Synthesis of 1,1,3,4-Tetramethyl-1-sila-2,4-Cyclopentadiene

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The compound 1,1,3,4-tetramethyl-1-sila-3-cyclopentene was obtained through the reaction of 2,3-dimethylbutadiene and dichlorodimethyl-silane in THF in the presence of sodium metal. After the bromination of this compound at 0°C for 2 hrs and dehydrobromination by using a base, we prepared 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene, which could undergo dimerization. The identification has been done by using ^1H-, ^{13}C- and C/H-Correlation two dimensional nmr spectroscopies.

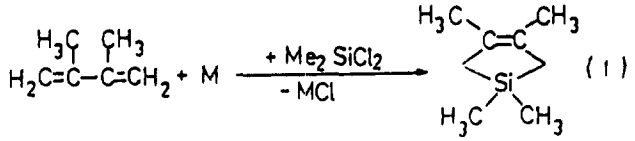
Introduction

It is well known that 1-silacyclopentadiene serves as a source of silylen formation via 7-silanorbornadiene.[1-3] On the other hand 1-silacyclopentadiene reacts with transition metal to give siloltransition metal complex.[4] From this point of view it has been a subject of much interest as a cyclopentadiene analogue. There are several reports to the synthesis of 1-silacyclopentadiene species. However their synthetic routes are rather restricted to the specified reaction types.[5-10] For example, the reaction of diphenylacetylene with lithium metal, followed by cyclization by using dimethyldichlorosilane affords the desired 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene. The success of this reaction is proved to be limited only in the case of disubstituted acetylene as a starting material. In order to develope a convenient preparative route leading to 1-sila-2,4-cyclopentadiene, we investigated the reaction of 2,3-dimethylbutadiene in the presence of sodium with dimethyldichlorosilane. 1,1,3,4-Tetramethyl-1-sila-3-cyclopentene thus formed was brominated and following dehydrobromination by using a base.

Results and Discussion

1,1,3,4-Tetramethyl-1-sila-3-cyclopentene was prepared from the reaction of 2,3-dimethylbutadiene with an alkali metal, followed by cyclization with dimethyldichlorosilane. The reaction of 2,3-dimethylbutadiene with metal and Me_2SiCl_2 was carried out using various alkali metals in THF and also in ether. These results are summarized in Table 1.[11]

The best result was obtained in the case of Na/THF medium is 65% yields. In the case of Na and K in ether it turned out to be polymerized and could not be distilled. From these results

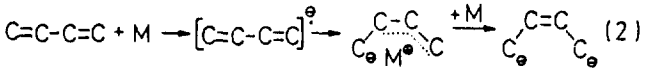


(1)

TABLE 1: Yields of 1,1,3,4-Tetramethyl-1-Sila-3-Cyclopentene

Metals	Solvents	Yields (%)
Li	Et_2O	25
Na	Et_2O	---
K	Et_2O	---
Li	THF	10-15
Na	THF	65

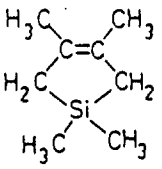
we would like to suggest the following two aspects: (a) In the step of cyclization with Me_2SiCl_2, *cis*-configuration of dianion must be formed. (b) Solvation effect to concerning the effective cationic character of metal influences the result of this reaction. This relationship is shown in (2).



(2)

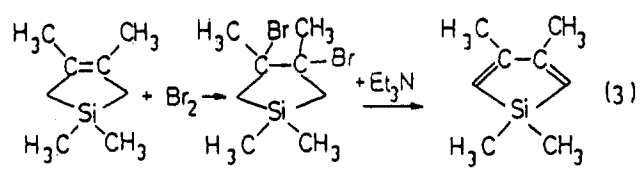
In this reaction, the radical anion is formed at the first step, followed by π-allylic electron delocalization. In this moment there may be an induced interaction between the metal cation and π-allylic electrons, which favours the formation of *cis*-configuration. In this sense the less solvated and therefore less shielded Na cation is more favorable than the more solvated and therefore more shielded Li cation. For the case of Na in ether and K in THF or in ether medium it might be suggested that the metallic characters are too strong to form π-allylic electron delocalization step and therefore polymerization being activated by anion radical proceeds. The formation of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene was confirmed with use of ^1H-, ^{13}C- and DEPT nmr spectroscopies. (See Table 2)

