quantum yield was 0.4. However, when methanol was omitted from the medium, no consumption of the starting oxide 16 was noted after 5 h. We therefore have observed the same situation as found in the 7-PNB series and are led to propose a similar mechanism involving a 5-coordinate intermediate that fragments to the observed products. Contrary to the literature,[18,19] no release of a 2-coordinate intermediate seems to occur.





Experimental Section

General. Proton NMR spectra (FT, $CDCl_3$) were obtained on a Varian XL-300 spectrometer. ^{31}P NMR spectra (FT, $CDCl_3$; proton-decoupled) were obtained either on this instrument or on an IBM NR-80 spectrometer. Compounds available from previous work included 4,[10], 9,[20] 12,[14] 13,[14] and 16.[10]

Photochemical Reactions. These were carried out in a Rayonet merry-go-round reactor with 16 low-pressure mercury lamps (253.7 nm). Solutions of the substrate and an alcohol trapping agent were placed in quartz NMR tubes and flushed with argon during the irradiation. The temperature was maintained at about 28–30 °C by placing the tube in an Ace Glass quartz water-cooled thermostat mounted in the center of the merry-go-round. Photochemical reactions in the absence of alcohol required prolonged times and the NMR tube was sealed in these experiments. Quantum yield measurements were performed as previously reported.[21] Changes in concentration of the substrate during the first 50% of the reaction were monitored by ^{31}P NMR spectroscopy; the irradiation was stopped 5–7 times, and peak areas were compared to that of a known concentration of $(EtO)_2P(O)OH$ in $CDCl_3$ contained in a sealed capillary as internal standard. The light density (except in experiments with $^{18}OH_2$) was 13.2×10^{-7} einstein/min × mL. The concentration of substrate decreased linearly. Sample preparation consisted of placing the substrate and trapping alcohol if used in the quartz tube, attaching this to a vacuum line, and distilling into it the solvent (usually 1,2-dichloroethane (DCE); dried over P_2O_5 on the line). The tube was then sealed.

Isotope Ratios. The ratio of ^{18}O to ^{16}O in the substrate remaining after a photolysis was determined by FAB mass spectrometry, using the ratio of the signals for $M^+ + 3$ to $M^+ + 1$. A PO Elektron (Ukraine) Model MI 1201E mass spectrometer equipped with a FAB ion source was used for these measurements. Samples (about 1 mg) were dissolved in 15 μL of thioglycerol; 1–2 μL were placed on the copper tip of a direct insertion probe. The sample was bombarded by 5 keV xenon atoms (incidence angle to the probe surface 45°). The positive ions were accelerated at 5 kV potential and detected in a Faraday cup collector system. The mean value of the isotopic ratio was obtained from 16

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[17] Quin, L. D.; Rao, N. S.; Topping, R. J.; McPhail, A. T. *J. Am. Chem. Soc.* **1986**, *108*, 4519.

[18] Tomioka, H.; Hirano, Y.; Izawa, Y. *Tetrahedron Lett.* **1974**, 1865.

[19] Tomioka, H.; Izawa, Y. *J. Org. Chem.* **1977**, *42*, 582.

[20] Quin, L. D.; Sadanani, N. D.; Sommese, A. G.; Ionkin, A. *J. Org. Chem.*, in press.

[21] Jankowski, S.; Quin, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 7011.

(generally) separate determinations of the *m/z* ratio for $M^+ + 3$ and $M^+ + 1$, each averaged over 10 measurements. Water with 74.8% enrichment of ^{18}O was supplied by Techsnabeksport, U.S.S.R., and used in the standard photolysis procedure as applied to phosphine oxide **12** (*vide infra*).

3-Methyl-1-(2,6-di-*tert*-butyl-4-methylphenoxy)-3-phospholene 1-Oxide (5). To a stirred solution of 2,6-di-*tert*-butyl-4-methylphenol (26.4 g, 0.12 mol) in 175 mL of benzene was added 75 mL of 1.6 M *n*-butyllithium (0.10 mol) in small portions. The resulting white suspension was stirred at room temperature for 1 h and then treated over a 10-min period with a solution of 1-chloro-3-methyl-3-phospholene 1-oxide (**4**, 15.0 g, 0.10 mol) in 100 mL of benzene. The resulting solution was stirred at room temperature for 3 h, and then solvent was removed with a rotary evaporator. The residue was taken up in $CHCl_3$ and chromatographed on silica gel with elution by $CHCl_3$. This afforded 13.5 g (40%) of **5**, ^{31}P NMR (in $CHCl_3$ with D_2O lock) δ 74.9. A sample recrystallized from CH_2Cl_2-hexane (1:1) had mp 103–104 °C. Anal. Calcd for $C_{20}H_{31}O_2P$: C, 71.86; H, 9.28. Found: C, 71.69; H, 9.22.

