Heteroatom Chemistry
Volume 4, Number 2/3, 1993

Photochemical Fragmentation of the 2-Phosphabicyclo[2.2.2]octa-5,7-diene Ring System as a Versatile Method for Generating 3-Coordinate Methylene Phosphine Oxides and Sulfides

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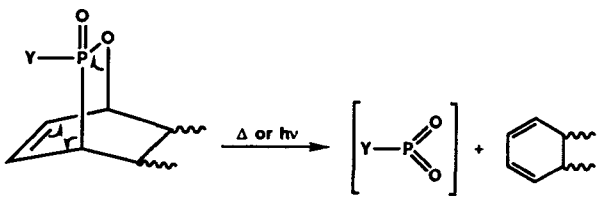
Received 17 June 1992

ABSTRACT

1,6-Dihydrophosphinine 1-oxides with 4-chloro-3(or 5)-methyl substituents give cycloadducts with dimethyl acetylenedicarboxylate having the 2-phosphabicyclo[2.2.2]octa-5,7-diene ring system that can be fragmented easily on irradiation with ultraviolet light (254 nm). The phosphorus-containing bridge is released as a derivative of the 3-coordinate methylene phosphine oxide species, R–P(O)=CH_2. This species is too reactive to observe but is readily trapped by an addition reaction with alcohols to give phosphinates (R = alkyl or aryl) or phosphonates (R = O-alkyl). These experiments constitute the first demonstration of the existence of RO–P(O)=CH_2. Phosphoryl oxygen in the cycloadducts has been replaced by sulfur, and these sulfides fragment smoothly on irradiation. The 3-coordinate species Ph–P(S)=CH_2 has been generated by other workers, but the species RO–P(S)=CH_2 was generated here for the first time. The power of the bicyclic fragmentation route for the generation of a variety of 3-coordinate P-methylene derivatives is made evident by this study.

The fragmentation of bridged, strategically unsaturated heterocyclic systems is a powerful technique for the generation of small molecules with multiple bonding at the heteroatom. We have exploited this method in several ways to generate phosphorus species with multiple bonds. We have, for example, successfully generated the unsaturated, 3-coordinate fragment $-PO_2$ attached to carbon [1,2], alkoxy [1,3], or amino groups [3–5], employing both thermal and photochemical fragmentation of derivatives of the 2,3-oxaphosphabicyclo[2.2.2]octa-5,7-diene ring system. The thermal fragmentation has been shown to occur by a concerted retro-cycloaddition [6] that accomplishes extrusion of the P–O bridging unit with the generation of a new P=O bond.



Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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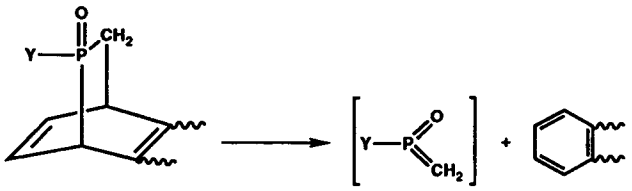
1042-7163/93/$5.00 + .25

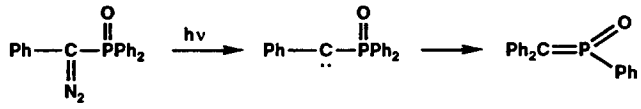
There are distinct advantages in the generation of reactive molecules by these methods; no added reagents are required, inert solvents can be used, and, at least in the photochemical method, quite mild conditions are employed.

When a methylene group replaces oxygen in the ring framework shown above, a similar pathway for fragmentation creates a multiple phosphorus–carbon bond, thereby providing derivatives with the 3-coordinate–P(O)=CH_2 group.



We had recognized this possibility several years ago and attempted to perform a thermal fragmentation on derivatives of the above bicyclic ring system but without encouraging results [7]. Deschamps and Mathey [8] also attempted the thermal fragmentation of a derivative of this ring system without success. Modification of the functionality at phosphorus can, however, lead to substances that do undergo smooth thermal fragmentation; Deschamps and Mathey converted phosphine oxide **1** to sulfide **2** and showed, from trapping reactions with alcohols and dienes, that the species methylenephenylphosphine sulfide (3) was released at 110°C in toluene. In our laboratory, we reduced phosphine oxide **4** to phosphine **5** and found [9] that thermal fragmentation occurred at quite low temperatures with the release of the 2-coordinate phosphaalkene **6**. The species Ph–P=CH_2 was generated similarly.

