Camphene-derived primary and hydroxymethyl phosphines†

Rebecca A. Berrigan,[a] Douglas K. Russell,[a] William Henderson,*[b] Meto T. Leach,[b] Brian K. Nicholson,[b] Gary Woodward[c] and Christopher Harris[c]

[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[b] *Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand. E-mail: w.henderson@waikato.ac.nz; Fax: +64 7 838 4219*
[c] *Rhodia Consumer Specialities Ltd, PO Box 80, Oldbury, West Midlands, UK B69 4LN*

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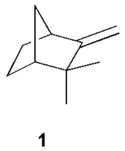
Thermal disproportionation of (2,2-dimethylbicyclo[2.2.1]hept-3-ylmethyl)phosphinic acid (*endo*-8-camphanylphosphinic acid, $camPO_2H_2$) yields the primary phosphine (2,2-dimethylbicyclo[2.2.1]hept-3-ylmethyl) phosphine ($camPH_2$). The compound has been characterised by NMR spectroscopy, and as its tris(hydroxymethyl)phosphonium chloride salt $[camP(CH_2OH)_3]Cl$, synthesised by reaction with excess formaldehyde and hydrochloric acid. The X-ray crystal structure of this phosphonium salt is reported, confirming the *endo* position of the phosphonium group. On treatment with triethylamine base, $camP(CH_2OH)_3{}^+Cl^-$ is converted to the hydroxymethylphosphine $camP(CH_2OH)_2$. The sulfide and selenide of this phosphine have been prepared, together with the platinum(II) complex *cis*-$[PtCl_2\{camP(CH_2OH)_2\}_2]$. The gas-phase decomposition of $camPH_2$ has been investigated using the technique of IR laser powered homogeneous pyrolysis. Results indicate the initial elimination of phosphine, followed by the rearrangement and decomposition of camphene through two distinct pathways.

Monoterpenes are readily accessible, chiral natural products, available in high enantiomeric purities and containing a range of functional groups for further chemical modification.[1] We are investigating the chemistry of a range of organophosphorus derivatives derived from monoterpenes, and in particular camphene **1**, which is a by-product of the pulp and paper industry. We have previously reported that the reaction of camphene with excess hypophosphorous acid under radical-catalysed conditions gives *endo*-8-camphanylphosphinic acid, $camPO_2H_2$, **2**, in good yields,[2] which forms a polymeric calcium salt.[3] In a separate study, we described the synthesis of uranyl nitrate complexes of some camphene-derived phosphorylic compounds.[4] In this paper we describe the synthesis and characterisation of some new camphene-derived phosphines, with emphasis on the primary phosphine $camPH_2$ and the hydroxymethylphosphine $camP(CH_2OH)_2$.



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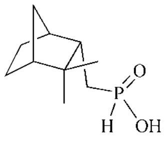

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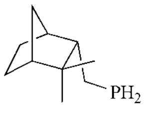
Results and discussion

Synthesis of the primary phosphine $camPH_2$, 3

The disproportionation of phosphinic acids of the type RP(O)(OH)H at elevated temperatures is known to be a useful route for the synthesis of primary phosphines, with the corresponding phosphonic acid RPO_3H_2 formed as a byproduct:[5,6]

$$3RPO_2H_2 \rightarrow RPH_2 + 2RPO_3H_2$$

Although such disproportionation reactions proceed with only a maximum 33% yield based on the starting phosphinic acid, the generally high purity of the distilled product, together with the ready accessibility of *endo*-8-camphanylphosphinic acid ($camPO_2H_2$), **2**, from inexpensive camphene **1** and hypophosphorous acid suggested that this route would be suitable for the synthesis of the new primary phosphine $camPH_2$, **3**. Thus, heating **2** to 220–240 °C resulted in pyrolysis, and phosphine **3** can be collected by distillation under reduced pressure (30 mm Hg). The phosphine is a colourless, low melting point solid that partly crystallises on standing. In other preparations the phosphine did not crystallise but instead was obtained as an air-sensitive, odorous liquid.



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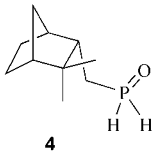

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Phosphine **3** has been characterised by ^{31}P NMR spectroscopy, which shows a characteristic resonance at δ −140.4, yielding a triplet in the ^1H-coupled spectrum, with $^1J(PH)$ 194.1 Hz. These values are very similar to those observed for other primary phosphines, which typically appear in the range δ −110 to −160,[7] for example $H_2PCH_2CH_2PH_2$ [δ −130.8, $^1J(PH)$ 193 Hz],[8] (η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2PH_2$) [δ −129.1, $^1J(PH)$ 194 Hz][9] and also PH_3 itself [$^1J(PH)$ 187 Hz].[10] The *endo*-disposition of the PH_2 group was confirmed by detailed analysis of the ^1H NMR spectrum (see experimental section). In the PH region of the ^1H NMR spectrum the PH_2 protons are highly coupled, giving two complex multiplets at δ 2.95 and 2.30. Although it was initially thought that each multiplet

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† Electronic supplementary information (ESI) available: IR and GC-MS data for the pyrolysis of phosphine 3. See http://www.rsc.org/suppdata/nj/b0/b006252i/

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Table 1 Bond lengths (Å) and angles (°) for **5**

