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2,6-Dimethoxyphenylphosphetane sulfide—synthesis, structure and exploratory photochemistry[☆]

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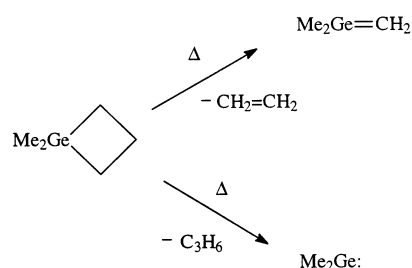
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Abstract

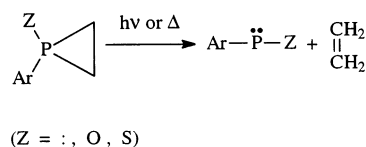
2,6-Dimethoxyphenylphosphetane sulfide has been synthesized by condensation of 2,6-dimethoxyphenylphosphine with 1,3-propanediol ditosylate and treatment of the resulting phosphetane with sulfur. Irradiation at 254 nm of the phosphetane sulfide was undertaken to determine the mode of photodissociation and the types of reactive intermediates produced. Evidence is presented for the formation of both the corresponding arylphosphinidene sulfide $\text{ArP}=\text{S}$ and the methylene(thio)phosphorane $\text{ArP}(\text{S})=\text{CH}_2$ as transient species. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Phosphetane sulfide; Phosphinidene sulfide; Methylene(thio)phosphorane

The ring-strain embodied in three- and four-membered heterocycles is known to facilitate their dissociation to reactive intermediates. In the silicon series siliranes have been found to be excellent precursors for the thermal and photochemical generation of silylenes R_2Si : [1], while siletanes have long been known to yield silenes $\text{R}_2\text{Si}=\text{CR}_2$ [2]. Germiranes are generally unstable [3], but germetanes seem capable of decomposing to either germynes R_2Ge : or germenes $\text{R}_2\text{Ge}=\text{CR}_2$, as the following example suggests [4]:



In recent work it has been demonstrated that phosphiranes and their chalcogenides are also efficient precursors for the photochemical and pyrolytic generation of phosphinidenes and their chalcogenides [5–9]:



Comparison of the reactivity of phosphinidenes $\text{R}-\text{P}$ (isolobal with nitrenes) and their chalcogenides $\text{R}-\text{P}=\text{O}$ and $\text{R}-\text{P}=\text{S}$ (long recognized as isolobal with carbenes) [10] is of current interest because the differences in the symmetry of their HOMOs should lead to differences in reaction pathways if transition-state structures maximize frontier orbital overlap [11]. While differences between ‘carbene-like’ $\text{R}-\text{P}=\text{Z}$ and ‘nitrene-like’ $\text{R}-\text{P}$ in the mechanisms of such reactions as addition to π -bonds remain to be firmly established, the evidence is mounting [9], and the prospects for the control of phosphinidene reactivity by altering their HOMO energies are excellent.

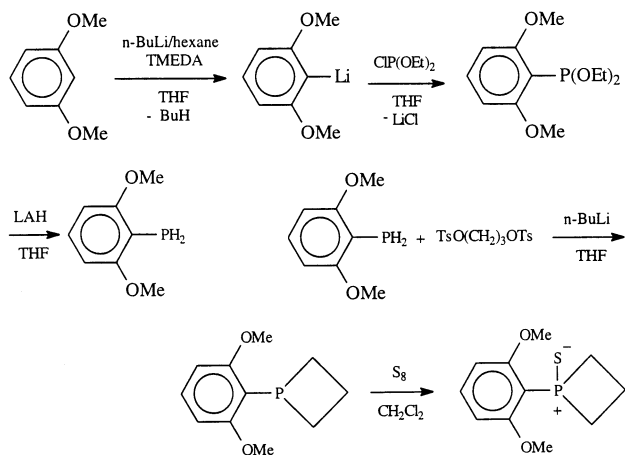
In the present work a chalcogenide of an arylphosphetane has been synthesized employing improvements

[☆] Dedicated to Professor Alan Cowley, on the occasion of his 65th birthday.

