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THE CHEMISTRY OF TRIMETHYLSILYLCARBENE

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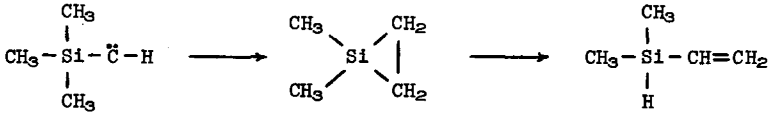
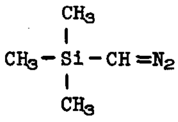
Trimethylsilylcarbene (1), generated by alpha-elimination of chloromethyltrimethylsilane by alkali metals at room temperature, is reported[1] to insert to 1,1-dimethyl-1-silacyclopropane (2)[2] which is then cleaved by the organo-metallic intermediates. 1,1-Dichloromethyltrimethylsilane and sodium-potassium vapor at 260°,[3] apparently via 1, gives vinyldimethylsilane (3), presumably by rearrangement of 2. We now summarize the properties of 1 as derived



1 2 3

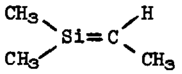
from trimethylsilyldiazomethane (4)[4] by thermolysis in the gas phase and by photolysis in solution.[5] The results are significant in that they reveal the marked ability of 1 to undergo methyl migration to 2-methyl-2-sila-2-butene (5) and products thereof.

Decomposition of 4 at 440° and 10 mm Hg pressure in a Pyrex flow system and collection of the effluent[6] at -78° yields 3[7] (3-4%), vinyltrimethylsilane[7,8] (6, ~ 3-4%), cis- and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (7, > 20% and 8, > 18%), 3,3,4,4-tetramethyl-3,4-disila-1-hexene (9, 4%) and involatile products. Silacyclopropane 2 was not detected. Disilacyclobutanes 7 and 8, assigned from their analyses, masses, ir absorptions, and nuclear magnetic resonances,[9] are apparently derived by dimerization of 5 in the reactor.[10] Silabutene 5 is trappable in the flow system with reactants other than itself in that (1) 4 and 2-propanol at 440° yields ethyldimethyl-2-propoxysilane (10, > 67%)[6,7] and (2) 4 and benzaldehyde at 425° gives cis- and trans-1-phenyl-1-propenes (11, 9% and 12, 12%).[10] Disilahexene 9 is presumably formed by addition of 3 to 5 and its structure was established upon its synthesis by cross-coupling ethyldimethylchlorosilane and vinyldimethylchlorosilane with lithium at 25° in hexamethylphosphoramide.



$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH=N_2$

4



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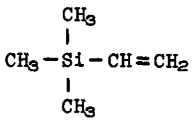
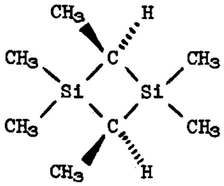


$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH=CH_2$

6



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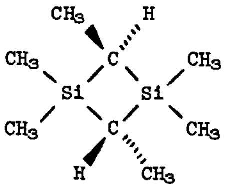

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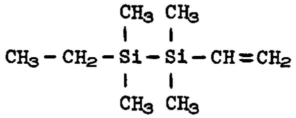
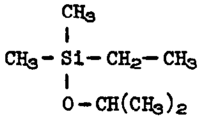


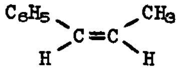
$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-\overset{CH_3}{\underset{CH_3}{Si}}-CH=CH_2$

9



$CH_3-\overset{CH_3}{\underset{O-CH(CH_3)_2}{Si}}-CH_2-CH_3$

10



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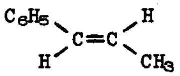