Synthesis of Bicyclic Phosphinate 6. A stirred solution of **5** (9.3 g, 0.028 mol) in 100 mL of dry $CHCl_3$ was treated dropwise with a solution of 4.8 g (0.030 mol) of bromine in 50 mL of $CHCl_3$. The temperature was maintained at 0 °C; after the addition was complete, the solution was stirred at room temperature for 1 h. Removal of solvent left a residue of crude 3,4-dibromo-1-(2,6-di-*tert*-butyl-4-methylphenoxy)-3-methylphospholane 1-oxide, ^{31}P NMR ($CHCl_3$ with D_2O as lock) δ 72.7. An accumulation of 20.9 g (0.040 mol) of the dibromide was used directly in the next step. It was dissolved in 60 mL of benzene and treated at room temperature with a solution of 12.4 g (0.072 mol) of *N*-phenylmaleimide and 12.7 g (0.126 mol) of triethylamine in 150 mL of benzene. This order of addition is necessary to avoid dimerization of the intermediate phosphole oxide. The mixture was stirred at room temperature for 48 h, the solid amine salt was removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was chromatographed on silica gel with hexane followed by hexane–$CHCl_3$ (1:1), which eluted the dimer of the phosphole oxide always formed as a byproduct (^{31}P NMR δ 81.4 and 72.0, d of d, $^3J_{PP} = 55$ Hz). Elution with $CHCl_3$ provided 5.4 g (25%) of **6** as a tan solid, ^{31}P NMR ($CHCl_3$ with D_2O as lock) δ 79.0. A sample was recrystallized from CH_2Cl_2–hexane, mp 246–247 °C. Anal. Calcd for $C_{30}H_{36}NO_4P$: C, 71.29; H, 7.13; N, 2.77. Found: C, 71.04; H, 7.48; N, 2.62.

Thermal Fragmentation of Phosphinate 6. A 0.30-g sample of phosphinate **6** was placed in the flask of a Kugelrohr apparatus and attached to three receiver bulbs. The sample was heated at 150 °C (0.40 mm) for 20 min. Yellow needles identified as 4-methyl-*N*-phenyl-1,2-dihydrophthalimide were collected in the first receiver. The apparatus was filled with argon and the first receiver removed. The thermolysis was continued at 250 °C (0.03 mm). White solid collected in the first receiver, and was resublimed into the last receiver. The solid, under argon, was taken up in $CHCl_3$; ^{31}P NMR indicated the major products to be trimer **1** (δ 128.5 (t, $^2J_{PP} = 10$ Hz) and 120.3 (d, $^2J_{PP} = 10$ Hz); lit.[3] δ 127.9 and 120.0, $J = 10$ Hz) and dimer **7** (δ 177.0; lit.[4] 176.5). Also present was a small, short-lived signal (about 3–4% of total signals) at δ 238 attributed to monomer **2**, a signal at δ 6.1 ($^1J_{PH} = 724$ Hz) probably due to the H-phosphonate **8** (R = H) from hydrolysis of monomer **1**, and δ 79.6 for sublimed phosphinate **6**. With the exception of the δ 79.6 signal, the spectrum resembled closely that for the sublimate from preformed[3] trimer **1**, subjected to a similar procedure (300–320 °C, 9 mm, 5 min).

Photochemical Studies on Phosphinate 6. Two milliliters of a 0.050 M solution of phosphinate **6** in 1,2-dichloroethane (DCE) was photolyzed for 3 h. There was no significant change in the size of the ^{31}P NMR signal; a trace of a new product with ^{31}P δ 5.6 (DCE; D_2O lock) and $^1J_{PH} = 720$ Hz was detected and is believed to be the H-phosphonate **8**, R = H, arising from the presence of water in the system. The structure was confirmed by spiking with an authentic sample available from another study[22] (mp 162–163 °C. Anal. Calcd for $C_{15}H_{25}O_3P$: C, 63.38; H, 8.80. Found: C, 63.25; H, 8.86. ^{31}P NMR ($CDCl_3$) δ 4.0, $^1J_{PH} = 708$ Hz).

A similar solution of phosphinate **6** in DCE that contained 10 equiv of ethanol was irradiated for 3 h. All starting **6** was consumed and the solution contained a ^{31}P NMR signal for the H-phosphonate **8** (R = Et), δ 5.6, $^1J_{PH} = 720$ Hz. The quantum yield was 0.14. Similarly, trapping with MeOH gave **8** (R = Me), δ ^{31}P 6.6 ($^1J_{PH} = 708$, $^3J_{PH} = 12.2$ Hz) and with *i*-PrOH gave **8** (R = *i*-Pr) δ ^{31}P 2.9 ($^1J_{PH} = 709$, $^3J_{PH} = 8.3$ Hz). Generally **8** was the only product observed in the ^{31}P NMR spectrum. On occasion a minor signal was also present about 1.5–2.0 ppm downfield of **8** which also exhibited one-bond H-coupling. These signals may arise from $(RO)_2PH(O)$. An authentic sample of **8** (R = Me) available from other studies[22] had ^{31}P ($CHCl_3$; D_2O lock) δ 6.0, $^1J_{PH} = 708$ Hz, $^3J_{PH} = 12.2$ Hz (Anal. Calcd for $C_{16}H_{27}O_3P$: C, 64.42; H, 9.06. Found: C, 64.71; H, 9.13). Addition to the product of photolysis of **6** in the presence of methanol caused enhancement of the ^{31}P NMR signals.

