Hz);  ${}^{13}C \{{}^{1}H\} NMR$  (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>2</sub>N (d,  $\delta$  43.04, J<sub>PNC</sub> = 12.9 Hz),  $C_5Me_5$  (s,  $\delta$  10.76),  $C_5Me_5$  (d,  $\delta$  130.4,  $J_{PC}$  = 11.8 Hz). Several pieces of spectroscopic evidence lead to the conclusion the  $Me_5C_5$  ring of 3 is not bonded in the monohapto manner: (i) The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3 indicate that the ring and Me carbons of the Me<sub>5</sub>C<sub>5</sub> moiety are equivalent; moreover, the equivalence of the methyl groups persists to -100 and -80 °C in <sup>1</sup>H and <sup>13</sup>C NMR experiments, respectively. (ii) The <sup>31</sup>P chemical shift of 3 (111.0 ppm)<sup>5</sup> is 33.8 ppm upfield (i.e., shielded) compared to that of the phosphorus(III) chloride precursor, 1. In all cases reported thus far, phosphenium ion formation via halide ion abstraction from precursor phosphorus(III) halides has been accompanied by a downfield <sup>31</sup>P NMR chemical shift of >100 ppm.<sup>7</sup> We attribute the upfield shift to multihapto bonding between P<sup>+</sup> and the Me<sub>5</sub>C<sub>5</sub> ligand and concomitant delocalization of the positive charge in the resulting cluster. Support for this suggestion is provided by the fact that  $\sim 100$  ppm upfield <sup>11</sup>B NMR chemical shifts have been observed<sup>8</sup> when pentahapto boron cations,  $[\eta^5-Me_5C_5)BX]^+$ , are formed via X<sup>-</sup> abstraction from the corresponding monohapto boron dihalides,  $(\eta^{1}$ - $Me_5C_5)BX_2$ .

Treatment of **2** with Al<sub>2</sub>Cl<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution results in the arsenium salt [(Me<sub>5</sub>C<sub>5</sub>)(Me<sub>2</sub>N)As]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup> (4).<sup>9</sup> <sup>-1</sup>H NMR (200 MHz) Me<sub>2</sub>N (s,  $\delta$  3.32) Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  2.17); <sup>13</sup>C {<sup>1</sup>H} NMR (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>2</sub>N (s,  $\delta$  38.14), Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  10.98), Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  126.88); <sup>27</sup>Al NMR (s, 103.5 ppm,  $w_{\rm h} \sim$  14 Hz). The <sup>1</sup>H and <sup>13</sup>C chemical shift equivalence of the Me<sub>5</sub>C<sub>5</sub> ring persisted to -80 °C.

The foregoing NMR observations on cations 3 and 4 are consistent with a static pentahapto structure (5) or with tri- and dihapto structures with low barriers to migration such as 6 and 7, respectively. Structure 6 is analogous to phosphonium or



arsonium ions, while 7 is, in essence, a phosphiran or arsiran stabilized by allyl cation attachment.<sup>10</sup> MNDO calculations<sup>11</sup> on  $[(Me_5C_5)(Me_2N)P]^+$  reveal the following: (i) the global minimum is 7, (ii) 5 and 6 do not correspond to minima,<sup>12</sup> and (iii) the barrier to circumannular migration of the Me<sub>2</sub>NP moiety in 7 via an  $\eta^1$  intermediate is very low (<2 kcal/mol).<sup>13</sup>

The reaction of  $(Me_5C_5)PCl_2$  with  $C_5H_5Li$  results in many products; however, the reaction of  $(Me_5C_5)AsCl_2$  with  $C_5H_5Li$ proceeds cleanly and results in  $(Me_5C_5)(C_5H_5)AsCl$  (8). <sup>1</sup>H NMR

(9) By analogy with phosphenium ions, two-coordinate arsenic cations,  $R_2As^+$ , are referred to as arsenium ions. In the adduct  $AsF_3 \cdot SbF_3$  there is a contribution made from the formulation  $[AsF_2]^+[SbF_6]^-$  in the solid state (Edwards, A. J.; Sills, R. J. C. J. Chem. Soc. A 1971, 942–945). However, compounds 4 and 9 constitute the first clear-cut examples of arsenium ions.

(10) Amido-substituted phosphirans have been described recently and found to exhibit relatively shielded <sup>31</sup>P NMR chemical shifts. Niecke, E.; Schoeller, W. W.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131-132. For the synthesis of other substituted phosphirans, see: Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *25*, 1097-1103.

(11) For MNDO parameters for third period elements, see: Dewar, M. J. S.; McKee, M.; Rzepa, H. J. Am. Chem. Soc. 1978, 100, 3607.

(12) The pentahapto structure (5) is computed to be 28.6 kcal/mol higher in energy than the dihapto structure (7).

