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STEREOSELECTIVE FORMATION OF SILACYCLOPENTANES BY THE REACTION OF SILACYCLOBUTANE WITH LITHIUM CARBENOIDS

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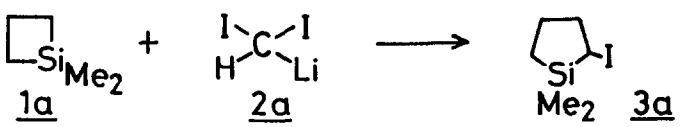
Summary: An addition of lithium diisopropylamide to a solution of 1,1-dimethyl-1-silacyclobutane and diiodomethane provided 1,1-dimethyl-2-iodo-1-silacyclopentane in good yield.

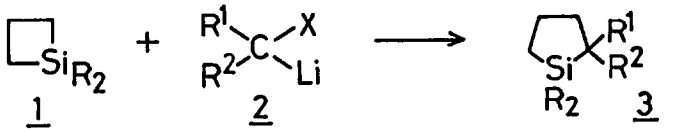
Dichlorocarbene[1] from $PhHgCCl_2Br$ or siglet methylene ($^1CH_2$)[2] generated by the photolysis of ketene reacts with silacyclobutane to give a mixture of a ring insertion product and a -C-H insertion product. Here we wish to report that treatment of silacyclobutane with lithium carbenoids provides silacyclopentanes exclusively with high stereoselectivity.

Butyllithium (1.6 M in hexane, 12.5 ml, 20 mmol) was added to a solution of diisopropylamine (2.0 g, 20 mmol) in THF (20 ml) at 0 °C. The resulting solution of lithium diisopropylamide was added dropwise to a solution of 1,1-dimethylsilacyclobutane (**1a**, 1.5 g, 15 mmol) and diiodomethane (5.4 g, 20 mmol) in THF (30 ml) over 30 min by syringe pump at -78 °C under an argon atmosphere. The resulting mixture was stirred at -78 °C for another 30 min after completion of the addition. Then cold bath was removed and the reaction mixture was allowed to come to room temperature. Workup (ethyl acetate, sat. NH_4Cl) followed by purification by silica-gel column chromatography gave 1,1-dimethyl-2-iodo-1-silacyclopentane (**3a**,[3] 3.0 g) in 83% yield.



The results are shown in Table 1. Not only dihalomethane but also benzyl bromide and iodomethyltrimethylsilane provided the corresponding 2-phenyl- and 2-trimethylsilyl-1-silacyclopentane in good yields upon treatment with lithium diisopropylamide in the presence of silacyclobutane. The substituents on silicon did not affect the reaction pathway. Thus, 1,1-diphenyl-, 1,1-dibutyl-, and 1,1-dihexynyl-1-

Table 1. Reaction between silacyclobutane and lithium carbenoids[a]



Entry	Silacyclobutane 1 R	Carbenoid 2 R^1	R^2	X	Product 3 Y(%)
1	Me	H	I	I	83
2	Me	H	Br	Br	57
3	Me	H	Cl	Cl	49
4	Me	n-Bu	I	I	59
5	Me	H	Ph	Br	61
6	Me	H	Me_3Si	I	56
7	Ph	H	I	I	72
8	Ph	H	Br	Br	74
9	Ph	H	Cl	Cl	72
10	n-Bu	H	I	I	85
11	n-Bu	H	Br	Br	79
12	n-BuC≡C	H	I	I	88

a) Silacyclobutane (1.5 mmol), dihalomethane (or benzyl bromide, iodomethyltrimethylsilane, 2.0 mmol), and lithium diisopropylamide (2.0 mmol) were employed.

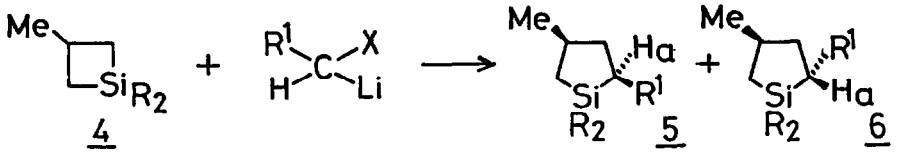
silacyclobutane reacted easily with lithium carbenoids as well as 1,1-dimethyl-1-silacyclobutane.

Several silacyclobutanes having substituent on four-membered ring carbon have been prepared and treated with lithium carbenoids. The reaction of 1,1,3-trimethyl-1-silacyclobutane (**4a**, R = Me) with CHI_2Li, $CHBr_2Li$, or PhCHBrLi gave the corresponding 2,4-disubstituted 1-silacyclopentane (**5** and **6**) with high stereoselectivity. The ratios of cis and trans isomer (**5**:**6**) were ca. 9:1 except for the reaction between **4b** and PhCHBrLi (Table 2).[4]

Cleavage of two Si-C bonds occurred in the case of 1,1,2-trimethyl-1-silacyclobutane (**7**). For instance, treatment of **7** with iodomethyllithium provided a mixture of cis-2-iodo-1,1,3-trimethyl-1-silacyclopentane (**8a**) and 2-iodo-1,1,5-trimethyl-1-silacyclopentane (**9a**) (**8a**/**9a** = 42/58). Treatment of **8e** with HBF_4 and H_2O_2 gave the diol ($1R^*,2S^*$) PhCH(OH)CH(Me)CH_2CH_2OH as a single stereoisomer, which was

identical with the sample prepared by the reduction of cis-γ-phenyl-β-methyl-γ-butyrolactone[5,6] (Table 3).

