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Preliminary communication

A NOVEL SYNTHESIS OF A *C*-UNSUBSTITUTED SILOLE

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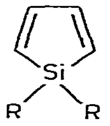
Summary

Flow pyrolysis of 4-allyl-4-methyl-4-silacyclopentene yielded the Diels—Alder dimers of 5-methyl-5-silacyclopentadiene (1-methylsilole) via sequential retro-ene extrusion of propene, 1,5-hydrogen migration to silicon, and dimerization. The monomeric silole is thermally produced in situ, and trapped by maleic anhydride.

Introduction

Although siloles (5-silacyclopentadienes) have proven to be quite interesting and important synthetic intermediates to ring systems such as 7-silanorbornadiene [1], siloxapinone [2], 1-silacyclopentadiene [3], and silepin [4], all of this work has been accomplished with siloles possessing at least two substituents on the ring-carbons. Reports of *C*-unsubstituted siloles have appeared in the literature four times. In 1961 Benkeser [5] reported that gas-phase pyrolysis (525—540°C) of a mixture of tetrachlorosilacyclopentanes, followed by $LiAlH_4$ reduction of Ic, afforded parent silole, Ia. Unfortunately, this work was not reproducible, and was retracted in 1964 [6]. Extensive investigation into the thermolyses of chlorinated silacyclopentanes by Nagai in 1968 provided no evidence which demanded even the intermediacy of siloles [7]. In 1962, Goubeau, Kalmar, and Hoffmann [8] reported that dehydrogenation of 54 g of 1,1-dimethyl-1-silacyclopentane at 460—480°C over 10% Pt/SiO_2 produced several drops of Ib. Likewise, Nefedov and Manakov [9] have reported that this dehydrogenation to Ib occurs at 600°C over an Al-Cu-K oxide catalyst (3%), or a Pt-C catalyst (9%). In neither case was the product completely characterized, and in neither case has further work appeared. We have been unable to reproduce these dehydrogenation results with repeated attempts and a variety of catalysts. Of course, the vague experimental details, low reported yields (a few drops [8], 3 or 9% [9]), and the difficulty of exactly reproducing catalysts make it difficult to make a definite statement on the authenticity of these results. Most recently Gaspar [10] has suggested structure Ia for a product from reaction of ^{31}Si atoms and butadiene. However, untill all other isomers have been excluded, this assignment must remain tentative, since the amounts produced in this reaction will never allow for complete spectroscopic identification. We present here a simple synthesis of 1-methylsilole (V) based on sequential retroene reaction and 1,5-sigmatropic migration of hydrogen to silicon.

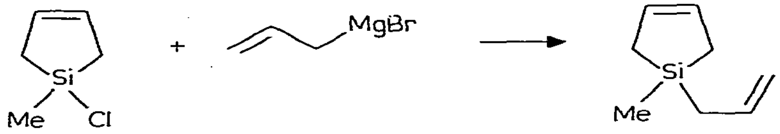


Silole
Ia, R=H
Ib, R=Me
Ic, R=Cl

(I)

