

CONCERNING PHOSPHIRENIUM CATIONS

Ronald Breslow\* and Lisa A. Deuring<sup>1</sup>

Department of Chemistry, Columbia University  
New York, New York 10027

**Abstract:** Tetraphenyl-, tetraethyl-, and 1,1-diphenyl-2,3-diethylphosphirenium cations can be prepared by extension of a previously described procedure, but base-promoted cyclizations of 1,3-dihalophosponium cations proceed to ring-opened products by an alternate pathway.

Phosphirenium cations are of considerable theoretical interest. A phosphorus d orbital could in principle be aimed between the p-orbitals of the carbon-carbon bond (1), permitting the Hückel-type three-orbital two-electron delocalization characteristic of cyclopropenyl cations. Such conjugation is also possible for thiirenium cations,<sup>2</sup> selenirenium cations,<sup>3</sup> thiirene oxides,<sup>4</sup> and thiirene dioxides.<sup>5</sup> However all of these except thiirene dioxides also have an unshared electron pair on the heteroatom, so they add some antiaromatic character<sup>6</sup> to the possible aromatic effects. Conjugative electron donation from a carbon p orbital to a heteroatom d orbital seems most likely for a heteroatom with a full positive charge, making the phosphirenium cation system particularly attractive.

We have been pursuing two general approaches to the system. In one of them, we have examined the elimination of two moles of HBr from a 1,3-dibromophosponium salt. This is analogous to the approach first used in the synthesis of diphenylcyclopropenone,<sup>7</sup> and subsequently successfully applied to the synthesis of diphenylthiirene dioxide<sup>5</sup> and oxide.<sup>4</sup> In the second approach we have explored the reaction of species such as diphenylchlorophosphine with acetylenes in the presence of Lewis acids. This is in analogy to the methods used<sup>2</sup> in the successful syntheses of thiirenium cations.

Treatment of a suspension of dibenzylidiphenylphosponium bromide (2) in ether with an excess of butyllithium afforded the dilithio derivative 3. This was added to excess bromine in ether to afford the dibrominated phosphonium cation 4 as a bromide salt; with AgBF<sub>4</sub> this was converted to 4-BF<sub>4</sub>. The salts of 4 were mixtures of the d,l and meso isomers (in varying ratios from run to run) with the expected <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P spectra. With triethylamine (in the presence of adventitious water) 4 was converted to the phosphine oxide 5. It was identified as the Z isomer, λ<sub>max</sub> (EtOH) 284 nm,<sup>8</sup> since it was not

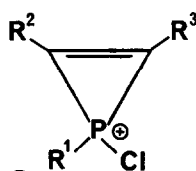
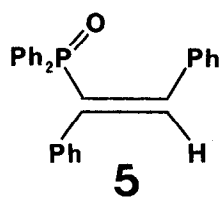
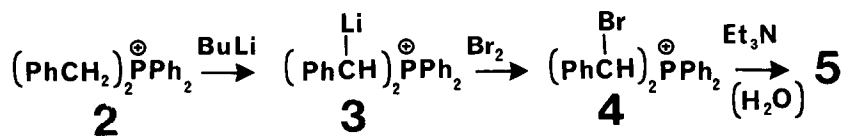
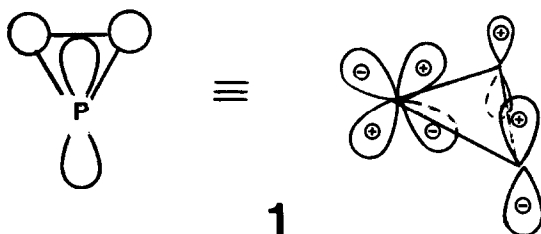
identical to the authentically prepared<sup>9</sup> E isomer,  $\lambda_{\max}$  (EtOH) 268 nm, but both were hydrogenated to the same dihydro derivative. One could imagine that 5 is derived from ring-opening of the tetraphenylphosphirenium cation 7, but such an opening would be expected to afford not the Z but the E isomer of 5. The work to be described shows that 5 is indeed not derived from 7.