TABLE 2: Nmr data for 1,1,3,4-Tetramethyl-1-sila-3-Cyclopentene



	^1H-nmr (ppm)	^{13}C-nmr (ppm)	
Si-CH_3	0.12	−1.8	Positive
=C-CH_3	1.68	19.2	Positive
=C-CH_2	1.30	25.4	Negative
C=C		130	

1,1,3,4-tetramethyl-1-sila-3-cyclopentene thus obtained was treated with bromine, followed by dehydrobromination by using triethylamine.



(3)

In the process (3), we have the best results in $CHCl_3$ medium by using pyridine as a catalyst. Here it must be expected that because +I-effect of methyl groups bonded to 3- and 4-positions the bromination will undergo easily. In fact it is not the case, and the reason is not clear. 1,1,3,4-Tetramethyl-1-sila-2,4-cyclopentadiene undergoes Diels-Alder reaction to

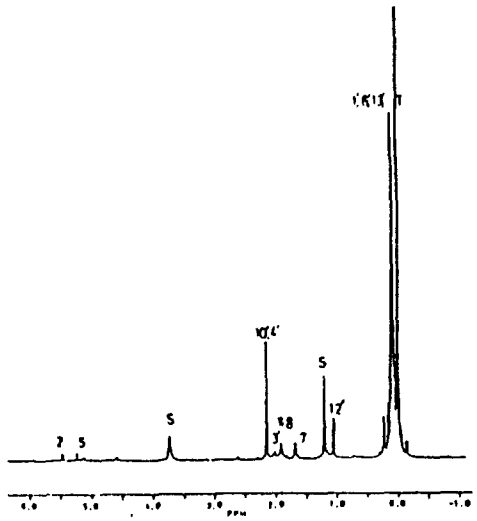


Figure 1. ^{1}H-nmr spectrum of 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene (monomer & dimer).

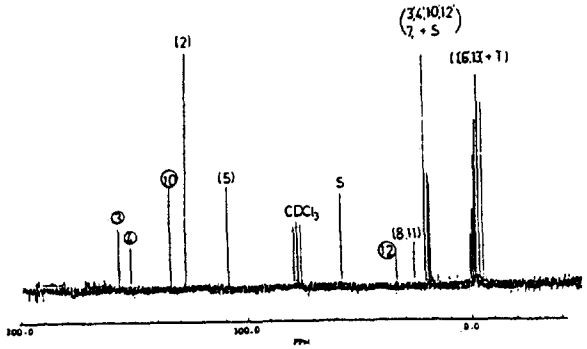


Figure 2. ^{13}C-nmr spectrum of 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene (monomer & dimer).

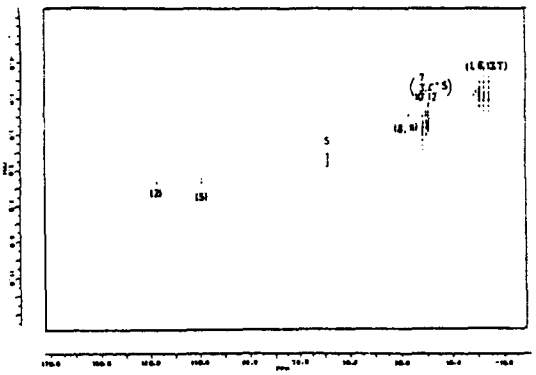
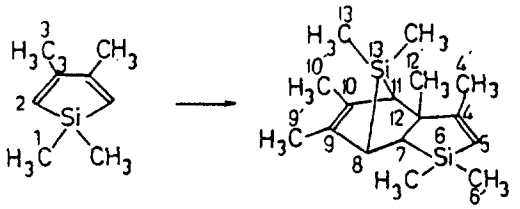


Figure 3. Two-dimensional spectrum of 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene (monomer & dimer).

form a dimer. Therefore we always found the mixtures of monomer and dimer.



