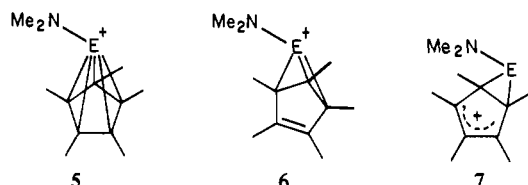


Hz); ^{13}C $\{^1\text{H}\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (d, δ 43.04, $J_{\text{PNC}} = 12.9$ Hz), C_5Me_5 (s, δ 10.76), C_5Me_5 (d, δ 130.4, $J_{\text{PC}} = 11.8$ Hz). Several pieces of spectroscopic evidence lead to the conclusion the Me_5C_5 ring of **3** is not bonded in the monohapto manner: (i) The ^1H and ^{13}C NMR spectra of **3** indicate that the ring and Me carbons of the Me_5C_5 moiety are equivalent; moreover, the equivalence of the methyl groups persists to -100 and -80 $^\circ\text{C}$ in ^1H and ^{13}C NMR experiments, respectively. (ii) The ^{31}P chemical shift of **3** (111.0 ppm)⁵ is 33.8 ppm *upfield* (i.e., shielded) compared to that of the phosphorus(III) chloride precursor, **1**. In all cases reported thus far, phosphonium ion formation via halide ion abstraction from precursor phosphorus(III) halides has been accompanied by a downfield ^{31}P NMR chemical shift of >100 ppm.⁷ We attribute the upfield shift to multihapto bonding between P^+ and the Me_5C_5 ligand and concomitant delocalization of the positive charge in the resulting cluster. Support for this suggestion is provided by the fact that ~ 100 ppm upfield ^{11}B NMR chemical shifts have been observed⁸ when pentahapto boron cations, $[\eta^5\text{-Me}_5\text{C}_5]\text{BX}^+$, are formed via X^- abstraction from the corresponding monohapto boron dihalides, $(\eta^1\text{-Me}_5\text{C}_5)\text{BX}_2$.

Treatment of **2** with Al_2Cl_6 in CH_2Cl_2 solution results in the arsenium salt $[(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{As}]^+[\text{AlCl}_4]^-$ (**4**).⁹ ^1H NMR (200 MHz) Me_2N (s, δ 3.32) Me_5C_5 (s, δ 2.17); ^{13}C $\{^1\text{H}\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (s, δ 38.14), Me_5C_5 (s, δ 10.98), Me_5C_5 (s, δ 126.88); ^{27}Al NMR (s, 103.5 ppm, $w_h \sim 14$ Hz). The ^1H and ^{13}C chemical shift equivalence of the Me_5C_5 ring persisted to -80 $^\circ\text{C}$.

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



arsenium ions, while **7** is, in essence, a phosphiran or arsanion stabilized by allyl cation attachment.¹⁰ MNDO calculations¹¹ on $[(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{P}]^+$ reveal the following: (i) the global minimum is **7**, (ii) **5** and **6** do not correspond to minima,¹² and (iii) the barrier to circumannular migration of the Me_2NP moiety in **7** via an η^1 intermediate is very low (<2 kcal/mol).¹³

The reaction of $(\text{Me}_5\text{C}_5)\text{PCl}_2$ with $\text{C}_5\text{H}_5\text{Li}$ results in many products; however, the reaction of $(\text{Me}_5\text{C}_5)\text{AsCl}_2$ with $\text{C}_5\text{H}_5\text{Li}$ proceeds cleanly and results in $(\text{Me}_5\text{C}_5)(\text{C}_5\text{H}_5)\text{AsCl}$ (**8**). ^1H NMR

(7) (a) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534-2540. (b) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475-3480. (c) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994-1001. (d) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789-797. (e) Baxter, S. G.; Cowley, A. H.; Collins, R. L.; Sena, S. F. *J. Am. Chem. Soc.* **1981**, *102*, 714-715.

(8) Jutzi, P.; Seufert, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 330-1. Jutzi, P.; Seufert, A.; Buchner, W. *Chem. Ber.* **1979**, *112*, 2488-93.