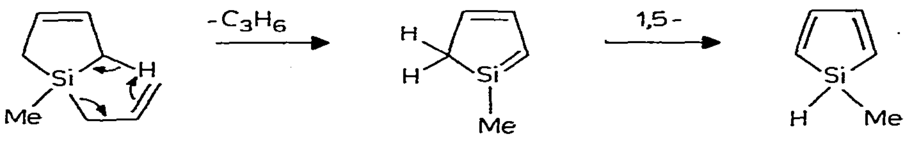
Results and discussion

Synthesis of the proposed precursor of V, 4-allyl-4-methyl-4-silacyclopentene (III), was initially attempted through magnesium-induced coupling of allylmethyldichlorosilane with either 1,3-butadiene or 1,4-dibromo-2-butene. In our hands these routes led to isolated yields of II which were unsatisfactory (<10%) for a synthetic intermediate. However, coupling of 4-methyl-4-chloro-4-silacyclopentene (II) [11] and allylmagnesium bromide afforded III in 72% isolated yield: b.p. 55°C/23 Torr; NMR (CCl_4): δ (ppm) −0.04 (s, 3H, SiMe), 1.05 (s(br), 4H, ring CH_2), 1.41 (center of apparent d of t actually overlapped d of d of d, J_{vic} = 8 Hz, $J_{1,3\text{-}trans} \sim J_{1,3\text{-}cis} \sim$ 1 Hz, allylic CH_2, 2H), 4.49—4.74 (vinyl mult., 2H), 5.29—5.72 (vinyl mult., 3H); calcd. for $C_6H_{14}Si$ m/e 138.0865, measured m/e 138.0862.



(II) (III)

On the precedent of the original work of Block [12] and our recent synthesis of a silabenzene [13], we expected III to eliminate propene via a retroene reaction to produce 1-methyl-1-silacyclopenta-1,3-diene (IV). Recent experience in our laboratories with transient 1-sila-1,3-butadienes [14] suggested that IV would rearrange to silole V via a 1,5-migration of hydrogen to silicon.



(III) (IV) (V)

Vacuum-flow pyrolysis of III (820°C, 4 × 10^{-4} Torr, quartz chip packed one ft tube) afforded a 71% yield of a light yellow oil (b.p. 42—44°C/0.1 Torr) whose mass spectrum* (m/e 192.0784, calcd. for $C_{10}H_{16}Si_2$, 192.0791) was in accord with that expected of a dimer of V. This was confirmed by the NMR spectrum* which is entirely consistent with that of Diels—Alder dimer VI existing as the inevitable mixture of isomers varying in stereochemistry at the two silicon atoms.

Heating of dimer VI at 150°C (evacuated, sealed tube; no solvent) with the reactive dienophiles maleic anhydride, TCNE, or dimethyl acetylenedicarboxylate, inevitably produced a violent explosion. Pyrolysis of VI through a quartz tube packed with quartz chips heated at 400°C, and immediate trapping at –196°C in a trap containing TCNE revealed no evidence of trapping of V upon warming to room temperature. Evidence that these explosions were indeed the result of cracking of VI and exothermic Diels—Alder reactions was obtained from a sealed-tube reaction of VI and perfluoro-2-butyne. When VI (0.2 g) and excess perfluoro-2-butyne were heated at 135°C for 13 h, the only identifiable product was *o*-bis(trifluoromethyl)benzene. It is reasonable to assume that this arises from cracking of VI to two molecules of V, Diels—Alder addition of the acetylene, and extrusion of methylsilylene. Conclusive evidence came from heating a dilute toluene solution of VI and maleic anhydride (sealed tube, degassed, 150°C, 4.5 h) which afforded a 96% yield of adduct VII as a viscous oil even after GLC purification. The mass spectrum [(m/e 194 (M^+, 0.9%), 165 ($M - HCO$, 43), 122 ($M - C_2O_3$, 75), 121 ($M - HC_2O_3$, 68), 120 ($M - H_2C_2O_3$, 32), 107 (m/e 122 – CH_3, 45), 105 (m/e 120 – CH_3, 41), 78 ($C_6H_6^+$, 100), 77 ($C_6H_5^+$, 26)], calcd. for $C_9H_{10}SiO_3$ 194.0399, measured m/e 194.0388) fit nicely for the Diels—Alder adduct. The NMR spectrum [δ (ppm) 0.10 (d, J 3 Hz, $h\nu$ at either H_c or $H_{c'}$ collapses to s(br), 3H, SiMe), 2.48 (very broad hump which sharpens with $h\nu$ at H_D, 2H, H_A), 3.46 and 3.54 (two identical d of d with overlapped inner peaks, $h\nu$ at H_A collapses each to a s, $J_{AB} \sim J_{aB} = 1.5$ Hz, each ~ 0.5 H, H_B and $H_{B'}$), 3.75 (q, J 3 Hz, $h\nu$ at SiMe collapses to s, 0.5 H, H_C), 4.54 (q(br), $J \sim 3$ Hz, $h\nu$ at SiMe collapses to s, 0.5 H, $H_{C'}$), 6.15 (m, $h\nu$ at H_A collapses to s, 2H, H_D)] clearly defines VII as an equal mixture of the two expected isomers with opposite stereochemistry at silicon.