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[5] in the condensation of primary phosphines with diol ditosylates originally developed by Oshikawa and Yamashita [12]. It has been established that the P–C bond forming steps are clean S_N2 processes occurring with inversion of absolute configuration, and thus, optically active phosphiranes could be synthesized from optically pure chiral diols [13]. This strategy was extended by Marinetti and coworkers to the synthesis of chiral phosphetanes [14].

The phosphetanes examined in this work were synthesized by the following route:



In Figs. 1 and 2 ORTEP drawings of the X-ray crystal structure of the phosphetane sulfide are shown [15]. Table 1 gives crystal data and structure refinement parameters and Table 2 presents selected bond lengths and angles. The phosphetane ring is puckered by 28.5° (dihedral angle between the planes C1–P1–C3 and C1–C2–C3) with S pseudo-axial and 34.2° with S pseudo-equatorial [16]. Such puckering of more highly substituted phosphetane chalcogenides has been noted,

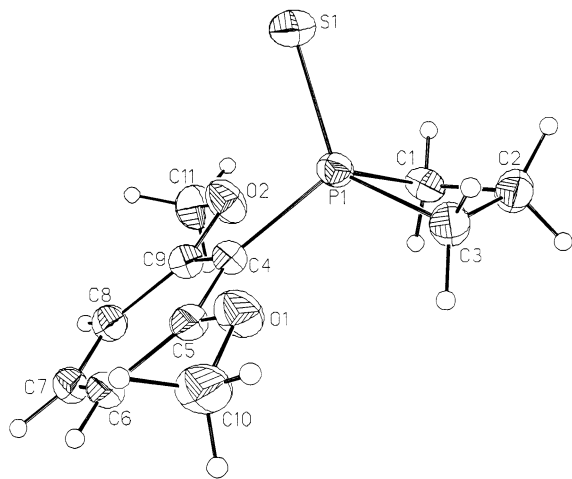


Fig. 1. ORTEP drawing of the X-ray crystal structure of 2,6-dimethoxyphenylphosphetane sulfide, S pseudo-axial, 25% thermal ellipsoids.

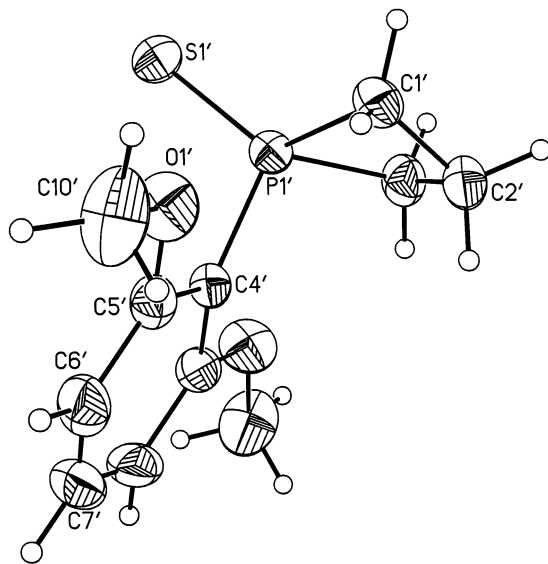


Fig. 2. ORTEP drawing of the X-ray crystal structure of 2,6-dimethoxyphenylphosphetane sulfide, S pseudo-equatorial, 25% thermal ellipsoids.

with a pucker angle of 17.6° for 1-L-menthyl-2,2,4,4-tetramethylphosphetane oxide [17]. A pucker angle of 24.4° has been calculated for unsubstituted phosphetane [18]. A larger pucker angle should favor extrusion of a phosphinidene chalcogenide upon photodissociation, relative to (2+2) cycloreversion. The reverse of such a cycloreversion, the (2+2) cycloaddition of phospho-alkene metal complexes to olefins has been accomplished by Marinetti and Mathey [19].