(9) By analogy with phosphonium ions, two-coordinate arsenic cations, R_2As^+ , are referred to as arsenium ions. In the adduct $\text{AsF}_3\cdot\text{SbF}_6^-$ there is a contribution made from the formulation $[\text{AsF}_2]^+[\text{SbF}_6]^-$ 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.

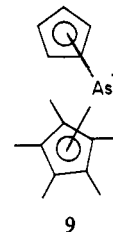
(10) Amido-substituted phosphirans have been described recently and found to exhibit relatively shielded ^{31}P NMR chemical shifts. Niecke, E.; Schoeller, W. W.; Wildbrecht, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131-132. For the synthesis of other substituted phosphirans, see: Chan, S.; 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 $[(\text{C}_5\text{H}_5)(\text{Me}_2\text{N})\text{P}]^+$. 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_5C_5 (s, 15 H, δ 1.73), C_5H_5 (s, 5 H, δ 5.74); ^{13}C $\{^1\text{H}\}$ NMR (20.0 MHz) (Me_4Si) Me_5C_5 (s, δ 132.6), Me_5C_5 (s, δ 12.37), C_5H_5 (br, δ 124.03). Treatment of **8** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 results in the arsenium salt $[(\text{Me}_5\text{C}_5)(\text{C}_5\text{H}_5)\text{As}]^+[\text{AlCl}_4]^-$ (**9**).⁹ ^1H NMR (200 MHz) Me_5C_5 (s, 15 H, δ 2.17), C_5H_5 (s, 5 H, δ 6.72); ^{13}C $\{^1\text{H}\}$ NMR (20.0 MHz) (Me_4Si) Me_5C_5 (s, δ 130.9), Me_5C_5 (s, δ 10.46), C_5H_5 (s, δ 119.8); ^{27}Al NMR (s, δ 103.5, $w_h \sim 14$ Hz). The chemical shift equivalence in both cyclopentadienyl rings persists to -80 $^\circ\text{C}$, and MNDO calculations on the model compound $(\text{C}_5\text{H}_5)_2\text{P}^+$ 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**.



Acknowledgment. We are grateful to the National Science Foundation (Grant CHE79-10155) and the Robert A. Welch Foundation for generous financial support.

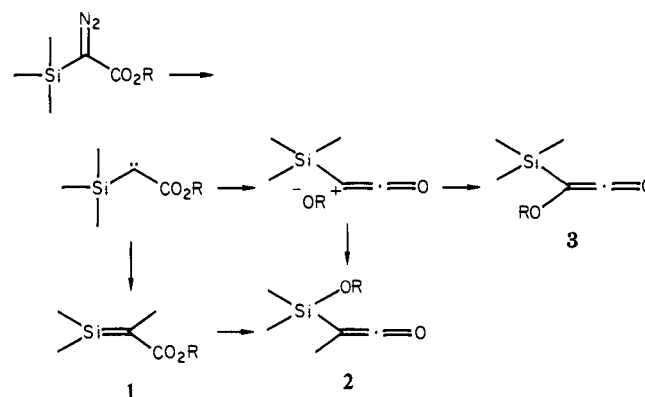
Isomerization of Silene to Ketene in the Photolysis of Pentamethyldisilyldiazoacetate

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Received April 2, 1981

We have recently presented evidence for the formation of a silene intermediate in the decomposition of ethyl (trimethylsilyl)diazoacetate.¹ The major question remaining is the source of alkoxysilylketene **2** in the gas-phase decomposition of the silyldiazoacetate.^{2,3} 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**.

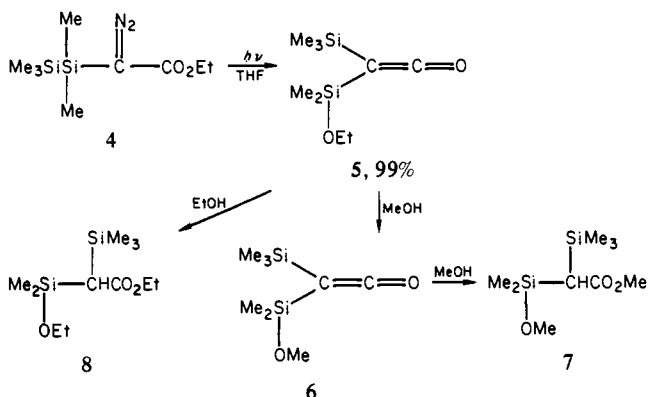
(1) Ando, W.; Hagiwara, T.; Migita, T. *J. Am. Chem. Soc.* **1973**, *95*, 7518.