P(1)–C(8)	1.794(3)	P(1)–C(13)	1.808(3)
P(1)–C(11)	1.819(3)	P(1)–C(12)	1.820(3)
O(1)–C(11)	1.412(4)	O(2)–C(12)	1.410(4)
O(3)–C(13)	1.419(3)	C(1)–C(2)	1.524(5)
C(1)–C(7)	1.539(5)	C(1)–C(6)	1.543(5)
C(2)–C(8)	1.542(4)	C(2)–C(3)	1.584(5)
C(3)–C(9)	1.518(5)	C(3)–C(10)	1.533(5)
C(3)–C(4)	1.548(5)	C(4)–C(7)	1.532(5)
C(4)–C(5)	1.542(5)	C(5)–C(6)	1.542(5)
C(8)–P(1)–C(13)	111.0(2)	C(8)–P(1)–C(11)	113.6(2)
C(13)–P(1)–C(11)	108.4(2)	C(8)–P(1)–C(12)	107.5(2)
C(13)–P(1)–C(12)	108.9(2)	C(11)–P(1)–C(12)	107.3(2)
C(2)–C(1)–C(7)	100.0(3)	C(2)–C(1)–C(6)	110.5(3)
C(7)–C(1)–C(6)	101.7(3)	C(1)–C(2)–C(8)	118.1(3)
C(1)–C(2)–C(3)	103.5(3)	C(8)–C(2)–C(3)	114.4(3)
C(9)–C(3)–C(10)	108.7(3)	C(9)–C(3)–C(4)	109.9(3)
C(10)–C(3)–C(4)	113.0(3)	C(9)–C(3)–C(2)	110.4(3)
C(10)–C(3)–C(2)	113.6(3)	C(4)–C(3)–C(2)	101.1(3)
C(7)–C(4)–C(5)	99.8(3)	C(7)–C(4)–C(3)	103.1(3)
C(5)–C(4)–C(3)	110.9(3)	C(4)–C(5)–C(6)	102.6(3)
C(5)–C(6)–C(1)	103.5(3)	C(4)–C(7)–C(1)	94.0(3)
C(2)–C(8)–P(1)	116.4(2)	O(1)–C(11)–P(1)	112.2(2)
O(2)–C(12)–P(1)		0(3)–C(13)–P(1)	107.3(2)

belonged to a given PH proton, no correlation was seen in the COSY45 spectrum, and instead the only correlation peaks observed for these multiplets was to the resonances assigned to the CH_2 protons $H_{8'/8''}$. Irradiation of the $H_{8'/8''}$ signals [δ 1.49] simplifies the PH multiplets to two sets of AB doublets, indicating that the PH protons are inequivalent.

An alternative route to camPH$_2$ has also been investigated, unsuccessfully. Attempted reduction of camP(O)Cl$_2$[4] to the primary phosphine **3** using excess $LiAlH_4$ furnished a solid material that despite showing ^{31}P NMR spectroscopic properties very similar to **3**, could not yield **3** by distillation, despite the use of high temperatures and low pressures (> 200 °C at 0.5 mm Hg). A similar difficulty in the isolation of a primary phosphine from a $LiAlH_4$ reaction mixture has been reported previously.[11]

The primary phosphine **3** is readily oxidised in air to the primary phosphine oxide **4**, which gives a resonance in the ^{31}P NMR spectrum at δ 9.2 appearing as a triplet resonance with ^1J(PH) 416.4 Hz. Similar values [δ 3.9, ^1J(PH) 457 Hz] have been reported for other primary primary phosphine oxides, such as $C_{12}H_{25}P(O)H_2$.[12] Approximately half of the phosphine had oxidised within 2 h exposure to air; other products of the oxidation process were not identified. Primary phosphine oxides $RP(O)H_2$ are known to be generally unstable towards disproportionation to the primary phosphine RPH_2 and the phosphinic acid RPO_2H_2.[5,13]

Synthesis and X-ray crystal structure of the phosphonium salt [camP(CH$_2$OH)$_3$]Cl, 5

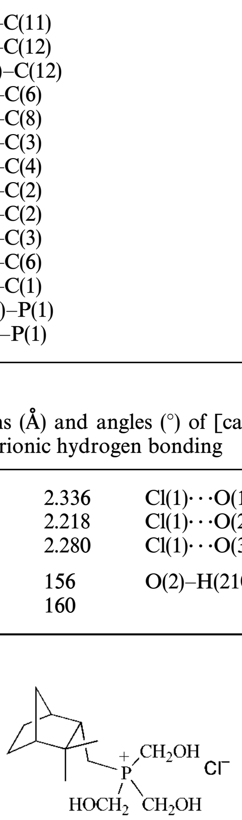
Primary (and secondary and tertiary) phosphines can be readily converted into air-stable, and typically crystalline, hydroxymethylphosphonium salts by reaction with an excess of formaldehyde and hydrochloric acid:[14]

$$RPH_2 + 3CH_2O + HCl \rightarrow [RP(CH_2OH)_3]Cl$$

Hydroxymethylphosphonium salts are useful precursors for the synthesis of hydroxymethylphosphines,[15,16] which are attracting renewed interest as water-soluble ligands for transition-metal centres,[16–18] in the functionalisation of amine-containing dendrimeric molecules,[19] and in the synthesis of various other types of phosphine ligands and their metal complexes.[20] The hydroxymethylphosphorus P–CH$_2$OH moiety can also be viewed as a masked P–H group; removal of formaldehyde can provide a route for regeneration of the P–H species. We have recently reported the synthesis of the surprisingly air-stable ferrocene-derived primary phosphine $FcCH_2PH_2$ by such a formaldehyde-elimination reaction.[9]

Table 2 Bond lengths (Å) and angles (°) of [camP(CH$_2$OH)$_3$]$^+$Cl$^-$, **5**, associated with interionic hydrogen bonding

Cl(1)· · ·H(110)	2.336	Cl(1)· · ·O(1)	3.104
Cl(1)· · ·H(210)	2.218	Cl(1)· · ·O(2)	3.029
Cl(1)· · ·H(310)	2.280	Cl(1)· · ·O(3)	3.067
O(1)–H(110)· · ·Cl(1)	156	O(2)–H(210)· · ·Cl(1)	170
O(3)–H(310)· · ·Cl(1)	160		