Solutions of the phosphetane sulfide were irradiated at 254 nm in order to determine what modes of photodissociation operate. In separate experiments, a 0.05 M solution of 2,6-dimethoxyphenylphosphetane sulfide in a 1:1 v/v mixture of CH_2Cl_2 and MeOH and a 0.1 M solution of the phosphetane sulfide in CD_3OD were irradiated at 254 nm. As indicated in Table 3, cyclopropane and propylene were detected in both experiments, and ethylene was found in the fully deuterated solvent that permitted its observation. The coproduct of unimolecular photoelimination of cyclopropane and propylene from the phosphetane sulfide should be 2,6-dimethoxyphenylphosphinidene sulfide ArP=S , and evidence for its formation is given below. The coproduct of unimolecular extrusion of ethylene from the phosphetane sulfide should be the methylene(thio)phosphorane ArP(S)=CH_2 , and evidence for its formation has also been found. Photoinduced ring expansion of the phosphetane sulfide can also be inferred. Complete characterization of the products has thus far been thwarted by difficulties in their purification from small-scale experiments.

Table 1
Crystal data and structure refinement parameters

Empirical formula	C ₁₁ H ₁₅ O ₂ PS
Formula weight	242.26
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	
<i>a</i> (Å)	12.1641(2)
<i>b</i> (Å)	29.7785(4)
<i>c</i> (Å)	10.1361(1)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	3671.59(9)
<i>Z</i>	12
<i>D</i> _{calc.} (Mg mm ⁻³)	1.315
Absorption coefficient (mm ⁻¹)	0.374
Crystal size (mm ³)	0.44 × 0.40 × 0.33
Theta range for data collection (°)	1.37–25.00
Index ranges	–15 ≤ <i>h</i> ≤ 15, –37 ≤ <i>k</i> ≤ 37, –12 ≤ <i>l</i> ≤ 12
Reflections collected	37930
Independent reflections	3302 [<i>R</i> _{int} = 0.14]
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3291/0/212
Goodness-of-fit on <i>F</i> ²	1.007
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.0947
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0886, <i>wR</i> ₂ = 0.1097
Extinction coefficient	0.0020(5)
Largest difference peak and hole (e Å ⁻³)	0.296 and –0.434

Consumption of the phosphetane sulfide was much more rapid in the mixed solvent system, in which the ³¹P chemical shift for the methanol adduct of the arylphosphinidene sulfide ArPH(S)OMe (55.9 ppm) [20] was observed. The corresponding deuterated adduct was not observed when the solvent was pure CD₃OD.

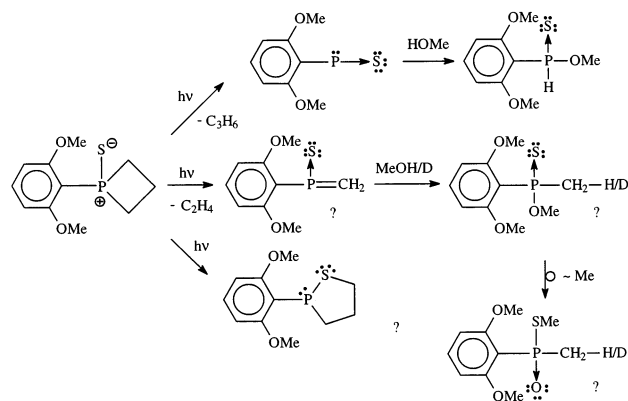
Table 2
Selected bond distances (Å) and angles (°) for compound 1

