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THERMAL GENERATION OF BIS(TRIMETHYLSILYL)METHYLSILYLENE. REARRANGEMENT OF THE SILYLENE TO A SILAETHYLENE VIA 1,2-SHIFT OF TRIMETHYLSILYL GROUP

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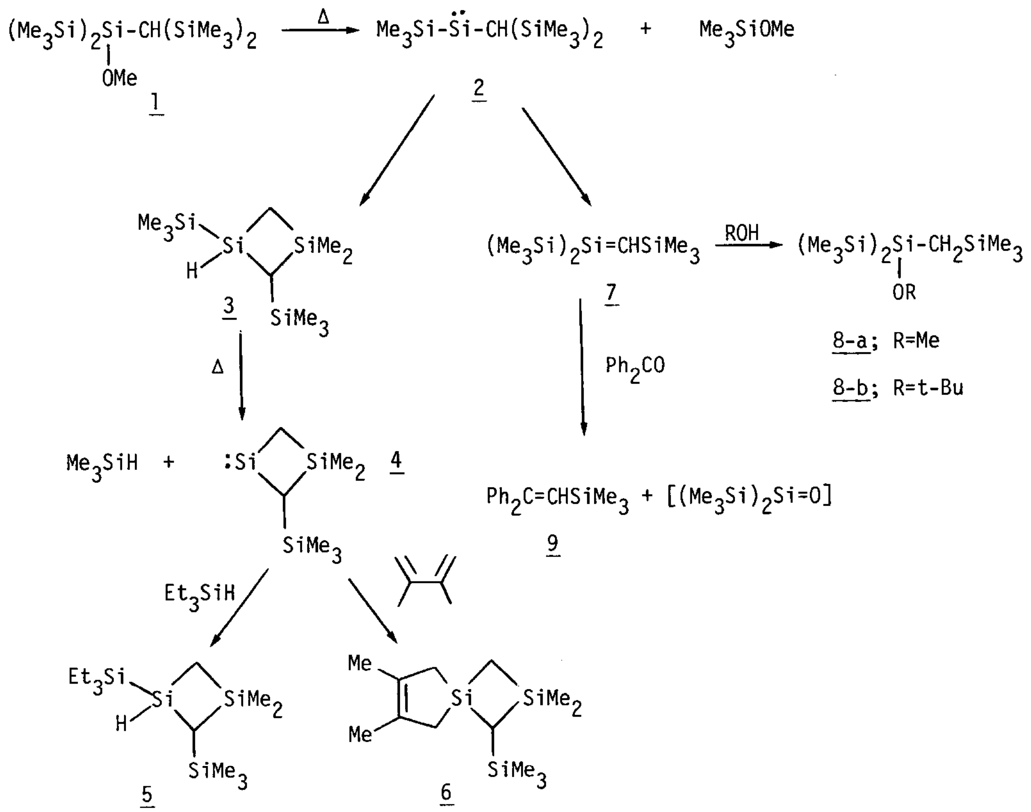
Abstract: The gas phase generation of bis(trimethylsilyl)methyltrimethylsilylsilylene through the pyrolysis of bis(trimethylsilyl)-methyl-di-(trimethylsilyl)-methoxysilane yielded a disilacyclobutane via intramolecular C-H insertion and a silaethylene intermediate by 1,2-shift of trimethylsilyl group.

In contrast to well documented rearrangement of silylcarbenes to silaethylenes,[1] little is studied on the rearrangement of silylenes to silaethylenes.[2] Recently, we and Barton have independently presented evidences for the thermally induced rearrangement of a cyclopropylsilylene to a silacyclobutene.[3,4] However, the reaction of the cyclopropylsilylene is the special case due to the inherent strain. We demonstrate here a strong evidence for the thermal rearrangement of bis(trimethylsilyl)methylsilylene to a silaethylene by 1,2-shift of trimethylsilyl group to a divalent silicon.[5]

