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# Generation of Methylenephosphine Oxides by Thermal Fragmentation of Derivatives of the 2-Phosphabicyclo[2.2.2]octa-5,7-diene Oxide Ring System

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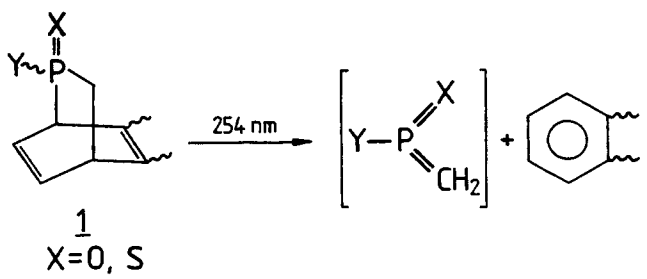
## ABSTRACT

*Differential thermal analysis and differential scanning calorimetry showed that the title compounds decomposed at 240–260°C with release of the fragment RP(O) = $CH_2$. Mass spectral studies also showed this to be a fragmentation pathway. The extruded methylenephosphine oxide could be trapped with ethanol, hydroquinone, or by reaction with the surface OH groups of silica gel.*

## *INTRODUCTION*

Derivatives of the 2-phosphabicyclo[2.2.2]-octadiene oxide ring system (**1**, X = O), prepared by the Diels-Alder cycloaddition of 1,6-dihydrophosphinine oxides with dimethyl acetylenedicarboxylate [1–3], are readily fragmented when irradiated with ultraviolet light [4]. This constitutes a useful technique for the generation of methylenephosphine oxides ($YP(O)CH_2$), which are of great interest as rare species with 3-coordinate phosphorus (Scheme 1). Methylenephosphine sulfides ($YP(S)CH_2$) have been generated in similar fashion from **1** (X = S) [4]. It has been noted in the literature that the methylenephosphine sulfides can also be generated by thermolysis of this bicyclic ring system (**1**, X = S) [3], but the oxides (**1**, X = O) are more resistant to thermal fragmentation [1,3] and have not yet been successfully used in this way as precursors of methylenephosphine oxides. We have explored the conditions needed for the practical thermal fragmentation of several oxides of Type 1. It will be seen that the thermolysis can indeed be performed successfully and the released methylenephosphine oxide trapped by reaction with hydroxylic reagents before it undergoes polymerization. Of particular significance is the discovery that silica gel is effective as a trapping agent through reaction of the OH groups on its surface. This is a process used in the Amherst laboratory




**1**
X=O, S

**SCHEME 1**

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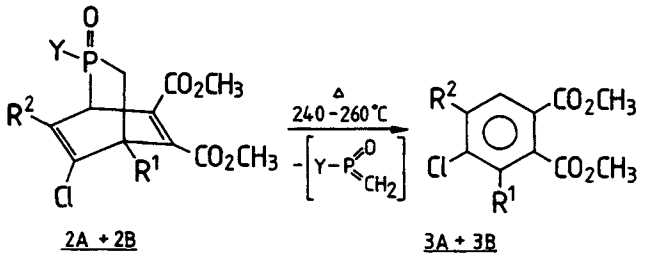



**SCHEME 2**

**TABLE 1** Thermal Parameters of the Cycloadducts (**2a–e**)[a]

| Compound | Decomposition Temperature[b] °C | Δm Measured (Calc.) % | ΔH kJ/mol$^{-1}$ |
|---|---|---|---|
| **a** | 235 (190–275) | 43 (38) | −178.0 |
| **b** | 240 (190–265) | 45 (48) | |
| **c** | 250 (210–280) | 47 (44) | |
| **d** | 260 (215–290) | 45 (46) | −119.7 |
| **e** | 260 (230–280) | 45[c] (46) | |

[a]The TG and DTA curves were obtained on a MOM derivatograph, while DSC measurements were performed on a 990 DuPont thermoanalyzer.
[b]The value for the minimum of the DTG curve; the range is given in parentheses.
[c]Including also the loss of weight at ≈210°C.

for the production of phosphorylated silica gels of various types that have value in special liquid chromatographic applications [5]. The functionality placed on the surface by the trapping with the methylenephosphine oxides is of a new type and will be included in later studies on chromatographic utility.

