

ordination site for entry of both stabilizing (e.g., phosphine) and reactive (e.g., benzene) ligands into the coordination sphere of the metal. In the intermediate formed immediately after the oxidative addition of benzene, the propene ligand serves as a "trap" for the metal-bound hydrogen, thus preventing reinsertion of benzene. Our results provide direct support for many alkene activation and isomerization mechanisms that have been postulated in the past.<sup>1</sup> However, these observations contrast strongly with mechanisms proposed for hydrido(allyl)metal complexes bound to silica.<sup>3</sup> Attached to the support, hydrido(allyl) complexes are suggested to coordinate 2 mol of phosphine without either  $\eta^3$ - $\eta^1$  isomerization or reductive elimination of propene. Perhaps most strikingly, exposure of the silica-supported hydrido(allyl) complexes to arenes produces catalytic arene hydrogenation—i.e., a reaction which leaves the hydrido(allyl) functionality intact—rather than decoordination, arene C-H activation, and alkene insertion, as we observe in our homogeneous system. We hope an understanding of the physical causes of these profound differences in reactivity will be achieved by continuing the direct study of the supported materials and pursuing the study of homogeneous models for such systems.

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**Supplementary Material Available:** Spectral and analytical data for the compounds 1–4 and 7–11 (3 pages). Ordering information is given on any current masthead page.

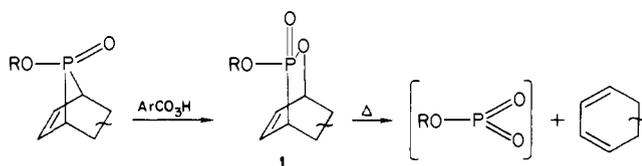
### Metaphosphate and Metaphosphonic Anhydride Formation by Thermolysis of 5,6-Oxaphosphabicyclo[2.2.2]octenes: Electrophilic $\alpha$ -Substitution on a Pyrrole

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We showed in earlier work<sup>1</sup> that a variety of cyclic phosphine oxides with highly contracted C–P–C angles readily undergo O-insertion into a C–P bond with peroxy acids. We have now found that strained cyclic phosphinates can undergo the same reaction and are converted to cyclic phosphonates. Of special interest are the phosphonates **1** arising from O-insertion into the 7-phosphanorbornene (7-PNB) framework, for these structures can in principle undergo fragmentation by retro-[4 + 2] cycloaddition to form the metaphosphate species  $\text{ROPO}_2$ . Meta-

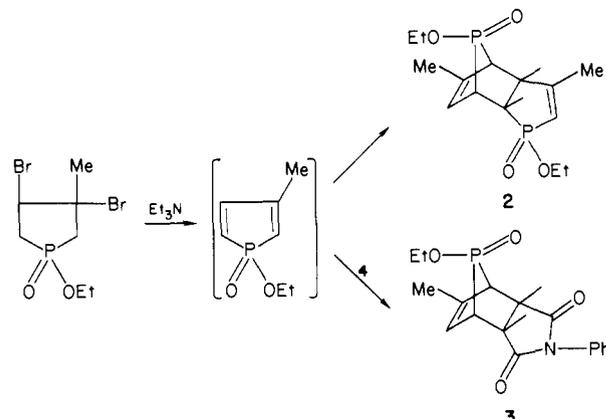


phosphates (and other low-coordination phosphorus species<sup>2</sup>) are of great current interest; the recently reviewed<sup>3</sup> pioneering work of F. H. Westheimer and associates has demonstrated that this highly reactive, polymerizable species has a momentary existence as a monomer and can be trapped with suitable reagents. We indeed have found that the thermolysis of the 5,6-oxaphosphabicyclo[2.2.2]octene system **1** opens a new and useful route to