(13) The low barrier for ring migration is estimated from a detailed calculation on the model compound  $[(C_3H_5)(Me_2N)P]^+$ . Justification for this extrapolation is found in the close agreement of the calculated energy differences for 5 and 7 and the analogous unpermethylated structures. (60 MHz) Me<sub>5</sub>C<sub>5</sub> (s, 15 H,  $\delta$  1.73), C<sub>5</sub>H<sub>5</sub> (s, 5 H,  $\delta$  5.74); <sup>13</sup>C {<sup>1</sup>H} NMR (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  132.6), Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  12.37), C<sub>5</sub>H<sub>5</sub> (br,  $\delta$  124.03). Treatment of **8** with a stoichiometric quantity of Al<sub>2</sub>Cl<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> results in the arsenium salt [(Me<sub>5</sub>C<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)As]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup> (9).<sup>9</sup> <sup>1</sup>H NMR (200 MHz) Me<sub>5</sub>C<sub>5</sub> (s, 15 H,  $\delta$  2.17), C<sub>5</sub>H<sub>5</sub> (s, 5 H,  $\delta$  6.72); <sup>13</sup>C [<sup>1</sup>H} NMR (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  130.9), Me<sub>5</sub>C<sub>5</sub> (s,  $\delta$  10.46), C<sub>5</sub>H<sub>5</sub> (s,  $\delta$  119.8); <sup>27</sup>Al NMR (s,  $\delta$  103.5, w<sub>h</sub> ~14 Hz). The chemical shift equivalence in both cyclopentadienyl rings persists to -80 °C, and MNDO calculations on the model compound (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>P<sup>+</sup> indicate that the bis(pentahapto) structure represents a global minimum which is 16 kcal/mol more stable than the bis(monohapto) structure. We therefore suggest the following structure for **9**.



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## Isomerization of Silene to Ketene in the Photolysis of Pentamethyldisilanyldiazoacetate

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We have recently presented evidence for the formation of a silene intermediate in the decomposition of ethyl (trimethylsilyl)diazoacetate.<sup>1</sup> The major question remaining is the source of alkoxysilylketene 2 in the gas-phase decomposition of the silyldiazoacetate.<sup>2,3</sup> The Wolff rearrangement may have a radical



or even ionic component. As an alkoxy group migrates to an adjacent position on its way to ketene 3, it finds itself in the neighborhood of a silicon atom and adds with or without simultaneous migration of a methyl group to give the ketene 2.

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Jutzi, P.; Seufert, A.; Buchner, W. Chem. Ber. 1979, 112, 2488-93.
(9) By analogy with phosphenium ions, two-coordinate arsenic cations,

Ando, W.; Hagiwara, T.; Migita, T. J. Am. Chem. Soc. 1973, 95, 7518.
 Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. J. Am. Chem. Soc. 1975, 97, 3818.

<sup>(3)</sup> Ando, W.; Sekiguchi, A.; Hagiwara, T.; Migita, T.; Chowdhry, V.; Westheimer, F. H.; Kammula, S.; Green, M.; Jones, M., Jr. J. Am. Chem. Soc. 1979, 101, 6393.

Another possibility may involve the isomerization of silene 1 to the rearranged ketene 2. Despite the amount of work done in this area, the mechanistic question for ketene 2 remains unresolved. We wish to present here definitive evidence for the isomerization of silene 1 to ketene 2.

One might expect that the trimethylsilyl group in the diazo compound 4<sup>4</sup> should have a considerably better migrating tendency than the methyl group. Photolysis of ethyl pentamethyldisilanyldiazoacetate (4) (0.89 mmol) for 2 h with a high-pressure mercury lamp in THF cleanly produced (ethoxydimethylsilyl)-(trimethylsilyl)ketene (5) in quantitative yield. The spectral data of 5 serve to establish the structure: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.22 (s, 9 H, SiMe<sub>3</sub>), 0.26 (s, 6 H, SiMe<sub>2</sub>), 1.17 (t, 3 H, OCCH<sub>3</sub>), and 3.68 (q, 2 H, OCH<sub>2</sub>); IR (NaCl) 2080 (C=C=O) and 1080 cm<sup>-1</sup> (Si-O-C); mass spectrum, m/e 216 (M<sup>+</sup>). The structure of



5 was further supported by reactions with alcohols. An interesting product, (methoxydimethylsilyl)(trimethylsilyl)ketene (6),<sup>5</sup> was obtained when treated with methanol. Methoxysilane 76 could be isolated on heating with methanol. Similarly, the reaction of 5 with ethanol gave the ethoxysilane  $8.^7$ 

Support for the intervention of the silene intermediate in the reaction of 4 was substantiated by photolysis in alcohols. Silene 9 was trapped as an alkoxysilane 10 in high yield.<sup>8</sup> Surprisingly, O-H insertion and Wolff rearrangement products were not observed by GLC analysis, whereas these were major reactions in ethyl (trimethylsilyl)diazoacetate.<sup>1-3</sup> Low-temperature photolysis of 4 in the rigid matrix of methanol/tetrahydro-2-methylfuran at -196 °C suppressed the isomerization of silene 9 to ketene 5 to some extent.

