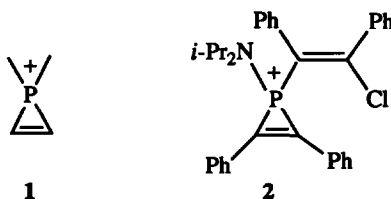


Evidence For The Rearrangement Of P-Chloro-Phosphirenium Ions To P-Vinyl-Phosphenium Ions

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Abstract: The formation of 1-diisopropylamino-2,3-diphenyl-1-(2-chloro-1,2-diphenylvinyl)phosphirenium ion (**2**), is postulated to proceed *via* the rearrangement of a P-chloro-phosphirenium ion to a P-vinyl-phosphenium ion.

The potential Hückel-type aromaticity of the phosphirenium ion ring system (**1**) 'remains one of the most intriguing questions of phosphorus heterocyclic chemistry'.³ The formal positive charge and the empty d-orbitals on the P atom are well suited to impart a stabilizing, conjugative interaction with the π -electrons of the 2p carbon orbitals.⁴



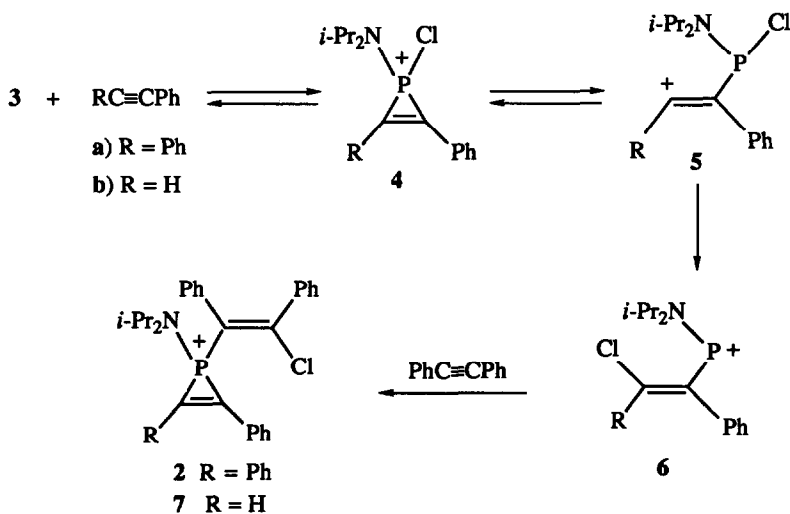
Previously, discrete phosphirenium ions were synthesized from the cycloaddition reaction of $\text{R}_2\text{PCl}_2 \cdot \text{AlCl}_3$ or $\text{R}_2\text{PCl} \cdot \text{AlCl}_3$ with alkynes.^{4,5} While the addition of a formal two-coordinate phosphorus cation (phosphenium ion) to an alkyne was first reported by Lochschmidt *et al.*,⁶ we recently reported the first X-ray crystal structure of a phosphirenium ion consisting of a 1:2 adduct (**2**) obtained from the reaction of $[\text{i-Pr}_2\text{NPCl}]^+[\text{AlCl}_4]^-$ (**3**)⁷ with diphenylacetylene.⁸ The short ring P-C bond (1.731 Å) and the long ring C-C bond length (1.36 Å) suggest the delocalized nature of the molecule. Herein, we describe the synthesis of **2** and evidence for the formation of P-vinyl-phosphenium ions from P-chloro-phosphirenium ions as a means of explaining the formation of the isolated product.

At 0 °C, 8.2 mmols of diphenylacetylene, dissolved in 7 mL of CH_2Cl_2 , was added dropwise to 8.2 mmols of a 0.5M CH_2Cl_2 solution of **3**. The reaction mixture was stirred at this temperature for 30 min. and then warmed to RT. The ³¹P NMR spectrum of the reaction mixture after 14h at RT showed a single signal at -75 ppm (relative to 85% D_3PO_4), indicative of phosphirenium ion formation. Surprisingly, an X-ray crystal structure of the product, obtained after a lengthy crystallization of the crude reaction product from CH_2Cl_2 at -35 °C, revealed the formation of **2**, in which two equivalents of diphenylacetylene were incorporated.

Similarly, examination of the ^{31}P NMR spectrum of the reaction of 1 eq of monophenylacetylene with 1 eq of phosphonium ion **3** shows rapid formation of a phosphirenium ion (major peak (>90%) at -84.3 ppm; minor peak (<10%) at $+380$ ppm). However, on standing at RT for 14h, the signal at -84.3 ppm virtually disappears concurrent with the growth of the signal at $+380$ ppm, indicative of phosphirenium ion formation. The results of these two experiments suggest the following reaction mechanism (Scheme 1).

The addition of phosphonium ion **3** to di- or monophenylacetylene seems to produce rapid formation of the 1:1 phosphirenium adduct (**4**). Ring opening of **4** to produce the unstable P-vinyl cation (**5**), 1,3-chloride migration to form the P-vinyl phosphonium ion (**6**), followed by reaction with another equivalent of acetylene could account for the final product (**2** or **7**). On the basis of its ^{31}P NMR spectrum, we assign the peak at $+380$ ppm in the monophenylacetylene reaction to **6b**.⁹ This proposed mechanism would also explain the *cis*-orientation of the phenyl groups on the exocyclic double bond in compound **2**.

