

The Tetra(vinyl)phosphonium Cation $[(\text{CH}_2=\text{CH})_4\text{P}]^+$

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Vinyl compounds $\text{CH}_2=\text{CHX}$ have a vast synthetic potential.¹ This wealth has been exploited most extensively in the realm of the simple olefins ethene, propene, or butadiene but also of the vinyl-halides, -ethers, -sulfides, -amines, -silanes, and -boranes, and of the large family of vinylmetallics.² Surprisingly, however, the chemistry of the vinyl compounds of *phosphorus* is not very well developed, and even some of the simple prototypes of this class have not yet been described.^{3,4} This is particularly true for the elusive tetra(vinyl)phosphonium cation $[(\text{CH}_2=\text{CH})_4\text{P}]^+$. Early reports of its synthesis have not been confirmed,^{5,6} and subsequent preparative attempts apparently have not met with success. It is also interesting to note that there is virtually no information on the synthesis, structure, and reactivity of tetra(vinyl)ammonium salts $[(\text{CH}_2=\text{CH})_4\text{N}]^+\text{X}^-$ or the arsenic, antimony, and bismuth analogues.

We have recently shown that with tri(vinyl)phosphine ($\text{CH}_2=\text{CH})_3\text{P}$, the most obvious potential synthon for the preparation of poly(vinyl)phosphonium cations, even simple quaternization, oxidation, or complexation reactions can lead to immediate polymerization of the substrate or its products.^{7,8} Therefore, there was a need for a synthetic strategy in which all sensitive vinyl groups are generated only in the final preparative step from substituents previously introduced at the common phosphonium center. After several unsuccessful experiments with reactions suggested by the literature,^{9–11} simple primary phosphines RPH_2 were tested as model substrates for hydrophosphination, before PH_3 could finally be considered as the *de novo* starting material.

At the exploratory stage,¹² cyclohexylphosphine (**1**) was first used for photochemical hydrophosphination of vinyl acetate in hexane with AIBN as a catalyst.¹³ Contrary to negative results reported in the literature,⁹ the tertiary phosphine **2** was readily obtained. Its quaternization with 2-iodo-ethanol afforded the quaternary salt **3** which upon acylation with acetic acid anhydride gave the symmetrical trifunctional derivative **4**. Treatment of **4** with sodium carbonate in refluxing dioxane led to conversion into cyclohexyl-trivinylphosphonium iodide (**5**) (Scheme 1). The structure of this salt has been confirmed in a single-crystal X-ray diffraction study (Figure 1).^{14a}

Encouraged by these results, phosphine gas was bubbled into a solution of vinyl acetate and AIBN in toluene under UV irradiation. After 4 h at 25 °C, tris(2-acetoxyethyl)phosphine (**6**) was obtained in 60% yield. This product was subjected consecutively to the same treatment as that described for the conversion of **3** into **4** and **5** to give the quaternary salts **7**, **8**, and finally **9a** (72% yield for the last two reactions)(Scheme 2).¹⁵

The course of the crucial last step was easily followed by ³¹P NMR spectroscopy, and all intermediates were detected (Supporting Information). The most important ones of these were characterized by their analytical and spectroscopic data, and the crystal structure of the first homoleptic salt (**8**) was determined (Figure 2).^{14b} The crystals contain two independent cations, each of which has *S*₄

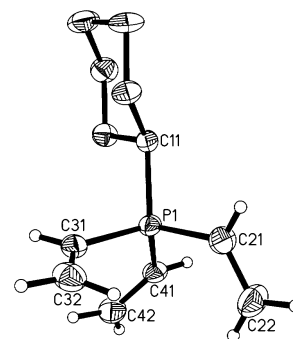
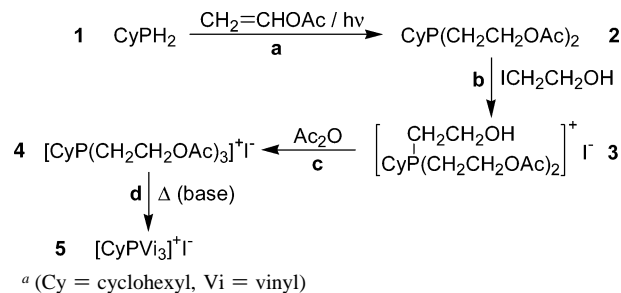
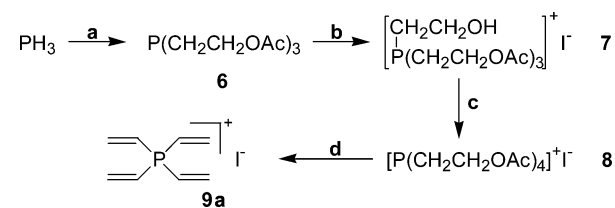


Figure 1. Molecular structure of the cation of **5**.