Thus, the thermally initiated retro-Diels -Alder reaction of VI can provide a convenient, in situ source of 1-methylsilole (V) for future synthetic efforts. We will continue to vary the substitution at silicon in an effort to lower the barrier for dimer to monomer conversion, and report those results in the complete manuscript.

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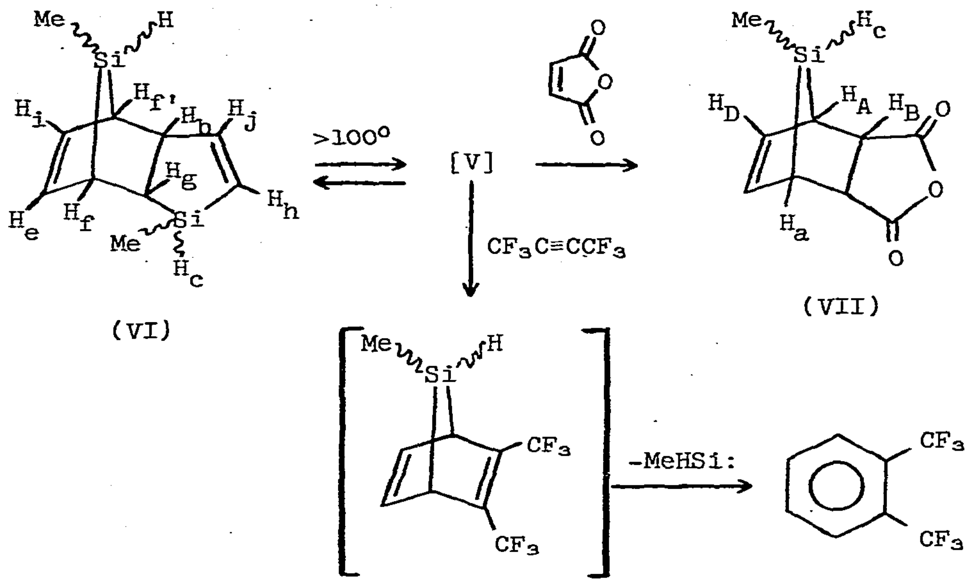
*Actually VI can be separated by preparative GLC into two fractions (assumed to be the *endo* and *exo*-adducts) which have essentially identical mass spectra: m/e (% rel. int.) 192 (27, M^+), 177 (29, $P - Me$), 164 (24, $P - C_2H_4$), 147 (72, silaindane – H), 145 (100, silaindene – H), 121 (45, m/e 147 – C_2H_2), 119 (17, m/e 145 – C_2H_2), 105 (39), 96 (72), 95 (46), 93 (43), 69 (45), 55 (56), 53 (56); the NMR spectrum (CCl_4) of the major fraction was the least complicated: δ (ppm) 0.42 (SiMe, center of three d's ca. 1/2/1), 1.84 and 2.00 (Hg, centers of two sets of d of d of d, $h\nu$ at H_b or H_f collapses to four d's), 2.83 (H_f and $H_{f'}$, center of complex mult., partially collapses with $h\nu$ at H_c, H_e, H_i or H_j), 3.39 (H_b, sym. apparent pentet), 4.00 (H_c, center of mult. which collapses to s(br) with $h\nu$ at SiMe), 4.91 (H_a, mult. collapsing to s with $h\nu$ at SiMe), 5.99 (H_h, d of d with low field d overlapping upfield part of H_i, $h\nu$ at H_c collapses to sharp d), 6.12 (H_i, t(br) collapsing to d with $h\nu$ at H_f). 6.72 (H_j, d(br) becoming sharp with $h\nu$ at H_c, or s(br) with $h\nu$ at H_h), 6.45 (t(br) collapses to d with $h\nu$ at H_f).



(VI)

(VII)

Acknowledgment

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