

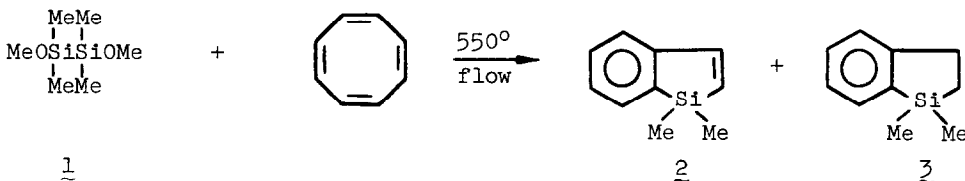
THE ADDITION OF DIMETHYLSILYLENE TO CYCLOOCTATETRAENE

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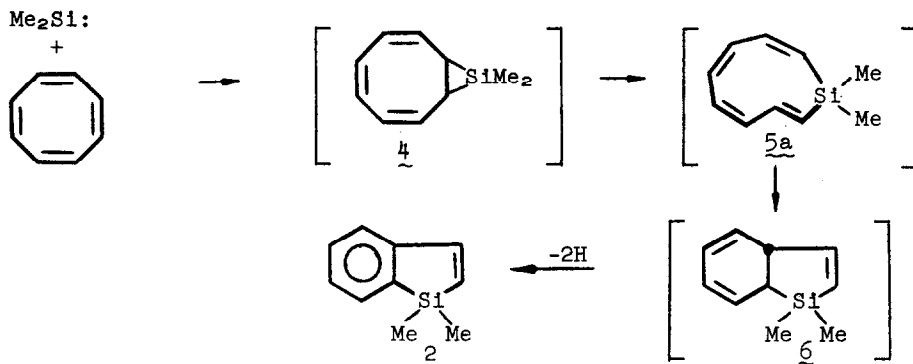
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In analogy with carbene chemistry,¹ the addition of a silylene ($R_2Si:$) to cyclooctatetraene (COT) could provide a direct entry into the unknown silonin (silanonatetraene) ring system. We report here preliminary results of studies which implicate silonin as a reaction intermediate.

1,2-Dimethoxy-1,1,2,2-tetramethyldisilane (1) is known to thermally decompose to dimethoxydimethylsilane and dimethylsilylene by an α -elimination process.² Gas-phase copyrolysis of 1 and COT in a nitrogen flow system at 450° yields 1,1-dimethyl-2,3-benzo-1-silacyclopentadiene (2) in 8% yield. After purification by gas chromatography, 2 is obtained as a colorless oil, m/e 160.0707, calcd. 160.0708. The nmr spectrum (CCl_4 , 100 MHz) contains an aromatic multiplet at δ 7.5-6.9 which overlaps a doublet at δ 7.25 ($J=10$ Hz) (5H), a doublet (1H, $J=10$ Hz) at δ 6.15 and a singlet (6H, $SiMe_2$) at δ 0.30. As the temperature of the copyrolysis is increased, the yield of 2 increases (30% at 550°) and a second major product, 1,1-dimethyl-2,3-benzo-1-silacyclopentene³ (3), (15% at 550°) is noted.



In view of the known thermal behavior of cyclononatetraene⁵ and certain of its heteroanalogs,⁶ the formation of the [4.3.0] ring system of 2 and 3 strongly indicates the intermediacy of silanonatetraene in this reaction. Conrotatory opening of initially formed 9,9-dimethyl-9-silabicyclo[6.1.0]nona-2,4-6-triene (4) would afford the cis, cis, cis, trans-isomer of 5a and ultimately closure to trans-fused 1,1-dimethyl-1-sila-8,9-dihydroindene (6).



