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Reaction of 6-Oxa-3-silabicyclo[3.1.0]hexanes with Phosphinimines. Synthesis of 6-Vinyl-1,3-dioxa-2,4-disilacyclohexanes

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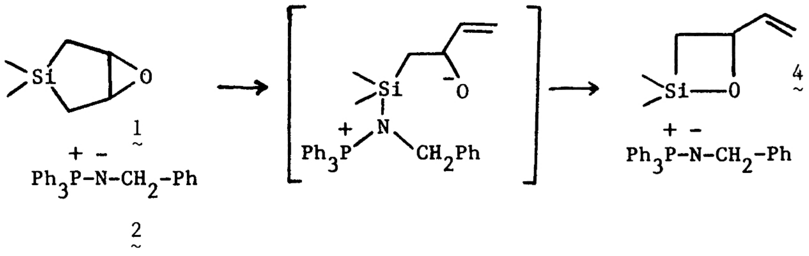
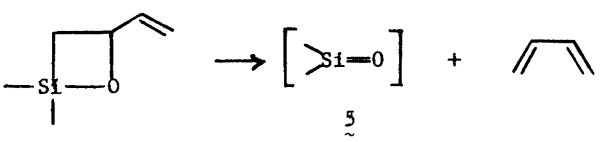
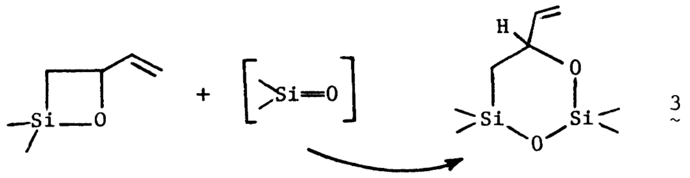
Reaction of 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]-hexane with N-benzyltriphenylphosphinimine yields 1,3-butadiene and 2,2,4,4-tetramethyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (3). A mechanism for the formation of 3 which involves the reaction of dimethylsilanone [$(CH_3)_2Si=O$] with 2,2-dimethyl-4-vinylsilaoxetane is proposed.

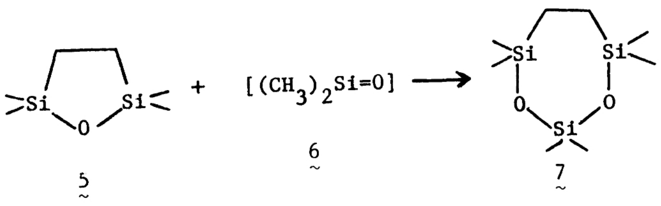
We reacted 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane 1 [1)] with N-benzyltriphenylphosphinimine (2) [2,3)] with the expectation that this reaction would yield 6-benzyl-3,3-dimethyl-6-aza-3-silabicyclo[3.1.0]hexane, since epoxides may be converted to aziridines by reaction with phosphinimines.[4)] In fact, this reaction takes a completely different course. On mixing 1 and 2 together at 130 °C a rapid reaction (1 h) occurs. The products are 1,3-butadiene, 2,2,4,4-tetramethyl-6-vinyl-1,3-dioxa-2,4-disilacyclohexane (3) (70%) [5,6)] as well as small amounts of hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4). The formation of these products may result from the following sequence of reactions. Nucleophilic attack by the negatively charged nitrogen of 2 does not take place on one of the epoxide carbons of 1 but rather on the silicon atom. This is followed by concerted heterolytic scission of one of the ring Si-C bonds and an adjacent C-O bond of the epoxide. This results in a zwitterionic species; the negative charge of which is centered on oxygen and the positive charge is carried by the tetravalent phosphorous atom. Intramolecular attack by the negatively charged oxygen on silicon with simultaneous rupture of the Si-N bond results in formation of 2,2-dimethyl-4-vinyl-2-silaoxetane (4) and regeneration of 2. Retro[2+2]cycloaddition of 4 leads to 1,3-butadiene and dimethylsilanone $[(CH_3)_2Si=O]$ (5).[7,8] Cyclooligomerization of 5 leads to D_3 and D_4, while insertion of 5 into the strained Si-O single bond of 4 leads to 3.







When 1 and 2 are mixed together with a three fold excess of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (6) and allowed to react as above 2,2,4,4-7,7-hexamethyl-1,3-dioxa-2,4,7-trisilacycloheptane (7) is isolated in addition to 1,3-butadiene, D_3, D_4, and 3. This provides additional evidence for the proposed reaction mechanism since the reaction of 6 and 5 has been previously shown to yield 7.[9-11]



Second, the observation that the reaction is catalytic (10 mol%) in 2 is consistent with the proposed mechanism. Fluoride ion (tetra-*n*-butylammonium fluoride) is significantly less effective, although similar results are observed.