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Reaction of the primary phosphine **3** with excess CH_2O/HCl under a nitrogen atmosphere gave the tris(hydroxymethyl)phosphonium salt **5** as a colourless crystalline solid. In order to verify the NMR spectroscopic evidence that the camphanyl skeleton of the compound was unaffected by the pyrolysis reaction used in the synthesis of **3**, a single-crystal X-ray diffraction study was carried out on **5**. Selected bond lengths and angles are given in Table 1, and interionic parameters in Table 2. The structure is shown in Fig. 1, together with the atom numbering scheme. The molecular structure confirms the presence of the *endo*-8-camphanyltris(hydroxymethyl)phosphonium cation, together with the chloride counter-anion. Only a relatively small number of structures have been previously reported for hydroxymethylphosphonium salts, for example [PhMe$_2$P{CMe(OH)C(O)Me}]Cl,[21] [Ph$_2$P(CH$_2$OH)$_2$]Cl[14] and [FcCH$_2$PMe(CH$_2$OH)$_2$]I (Fc = ferrocenyl).[22] The geometry around the phosphorus atom is essentially tetrahedral, with C–P–C bond angles lying in the range 107–114°. Overall, the structural features of the cation of **5** are similar to those of Ph$_2$P(CH$_2$OH)$_2$$^+$; the P–CH$_2$OH bond distances of **5** average to 1.816(3) Å, while in Ph$_2$P(CH$_2$OH)$_2$$^+$ the average is 1.830(3) Å. In the free hydroxymethylphosphines $(HOCH_2)_2CH_2CH_2P(CH_2OH)_2$[17] and $FcCH_2P(CH_2OH)_2$[22] the P–CH$_2$OH bond distances average 1.834(5) and 1.857(4) Å, respectively. The average C–O bond length of **5** [1.413(4) Å] is also comparable to the average C–O bond length of

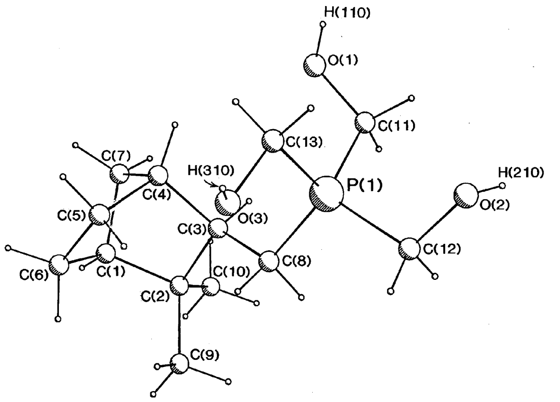


Fig. 1 Structure of the cation $[\text{camP(CH}_2\text{OH)}_3]^+$ of **5** determined by single-crystal X-ray diffraction as its chloride, showing the atom numbering scheme.

$\text{Ph}_2\text{P(CH}_2\text{OH)}_2^+$ [1.405(7) Å]. The P–C(8) bond length of **5** [1.794(3) Å] is similar to the average P–CH_3 bond length in the phosphonium salt $[\text{PhMe}_2\text{P\{CMe(OH)C(O)Me\}]Cl}$[21] [1.782(3) Å], the P–CH_2 bond in $[\text{FcCH}_2\text{PMe(CH}_2\text{OH)}_2]\text{I}$ [1.79(2) Å][22] and to the average C(sp^3)–P^+ bond distance in phosphonium salts [1.800(15) Å].[23]

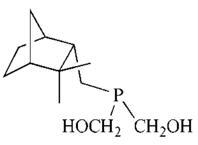
Examination of the cell packing diagram of **5** reveals that each chloride ion experiences interionic H-bonding to the hydroxyl groups of three different phosphonium cations. These interionic contacts, which have also been observed in the bis(hydroxymethyl)phosphonium salt $[\text{Ph}_2\text{P(CH}_2\text{OH)}_2]\text{Cl}$[14] and in $[\text{FcCH}_2\text{PMe(CH}_2\text{OH)}_2]\text{I}$,[22] are indicated by the short Cl···H distances given in Table 2. The Cl···O distances (3.03–3.10 Å) are typical for Cl···H–O hydrogen bonds of 2.99–3.05 Å.[24]

The phosphonium salt **5** has also been characterised by positive-ion electrospray mass spectrometry (ES-MS) and NMR spectroscopy. ES-MS in methanol solvent gave an intense ion due to $[\text{RP(CH}_2\text{OH)}_3]^+$ at *m*/*z* 261, with a smaller ion at *m*/*z* 557 assigned as the aggregate ion $[2\ \text{RP(CH}_2\text{OH)}_3 + \text{Cl}]^+$. We have previously described the utility of ES-MS in the characterisation of a wide range of hydroxymethylphosphonium salts.[25]

The ^{31}P-{^{1}H} NMR spectrum of **5** (δ 29.9) is consistent with values observed for other hydroxymethylphosphonium salts, for example $[\text{P(CH}_2\text{OH)}_4]\text{Cl}$ (δ 25.8).[26] ^{13}C-{^{1}H} and ^{1}H NMR spectra were fully assigned by use of one- and two-dimensional experiments and NOE data; full assignments are given in the experimental section. The ^{13}C-{^{1}H} spectrum of the camphanyl region showed the expected ten resonances; the quaternary carbon C(2), which showed coupling to ^{31}P (*J* 12.4 Hz), was readily assigned as the resonance at δ 37.6 from the DEPT spectrum. The methylene resonance showing a large ^1J(PC) coupling (38.3 Hz) is also readily assigned to C_8. The CH_2OH carbons appear at δ 50.7 and show characteristic coupling to ^{31}P of 54.7 Hz.

