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PHOTOLYSIS AND PYROLYSIS OF POLYSILYLATED DIAZOMETHANES. EFFECTIVE MIGRATING TENDENCY OF TRIMETHYLSILYL GROUP TO A CARBENE CENTER

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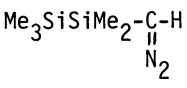
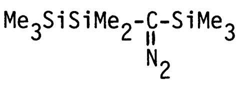
Photolysis and pyrolysis of polysilylated diazomethanes were investigated, and a selective migration of trimethylsilyl group to a carbene center was observed.

Research on silaethylenes has remarkably grown,[1] and one of the typical approach is the rearrangement of silylcarbenes in the photo and thermal decompositions of silyl diazo compounds.[2] In a previous paper, we reported that the migrating ability of the groups on silicon atom to a carbene center was not significantly influenced on the nature of substituents and depended on the statistical factor.[3] Since Si-Si bond has a character of donating effect of σ-electrons[4] and the bond is relatively weaker than that of Si-C,[5] silylcarbenes having Si-Si bond should undergo a selective migration of trimethylsilyl group by cleaving Si-Si bond. In this letter, we demonstrate an effective migration of trimethylsilyl group to a carbene center in the photo and thermal decompositions of polysilylated diazomethanes, 1, 2, and 3.



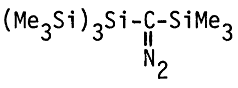
$\mathrm{Me_3SiSiMe_2{-}\underset{\underset{N_2}{\|}}{C}{-}H}$

1



$\mathrm{Me_3SiSiMe_2{-}\underset{\underset{N_2}{\|}}{C}{-}SiMe_3}$

2



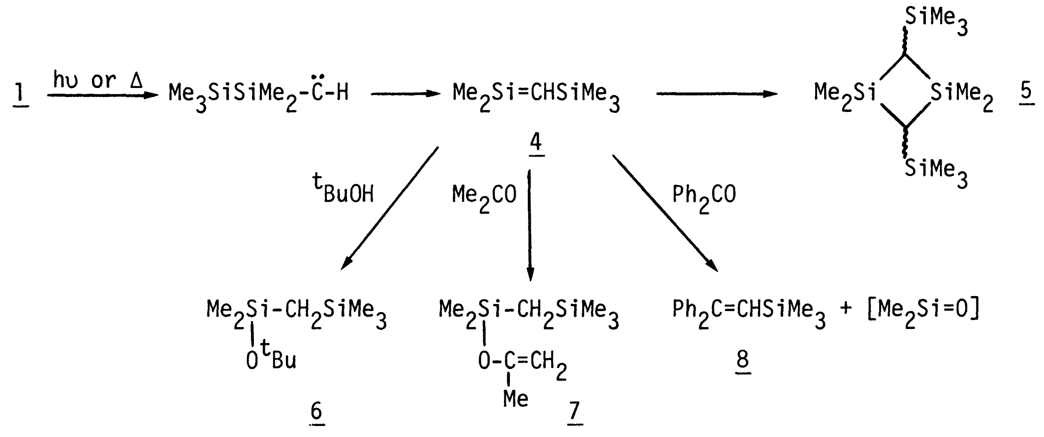
$\mathrm{(Me_3Si)_3Si{-}\underset{\underset{N_2}{\|}}{C}{-}SiMe_3}$

3

Pentamethyldisilanyldiazomethane 1[6] was prepared by the reaction of pentamethyldisilanylmethylmagnesium chloride and diphenyl phosphorazide in 50% yield according to the method of Shioiri.[7] Pentamethyldisilanyltrimethylsilyldiazomethane 2 was obtained in 93% yield by treating chloropentamethyldisilane with lithium trimethylsilyldiazomethane prepared from trimethylsilyldiazomethane and lithium diisopropylamide.[8)] Similarly, silyldiazomethane 3 was prepared quantitatively from tris(trimethylsilyl)chlorosilane and lithium trimethylsilyldiazomethane.[9)]