Scheme 1^a



Scheme 2



symmetry. The target compound tetravinylphosphonium iodide (**9a**) was also readily identified by conventional methods beyond doubt, but all attempts to grow single crystals failed. Therefore, **9a** was converted into the chloride (**9b**) with AgCl , the picrate (**9c**) with silver picrate, and the tetraphenylborate (**9d**) with NaBPh_4 , of which the latter finally gave a suitable crystalline specimen (orthorhombic, space group *Pnma*, *Z* = 4).^{14c}

In this salt, the smaller Vi_4P^+ cations occupy two distinct positions, which could be accounted for by a 1:1 disorder model. The structure of the cation is shown in Figure 3. The average P–C and C=C bond lengths are 1.798 and 1.249 Å, indicating standard single and double bonding, respectively, and the C–P–C and P–C=C angles are all close to the 109° and 120° reference values. The dimensions of the BPh_4^- anion show no anomalies.¹⁶

Tetraalkylphosphonium cations $[\text{R}_4\text{P}]^+$ are known to adopt conformations of high symmetry, preferentially of point groups *D*_{2d} and *S*₄, as observed for R = Et, ⁱPr, ^oPr,^{17–19} and for **8** (above).

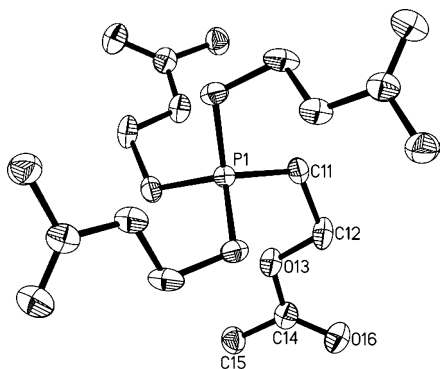


Figure 2. Molecular structure of the cation of **8**.

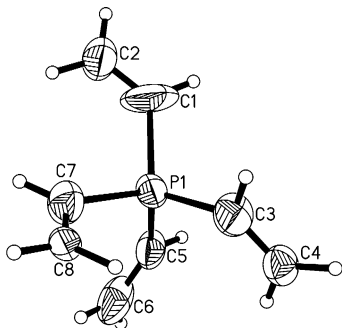


Figure 3. Molecular structure of the tetra(vinyl)phosphonium cation $[(\text{CH}_2=\text{CH})_4\text{P}]^+$ in the tetraphenylborate **9d**.

According to quantum chemical calculations, tetra(vinyl)element species $(\text{CH}_2=\text{CH})_4\text{E}$ ($\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) can adopt many conformations with very similar energies.^{20,21} Calculations carried out in the course of the present study have shown that the cations $[\text{Vi}_4\text{P}]^+$ with point groups of maximum attainable symmetry (D_{2d} and S_4) are higher in energy and that only a model of point group C_1 represents a pronounced minimum (Supporting Information). The cations of **9d** have no crystallographically imposed symmetry, but an analysis shows that three of the vinyl groups (with C3, C5, C7) form a propeller of approximate local C_3 symmetry, which is almost superimposable with the PVi_3 part of the $[\text{CyPVi}_3]^+$ cation (Figure 1). The array of the four vinyl groups in the $[\text{Vi}_4\text{P}]^+$ cation is thus in agreement with the quantum chemical calculations and is moreover exactly analogous to the molecular structures of tetra(vinyl)methane and -silane, which were determined only very recently by X-ray diffraction.^{22,23} In our own supplementary investigations, the tetra(vinyl)borate anion $[\text{B}(\text{CH}=\text{CH}_2)_4]^-$ was also found to have a similar conformation in its methyltriphenylphosphonium salt²⁴ (Supporting Information). Taken together, these results indicate that the structure shown in Figure 3 is probably not greatly influenced by packing forces but represents the intrinsic configuration and conformation of $(\text{CH}_2=\text{CH})_4\text{E}$ species.

Tetra(vinyl)phosphonium salts are very reactive toward nucleophiles and undergo a large variety of clean reactions, but the conditions have to be carefully chosen to avoid decomposition through random polymerization. Attempts to use **9a–d** for the preparation of the unknown pentavinylphosphorane, Vi_5P , have been unsuccessful.

Acknowledgment. Dedicated to Professor O. E. Scherer on the occasion of his 70th birthday.