Table 2. Reaction of 3-methyl-1-silacyclobutane with lithium carbenoids

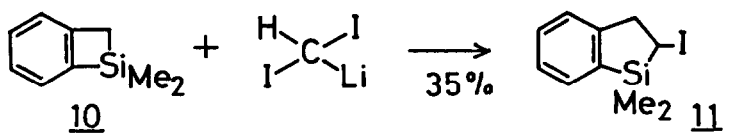


4a:	R = Me	R^1 = X = I	72%	**5a:6a** =	91	:	9
		R^1 = X = Br	58%	**5b:6b** =	89	:	11
		R^1 = Ph X = Br	23%	**5c:6c** =	95	:	5
4b:	R = Ph	R^1 = X = I	97%	**5d:6d** =	93	:	7
		R^1 = X = Br	88%	**5e:6e** =	93	:	7
		R^1 = Ph X = Br	43%	**5f:6f** =	35	:	65

Table 3. Reaction of 2-methyl-1-silacyclobutane with lithium carbenoids

7a:	R = Me	R^1 = X = I	55%	**8a:9a** =	42	:	58
		R^1 = X = Br	56%	**8b:9b** =	48	:	52
		R^1 = Ph X = Br	62%	**8c:9c** =	36	:	64
7b:	R = Ph	R^1 = X = I	90%	**8d:9d** =	45	:	55
		R^1 = Ph X = Br	45%	**8e:9e** =	30	:	70

Benzosilacyclobutene (**10**)[8] afforded the corresponding silacyclopentene **11**. In this case, one of C-Si bonds was cleaved selectively.[9]



References and Notes

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Serres, J. Organomet. Chem., **50**, 39 (1973).

2. H. M. Frey, R. Walsh, and I. M. Watts, J. Chem. Soc., Chem. Commun., **1989**, 284.
3. **3a**: Bp 73 °C (bath temp, 2 Torr); IR (neat) 2932, 1250, 1049, 840, 812, 783 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.11 (s, 3H), 0.32 (s, 3H), 0.60 (dd, J = 7.5, 7.5 Hz, 1H), 0.61 (dd, J = 7.0, 7.0 Hz, 1H), 1.48-1.73 (m, 1H), 1.68-2.16 (m, 3H), 3.18 (dd, J = 6.1, 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ-2.7, -2.5, 11.1, 13.0, 25.3, 39.6. Found: C, 29.96; H, 5.58%. Calcd for $C_6H_{13}ISi$: C, 30.00; H, 5.46%.
4. Assignments of the products were based on the examination of those ^1H NMR spectra. All the trans isomers, **6a-6f** exhibited the narrow signals for the protons (H_a) attached to carbon bearing R^1 group at lower field than those for protons in cis isomers **5a-5f**. The chemical shifts of protons (H_a) for **5a-5f** and **6a-6f** are as follows. **5a**: 2.91 (dd, J = 7.5, 12.5 Hz), **6a**: 3.41 (dd, J = 3.0, 5.5 Hz); **5b**: 3.45 (dd, J = 8.0, 12.0 Hz), **6b**: 3.80 (dd, J = 2.5, 5.5 Hz); **5c**: 2.36 (dd, J = 6.5, 13.0 Hz), **6c**: 2.58 (dd, J = 8.0, 8.0 Hz); **5d**: 3.44 (dd, J = 7.3, 13.0 Hz), **6d**: 3.91 (dd, J = 3.5, 5.5 Hz); **5e**: 3.71 (dd, J = 7.7, 12.5 Hz), **6e**: 4.05 (dd, J = 2.3, 4.5 Hz); **5f**: 3.02 (dd, J = 6.5, 14.0 Hz), **6f**: 3.21 (dd, J = 8.0, 8.0 Hz). Further support for the assignment has been given by the following transformation of **5f** and **6f** into the corresponding 1,4-diol ($HOCH_2CH(Me)CH_2CH(OH)Ph$) by the action of HBF_4 and H_2O_2 according to the reported procedure.(K. Tamao, J. Syn. Org. Chem. Jpn., **46**, 861 (1988); I. Fleming, R. Henning, and H. Plant, J. Chem. Soc., Chem. Commun., **1984**, 29). The diol ($1R^*,3R^*$) derived from **5f** was identical with a sample prepared by the reduction ($LiAlH_4$) of cis-α-methyl-γ-phenyl-γ-butyrolactone (E. Nakamura, H. Oshino, and I. Kuwajima, J. Am. Chem. Soc., **108**, 3745 (1986)). The other diol from **6f** was identical with that generated from trans-α-methyl-γ-phenyl-γ-butyrolactone.
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6. Treatment of **9e** with HBF_4 and H_2O_2 provided a 1,4-diol $PhCH(OH)CH_2CH_2CH(Me)OH$[7] as 2:1 stereoisomeric mixture.
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