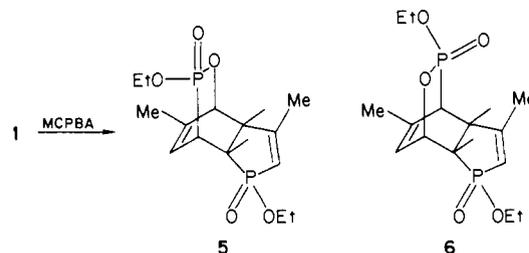
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metaphosphates. The temperature for generating this species is relatively low (100–110 °C), suggesting that practical applications may be derived from the high reactivity of the metaphosphates. In exploring this possibility, we have encountered a valuable property of metaphosphates that was suggested by their known<sup>4</sup> ability to perform electrophilic substitution on aniline derivatives: *N*-substituted pyrroles are highly effective trapping agents for metaphosphates and are phosphorylated specifically at the  $\alpha$ -position.

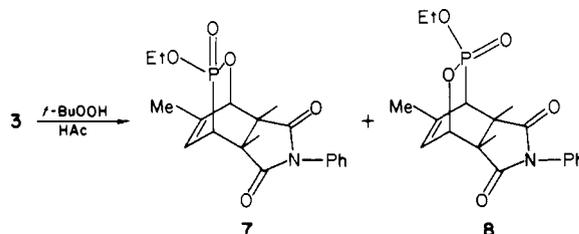
We have employed the 7-PNB phosphinates **2** and **3** in this



work. The former results from dimerization<sup>5</sup> of 1-ethoxy-3-methylphosphole oxide on formation, while **3** (mp 219–220 °C;  $\delta$  <sup>31</sup>P NMR (CDCl<sub>3</sub>) +80.1) is formed when the phosphole is generated in the presence of *N*-phenylmaleimide (**4**). Phosphinate **2** reacted completely in 18 h with *m*-chloroperbenzoic acid (MCPBA) at 25 °C, providing only one of the two possible O-insertion products **5** and **6**. The correct structure was easily



assigned from its <sup>31</sup>P NMR spectrum (phosphonate  $\delta$  +27.2, phosphine oxide  $\delta$  +67.2), which had signal splitting (63.5 Hz) clearly derived from the three-bond <sup>31</sup>P–<sup>31</sup>P connection of **5**. A purification procedure consisting of complexation of the benzoic acid with solid KF, chromatography on Florosil, and recrystallization from benzene–cyclohexane provided analytically pure<sup>6</sup> **5**; attempts to remove the benzoic acid with various bases were less effective.<sup>1</sup> Phosphinate **3** gave a nearly 1:1 mixture of O-insertion products **7** and **8** ( $\delta$  <sup>31</sup>P +25.6, +25.7, unassigned) with



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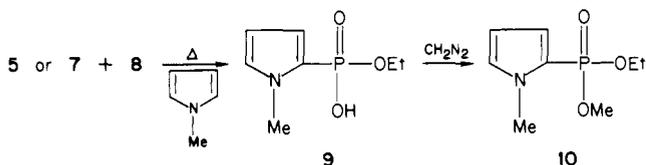
(6) The <sup>13</sup>C NMR spectra supported the structure, especially by showing direct attachment of O to bridgehead C ( $\delta$  79.3, <sup>2</sup>J<sub>POC</sub> = 7.5, J<sub>PCCC</sub> = 3.0 Hz). Anal. Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>P: C, 50.61; H, 6.67; P, 18.61. Found: C, 50.45; H, 6.75; P, 18.41.

MCPBA. *tert*-Butyl hydroperoxide in acetic acid (25 °C) gave a similar result, although isomer **8** was selectively destroyed during the isolation procedure (evaporation of volatiles, chromatography on silica gel with 5% methanol-chloroform).

When phosphonate **5** was heated in benzene at 80 °C, loss of the P bridge was complete after 1.5 h; a new  $^{31}\text{P}$  NMR signal at  $\delta +72.3$  was assigned to the residual dihydrophosphindole. The only other  $^{31}\text{P}$  NMR signals were found in the phosphate region (0 to -12 ppm) and apparently arose from reactions of the released metaphosphate. The mixture of phosphonates **7** and **8** gave a similar clean decomposition at 110 °C for 7 h.