## *RESULTS AND DISCUSSION*

### *Thermochemical Characteristics of the Fragmentation*

The behavior of several cycloadducts (**2a–e**) when heated in the dry state was first studied with differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. Both techniques showed that an exothermic decomposition occurred in the range of 200–280°C. When the temperature reached ≈240°C, mass spectral examination of the residual material showed that it contained dimethyl chloromethylphthalate isomers **3A** and **3B** ($M^+$ = 242 and 244 for the $^{35}Cl$ and the $^{37}Cl$ isotopes, respectively), as expected if the thermolysis involves the extrusion of the bridging C–P unit (Scheme 2). The decomposition temperatures and, in two cases, enthalpy values are recorded in Table 1.

At the conclusion of the DTA experiments, the weight loss was determined and found to exceed that expected for elimination of the bridging unit YP(O) = $CH_2$. The loss, in fact, agreed with the additional elimination of dimethyl ether from the ester groups to form the phthalic anhydride (Table 1), but it was not possible to obtain supporting evidence for this, due to the poor condition of the sample from the overheating. In the case of isopropyl ester **2e**, significant weight loss occurred at 210°C before the exothermic release of the P–C unit at 260°C and may be due to the elimination of propylene from the ester group. The weight loss of 13% agrees with that calculated for elimination of propylene (12%).

### *Fragmentation in the Mass Spectrometer*

The molecular ion formed from eight cycloadducts (**2a–h**, Table 2) under electron impact (EI) mass spectral conditions was quite unstable and amounted to only 1–4% relative abundance (RA). The molecular mass was, however, confirmed in each case by chemical ionization mass spectra obtained with isobutane. In all but one case (**2g**), the base peak in the EI spectra had $m/z$ = 211 (with the correct isotopic distribution), which corresponds to the fragment from loss of the bridging P–C unit and also one methoxy group from a carboxylate. Examination of metastable peaks revealed that the loss of the methoxy group preceded that of the bridging unit. In the case of **2g**, $m/z$ = 211 had 93% RA. The fragmentation occurred for this compound so as to give the positive ion corresponding to the bridging unit $[Me_2NP(O) = CH_2]^+$, $m/z$ = 105 with 19% RA. The structure of the ejected species was confirmed by HRMS ($M^+_{found}$ = 105.0314; $C_3H_8NOP$ requires 105.0343). The base peak for **2g** was, in fact, an ion with $m/z$ = 90, corresponding to $[MeNP(O) = CH_2]^+$. The stability of these N-containing fragments is of interest, for it may indicate that electron release from nitrogen is involved. Other fragmentation products were detectable in small amounts, but were of less interest. Some of these are recorded in Table 2.

### *Fragmentation in the Presence of Trapping Agents*

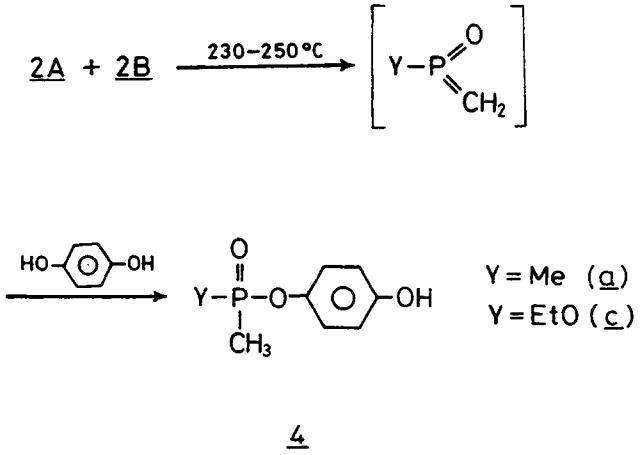
Because of the high temperature necessary to accomplish the generation of the methylenephosphine oxides, our first attempts at performing trapping reactions were based on the use of a non-

**TABLE 2** Mass Spectral Data of the Cycloadducts (**2a–h**)[a]
$R^1$ = Me $R^2$ = H (*A*) and $R^1$ = H $R^2$ = Me (*B*) Y = Me (*a*), Ph (*b*), EtO (*c*), *n*-PrO (*d*), *i*-PrO (*e*), PhO (*f*), $NMe_2$ (*g*) $R^1$ = $R^2$ = Me Y = EtO (*h*) *m/z* (Relative Intensity, %)