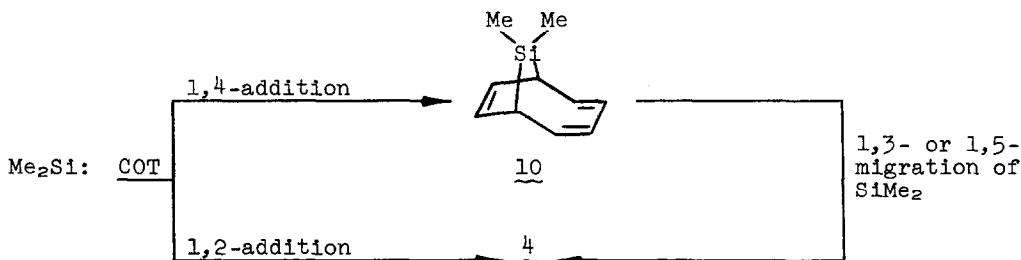
The origin of 2 is more obscure. Staley⁷ has suggested that the exclusive formation of the trans-8,9-dihydroindene from 9,9-dimethylbicyclo[6.1.0]nonatriene, instead of the usual cis-fused product, is due to an increase in the energy of activation for the rearrangement of 7a as the steric crowding of conformer 7a is translated into the resulting activated complex. This could bring about a reversal of the usual relative rates of rearrangement for the conformers of cis-bicyclo[6.1.0]nona-2,4,6-trienes. Anastassiou⁸ has recently demonstrated that a 9-*t*-butyl substituent forces conformational control over this rearrangement and that indeed the "folded" conformation (7) produces almost exclusively the cis-fused dihydroindene while the conformation corresponding to 8 yields predominantly the trans-fused isomer. Qualitatively the same factors should hold for 7b and 8b and 6 would be the expected product. It is therefore tempting to



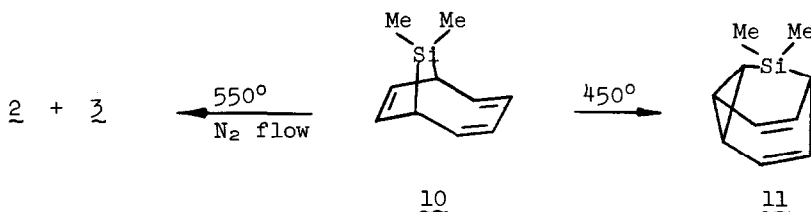
suggest that the rearrangement of 7b to cis-fused dihydrosilaindene (9) is competitive with the rearrangement of 8b at our temperatures. Conversion of 9 to 2 could occur by a symmetry allowed $\sigma^4_s + \pi^2_s$ thermal group transfer of hydrogen.⁹ Similar intramolecular group transfers of hydrogen in the isodrin series have been reported by Mackenzie.¹⁰ However it must first be experimentally determined whether or not the hydrogen transfer is intra- or intermolecular and such experiments are now in progress.



While the intermediacy of 4 is clearly implicated, its origin is uncertain. The addition of dimethylsilylene to 1,3-dienes produces the products of 1,4-addition (1-silacyclopent-3-enes) but vinyl silacyclopropanes, the 1,2-addition products, are thought to be likely intermediates in these reactions.¹¹ Therefore the formation of 4 can be envisioned as arising from either a 1,2-addition of dimethylsilylene or a 1,4-addition followed by a 1,3-¹² or 1,5-sigmatropic¹³ migration of silicon.



In order to test the reasonableness of this possibility, we have pyrolyzed 9,9-dimethyl-9-silabicyclo[4.2.1]nona-2,4,7-triene (10).¹⁴ The gas-phase, flow pyrolysis of 10 at 550° under identical conditions as employed for the silylene/COT reaction yielded 2 (33%) and 3 (11%). Thus it would appear that the thermal rearrangement of 10 proceeds on the same energy surface as the silylene/COT reaction. However, at 450° (flow) 10 is cleanly converted into a mixture (ca. 1:1) of 10 and 11.¹⁴ Since no 2 is found in this reaction and no 10 or 11 found in the silylene/COT reaction at 450° , we conclude that 10 is not an intermediate in the latter reaction. This conclusion strongly indicates the initial formation of 4 from the addition of $\text{Me}_2\text{Si:}$ to COT.



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