In the course of our studies on reaction of halophosphines and acetylenes with Lewis acids such as  $\text{SbF}_5$ , Hogeveen reported<sup>10</sup> the preparation of a series of chlorophosphirenium cations (6a-6f) from the reaction of  $\text{R}_2\text{PCl}_2$  and  $\text{AlCl}_3$  with acetylenes. Under similar conditions we find that  $\text{R}_2\text{PCl}$  species also react, so we were able to prepare  $\text{CDCl}_3$  solutions of tetraphenyl- (7), tetraethyl- (8), and 1,1-diphenyl-2,2-diethylphosphirenium (9) tetrachloroaluminate. For 9 the  $^1\text{H}$  NMR showed the ethyl signals at  $\delta$  1.40 ( $J_{\text{HH}} = 7.5$  Hz) and 3.07 ( $J_{\text{PH}} = 14.3$  Hz) and the expected phenyls. The  $^{13}\text{C}$  NMR showed  $\text{CH}_3$  at  $\delta$  12.38 and  $\text{CH}_2$  at 20.09, phenyl signals at 116.91 ( $J_{\text{PC}} = 102.5$  Hz), 133.81 ( $J_{\text{PC}} = 14.1$  Hz), 130.65 ( $J_{\text{PC}} = 17.1$  Hz), and 135.49 ( $J_{\text{PC}} = 4.9$  Hz). The ring carbons were at  $\delta$  135.05 ( $J_{\text{PC}} = 4.9$  Hz), while  $^{31}\text{P}$  was at  $\delta$  107.4 (vs.  $\text{P}(\text{OMe})_3$ ). The results for 8 were also as expected, with  $^{31}\text{P}$  at  $\delta$  108.3 and the  $^{13}\text{C}$  of the ring carbons at  $\delta$  133 ( $J_{\text{PC}} = 2$  Hz). The tetraphenyl derivative 7 was formed in lower (ca. 10%) yield, and showed a  $^{31}\text{P}$  signal at  $\delta$  111.45. These data are consistent with those reported<sup>10</sup> for compounds 6, and are as expected for the assigned structures. In particular, the very low P-C coupling constants within the ring are expected for strained bonds with high p character. The structures are also confirmed by the ready hydrolysis to products 10.

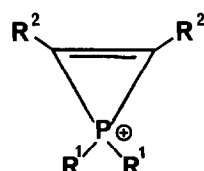
All three phosphirenium cation solutions were stable for 24 hours at room temperature, but reacted rapidly with  $\text{H}_2\text{O}$  (with or without added  $\text{Et}_3\text{N}$ ) to afford the corresponding E phosphine oxides 10 (characterized by H, P, and C NMR and mass spectroscopy). Since 5 and (10,  $\text{R}^1 = \text{R}^2 = \text{Ph}$ ) are not interconverted under these conditions, 5 cannot have been formed via phosphirenium cation 7. Instead we believe that 4 indeed cyclizes to 11, but that this undergoes ring opening by attack of hydroxide at phosphorus to yield 5, rather than eliminate  $\text{HBr}$  to afford 7.

The Hogeveen procedure, and our adaptation of it, yields a group of phosphirenium cation derivatives (6-9). Further work will be needed to determine whether these species show unusual conjugative stabilization, so that they could be classified as "aromatic".

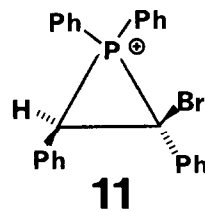
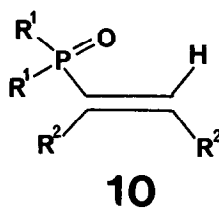
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- a  $R^1 = R^2 = \text{CH}_3, R^3 = \text{H}$
- b  $R^1 = R^2 = R^3 = \text{CH}_3$
- c  $R^1 = \text{CH}_3, R^2 = R^3 = \text{H}$
- d  $R^1 = \text{Ph}, R^2 = R^3 = \text{CH}_3$
- e  $R^1 = \text{Ph}, R^2 = \text{CH}_3, R^3 = \text{H}$
- f  $R^1 = \text{Ph}, R^2 = R^3 = \text{H}$



- 7**  $R^1 = R^2 = \text{Ph}$
- 8**  $R^1 = R^2 = \text{Et}$
- 9**  $R^1 = \text{Et}, R^2 = \text{Ph}$



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