S Pseudo-axial		S Pseudo-equatorial	
<i>Bond lengths</i> (Å)			
P(1)–C(4)	1.800(3)	P(1')–C(4')	1.801(4)
P(1)–S(1)	1.9523(10)	P(1')–S(1')	1.9605(14)
P(1)–C(1)	1.821(3)	P(1')–C(1')	1.832(3)
P(1)–C(3)	1.813(3)	P(1')–C(3')	1.832(3)
C(1)–C(2)	1.537(4)	C(1')–C(2')	1.532(4)
C(2)–C(3)	1.541(4)	C(2')–C(3')	1.531(4)
<i>Bond angles</i> (°)			
C(3)–P(1)–C(1)	78.67(12)	C(3')–P(1')–C(1')	76.7(2)
C(2)–C(1)–P(1)	88.6(2)	C(2')–C(1')–P(1')	88.5(2)
C(2)–C(3)–P(1)	88.7(2)	C(2')–C(3')–P(1')	88.5(2)
C(4)–P(1)–S(1)	114.24(9)	C(4')–P(1')–S(1')	109.69(12)
C(4)–P(1)–C(1)	111.82(12)	C(4')–P(1')–C(1')	108.71(13)
C(4)–P(1)–C(3)	113.11(12)	C(4')–P(1')–C(3')	108.71(13)

In both solvent systems, a major product observed in the ³¹P-NMR spectrum displays a chemical shift (20.8 ppm) appropriate for a tricoordinate phosphorus compound. Since a major product in both solvent systems was revealed by GC–MS analysis to be isomeric with the starting material, ring-expansion appears to be one of the photoprocesses [21].

The product chemical shift at 75.6 ppm formed in all the irradiations is consistent with a methanol adduct of ArP(S)=CH₂, or its rearrangement product [22], and GC–MS analysis revealed the formation of a product corresponding in mass to the addition of CH₃OH and CD₃OD, respectively to ArP(S)=CH₂ when these isotopomers were employed as solvent. Alcohol adducts of methylene(thio)phosphoranes generated by other routes, PhP(S)=CPh₂ [23], 2,6-Me₂PhP(S)=CPh₂ [24], and PhP(S)=CH₂, [25], have been observed.

The hydrocarbon coproducts of photolysis leave little doubt concerning the reactive intermediates formed upon fragmentation of the phosphetane sulfide, and the spectroscopic data recorded for the phosphorus-containing products of trapping experiments lend support to the following reaction scheme. However, it must remain tentative until the rearrangement and trapping products are fully characterized.



What is clear, however, is that the ultraviolet irradiation of phosphetane derivatives is a promising new source of reactive species.

1. Experimental

1.1. General data

All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Photolyses were carried out in a Rayonet RS photochemical reactor (model number RPR-208, 120 W radiated power) equipped with low-pressure mercury lamps emitting 254-nm radiation. ¹H-, ¹³C-, and ³¹P-NMR spectra were recorded on Varian XL-300, Gemini-300 (¹³C 75.4 MHz, ³¹P 121.4 MHz), XL-500 (¹³C

Table 3
Results of 254 nm irradiation of 2,6-dimethoxyphenylphosphetane sulfide

Solvent	Time (min)	Conversion (%)	³¹ P chemical shifts of products δ	Hydrocarbon yields (%)		
				<i>cyclo</i> -(CH ₂) ₃	Propene	Ethylene
MeOH-CD ₂ Cl ₂	40	83	4.2, 20.8, 55.9, 75.6	22	15	^a
CD ₃ OD	40	17	20.8, 70.4, 75.6	20	14	17
CD ₃ OD	130	76	20.8, 49.8, 70.4, 75.6	30	17	25
CD ₃ OD	190	89	20.8, 49.8, 70.4, 75.6	32	17	26

^a Not determined because of overlapping peaks in the ¹H-NMR spectrum employed to determine yields.

125 MHz, ³¹P 202.3 MHz) and XL-600 (¹³C 250 MHz) spectrometers. 85% H₃PO₄ was employed as an external standard for ³¹P spectra. Recorded yields are based on starting materials consumed and were determined by integration of ³¹P-NMR spectra. Combined gas chromatography–mass spectrometry was performed on a Hewlett-Packard Model 5890 Series II instrument fitted with a Quadrex 25-m \times 0.32 mm capillary column coated with 0.5 μ m polymethyl (5% phenyl) silicone bonded phase, connected to a Model 5971 Mass Selective detector (quadrupole mass filter), mass spectra recorded above *m/e* 40, ionization energy 70 eV.