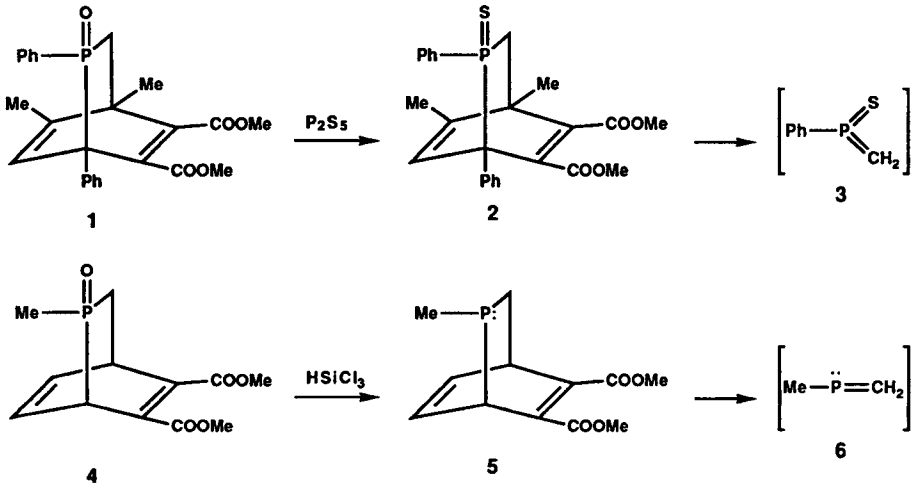
We have now found that the photochemical fragmentation of phosphine oxides in the 2-phosphabicyclo[2.2.2]octa-5,7-diene ring system occurs cleanly at room temperature, thus providing the first successful technique for the generation of methylenephosphine oxides, R–P(O)=CH_2. Such species polymerize rapidly and must be detected by trapping reactions, as with alcohols to form phosphinates. C-Arylated derivatives of this parent have been generated photochemically by Regitz and co-workers from α-azo phosphine oxides [10], but this method is not capable of extension to provide the parent methylene species.

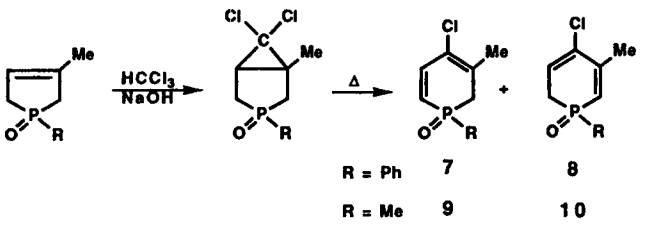


An important aspect of the heterocycle fragmentation approach to low-coordinate phosphorus species is that a variety of new compositions can conceivably be created by modifying the substitution pattern at phosphorus. In the present study, we have demonstrated the versatility of the approach by generating the first examples of methylene(oxo)phosphoranes with P-alkoxy groups (RO–P(O)=CH_2). The structure can be viewed as an intramolecular anhydride of a mono-alkyl methylphosphonate and is trapped by reacting it with hydroxy compounds to form the phosphonate. Similarly, we have generated, for the first time, the corresponding thiono derivative, RO–P(S)=CH_2, which gives a thionophosphonate on reaction with an alcohol.

Generation of P-Phenyl and P-Methyl Methylene Phosphine Oxides

The requisite 2-phosphabicyclo[2.2.2]octa-5,7-diene ring system is readily synthesized [7,8,11] by the Diels-Alder reaction of acetylenedicarboxylates with 1,6-dihydrophosphinine oxides. In the present study,