| | **2a** | **2b** | **2c** | **2d**[b] | **2e**[c] | **2f**[d] | **2g** | **2h** |
|---|---|---|---|---|---|---|---|---|
| $M^{+e,f}$ | 318 | 380 | 348 | 362 | 362 | 396 | 347 | 362 |
| | (4) | (1) | (1) | (1) | (1) | (3) | (1) | (4) |
| $M\text{-}CH_3\rceil^{+f}$ | 303[a] | 365 | 333 | 347 | 347 | 381 | 332 | 347 |
| | (8) | (9) | (6) | (4) | (1) | (14) | (7) | (25) |
| $M\text{-}CH_3O\rceil^{+f}$ | 287 | 349 | 317 | 331 | 331 | 365 | — | 331 |
| | (5) | (2) | (3) | (3) | (1) | (5) | — | (6) |
| $M\text{-}Cl\rceil^{+}$ | 283 | 345 | 313 | 327 | — | 361 | — | 327 |
| | (7) | (7) | (2) | (1) | — | (2) | — | (4) |
| $M\text{-}CH_3\text{-}CH_3OH\rceil^{+f}$ | 271 | 333 | 301 | 315 | 315 | 349 | 300 | — |
| | (12) | (7) | (2) | (1) | (1) | (8) | (5) | — |
| $M\text{-}CO_2CH_3\rceil^{+f}$ | 259 | 321 | 289 | 303 | 303 | 337 | 288 | 303 |
| | (78) | (44) | (29) | (12) | (5) | (91) | (31) | (40) |
| $M\text{-}CO_2CH_3\text{-}(Y\text{-}O)+H\rceil^{+f}$ | — | — | 261 | 261 | 261 | — | — | 275 |
| | — | — | (27) | (26) | (29) | — | — | (30) |
| $M\text{-}CH_3O\text{-}YP(O)CH_2\rceil^{+f}$ | 211 | 211 | 211 | 211 | 211 | 211 | 211 | 225 |
| | (100) | (100) | (100) | (100) | (100) | (100) | (93) | (100) |
| $YP(O)CH_2\rceil^{+}$ | — | — | — | — | — | — | 105 | — |
| | — | — | — | — | — | — | (19) | — |
| $YP(O)CH_2\text{-}CH_3\rceil^{+}$ | — | — | — | — | — | — | 90 | — |
| | — | — | — | — | — | — | (100) | — |

[a]Recorded on a MS 25 RFA spectrometer at 70 eV.
[b]$M\text{-}Pr\rceil^{+}$ (2%), [c]$M\text{-}Pr\rceil^{+}$ (2%), [d]$Ph^{+}$ (69%).
[e]Confirmed by CI mass spectra.
[f]The *m/z* values are listed for the $^{35}Cl$ isotope.

volatile hydroxy compound mixed in with the solid cycloadduct. Hydroquinone was used for this purpose, in five-fold excess. Thermolysis was performed at 230–250°C, as suggested from the DTA and DSC experiments. The products so obtained from the two cycloadducts **2a** and **2c** were purified by flash chromatography and analyzed by $^{31}P$ NMR. The $^{31}P$ NMR shift obtained for the product from **2a** ($\delta$ = 49.7) was of the proper magnitude for an ester of dimethylphosphinic acid (**4a**, cf. to $\delta$ = 52.6 for $Me_2P(O)OEt$ [3]), and a high-resolution mass spectral analysis of the product gave the correct value for $M^+$ (Scheme 3). Similarly, cycloadduct **2c** gave a product with $\delta^{31}P$ = 24.5, which is consistent with an ester of a phosphonic acid (**4c**, cf. to $\delta$ = 30.7 for $MeP(O)(OEt)_2$ [3]), again confirmed with high-resolution MS. Under these conditions, the yield of trapping products was low (≈7% in both cases), probably due to polymerization of the reactive intermediates.

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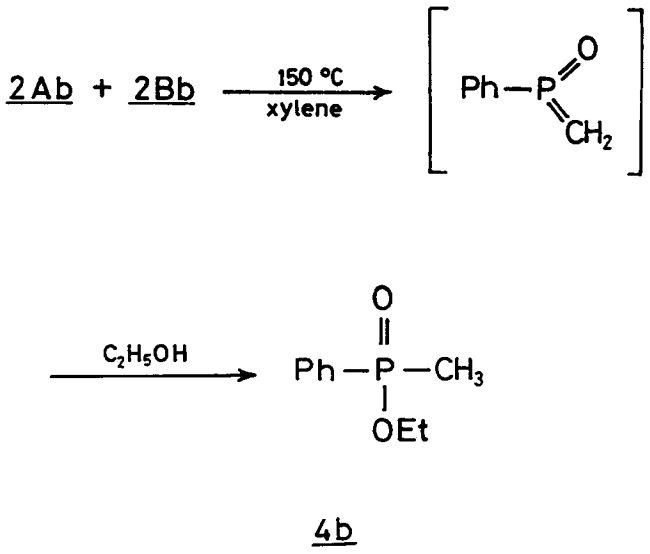
**SCHEME 3**