1.2. Materials

Benzene, THF, ether, and pyridine were dried by and distilled from benzophenone sodium ketyl under a nitrogen atmosphere immediately before use. Calcium hydride was the drying agent for pentane, cyclohexane, and hexane. CH₂Cl₂ was distilled from P₂O₅. The following were employed as received, except as noted: 2-bromomesitylene (Aldrich, 99%), ethylene (Aldrich, 99.9%), PCl₃ (Aldrich, 98%, distilled under N₂ before use), P(OEt)₃ (Aldrich, 98%), *n*-BuLi (Fisher, 1.6 M or Aldrich, 2.5 M in hexane), LiAlH₄ (Aldrich, 95%), 1,3-propanediol (Sigma, 98%), 1,3-dimethoxybenzene (Aldrich, 99%, distilled under N₂ from Na before use), TMEDA (Aldrich, 99%, dried with *n*-BuLi and distilled under N₂), *p*-toluenesulfonyl chloride (Aldrich, 98%), H₂O₂ (Aldrich, 30%), H₂O₂-urea complex (Aldrich, 98%), sulfur (Mallinckrodt, sublimed), benzene-*d*₆ (Aldrich, 99.6%), CD₂Cl₂ (Aldrich, 99.95%), CD₃OD (Aldrich, 99.8%), CDCl₃ (Aldrich, 99.8%), Ph₃P (Aldrich, 99%), W(CO)₆ (Aldrich, 99%), BH₃-SMe₂ (Aldrich, 2.0 M in Et₂O).

1.3. Chlorodiethylphosphite CIP(OEt)₂

Chlorodiethylphosphite CIP(OEt)₂ was synthesized as a colorless liquid, b.p. 56–58°C/30 Torr in a 53% yield (50 g) using the method of Cook et al [26]: ³¹P-NMR (121.4 MHz, CDCl₃) 166 (lit. [27] δ 165). There is a ca. 10% Cl₂POEt impurity: ³¹P-NMR δ 178 (lit. [21] 177).

1.4. 2,6-Dimethoxyphenylphosphine

A total of 13.8 g (0.1 mol) 1,3-dimethoxybenzene, 11.6 g (0.1 mol) TMEDA, and 150 ml THF were placed in a 500-ml three-necked flask equipped with a 100-ml pressure equalizing dropping funnel, magnetic stirring bar, septum, and a nitrogen inlet, and the reaction flask was cooled to 0°C. A total of 42 ml 2.5 M *n*-BuLi (0.105 mol) in hexane was slowly added to the mixture, which was then stirred for 4 h at room temperature (r.t.). The resulting yellowish solution of 2,6-dimethoxyphenyllithium was transferred by cannula to a 250-ml pressure-equalizing dropping funnel (flushed with nitrogen) that was installed on a 500-ml three-necked flask equipped with a magnetic stirring bar, nitrogen inlet and septum. 15.7 g (0.1 mol) CIP(OEt)₂ and 100 ml THF were placed in this flask which was equipped with a magnetic stirring bar, septum, and nitrogen inlet, and was cooled to 0°C. The solution of 2,6-dimethoxyphenyllithium was added slowly, and then the reaction mixture was stirred overnight. The mixture was concentrated to ca. 50 ml, and 300 ml pentane was added to precipitate LiCl. After filtration and removal of solvent, 24 g of an orange liquid was obtained whose ³¹P-NMR spectrum indicated that > 90% of the phosphorus containing compounds present was the target diethyl(2,6-dimethoxyphenyl)phosphite (δ 163, MS (EI) *m/e* (relative intensity) 258 (*M*⁺, 100), 227 (32), 201 (84), 183 (93), 171 (53), 155 (38), 141 (83)). This crude product was employed in the next step. LiAlH₄ (0.8 g, 0.2 mol) and 200 ml THF were placed in a 1 l three-necked flask equipped with a 150 ml pressure-equalizing dropping funnel, mechanical stirrer, and a Friedrichs condenser capped with a nitrogen inlet. After the slurry was cooled to –30°C with stirring, 19.4 g (0.179 mol) Me₃SiCl was added dropwise, and the mixture was allowed to warm to r.t. and stirred for 1.5 h. The mixture was cooled to 0°C and a solution of 23.3 g (0.090 mol) diethyl(2,6-dimethoxyphenyl)phosphite in 100 ml THF was added slowly. The mixture was stirred for 6 h, and ³¹P-NMR indicated complete conversion of the phosphite and a primary phosphine as the major product. After excess LiAlH₄ was quenched with 40 ml degassed MeOH, and