(2) Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3818.

(3) 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** should have a considerably better migrating tendency than the methyl group. Photolysis of ethyl pentamethyldisilyldiazoacetate (**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_4 , δ) 0.22 (s, 9 H, SiMe_3), 0.26 (s, 6 H, SiMe_2), 1.17 (t, 3 H, OCCH_3), and 3.68 (q, 2 H, OCH_2); IR (NaCl) 2080 ($\text{C}=\text{C}=\text{O}$) and 1080 cm^{-1} ($\text{Si}-\text{O}-\text{C}$); mass spectrum, m/e 216 (M^+). The structure of



5 was further supported by reactions with alcohols. An interesting product, (methoxydimethylsilyl)(trimethylsilyl)ketene (**6**),⁵ was obtained when treated with methanol. Methoxysilane **7**⁶ 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.⁸ Surprisingly, O-H insertion and Wolff rearrangement products were not observed by GLC analysis, whereas these were major reactions in ethyl (trimethylsilyl)diazoacetate.¹⁻³ Low-temperature photolysis of **4** in the rigid matrix of methanol/tetrahydro-2-methylfuran at $-196\text{ }^\circ\text{C}$ 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

(4) Compound **4** was prepared by the reaction of bis(pentamethyldisilyl) sulfide with diethyl mercuribis(diazoacetate) in 38% yield. NMR (CCl_4 , δ) 0.12 (s, 9 H, SiMe_3), 0.25 (s, 6 H, SiMe_2), 1.27 (t, 3 H, OCCH_3), and 4.13 (q, 2 H, OCH_2); IR (NaCl) 2100 (N_2) and 1690 cm^{-1} (CO_2); UV λ_{max} (MeOH) 381 nm (ϵ 125).

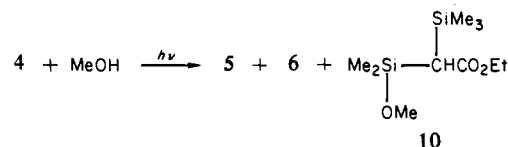
(5) Compound **6**: NMR (CCl_4 , δ) 0.20 (s, 9 H, SiMe_3), 0.22 (s, 6 H, SiMe_2), and 3.37 (s, 3 H, OMe); IR (NaCl) 2085 ($\text{C}=\text{C}=\text{O}$) and 1090 cm^{-1} (SiOC); mass spectrum, m/e 202 (M^+).

(6) Compound **7**: NMR (CCl_4 , δ) 0.11 (s, 9 H, SiMe_3), 0.14 (s, 3 H, SiMe_2), 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).

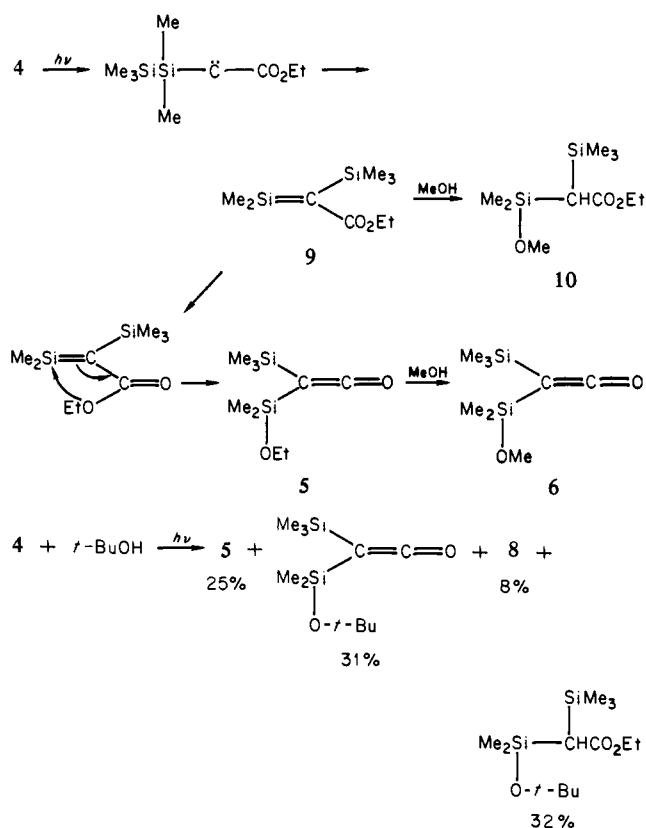
(7) Compound **8**: NMR (CCl_4 , δ); 0.11 (s, 9 H, SiMe_3), 0.15 (s, 3 H, SiMe_2), 0.18 (s, 3 H, SiMe), 1.13 (t, 3 H, OCCH_3), 1.20 (t, 3 H, OCCH_3), 1.66 (s, 1 H, SiCH), 3.66 (q, 2 H, OCH_2), and 4.02 (q, 2 H, OCH_2).