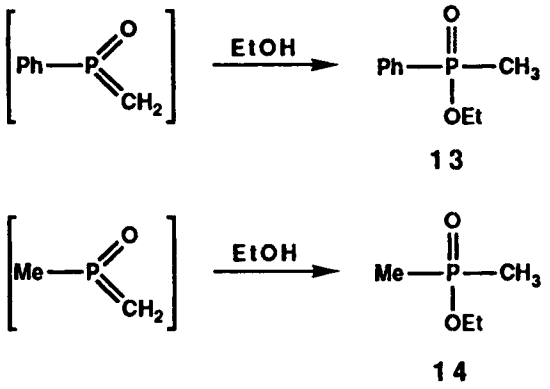


SCHEME 1

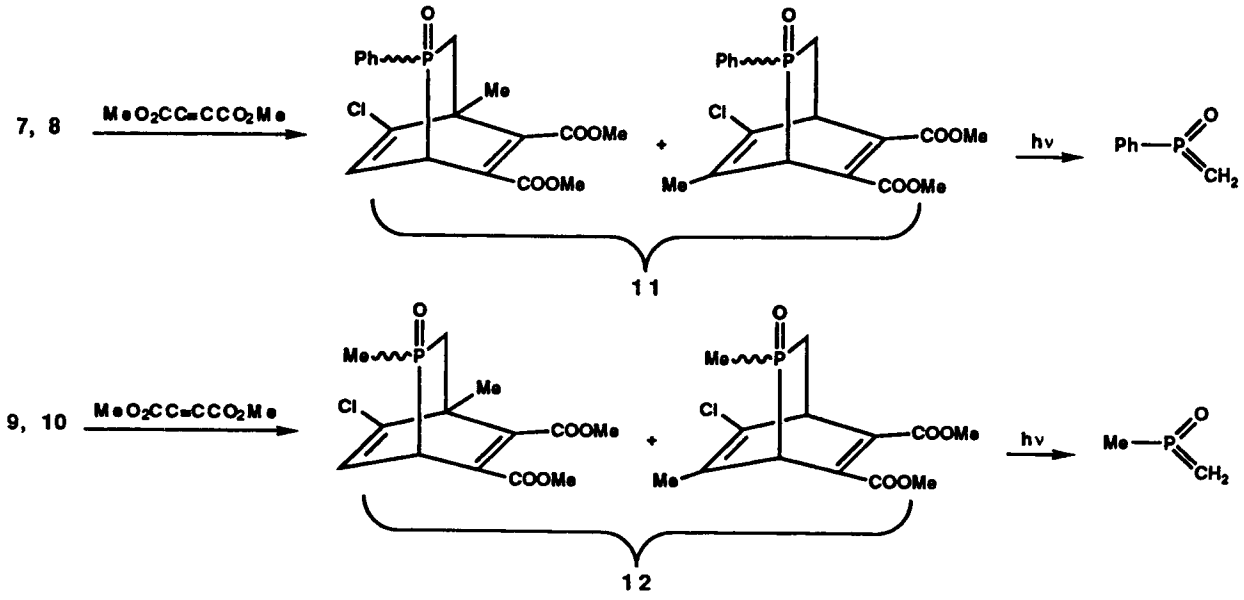
we have employed the method outlined in Scheme 1 for the synthesis of the required dihydrophosphinine oxides; experimental details have been published earlier [11].

The method is most readily applied to a 3-methyl-3-phospholene oxide as starting material, but, as seen in Scheme 1, this results in the formation of two isomeric dihydrophosphinine oxides, with the 4-chloro-3-methyl isomers (7 and 9) in predominance. The mixtures are not readily separated and are used directly in the cycloaddition with dimethyl acetylenedicarboxylate. Each dihydrophosphinine oxide gives two cycloadducts that differ in configuration at phosphorus (Scheme 2). The resulting 4-component mixture presents a formidable separation challenge but is nevertheless directly useful in the fragmentation process to generate the methylene phosphine oxides (Scheme 2), since all isomers release this fragment (not necessarily at the same rates). Partial mixture separation has been achieved in some cases in the study of the adducts [11], but there seems to be no advantage in the use of isomer-enriched samples.

Diels-Alder adduct mixtures **11** and **12** were readily fragmented when irradiated in acetonitrile with a medium-pressure Hanovia lamp (nominally 254 nm). Thus, after 2–4 hours of irradiation of a 0.1 mmol sample in a 5–10 mm quartz tube, none of the isomers remained. When ethanol was included in the photolysis medium, almost all of the phosphorus appeared in the desired form of ethyl methylphenylphosphinate (**13**) or ethyl dimethylphosphinate (**14**). Both are known compounds and were identified by ^{31}P NMR and gas chromatography-mass spectroscopy (GC-MS).



The use of trapping agents to detect a highly reactive intermediate always carries with it an uncertainty about a possible role for the agent *before* the fragmentation, thus preventing the development of a truly free species. We have addressed this question in a quantum yield study with a related derivative having a P-ethoxy group, as will be discussed in the next section. It was established that



SCHEME 2

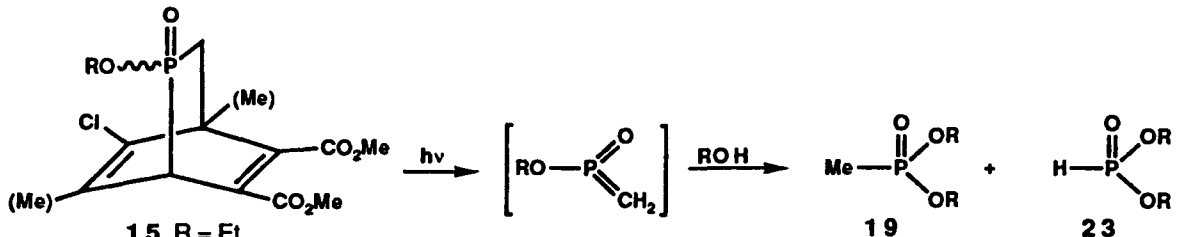
no role exists for the alcohol before the photolytic fragmentation has occurred.