Supporting Information Available: Crystallographic data of **5**, **8**, **9d**, and $[\text{Ph}_3\text{PMe}][\text{BVi}_4]$ (CIF) and syntheses and characterization of **2–5** and **9a–9d** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The sequence of reactions leading from **1** to **5** are described in full in the Supporting Information.
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- Crystal structures: (a) $[\text{CyVi}_3\text{P}]^+\text{I}^-$, **5** (143 K): monoclinic, space group $P2_1/n$, $Z = 4$; $a = 7.1098(1)$ Å, $b = 24.8571(6)$ Å, $c = 8.1218(2)$ Å, $\beta = 90.253(1)^\circ$. $R_1 = 0.0264$, $wR_2 = 0.0574$. (b) $\{\text{P}[\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{Me}]_4\}^+\text{I}^-$, **8** (143 K): tetragonal, space group $I4c2$, $Z = 8$; $a = 10.5930(10)$ Å, $c = 37.5286(6)$ Å. $R_1 = 0.0240$, $wR_2 = 0.0684$. (c) $[\text{Vi}_4\text{P}]^+[\text{BPh}_4]^-$, **9d** (143 K): orthorhombic, space group $Pnma$, $Z = 4$; $a = 19.3966(3)$ Å, $b = 13.7062(2)$ Å, $c = 9.9160(1)$ Å; $R_1 = 0.0496$, $wR_2 = 0.1229$. (d) $[\text{MePh}_3\text{P}]^+[\text{BVi}_4]^-$ (143 K): monoclinic, space group $P2_1/n$, $Z = 4$; $a = 10.3108(1)$ Å, $b = 14.5850(2)$ Å, $c = 15.6994(3)$ Å, $\beta = 100.1099(6)^\circ$. $R_1 = 0.042$, $wR_2 = 0.103$. For details see Supporting Information.
- 6–9a**: vinyl acetate (72.7 g, 0.84 mol) is dissolved in toluene (250 mL), 10 mg of AIBN is added, and phosphine gas PH_3 is bubbled into the solution at room temperature with stirring and irradiation with a UV lamp. After 4 h all volatile components are removed in a vacuum to leave a yellow oily product (**6**, 49.7 g, 60.7% yield), which should be kept under nitrogen below -32 °C. NMR (C_6D_6 , 20 °C), ^{31}P : -41.5 (s), ^{13}C : 169.9 (s, CO_2); 61.9 (d, $J = 20.8$), 26.9 (d, $J = 15.6$) for CH_2 ; 20.5 (s, Me). **6** (15 g, 51.3 mmol) is treated with 2-iodo-ethanol (12.0 g, 70 mmol) in tetrahydrofuran (30 mL) at 20 °C with stirring for 12 h. Removal of all volatiles in a vacuum gives a residue of compound **7** (17.9 g, 75% yield), which also needs to be kept below -32 °C to prevent decomposition. NMR (CDCl_3 , 20 °C), ^{31}P : 33.0 (s), ^{13}C : 170.1 (s, CO_2); 57.4 (d, $J = 6.9$), 21.9 (d, $J = 70.7$) CH_2 acetoxyethyl; 55.0 (d, $J = 8.5$), 24.3 (d, $J = 24.0$) CH_2 hydroxyethyl; 21.2 (s, Me). **7** (15 g, 32 mmol) is dissolved in acetic acid anhydride (50 mL) and refluxed for 10 h. Most of the solvent is evaporated and the residue treated again with fresh Ac_2O (40 mL) for 6 h under reflux. Excess reagent is removed in a vacuum and the residue washed with diethyl ether (3×50 mL). The remaining brown oil is extracted with chloroform to give a colorless solid which can be crystallized from acetone (**8**, mp 146 °C, 88% yield). NMR (CD_3CN , 20 °C), ^{31}P : 33.4 (s), ^{13}C : 170.9 (s, CO_2); 58.3 (d, $J = 5.7$), 21.7 (d, $J = 48.3$) CH_2 ; 21.1 (s, Me). **8** (15 g, 28 mmol) is refluxed with 15 g of soda in 80 mL of dioxane for 6 h. The reaction mixture is filtered, and the solids are extracted with hot acetonitrile. The product precipitates on cooling and addition of diethyl ether and can be crystallized from acetone/diethyl ether (**9a**, 6.13 g, 72% yield, mp 80 °C with decomposition). NMR (CD_3CN , 25 °C), ^{31}P : 9.7 (s); ^{13}C : 145.04 (s, $\text{C}\beta$), 118.1 (d, $J = 83.6$ C α). MS (FAB): m/z 139 (100%) $[\text{Vi}_4\text{P}]^+$.
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