A methoxysilane 1, the precursor of bis(trimethylsilyl)methylsilylene 2, was prepared by the photolysis of tris(trimethylsilyl)silyltrimethylsilyldiazomethane in methanol in 50% yield.[6] When a benzene solution of 1 was pyrolyzed in a vertical Pyrex tube packed with Pyrex chips at 450°C under flowing nitrogen, disilacyclobutane 3 and methoxytrimethylsilane were obtained as volatile products in 57 and 79% yields, respectively. Spectral data of 3 are consistent with the assigned structure, NMR(CCl_4,δ) -0.33(d,J=7Hz,1H, Si_3CH), -0.08(s,9H,$SiMe_3$), 0.09(s,9H,$SiMe_3$), 0.18(s,3H,SiMe), 0.24(s,3H,SiMe), and 4.35(q,J=7Hz,1H,SiH),[7] IR(NaCl) 2070 cm^{-1}(Si-H); Mass m/e 260 (M^+); Anal. Calcd for $C_{10}H_{28}Si_4$: C, 46.07, H, 10.82; Found: C, 46.05, H, 11.02%. We further copyrolyzed the compound 3 with triethylsilane and 2,3-dimethylbutadiene at 450°C, and obtained products 5 and 6, respectively, which probably arised from disilacyclobutanylidene 4.[8]



Disilacyclobutane 3 is easily rationalyzed as the insertion product of bis(trimethylsilyl)methylsilylene 2 into γ-C-H bonds on the methyl groups on silicon.[9] No evidence for the intermediacy of a silaethylene by the isomerization of 2 was found under the reaction conditions.

However, evidence that silaethylene 7 is indeed involved was obtained by the copyrolysis of 1 with alcohols. Thus, pyrolysis of a benzene/methanol solution of 1 at 450°C led to the formation of 3 (30%) and methoxysilane 8-a (30%), at least formally, by addition of the silaethylene 7 to the host alcohol, NMR(CCl_4,δ) -0.01(s,9H,$SiMe_3$), 0.03(s,9H,$SiMe_3$), 0.08(s,9H,$SiMe_3$), 0.14(s,2H, $SiCH_2Si$), and 3.31(s,3H,OMe); IR(NaCl) 1080 and 1040 cm^{-1}(Si-O-C); Mass m/e 292 (M^+). tert-Butanol also intercepts the silaethylene 7 to give tert-butoxysilane 8-b (60%) in addition to 3 (30%). Yields of the disilacyclobutane 3 decreases in the presence of the alcohols.

The intervention of the silaethylene 7 was further substantiated by the reaction of 1 with benzophenone, which acts as a trapping agent for silaethylenes.[10] Copyrolysis of 1 and a 10-fold excess of benzophenone afforded vinylsilane 9 (14%) along with 3 (2%) and tetraphenylethylene (76%). Vinylsilane 9 was evidently formed through the intermediacy of a labile silaoxetane in the reaction of the silaethylene 7 with benzophenone. At present time, we can not understand details for the formation of tetraphenylethylene, but we suspect the abstraction of oxygen from benzophenone by the electrophilic silylene 2 to produce diphenylcarbene which dimerizes to tetraphenylethylene.[2b] Since a major part of the silylene 2 is consumed by benzophenone, the yield of 3 remarkably decreases.

It is of quite interest to note that 1,2-migration of trimethylsilyl group to a silylene center prevails over that of a hydrogen. Such efficient rearrangement of trimethylsilyl group may arise from some interactions of vacant p-orbital of the silylene with the neighboring Si-C bond.

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5. Recently, Sakurai presented a clear evidence of a silylene to a disilaethylene rearrangement by 1,2-shift of trimethylsilyl group. H.Sakurai, H.Sakaba, and Y.Nakadaira, J. Am. Chem. Soc., 1982, 104, 6156.
6. Compound 1: mp. 140-142°C; NMR(CCl_4,δ) -0.02(s,18H,$SiMe_3$), 0.10(s,18H, $SiMe_3$), 3.33(s,3H,OMe), and the signal of the methin proton on the carbon is superimposed on those of trimethylsilyl groups; IR(KBr) 1100 and 1010 cm^{-1} (Si-O-C); Mass m/e 349 (M^+-15); Anal. Calcd for $C_{14}H_{40}Si_5O$: C, 46.08, H, 11.04; Found: C, 46.02, H, 11.23%.
7. The signals of the ring methylene protons of 3 are superimposed on those of two trimethylsilyl groups, but the integration of the silyl region signals shows these shoud arise from 27 protons in total.
8. All new compounds presented here showed NMR, IR, and Mass spectra as well as elemental analyses consistent with the structures assigned.
9. A referee pointed out the possibility of β-elimination of methoxytrimethylsilane from 1, instead of α-elimination. However, this is unlikely since methoxysilane, $Me_2Si(OMe)CH(SiMe_3)_2$, is stable under the reaction conditions.
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