Generation of P-Alkoxy Methylene Phosphine Oxides

Our previous studies [11] had also made available several P-alkoxy derivatives of the 2-phosphabicyclo [2.2.2]octa-5,7-diene 2-oxide ring system by the Diels-Alder reaction of P-alkoxy 1,6-dihydrophosphinine oxides with dimethyl acetylenedicarboxylate. If a methylene phosphine oxide were to be extruded from such a compound, it would be of a previously unknown type; there is no literature reference to the species $RO–P(O)=CH_2$. Accordingly, we have performed photolytic fragmentations of several of the bicyclic P-alkoxy derivatives (Scheme 3). In every case, the starting material was consumed on irradiation at 254 nm. When an alcohol was present, most of the phosphorus appeared in the form of the expected methylphosphonate. These products were identified by their ^{31}P NMR spectra and some by GC-MS; most were known in the literature. For example, from the ethanol trapping of the fragment released from ester **15**, there was obtained a product (**19**) with δ 30.7 ($CDCl_3$); a literature value [12] is δ 27.7 ($CDCl_3$). A spiking experiment with an authentic specimen confirmed the assignment. The identification of the main products as dialkyl methylphosphonates leads to the conclusion that the reactive intermediate released on irradiation of the esters is the hitherto unknown P-alkoxy methylene phosphine oxide.

An observation made for all of the products of the photolyses was that a small, variable amount of another alcohol-trapped extruded phosphorus species accompanied the main product. They were detected by ^{31}P NMR signals in the range δ 5–7. These products generally contributed about 5–10% to the total area of ^{31}P NMR signals. Thus, in the case of photolysis of ester **15**, a ^{31}P NMR analysis, under conditions of long pulse delay to allow for any differences in relaxation time among the species present, showed the amount to be 6.7%. When proton coupling was allowed, the signals split to doublets with the very large coupling constants (about 670 Hz) characteristic of a directly attached proton. The shifts and coupling constants were suggestive of a dialkyl H-phosphonate (23–26, Scheme 3); for example, the ethanol trapping product mixture from the photolysis of ethyl ester **15** and δ 7.5 with $^1J_{PH}$ = 690 Hz (δ 7.1–8.1, ^1J = 682–691 Hz has been reported [13]). The assignment of structure **21** to the major product was confirmed by spiking with an authentic specimen.

The origin of the side-products is uncertain at this time, and there is no explanation for the failure of comparable side-products to form when phosphine oxides rather than esters are irradiated. We eliminated the possibility that the differing behavior was due to the esters undergoing some photolytic cleavage of the P-alkoxy group, which is impossible for the phosphine oxides, by an experiment where the alcohol trapping agent carried a different alkyl group from that in the starting ester. Retention of the original P-alkoxy group would lead to a H-phosphonate with mixed alkoxy groups, whereas a preliminary cleavage of the P-alkoxy group would give a phosphonate with the same alkoxy groups. When isopropyl ester **18** was photolyzed in the presence of ethanol, the side-product had a ^{31}P NMR shift (δ 5.9) that was significantly different from that of diethyl H-phosphonate (δ 7.5) or of di-isopropyl H-phosphonate (δ 4.1) and can safely be assumed to be ethyl isopropyl H-phosphonate. Therefore, the original alkoxy group on P remains in place during the photolysis. In another experiment, it was shown that a typical dialkyl methylphosphonate main product (di-isopropyl, **22**) was, not unexpectedly, stable to the irradiation and did not undergo any C–P bond cleavage to give an H-phosphonate. To account for the formation of the H-phosphonate side-products, then, it is necessary to assume that the starting ester undergoes cleavage of both of its C–P bonds but in an unknown sequence. We do note that the H-phosphonate can arise from the addition of alcohol to a phosphenite (RO–P=O) as a reactive intermediate [14] formed



15, R = Et
16, R = Me
17, R = *n*-Pr
18, R = *i*-Pr

19 **20** **21** **22**

23 **24** **25** **26**

SCHEME 3

in a double C–P cleavage, but there is at present no evidence for such an intermediate.

Another minor product formed in approximately the same amount has a ^{31}P NMR signal close to 0 and has no attached proton. A dialkyl phosphate from oxidation of the H-phosphonate would fit these properties, and, in the case of the product from **15** with δ-1.7 (CH_3CN), this was confirmed by a spiking experiment. Thus, an authentic specimen of the suspected diethyl phosphate increased the intensity of the signal at δ-1.7.

The possibility that the trapping alcohol might give an adduct with the starting bridged compound and that this adduct fragments to give the observed trapping product was explored with the use of ethyl ester **15**. We observed that the rate of the photolytic fragmentation was semiquantitatively the same both in the presence and absence of the alcohol and that the quantum yield was 0.07 in both cases. It is appropriate, therefore, to ascribe the role of ethanol to a trapping reaction with free P-ethoxy methylene(oxo)phosphorane and not to the formation of adduct **27**, which then fragmented.