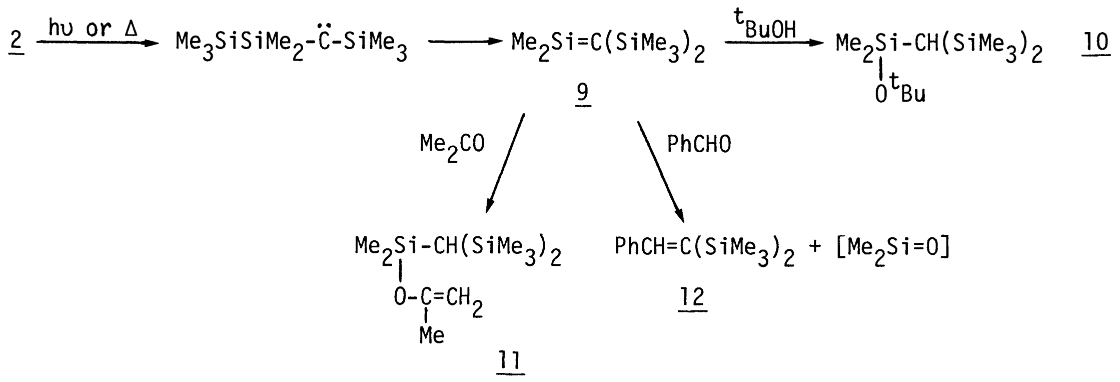
Flash vacuum pyrolysis of 1 at 450°C produced disilacyclobutane 5 in 47% yield (a mixture of trans and cis; ratio 59 : 41), apparently formed by the head-to-tail dimerization of silaethylene 4.[10)] The silaethylene 4 was further intercepted by alcohols and carbonyl compounds. When 1 was pyrolyzed with t-butyl alcohol through a vertical Pyrex tube packed with Pyrex chips at 450°C under flowing nitrogen, t-butoxysilane 6 was obtained in 52% yield. Copyrolysis of 1 with acetone gave silyl enol ether 7 in 54% yield, and with a 17-fold excess of benzophenone led to the formation of vinylsilane 8 in 58% yield which was formed by a Wittig-type reaction of 4 with the ketone.

Photolysis of 1 with a high pressure mercury lamp also yielded the silaethylene 4 which was successfully trapped by t-butyl alcohol and acetone to give the same products 6 and 7 in 41 and 28% yields, respectively. It is of quite interest to note that the exclusive migration of trimethylsilyl group to a carbene center was observed in both thermal and photochemical decompositions of 1, no detectable amounts of methyl migration product being formed.

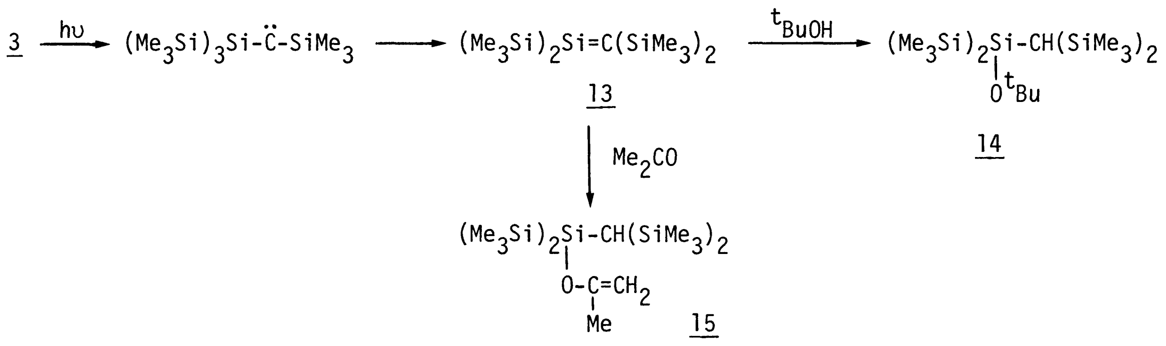


The similar silyl migration was observed in the reaction of 2. Thus, pyrolysis of 2 with t-butyl alcohol at 450°C under flowing nitrogen afforded only t-butoxysilane 10 in 59% yield by the reaction of silaethylene 9. Silyl enol ether 11 and vinylsilane 12 were formed in 52 and 48% yields, respectively when copyrolysis of 2 with acetone and benzaldehyde were conducted.

Photolyses of 2 in t-butyl alcohol and acetone also led to the same products 10 and 11 in 58 and 29% yields, respectively. No methyl migration could be found in the photo and thermal decompositions of 2.



