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# SYNTHESIS OF UNSATURATED ORGANOSILICON HETEROCYCLES - REACTION OF SILYLENES WITH CYCLIC DIENES

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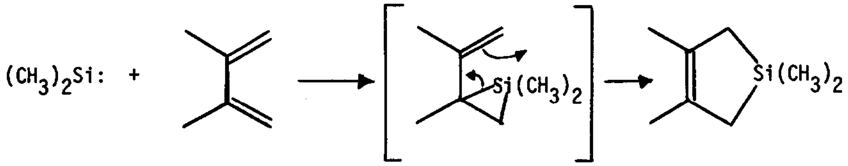
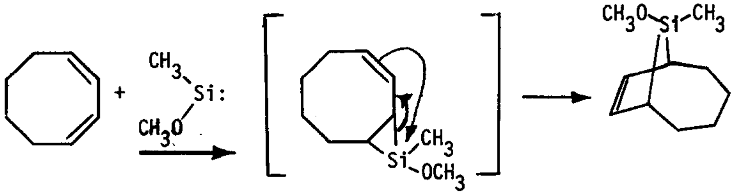
We have been concerned with improving synthetic routes to medium sized organosilicon heterocycles.[1,2] The modified acyloin reaction [3,4] on suitable organosilicon diesters has been the best entry into these ring systems.[1,5] However, problems remain with this approach. One is that the synthesis of suitable organosilicon diester substrates for the acyloin reaction requires many steps from commercially available dichlorosilanes. Second, the types of functionality bonded to silicon which are compatible with this approach are quite limited. Third, the heterocycle thus formed after hydrolysis of the trimethylsilyl protecting groups contains an α-hydroxy ketone functionality which in turn requires several steps to transform into a carbon-carbon double bond or a diene system.[2,6]

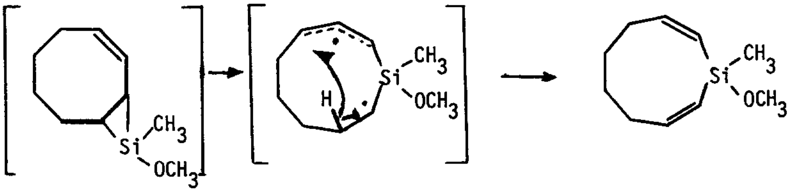
We would like to report an example of a one step synthesis of a medium sized organosilicon heterocycle possessing both unsaturation and functionality at the silyl center. Co-pyrolysis of 1,2-dimethyltetramethoxydisilane[7,8] with 1,3-cyclooctadiene in a flow apparatus at 350° yields 1-methoxy-1-methyl-1-sila-2,8-cyclononadiene in 25% yield. 1,2-Dimethyltetramethoxydisilane is known to undergo an alpha elimination under these conditions to yield trimethoxymethylsilane and methoxymethylsilylene.[9-11] Apparently methoxymethylsilylene reacts with 1,3-cyclooctadiene to yield the observed product. This is surprising since both dimethylsilylene and dimethoxysilylene have been observed to react with butadiene and 2,3-dimethyl butadiene to yield the appropriately substituted 1-sila-3-cyclopentenes.[11,12] A reaction sequence involving initial formation of a vinyl silacyclopropane intermediate which opens with carbon-silicon bond scission has been proposed.



A similar reaction pathway in the case of 1,3-cyclooctadiene would yield 9-methoxy-9-methyl-9-sila-bicyclo[4,2,1]non-7-ene. No such bicyclic silyl compound was detected.



An economical reaction sequence which can rationalize our results is the initial addition of methoxymethylsilylene to one of the carbon-carbon double bonds of the 1,3-cyclooctadiene to yield a vinyl silacyclopropane intermediate. However, this opens by carbon-carbon bond scission rather than carbon-silicon bond scission to yield an allylic radical and a radical center alpha to silicon. Transannular abstraction of a hydrogen atom by the remote end of the allylic radical in a 1,5-sense yields the product.



Similar results have been obtained with 1,3-cyclododecadiene. A related example has been reported by Russian workers who found that dichlorosilylene reacts with cyclopentadiene to yield 1,1-dichloro-1-silacyclohexa-2,4-diene.[13]

Clearly, the question of whether a vinyl silacyclopropane will open by carbon-silicon or carbon-carbon bond scission must be determined by factors which are as yet undetermined. The scope and generality of this reaction of methoxymethylsilylene with other cyclic dienes is under active study.

## Experimental

1-Methoxy-1-methyl-1-sila-2,8-cyclononadiene was prepared by reaction of 1,3-cyclooctadiene and 1,2-dimethyltetramethoxydisilane as follows. A pyrex pyrolysis tube was placed in a vertical tube oven. The tube (30 cm long, O.D. 12.5 mm, I.D. 9 mm) was packed with 1 cm long pieces of 3 mm Pyrex tubing. A pressure equalizing addition funnel and a nitrogen inlet were connected to the pyrolysis tube above the oven. The exit of the tube was connected to one neck of a two-neck flask which was immersed in a dry ice acetone bath. The second neck of this flask was connected to another dry ice acetone trap. The nitrogen flow rate was adjusted to 12 ml/min. The oven was heated to between 350°-370°. A mixture of 5.0 g (23.8 mmol) of 1,2-dimethyltetramethoxydisilane[7,8] and 10.5 g (97 mmol) of 1,3-cyclooctadiene was placed in the addition funnel. This mixture was added at a rate of 1 drop every 10 seconds. After the addition was completed and the apparatus cooled, the column was rinsed with 20 ml of $CH_2Cl_2$. The material from the two traps was combined and the $CH_2Cl_2$ removed by distillation through a 15 cm vacuum jacketed Vigreux column at atmospheric pressure. Unreacted 1,3-cyclooctadiene and trimethoxymethylsilane were removed by distillation under reduced pressure (20 mm). The pot residue was bulb to bulb distilled at 0.1 mm pressure. In this manner, 2.51 g of clear colorless liquid was obtained. 1-Methoxy-1-methyl-1-sila-2,8-cyclononadiene was obtained by preparative glpc on a 1/4" X 4' 20% DC-QF-1 on chromasorb P column at 120° (0.96 g, 25% yield). Nmr: s(3H) o.40δ, m(4H) 1.55δ, m(2H) 2.18δ, m(2H) 2.51δ, s(3H) 3.32δ, d(2H) 5.45δ, J = 14 Hz,[14] m(2H) 6.44δ. Ir: 1600 cm$^{-1}$ C=C; 1240, 830, and 800 cm$^{-1}$ Si-$CH_3$; and 1070 cm$^{-1}$ Si-$OCH_3$. Mass Spectrum at 70eV: Parent m/e = 182 (13%), P-$CH_3$ m/e = 167 (15.3%), P-$OCH_3$ m/e = 151 (2.4%). Analytical samples were purified by preparative glpc on a 1/4" X 18" 20% β,β-ODPN on chromasorb P column at 70°. Anal. Calcd. C, 65.87; H, 9.95. Found C, 65.66; H, 9.77.

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