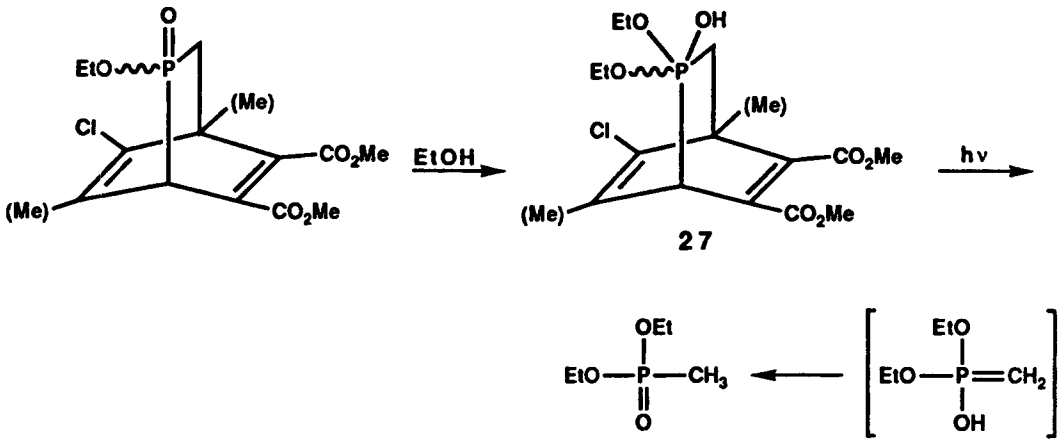
Generation of P-Phenyl Methylene Phosphine Sulfide

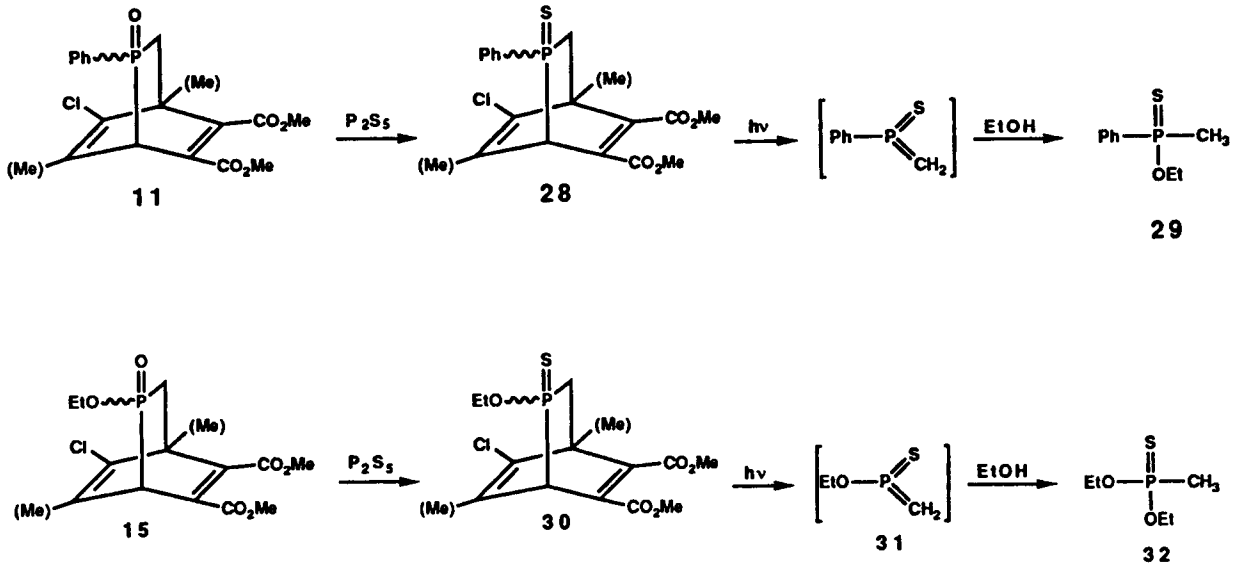
To explore the applicability of the photochemical method to the generation of thiono counterparts of the methylene phosphine oxides, the phosphoryl oxygens in the isomer mixture of P-phenyl phosphine oxides **11** were replaced with sulfur by refluxing in toluene with P_2S_5. The product **28** gave the expected downfield ^{31}P NMR shift (to δ 50–56) for the mixed sulfides. On photolysis in absolute ethanol at 254 nm, the sulfide mixture was completely consumed and the phosphorus product (**29**) had a ^{31}P NMR shift of δ 89.3 (ethanol). This matches closely the value (δ 89.6 in CH_2Cl_2) reported by Deschamps and Mathey [8] for the methanol trapping product of the same thiono-phosphorane when formed by thermolysis of a related phosphine sulfide (**2**). The identity of the ethanol trapping product was confirmed by GC-MS.