Similarly, the reaction of 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]-hexane[2] with 2 yields isoprene and 2,2,4,4,6-pentamethyl-6-vinyl-1,3-dioxa-

2,4-disilacyclohexane (8) (45%) [12] and 2,2,4,4-tetramethyl-6-isopropenyl 1,3-dioxa-2,4-disilacyclohexane (9) (23%) [13]. The formation of these products can be accounted for by a similar reaction scheme.

The scope of this unusual reaction is under active study. New compounds: 3, 8, and 9 were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR as well as GC-MS and high resolution mass spectrometry.

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References

1) G. Manuel, P. Mazerolles, and J. C. Florence, J. Organomet. Chem., 30, 5 (1971).
2) Yu. G. Gololobov, I. N. Zhumurova, and L. F. Kasukhin, Tetrahedron, 37, 437 (1981).
3) E. J. Corey, B. Samuelsson, and F. A. Luzzio, J. Am. Chem. Soc., 106, 3682 (1984).
4) R. Appel and M. Halstenberg, Chem. Ber., 109, 814 (1976).
5) The formation of 3 has been suggested on the basis of mass spectral data. However, 3 has not been isolated nor further characterized. I. M. T. Davidson, A. Fenton, G. Manuel, and G. Bertrand, Organometallics, 4, 1324 (1985).
6) 3: ^{1}H NMR δ: 0.152(s,3H), 0.161(s,3H), 0.178(s,3H), 0.201(s,3H), 0.87 (dd,1H, J = 12 and 3 Hz), 1.02(dd,1H, J = 12 and 11 Hz), 4.55(br.m,1H), 4.99(dd,1H, J = 11 Hz and 1.5 Hz), 5.17 (dt,1H, J = 17 and 1.5 Hz), 5.90 (ddd,1H, J = 17, 11, 6 Hz). ^{13}C NMR δ: 145.34, 112.45, 72.01, 26.94, 2.41, 1.33, 1.15, 0.03. ^{29}Si NMR δ: 11.01, 2.83. IR ν: 1645, 1259, 1100-1020, 984, and 918 cm^{-1}. High resolution MS ($M^{+\cdot}$): Calcd for $C_8H_{18}O_2Si_2$ 202.0845; Found 202.0846. Low resolution GC-MS m/e (rel. intensity): 202 (10.3%) $M^{+\cdot}$, 187 (12.1%) $M-15^{+}$, 149 (21.9%), 133(100%), 54(23.7%).
7) D. N. Roark and L. H. Sommer, J. Chem. Soc., Chem. Commun., 1973, 167.
8) T. J. Barton and J. A. Kilgour, J. Am. Chem. Soc., 96, 2278 (1974).
9) H. Okinoshima and W.P. Weber, J. Organomet. Chem., 155, 165 (1978).
10) T. H. Lane and C. L. Frye, J. Organometal. Chem., 172, 213 (1979).
11) G. Manuel, G. Bertrand, W. P. Weber, and S. A. Kazoura, Organometallics, 3, 1340 (1984).

12) **8**: ^{1}H NMR δ: 5.94(dd,1H, J = 17 and 11 Hz), 5.16(d,1H, J = 17 Hz), 4.92 (d,1H, J = 11 Hz), 1.39(s,3H), 1.145(dd,2H, J = 17 and 12 Hz), 0.15(s,12H). ^{13}C NMR δ: 148.71, 110.03, 76.93, 33.21, 30.67, 2.44, 2.22, 1.90,1.41. ^{29}Si NMR δ: 9.83, -6.17. IR $\bar{\nu}$: 1640, 1051, and 1024 cm^{-1}. High resolution MS $(M-15)^+$: Calcd for $C_8H_{17}O_2Si_2$ 201.0767; found 201.0766. Low resolution GC-MS m/e (rel. intensity) 201(60.1%) M-15$^+$, 189(11.7%), 173(17.6%), 149(41.0%), 133(100%), 68(41.9%).

13) **9**: ^{1}H NMR δ: 4.94(s,1H), 4.74(s,1H), 4.46(dd,1H, J = 12 and 2 Hz), 1.73 (s,3H), 1.07(dd,1H, J = 13 and 12 Hz), 0.83(dd,1H, J = 13 and 2 Hz), 0.205 (s,3H), 0.175(s,3H), 0.154(s,3H), 0.145(s,3H). ^{13}C NMR δ: 129.65, 109.54, 74.61, 73.70, 25.47, 1.11(2C), -0.06(2C). ^{29}Si NMR δ: 11.64, -2.81. IR $\bar{\nu}$: 1649, 1062 and 1054 cm^{-1}. High resolution MS $(M-15)^+$: Calcd for $C_8H_{17}O_2Si_2$ 201.0767; Found 201.0768. Low resolution GC-MS m/e (rel. intensity) 216(10.9%) $M^{+\cdot}$, 201(59.9%) M-15$^+$, 149(38.6%), 133(100%), 68(46.1%).

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