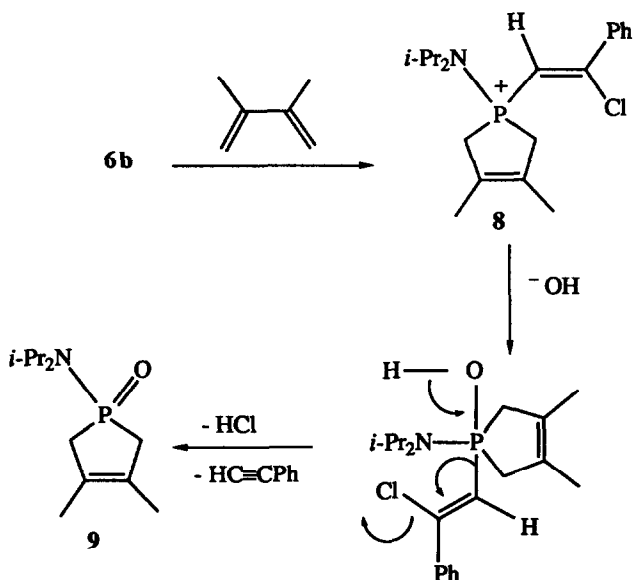
Scheme 1.



To confirm that a P-vinyl phosphonium ion could react with a second equivalent of an acetylene, **6b** was treated with 1 eq of diphenylacetylene. Examination of the ^{31}P NMR spectrum of this trapping experiment after 3h at RT showed quantitative formation of a new phosphirenium ion (-85.9 ppm), suggesting the formation of **7**. Inspection of the ^{13}C NMR spectrum of this compound indicated near quantitative consumption of the diphenylacetylene, thus ruling out the possibility of reformation of **4b**. The complicated vinyl/phenyl region of this spectrum precluded further characterization.

Since it is known that phosphonium ions react with butadienes to form the corresponding phospholenium ion,¹⁰ **6b** was also trapped with 2,3-dimethyl butadiene. The addition of 1 eq of 2,3-dimethyl butadiene to **6b** at 0°C yielded phospholenium ion (**8**) after 1 h at RT, which on hydrolysis gave phospholene oxide (**9**) in 89% isolated yield (Scheme 2).¹¹ Interestingly, the hydrolysis of the intermediate phospholenium ion proceeds with elimination of monophenylacetylene, as evidenced by its presence in the ^1H and ^{13}C NMR of the crude reaction mixture prior to purification.

Scheme 2.



The synthesis of **2** further exemplifies the utility of phosphonium ions for the facile synthesis of a variety of phosphorus-containing heterocycles,^{10,12} while the characterization of **6** represents the first example of a vinyl phosphonium ion.

References and Notes

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7. **3** is readily synthesized from the addition of freshly sublimed AlCl_3 to a CH_2Cl_2 solution of $i\text{-Pr}_2\text{NPCl}_2$ at -78°C followed by warming to RT. For a review of phosphonium ions see: Kemp, R. A.; Cowley, A. H. *Chem. Rev.* **1985**, *85*, 367.

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9. The peak at +380 ppm is in the region observed for known phosphonium ions. See ref. 7.

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11. The synthesis of **9** is as follows: 22 mmols of monophenyacetylene is added to a 0.5M CH_2Cl_2 solution of **3** at 0°C . The reaction mixture is warmed to RT and stirred for 24h at which time 22 mmol of 2,3-dimethyl butadiene is added to the solution. ^{31}P NMR indicates quantitative consumption of the phosphorus intermediates. The mixture is hydrolyzed by pipetting the solution into a saturated aqueous ammonium chloride solution. The organic layer is separated and the water layer extracted (2x 50 mL) with CH_2Cl_2 . The organics are combined, dried over magnesium sulfate, and the solvents removed to give 10.4 g of a yellow oil. The oil is refluxed for 16h in 200 mL of 1,4-dioxane in the presence of 70 mL of 0.6M NaOH. The reaction mixture is extracted with CH_2Cl_2 . The combined organic extracts washed with water and removed. Drying the resultant organic layer followed by removal of solvent yielded an amber oil that crystallized on standing. The compound was purified by vacuum sublimation at 100°C to provide 4.5 g (89%) of pure 1-diisopropylamino-3,4-dimethylphosphol-3-ene oxide (**9**). mp = $90\text{--}91^\circ\text{C}$. ^1H NMR: δ 3.29 (m, 2H, isopropyl CH); 2.42 (m, 4H, ring CH_2); 1.72 (s, 6H, ring CH_3); 1.26 (d, 12H, isopropyl CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 128.3 (d, $J_{\text{CP}} = 11.2$ Hz, C_3, C_4); 46.0 (s, $i\text{-pr}$ -CH); 39.2 (d, $J_{\text{CP}} = 82.4$ Hz, C_2, C_5); 23.0 (s, $i\text{-pr}$ - CH_3); 16.6 (d, $J_{\text{CP}} = 16.7$ Hz, ring CH_3). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{NOP}$: C, 62.86; H, 10.55; N, 6.11; Found: C, 63.70; H, 10.58; N, 6.32.

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