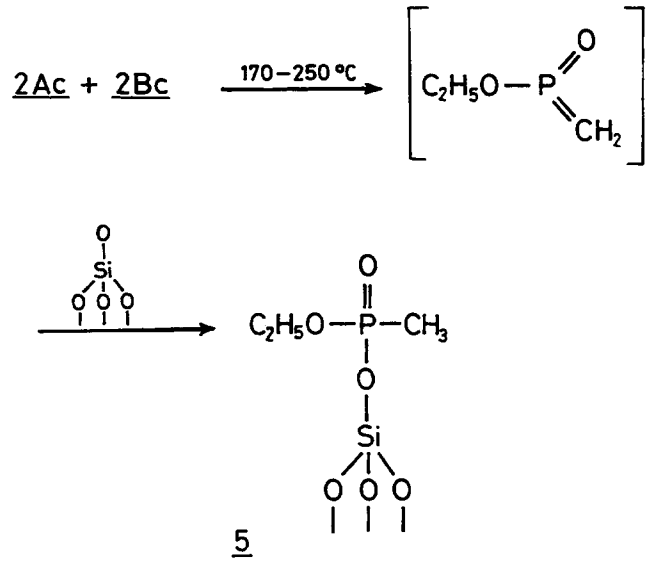
It was then found that the fragmentation of the P-phenyl cycloadduct (**2b**) could be effected in xylene solution at 150°C, but the reaction was quite slow (Scheme 4). Under these conditions, ethanol could be employed as the trapping agent. The progress of the reaction was monitored by $^{31}P$ NMR; the reaction was stopped after 10 hours, at which time about 10% of the starting compound remained unchanged. The only new $^{31}P$ NMR signal was that for the expected product, ethyl methylphenylphosphinate (**4b**, $\delta$ = 42.1; Ref. [2] $\delta$ = 42.1). However, the P-alkoxy cycloadducts (**2c–e**) remained unchanged even after 48 hours in refluxing xylene. The data in Table 1 also suggest their higher stability.

The next and critical experiments employed silica gel as the trapping agent. Ester **2c** was used for this purpose. A solution of the ester in dichloromethane was used to impregnate the silica gel; the dichloromethane was removed by evaporation,




**SCHEME 4**

and the residual solid was heated at 250°C for 5 minutes. A second sample was heated at 170°C for 3 hours. The samples were examined directly by solid-state $^{31}P$ NMR using the CP-MAS technique, as in our other studies [5]. The samples gave very similar spectra; the major signal appeared at $\delta$ = 19.5, with a minor signal as a shoulder at $\delta$ = 28.7. The major signal may be assigned to structure **5** (Scheme 5); the signal is several ppm upfield of that for an alkyl ester of a phosphonate (e.g., $MeP(O)(OEt)_2$, $\delta$ = 30.7 [3]), an effect observed consistently when phosphorus acids are silylated with simple reagents or when they are bonded to silica gel [5]. The minor signal probably arises from adsorbed ethyl methylphosphonate, which would be formed from the addition of water to the released methylenephosphine oxide. Traces of water are inevitably present and cause a minor complication in other studies on phosphorylations of silica gel [5].




**SCHEME 5**

We have therefore shown that silica gel is a highly effective trapping agent for methylenephosphine oxides. In spite of the high temperature requirement, the process can be easily conducted on the impregnated solid, thus making available a new type of functionalized silica. The photochemical generation of the methylenephosphine oxides from the cycloadducts is, of course, much faster and occurs at room temperature. However, this technique fails in the presence of suspended silica gel, and therefore the thermal method indeed has practical value.

## *EXPERIMENTAL*

The TG and DTA curves were determined with a MOM derivatograph using 50 mg samples in platinum crucibles in static air at a heating rate of 5°C $min^{-1}$. The DSC measurements were performed on a 990 DuPont thermoanalyzer at a heating rate of 5°C $min^{-1}$ in static air with 2 mg samples in aluminum crucibles.

Mass spectra were obtained on a MS 25-RFA spectrometer at 70 eV.

The $^{31}P$ NMR spectra were recorded with an IBM NR-80 instrument with 85% $H_3PO_4$ as external standard. CP-MAS $^{31}P$ NMR measurements were performed with a Bruker-200 solids spectrometer with $CaHPO_4$ as reference.

Phosphabicyclooctadienes **2a**, **c–e** were synthesized as described in Ref. [2]; three additional derivatives (**2b**, **2f**, and **2h**) were prepared by an extension of the earlier method.