We, therefore, have defined a set of photochemical conditions for the room-temperature generation of the methylene phosphine sulfide species, possibly of interest as precursors of methylphosphonothionates in a one-step process on reaction with complex alcohols.

Generation of P-Ethoxy Methylene Phosphine Sulfide

No examples of methylene phosphine sulfides with P-alkoxy groups have previously been mentioned in the literature. A precursor for this new species would result from the replacement of oxygen by sulfur in the phosphinates **15–18** used for the generation of P-alkoxy methylene phosphine oxides. This replacement was accomplished in the P-ethoxy derivative **15** by heating in CH_2Cl_2 with P_2S_5. The ^{31}P NMR signals for the mixed thionophosphinates (**30**) occurred at δ 92–97, the expected range (*e.g.*, $Me_2P(S)OMe$ δ 94.3 ($CDCl_3$) [15]). The thiophosphinate mixture was photolyzed in absolute ethanol at 254 nm in a 5 mm quartz tube. For a 24 mg charge, all of the starting material was consumed after 1 hour, and the only ^{31}P NMR signal appeared at δ 94.7 (ethanol). The expected product (**32**) is a known compound with δ 96 [16]. The identity of the product was confirmed by a GC-MS experiment. This result can be interpreted, as in other cases, as proving that the P-C bridging unit had been extruded, giving here the desired P-ethoxy methylene phosphine sulfide **31** for the first time. In this case, as in the P-phenyl sulfide **28**, there was no indication of the cleavage of a C–P bond to form an H-phosphonate by-product.





EXPERIMENTAL

General

Photolyses were conducted either in a cylindrical multilamp Rayonet apparatus for actinometry at 254 nm (125 W) or by an Ace Glass quartz, water-cooled immersion well with a 450 W Hanovia medium-pressure lamp (nominally 254 nm). The photolytic reactions were carried out in 5 or 10 mm EPR precision quartz tubes that were mounted in the Rayonet apparatus or were attached to the outer wall of the Ace immersion well. The reactions were followed by ^{31}P NMR to the disappearance of the starting material, using an IBM NR-80 spectrometer with D_2O for external locking and 85% H_3PO_4 as external standard. Downfield shifts have positive signs. Fourier transform ^1H spectra were recorded with a Varian XL-200 spectrometer in $CDCl_3$ with Me_4Si as internal standard. The MS data were obtained with a Hewlett-Packard GC-MS system, using a Hewlett-Packard Atomic Emission Detector set at the frequency for phosphorus (186 nm) and a Hewlett-Packard Mass Selective Detector (70 eV).

Reaction of Dimethyl Acetylenedicarboxylate with 1-Phenyl-1,6-Dihydrophosphinine Oxides **7** *and* **8**

A solution of 1.06 g (4.44 mmol) of P-phenyl-1,6-dihydrophosphinine oxides **7** and **8**, prepared as described previously [17], and 1.64 mL (13.3 mmol) of dimethyl acetylenedicarboxylate in 12 mL of toluene was refluxed under nitrogen for 15 hours. The ^{31}P NMR spectrum of the solution showed that all starting material (δ 10.0 and δ 11.0) had reacted. The solvent was removed *in vacuo*, and the residual oil had ^{31}P NMR signals (benzene) at δ 40.6, 40.0, 36.2, and 35.7. It was purified by chromatography on a silica gel (Aldrich 60–200 mesh) column with elution by benzene-acetone (2:3). The isomer mixture **11** (0.7 g, 1.84 mmol) had ^{31}P NMR signals (CH_3CN) at δ 42.9, 42.1, and 38.5 (3:3:1; the fourth isomer was lost in the purification procedure). No attempt was made to associate signals with particular isomeric forms. The proton NMR spectra for the isomer mixture contained overlapping signals, but features consistent with the adduct structure, and in resemblance to the P–CH_3 counterpart [11], were present: olefinic H at δ 6.67 (d of d, J = 5.2 and 7.2 Hz) and 6.15 (d of d, J = 6.0 and 7.1 Hz); 4-Me at δ 1.66–1.69; 6-Me and –CH_2 at δ 1.88–2.29. The mixture was used directly in photolysis experiments.