Photolysis of 3 in t-butyl alcohol cleanly produced t-butoxysilane 14 in 60% yield by the interception of silaethylene 13. Silyl enol ether 15 was also obtained by the photolysis of 3 in acetone in 38% yield.



In summary, the effective migrating aptitude of trimethylsilyl group to a carbene center was observed in the reactions of these polysilylated diazomethanes. This may reflect a vertical charge stabilization by the donating effect of Si-Si σ-electrons to the vacant p-orbital of the silylcarbenes.

References

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6) Compound 1: bp. 62-65°C/22 mmHg; NMR(CCl_4,δ) 0.12(s,9H,$SiMe_3$), 0.18(s,6H,$SiMe_2$), and 2.53(s,1H,CHN_2); IR(NaCl) 2050 cm^{-1}(N_2); Mass m/e 144 (M^+-28).

7) S.Mori, I.Sakai, T.Aoyama, and T.Shioiri, Chem. Pharm. Bull., 30, 3380 (1982).

8) Compound 2: bp. 79-80°C/3 mmHg; NMR(CCl_4,δ) 0.05(s,9H,$SiMe_3$), 0.09(s,9H,$SiMe_3$), and 0.12(s,6H,$SiMe_2$); IR(NaCl) 2025 cm^{-1}(N_2); Mass m/e 216 (M^+-28).

9) Compound 3: Purified by alumina column; NMR(CCl_4,δ) 0.17(s,9H,$SiMe_3$) and 0.22(s,27H,$SiMe_3$); IR(NaCl) 2020 cm^{-1}(N_2); Mass m/e 360 (M^+).

10) All new compounds presented here showed NMR, IR, and Mass spectra as well as satisfactory elemental analyses consistent with the structures assigned. Some representative data are as follows.

(a) Compound 5 (a mixture of trans and cis): NMR(CCl_4,δ) -0.43(s,Si_3CH), -0.40(s,Si_3CH), -0.10(s,$SiMe_3$), -0.09(s,$SiMe_3$), 0.15(s,$SiMe_2$), 0.20(s,$SiMe_2$), and 0.23(s,$SiMe_2$); Mass m/e 288 (M^+); Anal. Found: C, 50.02; H, 11.44%. Calcd for $C_{12}H_{32}Si_4$: C, 49.91; H, 11.17%.

(b) Compound 6: NMR(CCl_4,δ) -0.25(s,2H,$SiCH_2Si$), 0.00(s,9H,$SiMe_3$), 0.10(s,6H,$SiMe_2$), and 1.23(s,9H,t-Bu); IR(NaCl) 1050 cm^{-1}(Si-O-C); Anal. Found: C, 55.10; H, 12.21%. Calcd for $C_{10}H_{26}Si_2O$: C, 54.97; H, 11.99%.

(c) Compound 7: NMR(CCl_4,δ) -0.10(s,2H,$SiCH_2Si$), 0.04(s,9H,$SiMe_3$), 0.18(s,6H,$SiMe_2$), 1.72(s,3H,C=C-Me), and 3.92(br.s,2H,C=CH_2); IR(NaCl) 1640(C=C) and 1050 cm^{-1}(Si-O-C); Anal. Found: C, 53.08; H, 11.12%. Calcd for $C_9H_{22}Si_2O$: C, 53.39; H, 10.95%.

(d) Compound 10: NMR(CCl_4,δ) -0.80(s,1H,Si_3CH), 0.07(s,18H,$SiMe_3$), 0.16(s,6H,$SiMe_2$), and 1.22(s,9H,t-Bu); IR(NaCl) 1040 and 1010 cm^{-1}(Si-O-C); Anal. Found: C, 53.64; H, 12.01%. Calcd for $C_{13}H_{34}Si_3O$: C, 53.71; H, 11.79%.

(e) Compound 14: NMR(CCl_4,δ) -0.53(s,1H,Si_3CH), 0.06(s,18H,$SiMe_3$), 0.12(s,18H,$SiMe_3$), and 1.18(s,9H,t-Bu); IR(KBr) 1030 and 1015 cm^{-1}(Si-O-C); Anal. Found: C, 49.93; H, 11.57%. Calcd for $C_{17}H_{46}Si_5O$: C, 50.17; H, 11.39%.

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