Synthesis and chemistry of the phosphine camP(CH$_2$OH)$_2$, 6

Under a nitrogen atmosphere, the treatment of a deoxygenated solution of $[\text{camP(CH}_2\text{OH)}_3]^+\text{Cl}^-$, **5**, in water–dichloromethane with equimolar amounts of either KOH or Et_3N gives 8-camphanyl bis(hydroxymethyl)phosphine $\text{camP(CH}_2\text{OH)}_2$, **6** [$\delta$ ^{31}P −25.4]. The phosphine is easily separated from the by-products (baseH^+Cl^- and formaldehyde) from the organic phase, where it can be isolated as a colourless, air-sensitive oil. The use of triethylamine as the base appeared to promote the formation of formaldehyde adducts of the phosphine, $\text{camP[(CH}_2\text{O)}_n\text{CH}_2\text{OH]}_2$; such adducts were observed before in the synthesis of $\text{P(CH}_2\text{OH)}_3$ from $[\text{P(CH}_2\text{OH)}_4]^+\text{Cl}^-$ using NEt_3.[16] Removal of excess formaldehyde was achieved by heating the crude product to *ca.* 85 °C under vacuum, while bubbling nitrogen through the oil. The phosphine sulfide $\text{camP(S)(CH}_2\text{OH)}_2$, **7** [$\delta$ ^{31}P 55.6] was obtained in high yield by treatment of a deoxygenated water–dichloromethane mixture of the phosphonium salt **5** and excess powdered sulfur with KOH. The phosphine selenide $\text{camP(Se)(CH}_2\text{OH)}_2$, **8** [$\delta$ ^{31}P 43.4, ^1J(PSe) 683 Hz] was synthesised similarly, except that the reaction mixture was heated to facilitate reaction. The sulfide and selenide have NMR spectroscopic properties consistent with their formulations; indeed the signals assigned to C(1)–C(7), C(9) and C(10) appear remarkably constant, irrespective of the substituents on phosphorus. In the phosphine **6** and the sulfide **7** and selenide **8**, the two CH_2OH groups are inequivalent, in contrast to the precursor tris(hydroxymethyl)phosphonium salt **5**, where the three CH_2OH groups are equivalent.



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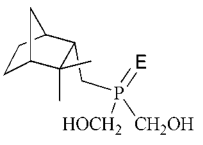


7, E = S
8, E = Se

Reaction of $\text{camP(CH}_2\text{OH)}_2$ with $[\text{PtCl}_2\text{(cod)}]$ (cod = cycloocta-1,5-diene) gave the platinum dichloride complex *cis*-$[\text{PtCl}_2\{\text{camP(CH}_2\text{OH)}_2\}_2]$, **9**. The presence of two chiral camphanyl groups suggested that diastereoisomers of **9** should exist. Although initial ^{31}P NMR studies at low field (36 MHz) showed only a single peak, at higher field (121 MHz) two separate peaks could be resolved, at δ 10.70 and 10.65, showing coupling to ^{195}Pt of 3420 Hz. This experiment shows that the phosphine $\text{camP(CH}_2\text{OH)}_2$ forms normal complexes, but is an example of an ampiphilic phosphine, with a combination of a bulky hydrophobic group and two smaller hydrophilic hydroxymethyl groups, which may find interesting applications.

Laser pyrolysis studies of camPH$_2$

A detailed study of the gas-phase decomposition of the new volatile primary phosphine **3** has been carried out; information on decomposition pathways of phosphines is of relevance for the design of new CVD systems for deposition of metal phosphide phases.[27] While it is noted that complex compounds such as **4** will probably be unsuitable for CVD applications, information from this study may prove useful in further understanding decomposition behaviour of more suitable phosphines. The rearrangement chemistry of monoterpenes such as camphene **1**, bornylene and tricyclene has been of interest, both in solution and in the gas phase.[27–29] The study of the gas-phase decomposition of this new terpene-derived primary phosphine permits an investigation of the rearrangement chemistry of this substituted camphene, as well as the role that the substituent may play in that rearrangement.

Infrared laser powered homogeneous pyrolysis (IR LPHP) was utilised in order to ensure that decomposition occurred solely in the gas phase. The specific details of the technique have been presented elsewhere,[30] but an overview of the process is as follows. A cylindrical Pyrex cell, capped at each end with a ZnSe window (transparent to IR) is filled with a small amount of the compound to be decomposed and a photosensitiser gas, in this case SF_6. Continuous CO_2 IR laser radiation is directed though the cell, absorbed by the photosensitiser and efficiently converted to heat.[31] The compound of interest is then pyrolysed thermally through collisional activation with the photosensitiser. Temperatures generated in the centre of the cell are typically as high as 1500

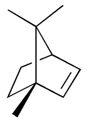
K. Homogeneous pyrolysis is ensured by the low thermal diffusion coefficient of SF_6, such that the pyrolysis region is confined to the centre of the cell, while the walls of the cell remain at room temperature. The contents of the cell, including decomposition products, can then be analysed directly by IR spectroscopy, or products can be condensed into detachable vessels suitable for analysis by GC-MS and ^1H NMR spectroscopy.

The range of compounds expected from this type of decomposition study of phosphine **3** warranted the utilisation of different spectroscopic techniques in order to unambiguously identify all products. IR spectroscopy was useful in the identification of smaller compounds, mostly produced in the final stages of decomposition. Tentative assignments from the IR spectrum could then be verified by subsequent ^1H NMR analysis. Separation and identification of the monoterpenes was achieved by GC-MS, this technique being useful to simultaneously present evidence of products for which observation had been masked in the previous spectra. The interpretation of data collected during the course of this study is presented in Table 3. To simplify discussion of the multiple conversions and decomposition pathways observed in this study, an overview is presented in Scheme 1. Justification for the assigned pathways and products is presented in the following discussion.