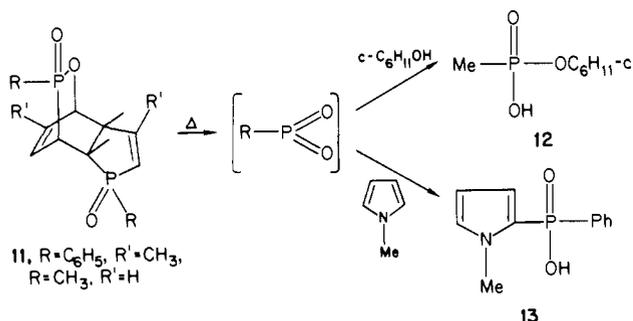
Trapping of the P fragment was accomplished by replacing the inert solvent with methanol (forming  $\text{MeOPO}(\text{OH})(\text{OEt})$  at 80 °C, 1.5 h) or dicyclohexylamine (forming  $(\text{C}_6\text{H}_{11})_2\text{NPO}(\text{OH})(\text{OEt})$  at 100 °C, 2 h). In each case, the phosphate derivatives were the major products by  $^{31}\text{P}$  NMR analysis ( $\delta -0.4$  and  $+5.2$ , respectively) and the signals upfield of  $\delta 0$  were eliminated.

The thermolysis of the cyclic phosphonates was also conducted in *N*-methylpyrrole at 110 °C. The product had  $\delta^{31}\text{P} +20.0$  and accounted for about 80% of the expelled phosphorus. To establish the identity of the product as **9**, it was isolated after esterification with  $\text{CH}_2\text{N}_2$  and Kugelrohr distillation (90 °C, 0.3 mm). The phosphonate **10** had the expected MS and NMR properties.<sup>7</sup> The



yield of **10** was reduced to 23% during the isolation procedure, but this value is not representative of the efficiency of the trapping. No  $\beta$ -substitution product was formed. The diethyl ester corresponding to **10** has been previously prepared by another method.<sup>8</sup>

The 5,6-oxaphosphabicyclo[2.2.2]octene system has also been found to be an excellent generator of metaphosphonic anhydrides when the phosphorus bears a carbon substituent. This process was suggested, but not explored, by Kashman and Awerbouch,<sup>9</sup> who first synthesized such bicyclic compounds. Sigal and Loew<sup>10</sup> later generated mesitylphosphonic anhydride by this approach; the bicyclic precursor was generated by Diels-Alder reactions of mesitylbutadienylphosphinate, but the temperatures required caused prompt decomposition of the intermediates, which were never observed directly. We found that heating **11**<sup>1</sup> in alcohols resulted in virtually complete interception of the expelled P fragment, forming half-esters of phosphonic acids (e.g., **12**,  $\delta^{31}\text{P} +28.6$ ).



The process may have synthetic significance for specialized phosphonates. Of significance also was the effective trapping of  $\text{PhPO}_2$  by *N*-methylpyrrole, forming **13**<sup>11</sup> (isolated as the *p*-

(7) Calcd for  $\text{C}_8\text{H}_{14}\text{NO}_3\text{P}$  ( $M^+$ ) 203.0711, found,  $m/z$  203.0713;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.30 (t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ ), 3.7 (s,  $\text{NCH}_3$ ), 3.75 (d,  $^3J_{\text{PH}} = 9.4$  Hz,  $\text{OCH}_2$ ), 4.10 (2 H, m,  $\text{OCH}_2$ ), 5.9-7.4 (3 H, m,  $=\text{CH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.3 (d,  $J = 6.6$  Hz,  $\text{CH}_2\text{CH}_3$ ), 36.3 ( $\text{NCH}_3$ ), 52.2 (d,  $J = 5.5$  Hz,  $\text{OCH}_2$ ), 61.7 (d,  $J = 5.5$  Hz,  $\text{OCH}_2$ ), 107.6 (d,  $J = 224.4$  Hz, C-2), 111.8 (d,  $J = 11.0$  Hz, C-4), 123.6 (d,  $J = 15.4$  Hz, C-5), 129.3 (d,  $J = 23.0$  Hz, C-3);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta +19.4$ .