filtration, the yellowish filtrate was concentrated and product collected by reduced pressure distillation 90–100°C/ca. 1 Torr, yielding 10.2 g (55%) of crude product. Recrystallization from hexane at –20°C provided colorless crystals, m.p. 39.5°C of 2,6-dimethoxyphenylphosphine: ^{31}P -NMR (121.4 MHz, C_6D_6) δ –172 (t, $J_{\text{H-P}} = 205.2$ Hz); ^1H -NMR (300 MHz, C_6D_6) δ 3.32 (s, 6 H, OCH_3), 4.06 (d, 2 H, $J_{\text{P-H}} = 210.6$ Hz, PH_2), 6.25 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz, *m-H*), 7.02 (t, 1H, $J_{\text{H-H}} = 8.2$ Hz, *o-H*); $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.4 MHz, CD_3CN) δ 57.0 (s, OCH_3), 105.1 (d, $J_{\text{P-C}} = 17.4$ Hz, *m-C*), 118.6 (s, *ipso-C*), 130.8 (s, *p-C*), 161.6 (d, $J_{\text{P-C}} = 4.6$ Hz, *o-C*); MS (EI) *m/e* (relative intensity) 170 (M^+ , 100), 153 (23), 138 (46), 109 (20).

1.5. 1,3-Propanediol ditosylate

1,3-Propanediol ditosylate was synthesized using the method of Corey and Mitra [28] in a 69% yield (68 g, recrystallized from EtOH), m.p. 125–126°C (lit. [23] 126–127°C).

1.6. 2,6-Dimethoxyphenylphosphetane sulfide

To 2.28 g (5.93 mmol) 1,3-propanediol ditosylate in a 250 ml Schlenk flask containing a magnetic stirring bar and capped with a septum was added 1.00 g (5.88 mmol) 2,6-dimethoxyphenylphosphine and 150 ml THF. Then 7.5 ml of 1.6 M *n*-BuLi was added dropwise by syringe to the stirred reaction mixture which had been cooled to 0°C. The mixture was stirred for 60 min and a ^{31}P -NMR spectrum of an aliquot revealed that no primary phosphine (δ –172) remained, and a single major product (δ –10.8) had been formed. After excess *n*-BuLi was quenched with 0.1 ml (0.8 mmol) Me_3SiCl and excess Me_3SiCl solvent was removed under vacuum, 150 ml pentane was added to precipitate lithium salts. Filtration and evaporation of the solvent yielded 1.05 g (86%) 2,6-dimethoxyphenylphosphetane as a slightly yellow liquid containing no other phosphorus compounds: ^{31}P -NMR (121.4 MHz, CD_2Cl_2) δ –10.86. Further purification was discouraged by its instability.