### *4- and 6-Methyl-5-chloro-2-dimethylamino-7,8-di(methoxy-carbonyl)-2-phosphabicyclo[2.2.2]octa-5,7-diene 2-Oxide.* (**2Ag** *and* **2Bg**)

To 1.0 g (2.87 mmol) of the P-ethoxy compound (**2c**) in 20 mL of dichloromethane was added 0.63 g (3.02 mmol) of phosphorus pentachloride. The contents of the flask were stirred for 15 minutes at room temperature and for 3.5 hours at reflux. Evaporation of the volatile components in vacuo provided the P-chloro compound (**6**) in a form suitable for further transformation. Mass spectroscopy *m/z* (relative intensity) 338 (4), 323 (9), 307 (9), 303 (4), 279 (38), 211 (100).

Intermediate **6** from the previous reaction was dissolved in 20 mL of benzene, and 0.39 g (8.67 mmol) of dimethylamine in 10 mL of benzene was added dropwise at 0°C. After completion of the addition, the cooling bath was removed and the mix-

ture stirred at room temperature for 3 hours. The precipitate was filtered off and the filtrate evaporated. The residue so obtained was purified by column chromatography (silica gel, 2% methanol in chloroform) to give 0.40 g (40%) of **2g** as a mixture of four isomers: $^{31}P$ NMR ($CDCl_3$) $\delta$ = 51.7, 51.3, 48.2, and 47.7; $^1H$ NMR ($CDCl_3$) $\delta$ 2.65 (d, $^3J_{PH}$ = 11 Hz) and 2.67 (d, $^3J_{PH}$ = 11 Hz), total intensity 6H, for the $NMe_2$ groups of the isomers; 3.83 (s), 3.80 (s), and 3.79 (s), total intensity 6H, for the $CO_2Me$ groups of the isomers: IR (neat) 1720, 1640, 1260 $cm^{-1}$; MS, Table 2.

### *Thermal Fragmentation of the Isomers,* (**A** *and* **B**) *of P-Methyl and P-Ethoxy Phosphabicyclooctadienes* (**2a** *and* **2c**) *in the Presence of Hydroquinone*

A mixture of 0.4 g (1.15 mmol) of **2a** (consisting of four isomers with $\delta^{31}P$ = 57.2, 56.7, 55.4, and 53.7) and 0.38 g (3.54 mmol) of hydroquinone was heated at 230°C for 7 minutes. The resulting material was taken up in chloroform and purified by column chromatography (silica gel, 3% methanol in chloroform) to give 15 mg (7%) of **4a**. The $^{31}P$ NMR (THF) $\delta$ 49.7; $M^+_{found}$ = 186.0494, $C_6H_{11}O_3P$ requires 186.0446.

Heating **2c** at 170°C for 12 hours resulted in 6% of **4c** after a similar work-up procedure: $^{31}P$ NMR ($CDCl_3$) $\delta$ + 24.5; $M^+_{found}$ = 216.0569, $C_9H_{13}O_4P$ requires 216.0551. The phthalate (**3**) could also be obtained from the mixture (11%): MS, *m/z* (relative intensity) 242 ($M^+$, 6), 211 (100), 152 (70).

### *Thermal Fragmentation of the Isomers* (**A** *and* **B**) *of P-Phenyl Phosphabicyclooctadiene* (**2b**) *in Xylene Solution in the Presence of Ethanol*

A solution of 21 mg (0.55 mmol) of phosphine oxide **2b** (a mixture of two isomers [2] with $\delta^{31}P$ = 43.8 (major) and 40.0 (minor)) and 0.1 mL of ethanol in 0.5 mL of 1,2-xylene was heated in a sealed 5 mm NMR tube at 150°C for 15 hours. The $^{31}P$ NMR spectrum showed that 10% of the starting material was still unreacted. The reaction product had $\delta^{31}P$ = 39.3 and was identical to a sample of ethyl methylphosphinate (**4b**) prepared earlier [2].

### *Phosphorylation of Silica Gel by the Thermal Fragmentation of the P-Ethoxy Phosphabicyclooctadiene* (**2c**)

Silica gel (1.0 g, Aldrich, 70–230 mesh[5]) was added to 0.31 g of phosphinic ester **2c** in 20 mL of dichloromethane, and the solvent was removed under reduced pressure. The impregnated silica gel so obtained was heated in a sealed tube at 250°C for 5 minutes: CP-MAS $^{31}P$ NMR $\delta$ 19.4. A second sample was heated at 170°C for 3 hours: CP-MAS $^{31}P$ NMR $\delta$ 19.5.

## *ACKNOWLEDGMENT*

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