The first observed step in the decomposition of phosphine **3** is almost certainly the elimination of phosphine (PH_3), confirmed by the detection of a clear phosphine signal in the IR spectrum, as well as an absence of any other phosphorus-containing products. Camphene **1**, the other expected product, showed strong signals in the ^1H NMR and GC-MS spectra.

Following the elimination of phosphine, all remaining products are likely to arise from the rearrangement and decomposition of camphene. The rearrangement chemistry of camphene at elevated temperatures has been previously documented.[38] Those reported experiments were carried out in a hot-walled vessel, providing some heterogeneous decomposition, yet the results provide an indication of conversions that may be expected in this work. The investigation of the decomposition behaviour of camphene **1**, bornylene **10**, and tricyclene **11** indicated that at moderate temperatures (340–360 °C) camphene was converted to tricyclene only, in almost quantitative yields. Tricyclene was not observed to revert, producing only trace amounts of camphene.

After elimination of phosphine, subsequent rearrangement and decomposition of camphene then followed two major pathways. The first (Scheme 1, pathway A) was through the initial rearrangement of camphene to tricyclene; signals are observed corresponding to xylenes, toluene and benzene (see Electronic supplementary information), with further decomposition products apparent as methane and acetylene. To produce this range of substituted arenes, it is probable that tricyclene has decomposed *via* a bridge-opening mechanism, then through an intermediate such as a substituted cyclohexadiene or *p*-cymene.[39]



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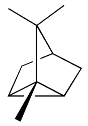

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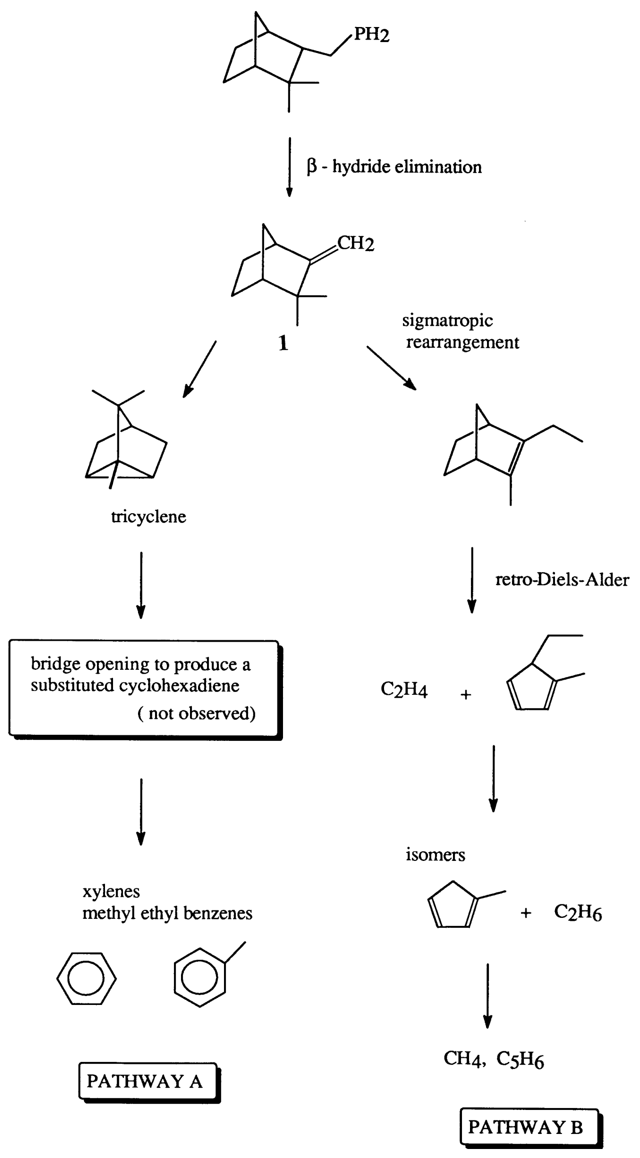
A second decomposition pathway seems to be available for camphene (Scheme 1, pathway **B**). Products indicative of a retro Diels–Alder pathway in the decomposition of camphene are observed, such as cyclopentadiene (IR stretch observed at 663 cm^{-1}) and ethylene. Recognising that conversion of camphene to bornylene is unlikely,[38] we postulate a [1,3] sigmatropic rearrangement of camphene to produce methylethylnorbornene (Scheme 1). This may then give rise to retro-Diels–Alder decomposition producing methylethylcyclopentadiene and ethylene. Cyclopentadiene and ethylene signals are clearly observed in ^1H NMR, IR and GC-MS spectra, and methylcyclopentadienes are observed using GC-MS (see Electronic supplementary information). A large signal for ethane is observed in ^1H NMR spectra, possibly resulting from bond homolysis of the ethyl group from methylethylcyclopentadiene.

When considering strictly gas-phase decomposition processes, precedent for this work arises in a decomposition study of isobornyl acetate,[39] using the same gas-phase decomposition technique (IR LPHP). Pyrolysis of this compound, even at mild temperatures, produced a range of compounds not dissimilar to those observed in this study and retro Diels–Alder decomposition of bornylene was postulated as the source of cyclopentadiene signals in the GC-MS. After noting the failure of camphene to convert to bornylene,[38] and confirmation of only traces of bornylene present in the GC-MS traces, it is suggested that in this study, retro-Diels–Alder decomposition products arise from camphene alone.