To a solution of the crude 2,6-dimethoxyphenylphosphetane (1.05 g, 5.00 mmol) in 30 ml CH_2Cl_2 contained in a 100 ml flask with a magnetic stirring bar was added 1 g (31 mmol) sulfur. After 45 min of stirring ^{31}P -NMR spectroscopy indicated that the phosphetane (δ –10.86) was completely converted to a new product (δ 50.1). The solvent was removed under vacuum, and addition of 5 ml CH_2Cl_2 dissolved the product and allowed the excess sulfur to be removed by filtration, yielding 1.185 g (98%) crude product as a light-yellow oil. Chromatography on silica gel with CH_2Cl_2 eluent yielded 0.72 g (60%) of a light-yellow solid, from which

light-yellow crystals were obtained by recrystallization from 1:9 CH_2Cl_2 –EtOAc: m.p. 119–120°C; ^{31}P -NMR (121.4 MHz, CD_2Cl_2) δ 50.1; ^1H -NMR (300 MHz, CD_2Cl_2) δ 1.90–3.28 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.88 (s, 6H, OCH_3), 6.61 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz, *m-CH*), 6.63 (d, 1H, $J_{\text{H-H}} = 8.4$ Hz, *m-CH'*) 7.42 (t, 1H, $J_{\text{H-H}} = 8.4$ Hz, *p-CH*); $^{13}\text{C}\{^1\text{H}\}$ -NMR (150.9 MHz, CD_2Cl_2) δ 16.8 (d, $J_{\text{P-C}} = 19.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 38.5 (d, $J_{\text{P-C}} = 53.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 56.3 (s, OCH_3), 104.7 (d, $J_{\text{P-C}} = 4.7$ Hz, *m-C*), 111.8 (d, $J_{\text{P-C}} = 61.0$ Hz, *ipso-C*), 134.0 (s, *p-C*), 161.1 (s, *o-C*); MS (EI) *m/e* (relative intensity) 242 (M^+ , 97), 199 (25), 185 (37), 167 (100), 153 (44). Anal. Calc. for $\text{C}_{11}\text{H}_{13}\text{O}_2\text{PS}$: C, 54.53; H, 6.25; observed: C, 54.51; H, 6.35%.

2. X-ray diffraction study

A crystal of appropriate dimensions was mounted on a glass fibers in a random orientation. Preliminary examination and data collection were performed employing a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer using graphite monochromated Mo– K_α radiation ($\lambda = 0.71073$ Å) equipped with a sealed tube X-ray source at r.t. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ω) scans. A typical data set collected consists of 4028 frames of intensity data collected with a frame width of 0.3° in ω and counting time of 15 s per frame at a crystal to detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages [29] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections ($\theta < 25^\circ$). Collected data were corrected for systematic errors using SADABS [30] based upon the Laue symmetry using equivalent reflections. The integration process yielded 37930 reflections of which 3302 ($2\theta < 50^\circ$) were independent reflections.

Crystal data and intensity data collection parameters are listed in Table 1.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package [31]. The structure was solved by direct methods and refined successfully in the space group *Pnma* with $z = 12$ suggesting 1.5 molecules per asymmetric unit. No missing symmetry was confirmed by Platon. Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding model (AFIX

m3). The final residual values were $R(F) = 4.66\%$ for 2104 observed reflections [$I > 2\sigma(I)$] and $wR(F_2) = 10.97\%$; $s = 1.07$ for all data. Structure refinement parameters are listed in Table 1. Selected geometrical parameters are listed in Table 2. A projection view of the molecule with non-hydrogen atoms represented by 25% probability ellipsoids showing the atom labeling is presented in Figs. 1 and 2.

3. Ultraviolet irradiation of 2,6-dimethoxyphenylphosphetane sulfide

3.1. Gas mixture preparation

A small quantity of propene was prepared sweeping the product with a slow stream of nitrogen from a reaction mixture prepared by dropping freshly distilled 2-bromopropane into a gently refluxing 4 M solution of NaOH in EtOH [32]. The propene was collected in a liquid nitrogen trap from which it was transferred by trap-to-trap distillation on a vacuum line to a 4 mm o.d. Pyrex tube into which ethylene was condensed from a metal cylinder. A small quantity of cyclopropane was prepared by sweeping the product with a slow nitrogen stream from a reaction mixture prepared by dropping freshly distilled 1,3-dibromopropane into a suspension of zinc powder in a gently refluxing mixture of 75% EtOH and 25% H₂O [33].