(4)

We confirmed the structure of this Diels-Alder dimer by using mass spectrum (found m/e at 276) and ^{1}H-decoupling, ^{13}C- and C/H-correlation two dimensional nmr spectroscopies.

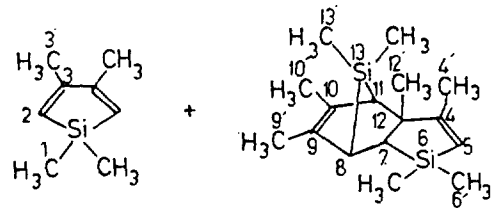
In Figure 1 and 2, all of the signals are perhaps assigned to every corresponding protons and carbons in the sense of usual chemical shift mode. To make sure whether these assignments are really correct, we have studied the C/H correlation two dimensional nmr spectrum.

TABLE 3:

Symbol	Pos.	^{1}H-nmr (ppm)	^{13}C-nmr (ppm)	2-Dimensional ^{1}H	2-Dimensional ^{13}C	2-Dimensional multi.
Si-C$\underline{H}_3$	$C_{13'}$	0.1	−1.2	0.1	−1.2	Q
	$C_{6'}$	0.14	−2.3	0.14	−2.3	Q
	$C_{1'}$	0.16	−4.5	0.16	−4.5	Q
−C$\underline{H}_3$	$C_{12'}$	1.0	17.5	1.0	17.5	Q
=C-C$\underline{H}_3$	$C_{10'}$	2.1	21	2.1	21	Q
	$C_{3'}$	2.0	19.2	2.0	19.2	Q
	$C_{4'}$	2.1	19.5	2.1	19.5	Q
-C$\underline{H}$	C_{11}	1.9	26	1.9	26	D
	C_8	1.9	26	1.9	26	D
	C_7	1.7	19.5	1.7	19.5	D
=C$\underline{H}$	C_2	5.6	126.5	5.6	126.5	D
	C_5	5.4	109.5	5.4	109.5	D
-$\underline{C}$-	C_{12}		32.5		—	
	C_{10}		134		—	
	C_3		151		—	
$H_3C-\underline{C}=$	C_4		156.7		—	

As expected, we found all the the C/H-correlated signals at the position with corresponding multiplicity where they are found independently in ^{1}H-and ^{13}C-nmr. On the other hand the signals of carbon without proton disappeared in this spectrum. We summarized these results in Table 3.

nmr spectral data of



Experiments

1,1,3,4-*Tetramethyl*-1-*sila*-3-*cyclopentene*. 2,3-Dimethylbutadiene 5.6m*l* (50mmol) in 10m*l* of THF were dropped slowly into 6m*l* (50mmol) of dimethyldichlorosilane and 2.4g(100mmol) of sodium metal in 70ml THF under dried nitrogen atmosphere. It was stirred further at room temperature for two days. Fom this reaction mixture THF-solvent was removed under reduced pressure. Thereafter ether was added and unsoluble NaCl was separated by filtration.

After ether was evaporated from the filtrate, the reaction product was distilled at 65°C, 41mmHg to give 4.3g (65% yield) of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene. Mass spectrum m/e calcd. for $C_8H_{16}Si$, 140.30, found 140, ir (neat) ν Si-CH_3 = 1242cm^{-1}(s), δSi-$CH_3$5865cm^{-1}(m), ^{1}H-nmr in $CDCl_3$ (ppm) 0.12 (Si-CH_3, S), 1.30 (C-CH_2, S), 1.68 (C-CH_3, S) ^{13}C-nmr in $CDCl_3$ (ppm), −1.8 (Si-CH_3, DEPT positive), 19,2(C-CH_3, DEPT positive), 25.4 (Si-CH_2, DEPT negative), 130 (C=C).