Fragmentation of 1-Adamantyl Ester 9. A DCE solution that was 0.108 M in phosphinate **9** and 0.554 M in methanol was irradiated for 3 h. All starting **9** was consumed, and the only product **11** had ^{31}P NMR δ 2.0, $^1J_{PH} = 687$ Hz. The quantum yield was 0.14.

Photochemical Studies on Phosphine Oxide 12. Oxide **12** in DCE solution was unaffected by irradiation for 3 h. In methanol solution, or in DCE containing a few equivalents of methanol, **12** was completely consumed and the product was **14**, ^{31}P NMR δ 26.8, $J = 568$ Hz; lit.[21] δ 27.3, $J = 576$ Hz. In acetonitrile–DCE (4:1) that was 0.068 M in **12** and 0.213 M in water, photolysis gave PhPH(O)OH, δ 18.0, $^1J_{PH} = 560$ Hz (lit.[23] δ 20, $J = 560$), with a quantum yield of 0.51.

The exchange of ^{18}O for ^{16}O at the P=O group was determined by photolyzing a solution of 0.189 g (0.50 mmol) of **12** in 10 mL of acetonitrile (freshly distilled from P_2O_5) that contained 20 mg (1 mmol) of $^{18}OH_2$ (74.8% ^{18}O). The unreacted **12** was recovered after the periods of irradiation by separation on PLC silica gel plates (Merck) with chloroform–2-propanol (10:1) as eluant, and analyzed by FAB MS. For a sample of the solution before photolysis, the recovered **12** had the ratio of *m/z* for M + 3 to M + 1 of 0.0654 ± 0.0018. The solution was irradiated with light intensity 25×10^{-7} einstein/min × mL for 1 min (2.5% of **13** consumed; by ^{31}P NMR analysis), 15 min (37.5%), and 30 min (75%). The M + 3 to M + 1 ratios were 0.0678 ± 0.0014, 0.0745 ± 0.0014, and 0.0856 ± 0.0010, respectively. The same experiment was carried out with $^{16}OH_2$ to determine a baseline value for $M^+ + 3$ to $M^+ + 1$ when no exchange is possible; the ratio was 0.0668 ± 0.0019 after 75% of **12** had been fragmented. Therefore, the increase in the ratio to 0.0856 ± 0.0010 at 75% reaction when $^{18}OH_2$ was present is proved to arise from true isotope exchange. The exchange occurring on heating a solution of 17.7 mg (0.047 mmol) of **12** in 1.0 mL of acetonitrile containing 10 mg (0.5 mmol) of the 74.8% enriched $^{18}OH_2$ was also determined. The ratio of $M^+ + 3$ to $M^+ + 1$ was 0.830 ± 0.0016. ^{31}P NMR analysis showed no decomposition of the starting **12**.

Photochemical Studies on Phosphine Sulfide 13. A solution of 25 mg of phosphine sulfide **13** in 1 mL of dry DCE was placed in a 10-mm quartz NMR tube, purged with argon, and then irradiated at 254 nm in the Rayonet apparatus for 1 h. The only ^{31}P NMR signal observed was that for starting **13**. When the experiment was repeated using methanol in place of DCE, photolysis was complete in 1 h; the only ^{31}P NMR signal appeared at δ 69 ($^1J_{PH} = 528$ Hz) for thiophosphonate **15**.[13]

Photochemical Studies on 3-Phospholene Oxide 16. Two milliliters of a 0.100 M solution of phospholene oxide **16** in DCE was irradiated for 5 h. No consumption of **16** was detected. Similar solutions were made 0.202, 0.538, and 0.955 M in ethanol. After 4 h of irradiation, all starting **16** had been consumed, and the H-phosphinate **14** (^{31}P δ 26.8, $J = 568$ Hz) was formed. The quantum yields were 0.50 ± 0.02, 0.43 ± 0.04, and 0.40 ± 0.06, respectively. The quantum yield was also determined for a solution of **16** (0.100 M) and 1-adamantanol (0.311 M) and found to be 0.45. The product had ^{31}P δ 12.7, $J = 550$ Hz in the solution.

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