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toluidine salt). The ability of metaphosphonic anhydrides to function as electrophilic substitution agents in solution has not previously been recognized, although the cyclization of *o*-biphenylmetaphosphonic anhydride<sup>12</sup> when formed at 600-800 °C is another example of electrophilic substitution. Other applications of the phosphorylating ability of this species are under study.

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(11) Calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_3\text{P}$  ( $M^+$ ) 221.0606, found,  $m/z$  221.0607;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.30 ( $\text{NCH}_3$ ), 5.6-7.3 (3 H, m,  $=\text{CH}$ ), 7.3-7.9 (5 H, Ar H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  35.4 ( $\text{CH}_3$ ), 110.6 (d,  $J = 12.1$  Hz, C-4), 111.8 (d,  $J = 112.0$  Hz, C-2), 123.7 (d,  $J = 12.1$  Hz, C-5), 127.3 (d,  $J = 19.8$  Hz, C-3), 130.0 (d,  $J = 9.0$  Hz, phenyl ortho C), 128.1 (d,  $J = 13.2$  Hz, phenyl meta C), 130.4 (phenyl para C, ipso C not observed);  $\delta^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $+9.8$ .

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### Structure of the $\text{C}_4\text{H}_6\text{CH}_3^+$ Cation. $^{13}\text{C}$ and $^1\text{H}$ NMR Spectroscopic Investigation of Equilibrium Isotope Effects in Deuterated Methylcyclobutonium Ions<sup>1</sup>

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The dominant structure in the dynamic equilibrium of the 1-methylcyclobutyl/1-methylcyclopropylcarbonyl cation<sup>2</sup> ( $\text{C}_4\text{H}_6\text{CH}_3^+$ ) **1** has been in dispute for more than a decade.<sup>2-5</sup> Recently two different structures have been suggested for **1** on the basis of  $^{13}\text{C}$  NMR spectroscopic studies.<sup>4,5</sup> These structures are an  $\text{sp}^3$  hybridized cyclobutyl cation<sup>4</sup> and a bicyclobutonium ion, considered to be either a single minimum or a set of fast equilibrating less symmetric cations claimed to be indistinguishable from the symmetric one.<sup>5</sup>

A comparison of the deuterium equilibrium isotope effects (EIE)<sup>6</sup> in cation **1** and in related model cations **2** and **3** appeared suitable to clarify the controversy concerning the structure of **1**.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a mixture of **1** and  $\text{CD}_2$ -labeled **1** (**1-*d*<sub>2</sub>**) show isotopic perturbation for the averaged signal of the three methylene groups, whereas the other peaks are unaffected. The peak for the nondeuterated methylene groups in **1-*d*<sub>2</sub>** is shifted upfield compared to the unlabeled ion **1** between 1.45 (-80 °C) and 1.22 ppm (-56 °C) in the  $^{13}\text{C}$  NMR, and between 0.043 (-110 °C) and 0.041 ppm (-90 °C) in the  $^1\text{H}$  NMR spectrum. This indicates a definite EIE on a fast rearrangement of *degenerate* cations.

In the  $\text{C}_4\text{H}_5\text{DCH}_3^+$  cation (**1-*d***) the signal for the proton geminal to deuterium moves downfield between 0.099 (-110 °C) and 0.063 ppm (-50 °C) whereas the remaining methylene protons show a small upfield shift. The EIE is observed most clearly in the  $^{13}\text{C}$  NMR spectrum of a mixture of **1-*d*** and **1** (Figure 1a). The triplet ( $J_{\text{CD}} = 25.3$  Hz) of the deuterated carbon in **1-*d*** is shifted downfield between 0.898 (-80 °C) and 0.670 ppm (-46

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