Conversion of Mixed P-Phenyl Oxides **11** *to Sulfides* (**28**)

A solution of 20 mg (0.0525 mmol) of the 3-component mixture of isomeric forms of **11** prepared above and 35 mg (0.158 mmol) of phosphorus pentasulfide in 1 mL of dry methylene chloride was stirred at room temperature for 3 days. The ^{31}P NMR spectrum (CH_2Cl_2) showed that all starting material was consumed, and the product gave signals for isomers of **28** at δ 51.4 (major), 50.6, 54.0, and 56.6 (cf. to δ 58.7 (CH_2Cl_2) for **2**[8]). The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue of **28** was used directly in photolysis experiments.

Conversion of Mixed Ethyl Phosphinates (**15**) *to Thionophosphinates* **30**

A solution of a mixture of phosphinates **15** (0.5 g, 1.43 mmol) obtained in previously reported work

[11] in 20 mL of dry toluene (deoxygenated with nitrogen) was treated with 0.43 g (1.93 mmol) of phosphorus pentasulfide. The mixture was refluxed under nitrogen for 8 hours. The solvent was removed *in vacuo*, and the residue was purified by chromatography on a silica gel column with elution by 1% methanol in chloroform. The product (0.25 g, 48%) had ^{31}P NMR signals ($CDCl_3$) at δ 96.7 and 92.2 (approximately 1:1); no signals for starting **15** were present. The product required storage under nitrogen in a refrigerator and was used directly in photolysis experiments.

Photolysis of Mixed Isomers of P-Methyl Phosphine Oxide **12**

A solution of 0.1 g (0.31 mmol) of a mixture of two isomers **12** (^{31}P NMR δ 52.6 and 48.9; available from previously reported work [11]) in 50 mL of acetonitrile containing 3 mL of absolute ethanol was irradiated in the Ace reactor with the Hanovia lamp for 7 hours at room temperature. Solvent was evaporated and the ^{31}P NMR spectrum ($CDCl_3$) showed peaks at δ 52.42 (98%) and 52.56 (2%). The former peak was assigned to ethyl dimethylphosphinate (**14**); an authentic sample prepared according to Kosolapoff and Watson [18] had δ 52.4, and spiking the reaction mixture with the known caused intensification of the peak at δ 52.4. The minor peak at δ 52.56 may be due to unchanged **11** or dimethylphosphinic acid (also δ 52.6); it was intensified by addition of an authentic sample of the acid.

A similar result was obtained when the single isomer of **12** (0.08 g) with δ 52.95 ($CDCl_3$) was irradiated in the same way for 2.5 hours in 50 mL of dioxane containing 3 mL of ethanol; the photo product had a peak at δ 52.46, intensified on addition of known **14** and distinguishable from that of starting material at δ 52.95.

Photolysis of Mixed Isomers of P-Phenyl Phosphine Oxides **11**

A solution of 10 mg (0.026 mmol) of isomers of **11** with ^{31}P NMR δ 43.3 and 39.6 (1:5) in 0.8 mL of dry methylene chloride containing 25 μL (0.42 mmol) of absolute ethanol was placed in a 5 mm quartz tube. The tube was subjected to irradiation with the Rayonet apparatus for 2.5 hours at room temperature. The ^{31}P NMR spectrum showed that all starting material had been fragmented and the only product had δ 42.1 (CH_2Cl_2); δ 42.0 (MeCN) has been reported [19] for the related ethyl ethylphenylphosphinate. The identification of the product as **13** was confirmed by GC-MS. Calcd for $C_9H_{13}O_2P$: M^+ 184; found m/z 184 (9.2%), 141 (100%).

Photolysis of P-Phenyl Phosphine Sulfide **28**

The sample of **28** prepared from 20 mg of mixed oxides **11** was dissolved in 0.6 mL of absolute ethanol in a 5 mm quartz tube and protected by argon. The tube was irradiated in the Rayonet apparatus for 1 hour. Analysis by ^{31}P NMR showed that all starting **28** was consumed and the major product had δ 89.3 (EtOH). This signal is assigned to ethyl methylphenylphosphonothionate (**29**, cf. to δ 89.6 (CH_2Cl_2) for the methyl ester [8]) and confirmed by GC-MS. Calcd for $C_9H_{13}OPS$, M^+ 200; found m/z 200 (65%), 156 (100%).

Photolysis of Phosphinate Esters (**15–18**)

a. Ethyl Ester **15**. A 0.16 g sample of a mixture of four isomers of **15** (δ ^{31}P NMR ($CDCl_3$) 57.6, 57.2, 55.7, and 54.1; ratio 32:23:28:17; available from previously reported work [11]) in 50 mL of dry acetonitrile containing 4 mL of dry ethanol was irradiated in the Ace reactor for 7 hours. Evaporation of solvent left a brown oil; ^{31}P NMR ($CDCl_3$) δ 30.7 (major), 7.53 (minor), and −0.87 (minor). The peak at δ 30.7 was assigned to diethyl methylphosphonate, **19** (Ref. [14] δ 27.7 in $CDCl_3$) by spiking with an authentic sample (Aldrich). The peak at δ 7.53 had $^1J_{PH}$ 690 Hz, as did an authentic sample of diethyl H-phosphonate (**23**). The ^{31}P NMR signal at δ −0.87 was intensified on addition of authentic diethyl phosphate.