Thus, the results of the present study concur largely with those observed previously for the decomposition of bornylene;

Table 3 Identification of products from the IR LPHP decomposition of phosphine **3**

Compound	Method of identification	Lit. values (ref.)
Phosphine	IR: ν_1 (P–H) 2320, ν_3 (P–H) 2325 cm^{-1}	2321, 2327 cm^{-1} (32)
Methane	IR: ν_3 (C–H) 3016, ν_2 (C–H) 1306 cm^{-1} ^1H NMR: δ 0.21 (s)	3020, 1306 cm^{-1} (33) δ 0.40 (34)
Acetylene	IR: ν_5 (C–H) 729 cm^{-1}	729 cm^{-1} (34)
Ethene	IR: ν_7 (C–H) 1889 cm^{-1} ^1H NMR: δ 5.4 (s)	1890 cm^{-1} (33) δ 5.28 (34)
Ethane	^1H NMR: δ 0.86 (s)	δ 0.86 (34)
Cyclopentadiene	IR: ν_{26} (C–H) 663 cm^{-1} GC-MS	663 cm^{-1} (35)
Methylcyclopentadienes	GC-MS	
Benzene	IR: ν_4 (C–H) 674 cm^{-1} ^1H NMR: δ 7.35 (s) GC-MS	671 (32), 673 cm^{-1} (36) δ 7.15 (37)
Toluene	IR: (C–H) 694 cm^{-1} ^1H NMR: δ 7.18 (m) GC-MS	694 cm^{-1} (36) δ 7.01 (37)
Xylenes	GC-MS	
Camphene	^1H NMR GC-MS	(37)
Bornylene	GC-MS	
Tricyclene	GC-MS	

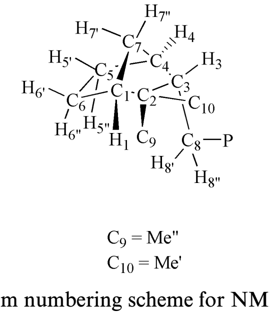


Scheme 1

however, we propose that in addition to bornylene, camphene is also a candidate for retro-Diels–Alder decomposition by first undergoing a sigmatropic rearrangement.

Experimental

All reactions were carried out under a nitrogen atmosphere, since the primary phosphine **3** is oxygen-sensitive. ^1H and ^{31}P NMR spectra (see Scheme 2 for atom numbering) were recorded on a Bruker AC300P instrument, at 300.13 and 75.47 MHz, respectively. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. Electrospray ionisation mass spectra were recorded on a VG Platform II instrument, using methanol as the mobile phase; further details are available elsewhere.[25]



Scheme 2 Atom numbering scheme for NMR assignment.

Syntheses

endo-8-Camphanylphosphinic acid **2** was synthesised according to the literature procedure.[2,3] Formaldehyde, triethylamine, sulfur, selenium, hydrogen peroxide and hydrochloric acid were all LR grade materials and were used as received. The complex [$PtCl_2$(cod)] was prepared by the literature procedure.[40]

***endo*-8-Camphanylphosphine, 3.** For the pyrolysis reaction a sample of crude camPO_2H_2, **2** (obtained by benzoyl peroxide catalysed addition of H_3PO_2 to camphene) was used, which was found to be 93% **2** and *ca.* 7% dicamphanylphosphinic acid $(cam)_2P(O)(OH)$

A 1 L, five-necked round-bottom flask, equipped with an overhead mechanical stirrer, temperature probe and apparatus for vacuum distillation, was charged with solid **2** (270 g, 1.34 mol) under an atmosphere of dry nitrogen. The flask was heated (electric isomantle), with stirring, until the solid **2** had formed a melt (*ca.* 70 °C). At this point, the system was placed under reduced pressure (30 mm Hg). The reactor temperature was slowly increased to above 200 °C. Pyrolysis occurred in the temperature range 220–240 °C. Material was evolved from the reactor with a boiling range of 155–160 °C (distillation head temperature). A total of 60 g of a colourless liquid was produced (82% yield based on **2**), some of which crystallised on standing. ^{31}P NMR specroscopy showed that a total of 93.5% of primary alkylphosphine had been produced by this method. ^{31}P NMR: δ −140.4, ^1J(PH) 194 Hz. ^1H NMR ($CDCl_3$): δ 2.95 (m, br, PH_2), 2.30 (m, PH_2)^a, 2.25 (s, br, 1H, H_4)^a, 1.74 (s, br, 1H, H_3), 1.60 (d, 1H, $H_{7''}$, ^2J 12.1)^a, 1.54 (m, 1H, $H_{6''}$)^b, 1.49 (s, br, 2H, $H_{8'/8''}$)^b, 1.46 (s, br, 1H, H_1)^b, 1.25 (m, br, 3H, $H_{6'}$, $H_{5'/5''}$)^b, 1.14 (d, $H_{7'}$, ^2J 12.1 Hz)^a, 0.91 (s, 3H, Me′) and 0.80 (s, 3H, Me″) (^{a} partially overlapping signals; ^{b} overlapping signals).