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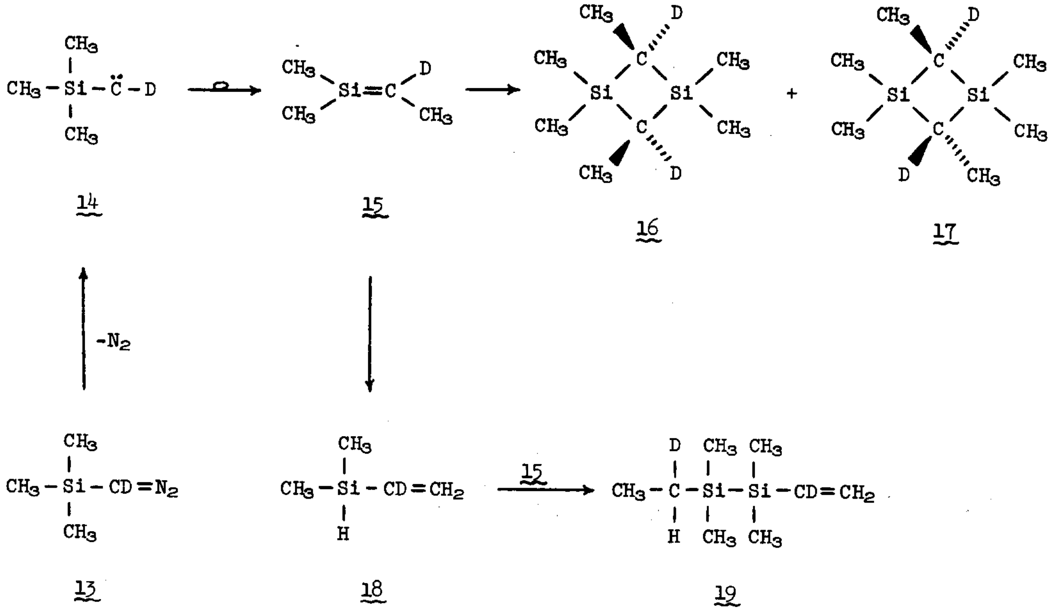
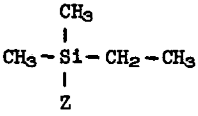
Major concerns of this investigation are the mechanisms of transformation of 1 to 5 and to 3. Carbene 1 might rearrange directly to 5 or/and insert to form 2 which then undergoes ring opening and hydrogen migration to 5.[11] Vinylsilane 3 may be produced by isomerization of 2 as derived from 1[3] or by rearrangement of 5. Methyl migration in conversion of 1 to 5 is revealed by thermolysis of α-deuteriotrimethylsilyldiazomethane (13)[12] at 425° to cis- and trans-1,3-dideuterio-1,2,2,3,4,4-hexamethyl-1,3-disilacyclobutanes[6] (16 and 17; > 40%). The stereochemistry and the location of deuterium in 16 and 17 are derived from their nuclear magnetic resonances.[13] The fact that the dideuteriodisilacyclobutanes 16 and 17 do not contain deuterium in their methyl groups indicates that 14 undergoes methyl migration to 15[11] which dimerizes to 16 and 17 and excludes isomerization of 1 to 2 as a path to 5.

The deuteriovinyldimethylsilane and the deuteriovinyltrimethylsilane formed from 13 at 425° are in insufficient quantity to determine the positions of their deuterium. There is produced however 3,3,4,4-tetramethyl-3,4-disila-1-hexene (19) which from its nmr, contains deuterium only at the 2- and 5-positions.[6,14] On the basis that 19 is formed from 15 and

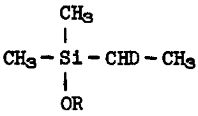


18, it appears that 15 isomerizes to 18 (thus $5 \xrightarrow{h\nu} 3$) and 3 does not arise from rearrangement of 2. Investigation of the details of formation of 3 is in progress.

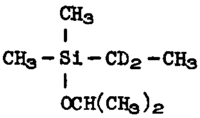
Photolysis of 4 at 25° in various alcohols and in diethylamine was then studied. Cationic cleavage of 4 in the dark by methanol occurs fairly rapidly to form trimethylmethoxysilane (~ 100%)[7] and methyl ether (~ 100%).[7] The cationic path for decomposition of 4 is indicated further by reaction with 2-propanol upon addition of hydrochloric acid to give trimethylisopropoxysilane,[7] hexamethyldisiloxane,[7] and methyl isopropyl ether[7] in > 90% yield. Alteration of 4 does not occur in diethylamine, 3-ethyl-3-pentanol, 2-methyl-2-propanol, or even 2-propanol for more than 12 hours and these systems photolyze (450 watt high pressure Hg arc) in < 2-3 hours to ethyldimethyl-N,N-diethylaminosilane (20),[7] ethyldimethyl-(3-ethyl-3-pentoxy)silane (21),[7] ethyldimethyl-2-propoxysilane (22), and 10 in > 55, 69, 47, and 66% yields, respectively.[6] Irradiation of 4 in 3-ethyl-3-pentanol-OD, 2-methyl-2-propanol-OD, and 2-propanol-OD, respectively, yields 23, 24, and 25.[6,15] Formation of these products and in particular photolysis of 13 in 2-propanol-OD[6,16] to give α,α-dideuterioethyldimethyl-2-propoxysilane (26) in which the methyl portion of its ethyl group does not contain deuterium provide further evidence that 1 undergoes methyl migration to 5.[17,19]



