REACTIONS OF 1-METHYL-1-β-PYRIDYL-1-SILACYCLOBUTANE WITH OPENING AND RETENTION OF THE SILICON–CARBON RING

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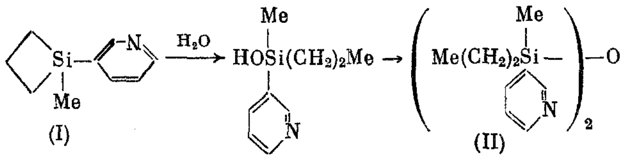
β-Pyridyl derivatives of silanes and olefins are less reactive than the corresponding α- and γ-pyridyl derivatives [1, 2].

However, as reported in the present article, the β-pyridyl derivative of a monosilacyclobutane, e.g., 1-methyl-1-β-pyridyl-1-silacyclobutane (I), readily adds water to form the corresponding silanol and then siloxane (II).

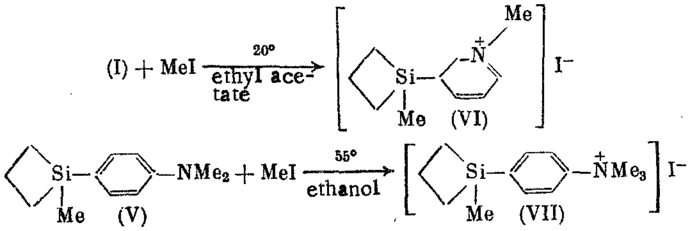


Thus, in the synthesis of (I) according to our previous procedure [3] (see the Experimental section), the isolation of (I) as a free base requires that the complex of (I) with MgClBr be decomposed with water, constantly extracting the desired product into ether–hexane. The time of contact of (I) with water is thus shortened, and effective drying with alumina and molecular sieves permits the preparation of pure (I) in 65% yield. If, on the other hand, these operations are carried out slowly and there is prolonged contact with water while the temperature is above 35°C, the yield of (I) is sometimes reduced to 10–20% due to the addition of water to the silacyclobutane (SCB) ring.

PMR monitoring of the diminution of the signals of the ring α- and β-CH_2 groups with $CHCl_3$ as the internal standard was used to evaluate the activity of (I) and also of 1-methyl-1-m-tolyl- (III) and 1-phenyl-1-p-dimethylaminophenyl-1-silacyclobutanes (IV) in the reaction in deuteroacetone. The rate of addition of water to (I) at 100°C is greater than that for (III) by more than a factor of 1000 (Table 1). At ∼20°C, (III) is completely inert, while about 15% (I) is consumed in 72 h. Even the contact of (I) with atmospheric moisture for more than 6 months leads to its complete conversion to siloxane (II), as indicated by vacuum distillation (the product obtained was identical to that isolated upon the reaction with H_2O in acetone).

This unusually high tendency of (I) to undergo ring opening is apparently related to protonation of the nitrogen atom and further reaction of the protonated form. The question of the mechanism of this reaction has remained open since its solution requires kinetic studies which might provide information on the reaction order and the activation parameters and isotope effect of this reaction.

The quaternization of (I), as expected, proceeds smoothly with retention of the four-membered ring and more readily than in the case of 1-methyl-1-p-dimethylaminophenyl-1-silacyclobutane (V) (heating at reflux in ethanol or ethyl acetate is not required).



A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1906–1909, August, 1985. Original article submitted October 12, 1984.

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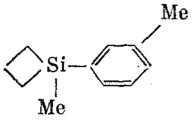
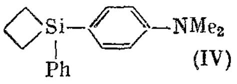
TABLE 1. Addition of Water to Monosilacyclobutanes in CD_3COCD_3

SCB	SCB:H_2O ratio	T., °C	Time, h	Conversion of SCB, %
(I)	1 : 6	100	0,25	34,4
			0,75	100
		20	24	7,8
 (III)	1 : 9	100	0,25	0
			10	0
			72	0,1
		20	30 days	0
 (IV)	1 : 6	100	6	Traces
			24	0,3
		20	10 days	0

The mass spectrum of the gas phase after heating (VI) at 60°C contains peaks with m/z = 178 ($[M - I]^{+\cdot}$, trace), 177 ($[M - HI]^{+\cdot}$, trace), and 163 ($[M - CH_3I]^{+\cdot}$, trace). Base (I) is present in the gas phase after heating (VI) at 180°C. The IR spectra of (VI) and (VII) contain all the band characterizing the silacyclobutane ring at 930, 1125, and 1185 cm^{-1}.