[camP$(CH_2OH)_3$]Cl, 5. To *endo*-8-camphanylphosphine, **3** (9.7 g), was added dropwise with stirring, 60 mL of a 1 : 1 mixture of deoxygenated 37% aqueous formaldehyde and concentrated hydrochloric acid. The two immiscible layers were stirred vigorously for 2 days, after which the resulting white solid was filtered off, washed with a small amount of cold water and recrystallised from methanol–petroleum spirit, to give the phosphonium salt **5** as a white solid (9.2 g, 54%), mp 137–139 °C. Anal. found: C, 52.4; H, 9.0; $C_{13}H_{26}ClO_3P$ requires C, 52.7; H, 8.9%. Positive-ion ES-MS (MeOH, cone voltage 45 V): *m/z* 261 $[M]^+$, 557 $[2M + Cl]^+$ (M^+ = phosphonium cation). ^{31}P-{^1H} NMR (CD_3OD): δ 29.9 (s). ^{13}C-{^1H} NMR (CD_3OD): δ 50.7 [d, CH_2OH, ^1J(PC) 54.7], 48.1 (s, C_1), 43.6 [d, C_3, ^2J(PC) 4.9], 42.3 (s, C_4), 38.5 [d, C_2, ^3J(PC) 12.4], 36.9 (s, C_7), 31.1 (s, C_{10}), 24.4 (s, C_6), 21.3 (s, C_9), 19.7 (s, C_5), and 11.8 [d, C_8, ^1J(PC) 38.3 Hz]. ^1H NMR (CD_3OD): δ 4.70 (s, br, CH_2OH), 2.55 (m, br, 2H, $H_{8'/8''}$), 2.33 (m, br, 1H, H_4), 2.02 (m, br, 1H, H_3), 1.98 (s, 1H, H_1), 1.85 (m, 1H, $H_{7''}$), 1.73 (m, 1H, $H_{6''}$), 1.48 (m, br, $H_{5'/5''}$), 1.46 (m, 1H, $H_{6'}$), 1.43 (d, 1H, $H_{7'}$, ^2J 10.8 Hz), 1.12 (s, 3H, Me′) and 0.99 (s, 3H, Me″).

Synthesis of camP$(CH_2OH)_2$, 6, using KOH. Under a nitrogen atmosphere, $[camP(CH_2OH)_3]^+Cl^-$, **5** (1.00 g, 3.4 mmol), was added to water (30 mL) and dichloromethane (30 mL). While stirring vigorously, KOH (0.21 g, 3.7 mmol) in deoxygenated water (10 mL) was added dropwise. After 2 h the dichloromethane layer was withdrawn by syringe and evaporated to dryness under reduced pressure to give camP$(CH_2OH)_2$, **6** (0.62 g, 80%), as an air-sensitive colourless oil. ^{31}P-{^1H} NMR ($CDCl_3$): δ −25.4 (s). ^{13}C-{^1H} NMR: δ

61.3 [d, ^1J(PC) 14.9, CH_2OH], 61.0 [d, ^1J(PC) 14.9, CH_2OH], 49.0 (s, C_1), 47.6 [d, ^2J(PC) 13.1, C_3], 42.3 [d, ^3J(PC) 7.5, C_4], 37.6 [d, ^3J(PC) 9.8, C_2], 37.0 (s, C_7), 32.3 (s, C_{10}), 24.7 (s, C_6), 21.7 (s, C_9), 19.9 (s, C_5), 14.8 [d, ^1J(PC) 9.2 Hz, C_8]. ^{1}H NMR: δ 4.30 (br, s, OH), 4.19–4.09, 3.99–3.91 (4H, br, m, CH_2OH)^b, 2.15 (1H, br, s, H_4), 1.68 (1H, br, s, H_1), 1.60–1.57 (2H, m, $H_{8'/8''}$), 1.55 (1H, d, ^2J 10.2, $H_{7''}$)^b, 1.49 (1H, m, $H_{6''}$)^b, 1.47 (1H, br, s, H_3)^b, 1.32–1.10 (2H, br, m, $H_{5'/5''}$)^b, 1.18 (1H, m, $H_{6'}$)^b, 1.10 (1H, d, ^2J 10.2 Hz, $H_{7'}$), 0.89 (3H, s, Me′), 0.79 (3H, s, Me″). (^{b} overlapping signals).

Synthesis of camP(CH_2OH)$_2$, 6 using triethylamine. Under a nitrogen atmosphere, [camP(CH_2OH)$_3$]$^+$Cl$^-$, **5** (1.00 g, 3.4 mmol), was added to water (30 mL) and dichloromethane (30 mL). While stirring vigorously, Et_3N (0.38 g, 3.7 mmol) in deoxygenated water (10 mL) was added dropwise. After 2 h the dichloromethane layer was removed by syringe and evaporated to dryness under reduced pressure to give a colourless oil. ^{31}P NMR showed three components at δ −25.2, −28.1 and −35.3. Heating to 85 °C under vacuum with a nitrogen bleed for 4 h removed the formaldehyde adducts at δ −28.1 and −35.3, leaving pure **6** (0.52 g, 66%).