The cyclopropane was collected in a liquid nitrogen trap and transferred to the pyrex tube containing ethylene and propene. CD₃OD was added as solvent and the solution degassed to 10⁻⁴ Torr by three freeze-pump-thaw cycles. The ¹H-NMR spectrum of this sample facilitated detection and yield determination for ethylene (δ 5.34), propylene (δ 1.65–1.70, 4.80–5.04, and 5.71–5.86) and cyclopropane (δ 0.31) among the irradiation products.

4. Irradiation of 2,6-dimethoxyphenylphosphirane sulfide in 1:1 CH₃OH–CD₂Cl₂

A 0.05 M solution of 2,6-dimethoxyphenylphosphetane sulfide was prepared by dissolving 5.0 mg (0.021 mmol) of the crystalline compound in a mixture of 0.2 ml CD₂Cl₂ and 0.2 ml CH₃OH. The solution was placed in a 4 mm o.d. quartz tube, which was sealed with a torch after three cycles of freeze-pump-thaw degassing at 10⁻⁴ Torr. This sample was irradiated at 254 nm at 15°C for 40 min. ³¹P- and ¹H-NMR spectra were recorded before and after irradiation, and indicated 83% conversion of the phosphetane sulfide. The NMR results are included in

Table 3. The largest peak in the GC–MS integrated ion current mass chromatogram (C₂H₄ and C₃H₆ not detectable under these conditions) corresponds to a product isomeric with the starting phosphetane sulfide, retention time 13.2 versus 13.9 min: MS (EI) m/e (relative intensity) (M^+ , 99), 199 (29), 185 (28), 167 (100), 153 (42), 63 (29). The second largest product peak has a parent mass compatible with an adduct of CH₃OH to ArP(S)=H₂: MS (EI) m/e (relative intensity) 246 (M^+ , 8), 232 (65), 200 (52), 185 (100), 167 (43), 153 (35), 139 (25), 123 (13), 109 (19), 93 ((19), 77 (15), 63 (25).

5. Irradiation of 2,6-dimethoxyphenylphosphetane sulfide in CD₃OD

A 0.1 M solution prepared by dissolving 10 mg (0.041 mmol) 2,6-dimethoxyphenylphosphetane sulfide crystals in 0.4 ml CD₃OD was placed in a mm o.d. quartz tube which was sealed with a torch after the solution was degassed by three freeze-pump-thaw cycles at 10⁻⁴ Torr. The sample was irradiated at 254 nm, 15°C, and ³¹P-NMR spectra were recorded before irradiation and after 40, 130, and 190 min. NMR data are included in Table 3. The largest product peak in the GC–MS integrated ion current mass chromatogram was the same compound isomeric with the starting phosphetane sulfide found upon irradiation in CH₃OH–CDCl₂. The mass spectrum of the second most abundant ‘heavy’ product (under conditions not allowing detection of C₂H₄ and C₃H₆) is compatible with an adduct of CD₃OD to ArP(S)=CH₂: MS (EI) m/e (relative intensity) 250 (M^+ , 4), 236 (57), 203 (28), 202 (29), 201 (32), 185 (100), 167 (33), 153 (33), 139 (24), 123 (14), 110 (15), 96 (27), 77 (14), 63 (23).

6. Supplementary material

For the X-ray crystal structures illustrated in Figs. 1 and 2 and the subjects of Tables 1 and 2, complete listings of atomic coordinates and the geometrical parameters for the non-hydrogen atoms, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms have been deposited with the Cambridge Crystallographic Data Center (CCDC 116777). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Tables of calculated and observed structure factors are available in electronic format.

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