In contrast to (VI), (I) is stable to the action of water. An unchanged IR spectrum was obtained upon heating a 10% aqueous solution of (VI) for 1 h at 70°C and then at 100°C at 0.01 mm to remove water.

Complexation with $NiCl_2$ is another reaction of (I) which occurs with retention of the ring. The reaction of (I) with $NiCl_2$ was carried out according to our previous work [3].

$$(I) + NiCl_2 \xrightarrow[\text{ethanol}]{50^\circ} 2(I) \cdot NiCl_2$$

After recrystallization, the crystals of the complex of (I) with $NiCl_2$ were dried, in contrast to our previous procedure [3],* at ≤ 55°C in vacuum using a drying pistol heated by acetone vapor to constant weight. The blue-green complex thus obtained was shown by elemental analysis to correspond to $2(I) \cdot NiCl_2$. This complex is soluble in methanol and ethanol up to about 10% at 25°C. The IR spectrum of this complex confirms the presence of a silacyclobutane ring [3].

Thus, the endocyclic Si–C bond in (I) is split by the action of water much more readily than for other silacyclobutanes. On the other hand, the reactions of (I) with MeI (quaternization) and $NiCl_2$ (complexation) at the nitrogen atom proceed readily with retention of the silacyclobutane ring.

EXPERIMENTAL

Samples of 1-methyl-1-p-dimethylaminophenyl-1-silacyclobutane and 1-methyl-1-m-tolyl-1-silacyclobutane were obtained according to our previous procedure [4] while a sample of 1-phenyl-1-p-dimethylaminophenyl-1-silacyclobutane was obtained according to our earlier work [5].

The IR spectra were taken on UR-20 and Specord 75 IR spectrometers. The PMR spectra of the silacyclobutanes were taken on a Varian T-60 spectrometer in CCl_4. In order to determine the fraction of ring opening, the spectra were taken in deuteroacetone with $CHCl_3$ as the internal standard. The ^{29}Si NMR spectra were taken on a Tesla BS-487 spectrometer equipped with an attachment for heteronuclear double resonance. The resonance absorption was recorded in the $^1H-\{^{29}Si\}$ INDOR mode. The ^{13}C NMR spectrum was taken on a Varian XL-100-12 spectrometer, and the mass spectra were taken on an LKB-2091 mass spectrometer.

1-Methyl-1-β-pyridyl-1-silacyclobutane (I). A solution of about 1.0 mole 1-methyl-1-chloro-1-silacyclobutane in an equal volume of ether was added over 2 h to an ethereal solution of 0.25 mole β-pyridylmagnesium bromide prepared according to Wibaut and van der Voort

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*The composition of the complex obtained in our previous work [3], in which the drying step was carried out in vacuum at 100°C, was close to $Ni(I)Cl_2$.

[6]. The reaction mixture was heated at reflux for 4 h, and the solvent was removed. 1-Methyl-1-ethyl-1-silacyclobutane was condensed at ∿100 mm in a trap. Then, 0.75 liter 1:1 ether–hexane was added to the residue. The residue was decomposed by water with cooling. The aqueous layer was extracted with ether, and the combined organic layers were dried initially with anhydrous alumina and then with molecular sieves. After filtration and removal of the solvents, the residue was distilled in vacuum to yield 26.1 g (64%) (I), bp 76-78.5°C (2.5 mm), n_D^{20} 1.5343, d_4^{20} 0.9706. PMR spectrum (δ, ppm): 0.5 s (3H, $Si-CH_3$), 1.15 m (4H, $\alpha-CH_2$), 2.12 m (2H, $\beta-CH_2$), 7.07 m (1H, β-H Py), 7.7 m (1H, γ-H Py), 8.48 m (1H, $\alpha-H_{NCHCH}$ Py), 8.73 m (1H, $\alpha-H_{NCHCSi}$ Py). ^{13}C NMR spectrum (δ, ppm, in C_6D_6): −1.7 (CH_3Si), 14.5 (C_α), 18.6 (C_β), 123.2, 133.1, 140.8, 151.2, 154.7 (β-pyridyl C atoms). ^{29}Si NMR spectrum (δ, ppm from TMS): 11.58. Mass spectrum, m/z (rel. intensity, %): 163 $[M]^{+\cdot}$ (20), 148 $[M - CH_3]^{+\cdot}$ (1.5), 135 $[M - C_2H_4]^{+\cdot}$ (100), 122 (10), 121 (6.5), 120 $[M - CH_3 - C_2H_4]^{+}$ (50), 108 (10.5), 107 (5), 106 (11), 93 (11.5), 80 (4), 79 (5.5), 67 (6.5), 53 (8.5).