camP(S)(CH_2OH)$_2$, 7. Under a nitrogen atmosphere, [camP(CH_2OH)$_3$]$^+$Cl$^-$, **5** (0.50 g, 1.7 mmol), and excess powdered sulfur (1 g) were added to a mixture of deoxygenated water (20 mL) and dichloromethane (30 mL). While stirring, KOH (0.12 g, 2.1 mmol) in deoxygenated water (10 mL) was added dropwise. After 24 h the organic layer was removed, dried over anhydrous $MgSO_4$, and evaporated to dryness to give a pale yellow solid. This was recrystallised from dichloromethane–petroleum spirit to give the product **7** as a pale yellow crystalline solid, 0.35 g (60%). Anal. found: C, 55.1; H, 8.8; $C_{12}H_{23}O_2PS$ requires C, 54.9; H, 8.8%. Mp 81–82 °C. ES-MS (positive ion with added $AgNO_3$): *m/z* 412 [M + Ag + MeCN]$^+$, 633 [2 M + Ag]$^+$. ^{31}P-{^{1}H} NMR: δ 55.6 (s). ^{13}C-{^{1}H} NMR: δ 60.5 [d, ^1J(PC) 30.5, CH_2OH], 59.7 [d, ^1J(PC) 30.5, CH_2OH], 48.3(s, C_1), 44.1 [d, ^2J(PC) 3.3, C_3], 42.1 [d, ^3J(PC) 1.5, C_4], 38.0 [d, ^3J(PC) 11.7, C_2], 37.2 (s, C_7), 31.7 (s, C_{10}), 24.6 (s, C_6), 22.1 (s, C_9), 21.8 [d, ^1J(PC) 17.6 Hz, C_8], 20.2 (s, C_5). ^{1}H NMR: δ 4.00 (2H, br, m, CH_2), 3.98 (2H, br, m, CH_2), 3.37 (2H, br, s, OH), 2.29 (1H, br, s, H_4), 2.05, 1.82 (2H, br, m, $H_{8'/8''}$)^a, 1.93 (1H, dt, ^2J 12.1, ^3J 3.1, H_3), 1.77 (1H, br, s, H_1)^a, 1.67 (1H, d, ^2J 10.0, $H_{7''}$), 1.55 (1H, m, $H_{6''}$), 1.30 (2H, br, m, $H_{5'/5''}$)^b, 1.28 (1H, m, $H_{6'}$)^b, 1.20 (1H, d, ^2J 10.0 Hz, $H_{7'}$), 0.97 (3H, s, Me′), 0.80 (3H, s, Me″) (^{a} partially overlapping signals; ^{b} overlapping signals).

camP(Se)(CH_2OH)$_2$, 8. Under a nitrogen atmosphere, KOH (0.094 g, 1.7 mmol) was added to [camP(CH_2OH)$_3$]$^+$Cl$^-$, **5** (0.47 g, 1.6 mmol), and excess powdered selenium (0.7 g) in deoxygenated water (30 mL). The mixture mixture was heated to 85 °C for 4 h. After cooling to room temperature the aqueous phase extracted with dichloromethane (30 mL) and the dichloromethane removed under reduced pressure. The crude product was recrystallised from dichloromethane–light petroleum to give the selenide **8** as a white crystalline solid (0.44 g, 70%). Anal. found: C, 46.6; H, 7.6; $C_{12}H_{23}O_2PSe$ requires C, 46.4; H, 7.5%. Mp 90–92 °C. ^{31}P-{^{1}H} NMR: δ 43.4 [s, ^1J(PSe) 683 Hz]. ^{13}C-{^{1}H} NMR: δ 59.8 [d, ^1J(PC) 47.4, CH_2OH], 59.4 [d, ^1J(PC) 47.4, CH_2OH], 48.4 (s, C_1), 44.8 [d, ^2J(PC) 3.0, C_3], 42.0 (s, C_4), 37.0 [d, ^3J(PC) 11.4, C_2], 37.2 (s, C_7), 31.7 (s, C_{10}), 24.7 (s, C_6), 22.4 (s, C_9), 21.1 [d, ^1J(PC) 39.2 Hz, C_8], 20.2 (s, C_5).

***cis*-[$PtCl_2${camP(CH_2OH)$_2$}$_2$], 9.** Under a nitrogen atmosphere, [$PtCl_2$(cod)] (0.18 g, 0.47 mmol) in deoxygenated dichloromethane (10 mL) was added to a solution of camP(CH_2OH)$_2$, **6** (0.22 g, 0.95 mmol), in deoxygenated dichloromethane (5 mL), to precipitate **9** as a white solid. Diethyl ether (30 mL) was added to facilitate precipitation. The white solid was filtered off, washed with ether and dried under vacuum. Anal. found: C, 39.75; H, 6.5; $C_{24}H_{46}O_4PCl_2Pt$ requires C, 39.7; H, 6.4%. Mp 219–223 °C. ^{31}P-{^{1}H} NMR: δ 10.70 [s, ^1J(PtP) 3420] and 10.65 [s, ^1J(PtP) 3420 Hz].

X-Ray crystal structure of [camP(CH_2OH)$_3$]Cl, 5

Colourless needles were obtained upon slow evaporation of a methanol solution of the compound.

Crystal data. $C_{13}H_{26}ClO_3P$: *M* 296.76, monoclinic, space group $P2_1/c$, $a = 16.504(7)$, $b = 7.561(5)$, $c = 12.142(3)$ Å, $\beta = 92.54(2)°$, $U = 1513.7(12)$ Å^3, $T = 130$ K, $Z = 4$, μ(Mo-Kα) = 0.357 mm^{-1}, 2798 reflections measured to $2\theta = 50°$, 2657 unique ($R_{int} = 0.0272$), which were all used in the refinement. Final R_1 (2σ data) 0.0467, wR_2 (all data) 0.1100.

CCDC reference number 440/232. See http://www.rsc.org/suppdata/nj/b0/b006252i/ for crystallographic files in .cif format.

Decomposition studies

FTIR spectra were recorded using a Perkin Elmer BIORAD Digilab FTS-60 IR spectrometer with resolution set at 1 cm^{-1}. ^{1}H NMR spectra were acquired using a Bruker 200 MHz spectrometer; all spectra were recorded in either $CDCl_3$ or d^8-toluene. GC-MS traces were collected using a HP 5890 series II gas chromatograph coupled to a HP 5971 series mass spectrometer. Gas chromatography was performed using a 30 m HP5 open bore column with a 0.25 μm thick inner coating, set at 35 °C. Operating conditions were optimised using a linear flow velocity of 29.4 cm s^{-1}, volume flow rate of 0.866 mL min^{-1} and a split ratio of 1 : 37. All samples were injected as a solution in dry diethyl ether. Mass spectral results were collected using Hewlett Packard MS Chem Station software, and products identified with the aid of the HP NIST/EPA/NIH mass spectral library.

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