

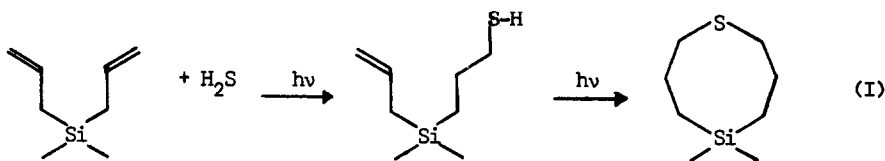
ADDITION OF H₂S TO α,ω-DIENES TO YIELD MEDIUM SIZED HETEROCYCLES
 1,1-DIMETHYL-1-SILA-5-THIACYCLOOCTANE

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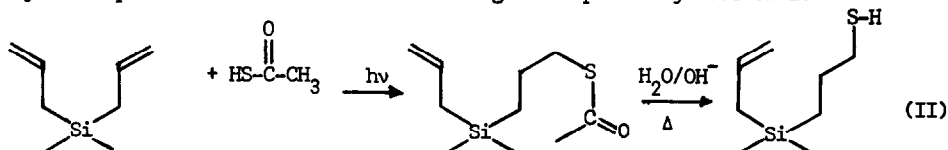
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(Received in USA 16 April 1973; received in UK for publication 7 July 1973)

We should like to report that H₂S adds to dimethyldiallylsilane¹ upon irradiation with a 450 W medium pressure Hanovia lamp in a dilute pentane solution at -78°C to form 1,1-dimethyl-1-sila-5-thiacyclooctane (I) in 25% isolated yield. This is remarkable considering the problems involved in synthesis of medium sized ring compounds from alicyclic precursors and the variety of competing pathways open to a thiyl radical intermediate. Clearly the intramolecular radical addition of the S-H bond in dimethylallyl-3-mercaptopropylsilane (II) to the carbon-carbon double bond of the allyl group is critical to the success of the reaction.



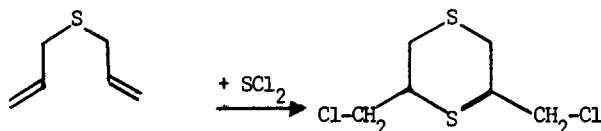
We have prepared II independently by the photochemical addition of thiolacetic acid to an excess of dimethyldiallylsilane followed by hydrolysis of the thiolacetate with aqueous base. Photolysis of pure II under similar conditions gave comparable yields of I.²



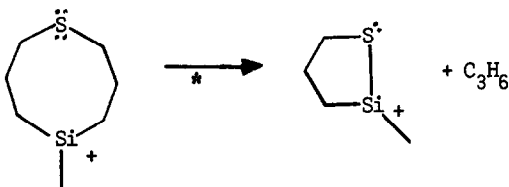
In a related study Surzur has shown that the direction of intramolecular addition of a thiyl radical to a terminal carbon-carbon double bond is strongly influenced by temperature.^{3,4} Thus 1-mercapto-5-hexene was cyclized to a mixture of 1-thia-2-methylcyclohexane and 1-thia-cycloheptane in which the six membered ring predominates at high temperature while the seven membered ring predominates at low temperature (-65°C). In our system six, seven, and eight membered rings are all possible. Apparently formation of the eight membered ring is highly favored at low temperature.

Our result is particularly interesting in that ring closure of ω-chlorosulfides RS-(CH₂)_nCl

to form cyclic sulfonium salts fails for cycles containing from 7 to 12 atoms.⁵ The fact that both C-Si (1.87 Å) and C-S (1.82 Å) bonds are longer than C-C single bonds may make formation of I more like cyclization of a nine membered than an eight membered all carbon ring system.⁶ Further sulfur dichloride adds to diallylsulfide⁷ and related systems⁸ in the opposite sense to yield the 2,5-di-chloromethyl-1,3-dithiacyclohexane.⁷



Sulfide I was distilled at 125°/25mm. Any non-cyclized II was removed by extraction with aqueous NaOH. Final purification of I was by gplc on a 10' x 1/4" Apiezon L column at 220°C. Nmr CS₂ solvent at 100 MHz on a Varian HA-100 s(6H) 10.13τ, m(4H) 9.51τ, m(4H) 8.39τ, t(4H) 7.69τ J = 6 Hz. Ir (CH₃)₂Si 1250 cm⁻¹ and 840 cm⁻¹. Analysis calcd. for C₈H₁₈SSi: C, 55.10; H, 10.40%, found: C, 55.09; H, 10.21. The mass spectrum of I is quite interesting. The parent ion at m/e = 174 is quite weak. Loss of a methyl group from the quaternary silyl center leads to a P-15 ion at m/e = 159 which is quite intense. Loss of C₃H₆ from the P-15 ion leads to the base peak at m/e = 117. A metastable peak at m* = (117)²/159 = 86.1 in support of this process is observed. Quite possibly this ion arises by transannular interaction of the siliconium ion center with the electron rich sulfur atom with concurrent loss of C₃H₆.



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Acknowledgements

This work was supported in part by the Air Force Office of Scientific Research - Grant No. 73-2424