Dimethyl-dipropyl-di-β-pyridylsiloxane (II). A tenfold excess of water in acetone was added to 4.1 g (∿25 mmoles) 1-methyl-1-β-pyridyl-1-silacyclobutane (I) and heated at reflux for 10 h. After solvent removal, the residue was distilled in vacuum to give a 70% yield of (II), bp 165-168°C (1.5 mm), n_D^{20} 1.5182. PMR spectrum (δ, ppm): 0.37 s (6H, CH_3Si), 0.6-1.7 m (14H, C_3H_7), 7.07 m (2H, β-H Py), 7.65 m (2H, γ-H Py), 8.5 m (4H, α-H Py).

Iodomethylate of 1-Methyl-1-β-pyridyl-1-silacyclobutane (VI). A sample of 6 mmoles (I) was added to a solution of 30 mmoles CH_3I in 3 ml ethyl acetate. The solution gradually became yellow and the reaction mixture separated into two layers. The upper layer was a light-yellow solution and then the lower layer was an orange liquid. Removal of the solvent in vacuum gave solid, yellow crystalline iodomethylate (VI), which is soluble in water. The yield was 80%. After recrystallization from ethyl acetate, mp 124-126°C. PMR spectrum (δ, ppm): 0.66 s (3H, CH_3Si), 4.4 s (3H, $\overset{+}{N}CH_3$), 1.1-2.5 m (6H, $\alpha-CH_2$ and $\beta-CH_2$), 7.8-8.9 m (4H, β-pyridyl).

Complex of 1-Methyl-1-β-pyridyl-1-silacyclobutane with $NiCl_2$, $2(I)\cdot NiCl_2$. A solution of 6 mmoles (I) in 4 ml ethanol was added to a solution of 1.25 mmoles $NiCl_2$ in 6 ml abs. ethanol heated to 50°C. After cooling, the solution was concentrated in vacuum. The solid precipitate was recrystallized from 1:3 ethanol–heptane and dried in a vacuum pistol heated with acetone vapor (∿55°C). The yield of this complex was 85%. The IR spectrum has bands at 930, 1122 (split), and 1185 cm^{-1} characteristic for the silacyclobutane ring. Found, %: C 47.01; H 5.73; Si 12.22; Ni 12.5. $C_{18}H_{26}Cl_4N_2Si_2Ni$. Calculated, %: C 47.39; H 5.70; Si 12.33; Ni 12.88.

Iodomethylate of 1-Methyl-1-p-dimethylaminophenyl-1-silacyclobutane (VII). A solution of 3.54 g (24.8 mmoles) MeI in a twofold volume of ethanol was added to a solution of 4.94 g (24 mmoles) (V) in 10 ml ethanol and heated at 55°C for 40 min. The residue formed after cooling was filtered off and recrystallized from ethyl acetate to give a 90% yield of the product, mp 157-157.5°C. Found, %: C 45.17; H 6.67; Si 7.88; N 4.5. $C_{13}H_{22}SiNI$. Calculated, %: C 44.96; H 6.38; Si 8.08; N 4.03; I 36.54.

CONCLUSIONS

1. An anomalously high tendency was found for 1-methyl-1-β-pyridyl-1-silacyclobutane to undergo opening of the silacyclobutane ring by the action of water.

2. The quaternization of 1-methyl-1-β-pyridyl-1-silacyclobutane by methyl iodide at the nitrogen atom in the silacyclobutane substituent and complexation with $NiCl_2$ proceed with retention of the silacyclobutane ring.

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