In another experiment, a quantitative analysis of the photolysis product mixture was performed by ^{31}P NMR at long pulse delay (50 seconds). The ratio of compounds **19**, **23**, and diethyl phosphate was 2.87:0.23:0.38.

b. Methyl Ester **16**. A solution in 2.5 mL of methanol and 50 mL of acetonitrile of 0.24 g of the mixed isomers of **16** with ^{31}P ($CDCl_3$) δ 59.5, 58.9, 57.9, and 55.5 (ratio 36:22:12:30) available from previous work [13] was photolyzed as above for 5 hours. The product had a major ^{31}P NMR ($CDCl_3$) peak at δ 33.5 (Ref. [20] δ 31.5 in CCl_4) with minor peaks at δ 10.8 and 1.67. The δ 10.8 peak was split to a doublet ($^1J_{PH}$ = 698 Hz) of septets ($^3J_{PH}$ = 12.3 Hz) which conclusively identified the substance as dimethyl H-phosphonate (**24**) (Ref. [21] δ 11, $^1J_{PH}$ = 698 Hz, $^3J_{PH}$ = 12.2 Hz).

c. Isopropyl Ester **18**. A mixture (0.1 g) of the isomers of **18** with ^{31}P NMR δ 55.67 and 53.61 was photolyzed as above in 3.4 mL of isopropyl alcohol and 50 mL of acetonitrile. The product had a major ^{31}P NMR ($CDCl_3$) signal at δ 28.1 and minor signals at δ 4.13 ($^1J_{PH}$ = 687 Hz) and δ 0.87. The signal at δ 28.1 was assigned to di-isopropyl methylphosphonate, **22** (Ref. [22] δ 27.4; δ 28.2 was obtained for an authentic specimen). GC-MS showed no signal for M^+ (180); the base peak (100%) had m/z 97

(possibly $MeP(OH)_3^+$) and $M^+ - C_3H_2O$ at 123 (52.5%). The signal at δ 4.13 was derived from diisopropyl H-phosphonate **26** (Ref. [21] δ 4.2, $^1J_{PH}$ = 690 Hz). The GC-MS showed no signal for M^+ (166) but had the base peak at m/z 83 (possibly $HP(OH)_3^+$) with major signals at m/z 151 (10%, $M^+ - CH_3$) and 109 (75.4%). Photolysis (13 hours) of **18** (50 mg) in 50 mL of CH_3CN and 4 mL of EtOH gave a product with δ ^{31}P 28.4 (CH_3CN), presumably the shift of ethyl isopropyl methylphosphonate, with minor signals at δ 5.8 and 0.88. The photolysis of **16** in CH_3CN with isopropyl alcohol as the trapping agent as above gave the same product with δ ^{31}P 28.9 (CH_3CN) and the minor by-product at δ 5.6.

d. Propyl Ester **17**. The experiment was performed as above on 0.16 g of a mixture of **17** with ^{31}P ($CDCl_3$) δ 57.49, 56.62, 55.57, and 53.91 (ratio 32:31:24:12) available from previous work [7]. The product, after 6 hours of photolysis in 5 mL of propyl alcohol and 50 mL of acetonitrile, contained no starting material signals and had a major signal at δ 30.7 for **21** with minor signals at 8.01 and −0.64. The signal at δ 8.01 was split to a doublet ($^1J_{PH}$ = 694 Hz) by hydrogen and is assigned to dipropyl H-phosphonate, **25** (Ref. [21] δ 6.5–7.4, $^1J_{PH}$ = 685 Hz).

Photolysis of Mixed Ethyl Thiophosphinates **30**

A solution of 15 mg (0.04 mmol) of ester **30** in 0.6 mL of absolute ethanol was irradiated with the Hanovia lamp in a 5 mm quartz tube for 2.5 hours. The ^{31}P NMR spectrum (ethanol) showed that all of the starting ester **30** had been consumed and the only product **32** had δ 94.7 (Ref. [16] δ 96). Structure **32** was confirmed by GC-MS. Calcd for $C_5H_{13}O_2PS$, M^+ 168; found, m/z 168 (92%), 79 (100%).

ACKNOWLEDGMENT

We are grateful to the donors of the Petroleum Research Fund of the American Chemical Society for a grant in support of this work. One of the authors (GK) acknowledges the support of OTKA through Grant No. 1170.

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