1,1,3,4-*Tetramethyl*-1-*sila*-2,4-*cyclopentadiene*. Br_2 2.5ml (50mmol) in $CHCl_3$ was slowly dropped at 0°C under stirring to 7g (50mmol) of 1,1,3,4-Tetramethyl-1-sila-3-cyclopentene

in 50ml of $CHCl_3$ in the presence of a catalytic amount of pyridine. The reaction mixture was stirred overnight at room temperature. Without separation of the brominated product, 14ml (100mmol) of triethylamine in 10ml of $CHCl_3$ was added and stirred additionally for 3 hrs.. The colorless triethylammonium bromide was filtered off and $CHCl_3$ solvent was removed under reduced pressure. The reaction product was distilled under reduced pressure to give 3.3g (48% yield) of a mixture of 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene monomer (dominated at 77—80°C, 60mmHg) and a dimer (dominated at 90-98°C, 30mmHg). Mass spectrum, m/e, calcd. for $(C_8H_{14}Si)_2$, 276.56, found 276, ir (neat) ν Si-CH_3 = 1250cm^{-1}(s), δ Si-CH_3 = 820cm^{-1}(m), ^{1}H-nmr. ^{13}C-nmr and C/H-correlation two dimensional nmr (see Table 3).

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Synthetic Studies Related to Ezomycins and Octosyl Acids. Synthesis of Heptofuranose Nucleosides

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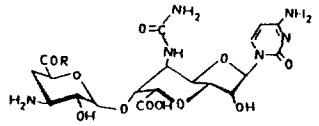
1-[Ethyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hept-5-enofuranosyluronate] uracil (**12**) was synthesized. Other various heptofuranose nucleosides were also synthesized from uridine and adenosine by two-carbon chain extension using Wittig reaction.

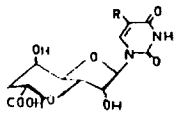
Introduction

The ezomycin complex[1,2] and octosyl acids[3] were recently isolated from the fermentation broth of two different strains of *Streptomyces*. Eight components, namely ezomycins A_1(1), A_2(2), B_1, B_2, C_1, C_2, D_1, and D_2 have been isolated from the ezomycin complex, and three octosyl acids, namely octosyl acids A(3), B(4), and C have been identified.



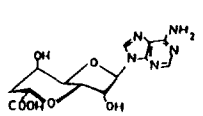
1 R = NHCHCH$_2$CH$_2$SCH$_2$CHNH$_2$ (COOH, COOH)

2 R = OH



3 R = COOH

4 R = CH_2OH



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The degradative and spectroscopic studies of ezomycins[4] and octosyl acids[3] revealed that an unusual higher-carbon sugar, namely a 3,7-anhydroocturonic acid, was a common structural backbone of these two series of compounds. The 3,7-anhydroocturonic acid is the first octose derivative containing a rigid bicyclic system in which a furanoid ring is *trans*-fused to a pyranoid ring. In spite of their structural similarities, the ezomycins and octosyl acids show marked differences in biological activities. Thus, whereas the ezomycins are antifungal antibiotics,[2] the octosyl acids are devoid of any such activity. However, the adenine analog (**5**) of the octosyl acids, readily obtained from *3* by transglycosylation,[5,6] was found to be an inhibitor of cyclic-AMP phosphodiesterases from various animal tissues.[6] In fact, octosyl acids 3 and 4 may be regarded as carboanalogs of 3′, 5′-cyclic nucleotides. The unique structures and the biological activities of the ezomycins and the octosyl acids have inspired various studies related to these compounds during the past several years. For example, a biosynthesis of octosyl acid A has been accomplished by Sato *et al.*,[7] and a ^{13}C NMR spectroscopic study of the ezomycins has been also reported.[8]

Although total synthesis of ezomycins and octosyl acids has not been accomplished yet, a few methods of approach toward their synthesis have been explored by synthesizing model compounds.[9-12] Among them, the methods devised by Hanessian *et al.*[11] and by Kim *et al.*[12] are promising ones for the eventual