Similar results were obtained with tert-butyl alcohol, but the results suggest that the relative difficulty in the reaction of the silene with a steric hindered alcohol is reflected in increasing amounts of ketene 5.9

SiMe), 0.18 (s, 3 H, SiMe), 1.70 (s, 1 H, SICH), 3.41 (s, 3 H, OMe), and 3.56 (s, 3 H, OMe). (7) Compound 8: NMR (CCl<sub>4</sub>,  $\delta$ ); 0.11 (s, 9 H, SiMe<sub>3</sub>), 0.15 (s, 3 H, SiMe), 0.18 (s, 3 H, SiMe), 1.13 (t, 3 H, OCCH<sub>3</sub>), 1.20 (t, 3 H, OCCH<sub>3</sub>), 1.66 (s, 1 H, SiCH), 3.66 (q, 2 H, OCH<sub>2</sub>), and 4.02 (q, 2 H, OCH<sub>2</sub>). (8) Compound 10: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.09 (s, 9 H, SiMe<sub>3</sub>), 0.13 (s, 3 H, SiMe), 0.17 (s, 3 H, SiMe), 1.21 (t, 3 H, OCCH<sub>3</sub>), 1.67 (s, 1 H, SiCH), 3.38

(s, 3 H, OMe), and 4.00 (q, 2 H, OCH<sub>2</sub>). The structure of 10 was also confirmed by the exchange reaction of the methoxy group on silicon atom with alcohols.

(9) (*tert*-Butoxydimethylsilyl)(trimethylsilyl)ketene: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.21 (s, 9 H, SiMe<sub>3</sub>), 0.28 (s, 6 H, SiMe<sub>2</sub>), and 1.27 (s, 9 H, *t*-Bu); IR (NaCl) 2080 (C=C=O) and 1045 cm<sup>-1</sup> (SiOC); mass spectrum, m/e 244 (M<sup>+</sup>). Ethyl  $\alpha$ -(*tert*-butoxydimethylsilyl)- $\alpha$ -(trimethylsilyl)acetate: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.10 (s, 9 H, SiMe<sub>3</sub>), 0.18 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe), 1.20 (t, 3 H, OCCH<sub>3</sub>), 1.24 (s, 9 H, *t*-Bu), 1.62 (s, 1 H, SiCH), and 3.97 (q, 2 H, OCH<sub>2</sub>).



Most convincingly, silene 9 can be trapped with carbonyl compounds. Silenes are known to react with carbonyl compounds to give alkenes or silvl enol ethers through the intermediacy of labile 1,2-silaoxetanes.<sup>10</sup> Photolysis of 4 (0.82 mmol) containing excess amounts of cyclohexanone (58 mmol) gave silyl enol ether  $11^{11}$  in 30% yield and ketene 5 in 53% yield. The silvl enol ether



11 is obtained probably by isomerization of a 1,2-silaoxetane via C-C bond cleavage.<sup>10</sup> However, the reaction in acetone or 2,3dimethyl-1,3-butadiene gave only the ketene 5 due to their low reactivities.

In summary, it is now clear that the silene having an ester group rearranges to the alkoxysilylketene 5 by migration of the alkoxy group to silicon. The intermediate silene was successfully trapped by alcohols and a carbonyl compound.

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<sup>(4)</sup> Compound 4 was prepared by the reaction of bis(pentamethyldisilanyl) sulfide with diethyl mercuribis(diazoacetate) in 38% yield. NMR (CCl<sub>4</sub>,  $\delta$ ) 0.12 (s, 9 H, SiMe<sub>3</sub>), 0.25 (s, 6 H, SiMe<sub>2</sub>), 1.27 (t, 3 H, OCCH<sub>3</sub>), and 4.13 (q, 2 H, OCH<sub>2</sub>); IR (NaCl) 2100 (N<sub>2</sub>) and 1690 cm<sup>-1</sup> (CO<sub>2</sub>); UV  $\lambda_{max}$ (MeOH) 381 nm (e 125).

<sup>(5)</sup> Compound 6: NMR (CCl<sub>4</sub>, δ) 0.20 (s, 9 H, SiMe<sub>3</sub>), 0.22 (s, 6 H SiMe<sub>2</sub>), and 3.37 (s, 3 H, OMe); IR (NaCl) 2085 (C=C=O) and 1090 cm<sup>-1</sup>

<sup>(</sup>SiOC); mass spectrum, m/e 202 (M<sup>+</sup>). (6) Compound 7: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.11 (s, 9 H, SiMe<sub>3</sub>), 0.14 (s, 3 H, SiMe), 0.18 (s, 3 H, SiMe), 1.70 (s, 1 H, SiCH), 3.41 (s, 3 H, OMe), and

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**<sup>1975</sup>**, 8, 18. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, 79, 529. (11) Compound **11**: NMR (CCl<sub>4</sub>,  $\delta$ ) 0.10 (s, 9 H, SiMe<sub>3</sub>), 0.23 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 1.21 (t, 3 H, OCCH<sub>3</sub>), 1.76 (s, 1 H, SiCH), 1.38–2.22 (m, 8 H, aliphatic CH), 4.02 (q, 2 H, OCH<sub>2</sub>), and 4.78 (m, 1 H, C=CH); IR (NaCl) 1705 (CO<sub>2</sub>) and 1670 cm<sup>-1</sup> (C=C); mass spectrum, *m/e* 314 (M<sup>+</sup>). 314 (M<sup>+</sup>).