$CH_3-\overset{CH_3}{\underset{Z}{Si}}-CH_2-CH_3$



$CH_3-\overset{CH_3}{\underset{OR}{Si}}-CHD-CH_3$



$CH_3-\overset{CH_3}{\underset{OCH(CH_3)_2}{Si}}-CD_2-CH_3$

20, $Z = N(C_2H_5)_2$
21, $Z = OC(C_2H_5)_3$
22, $Z = OC(CH_3)_3$

23, $R = C(C_2H_5)_3$
24, $R = C(CH_3)_3$
25, $R = CH(CH_3)_2$

26

Further study of 1, as derived by alpha-elimination methods, is in progress.

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1. J. W. Connolly and G. Urry, J. Amer. Chem. Soc., 86, 619 (1964).
2. Silacyclopropanes have been reported by R. L. Lambert, Jr., and D. Seyferth, ibid., 94, 9246 (1972), Y. Nakadaira, S. Kanouchi, and H. Sakurai, ibid., 96, 5623 (1974), and M. Ishikawa and M. Kumada, J. Organometal. Chem., 81, C3 (1974).
3. P. S. Skell and E. J. Goldstein, J. Amer. Chem. Soc., 86, 1442 (1964).
4. D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, J. Organometal. Chem., 44, 279 (1972).
5. R. N. Haszledine, D. L. Scott, and A. E. Tipping, J. Chem. Soc. Perkin I, 1440 (1974) report that 1 inserts into trimethylsilane without rearrangement.
6. All volatile products were separated on SE-30 or XE-60 glc columns and have proper analyses and/or exact masses.
7. Identified by comparison with authentic standards.
8. The origin of 6 (possibly from 3 and 4) is not clear.
9. Nmr ($CDCl_3$): 7, δ 0.20, 0.24, 0.37 (s+s+m, 14H, Si-CH_3 and C-H) and 1.00 (d, 6H, C-CH_3); 8, δ 0.18 (s, 12H, Si-CH_3), 0.45 (m, C-H, 2H), and 1.10 (d, 6H, C-CH_3).
10. For related reactions of sila-alkenes, see P. Boudjouk and L. H. Sommer, Chem. Commun., 54 (1973), L. H. Sommer and D. N. Roark, ibid., 167 (1973) and references therein.
11. It is unlikely that 5 is formed from 1 in the gas phase by protonation, rearrangement, and deprotonation.
12. Prepared from 4 by addition of methyllithium at -15° and then D_2O.
13. Nmr ($CDCl_3$): 16, δ 0.17 and 0.20 (s+s, 12H) and 1.08 (m, 6H); 17, δ 0.20 (s, 12H) and 1.08 (m, 6H).
14. Nmr ($CDCl_3$): 19, δ 0.07 and 0.17 (s+s, 12H), 0.67 (m, 1H), 1.00 (m, 3H), 5.65 (m, 1H), and 5.97 (m, 1H).
15. The nmr of 23, 24, and 25 reveal that deuterium is exclusively in the α-positions of their ethyl groups.
16. Photolysis of 13 (96% α-D) and 2-propanol-OD (86% D) gives, based on nmr, 26 (67-75%) and 25 (25-33%) in 53% yield.
17. This behavior of 4 is analogous to photolysis of ethyl trimethylsilyldiazoacetate in alcohols to give ethyl 2-(alkoxydimethylsilyl)propionates; W. Ando, T. Hagiwara, and T. Migita, J. Amer. Chem. Soc., 95, 7518 (1973).
18. Cationic conversion of 1[11] to 21-25 by photolysis of 5 in alcohols cannot as yet be excluded as a mechanistic possibility. It is noted, however, that t-butylcarbene, presumably generated in thermolysis of 1-diazo-2,2-dimethylpropane, is not protonated by hindered alcohols; J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, ibid., 90, 531 (1968).
19. T. J. Barton, J. A. Kilgour, R. R. Gallucci, A. J. Rothschild, J. Slutsky, A. D. Wolf, and M. Jones, Jr., ibid., 97, 657 (1975) report that the phenyltrimethylsilylcarbene does not undergo insertion to 1,1-dimethyl-2-phenyl-1-silacyclopropane.

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