(8) Compound **10**: NMR (CCl_4 , δ) 0.09 (s, 9 H, SiMe_3), 0.13 (s, 3 H, SiMe_2), 0.17 (s, 3 H, SiMe), 1.21 (t, 3 H, OCCH_3), 1.67 (s, 1 H, SiCH), 3.38 (s, 3 H, OMe), and 4.00 (q, 2 H, OCH_2). The structure of **10** was also confirmed by the exchange reaction of the methoxy group on silicon atom with alcohols.

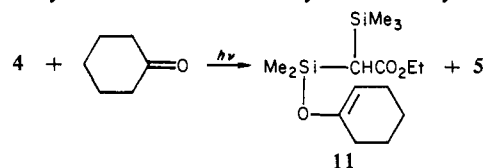
(9) (*tert*-Butoxydimethylsilyl)(trimethylsilyl)ketene: NMR (CCl_4 , δ) 0.21 (s, 9 H, SiMe_3), 0.28 (s, 6 H, SiMe_2), and 1.27 (s, 9 H, *t*-Bu); IR (NaCl) 2080 ($\text{C}=\text{C}=\text{O}$) and 1045 cm^{-1} (SiOC); mass spectrum, m/e 244 (M^+). Ethyl α -(*tert*-butoxydimethylsilyl)- α -(trimethylsilyl)acetate: NMR (CCl_4 , δ) 0.10 (s, 9 H, SiMe_3), 0.18 (s, 3 H, SiMe_2), 0.23 (s, 3 H, SiMe), 1.20 (t, 3 H, OCCH_3), 1.24 (s, 9 H, *t*-Bu), 1.62 (s, 1 H, SiCH), and 3.97 (q, 2 H, OCH_2).



room temperature	0%	23%	70%
$-196\text{ }^\circ\text{C}$	11%	4%	83%



Most convincingly, silene **9** can be trapped with carbonyl compounds. Silenes are known to react with carbonyl compounds to give alkenes or silyl enol ethers through the intermediacy of labile 1,2-silaoxetanes.¹⁰ 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 silyl enol ether



11 is obtained probably by isomerization of a 1,2-silaoxetane via C-C bond cleavage.¹⁰ However, the reaction in acetone or 2,3-dimethyl-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.

Acknowledgment. We acknowledge partial support by the Ministry of Education, a Grant for Scientific Research (447019), and the Shinetsu Chemical Co. We gratefully thank Professor T. J. Barton for many helpful discussions.

(10) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(11) Compound **11**: NMR (CCl_4 , δ) 0.10 (s, 9 H, SiMe_3), 0.23 (s, 3 H, SiMe_2), 0.26 (s, 3 H, SiMe), 1.21 (t, 3 H, OCCH_3), 1.76 (s, 1 H, SiCH), 1.38-2.22 (m, 8 H, aliphatic CH), 4.02 (q, 2 H, OCH_2), and 4.78 (m, 1 H, $\text{C}=\text{CH}$); IR (NaCl) 1705 (CO_2) and 1670 cm^{-1} ($\text{C}=\text{C}$); mass spectrum, m/e 314 (M^+).