Chemistry of Heterocyclic Compounds, Vol. 39, No. 11, 2003

NEWS

SILACYCLES IN 2003. SECOND EUROPEAN ORGANOSILICON DAYS CONFERENCE

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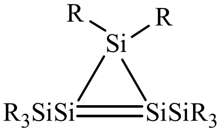
The Second European Organosilicon Days conference took place in Munich at the Technical University from September 11 through September 12, 2003. The first conference, which had been devoted to silicon chemistry, occurred in Munich in 2001. About 400 scientists from Europe, the USA, Canada, Japan, China, and Russia participated in the conference.

All aspects of the chemistry of organosilicon compounds were discussed at the conference, including synthesis of novel silacycles and siloxanes, and also the biological activity of novel organosilicon derivatives and the use of polysiloxanes in medicine and industry.

The plenary lecture by Professor M. Kira (Tohoku University, Japan) focused on synthesis of small silacycles containing a Si=Si bond in the ring (**1-3**):



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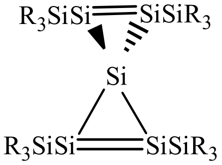

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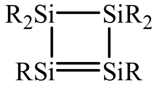

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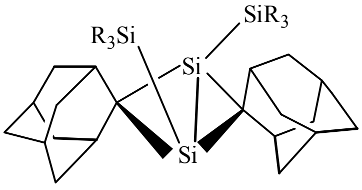
Owing to the difference between the electronic and steric effects of the trialkylsilyl substituents, these disilenes are interesting systems for studying structure, electronic spectra, and chemical reactions. Tetrasilyldisilenes are useful reagents for synthesis of novel types of organosilicon compounds such as η^2-disilene complexes of transition metals and also 1,3-disilabicyclo[1.1.0]butane **4**.



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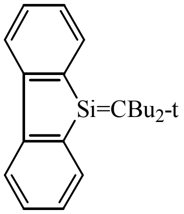

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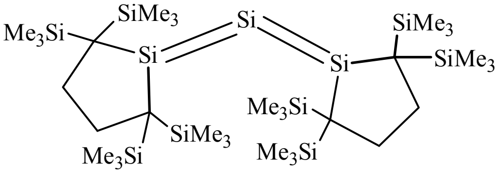

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1745-1748, November, 2003.

Professor R. West (University of Wisconsin, USA) reported on synthesis of silafulvene **5** by reaction of the 9-silafluorene dianion with di-*tert*-butyl ketone, and also a study of its structure and chemical transformations.

The first representative of the trisilaallenes **6** has been synthesized, in which the silicon atom is *sp*-hybridized (Professor M. Kira, Tohoku University, Japan).

The chemistry of alkyl-substituted octasilacubanes, which were first obtained in 1992, has been further developed in research by Japanese scientists (Professor M. Unno, Gunma University, Japan). Thus Br_2 or I_2 halogenation of octasilacubane $(RSi)_8$ (R = CMe_2CHMe_2, *t*-$BuMe_2Si$) has been carried out, as a result of which the corresponding dibromides and diiodides have been obtained. The reaction of octasilacubane (R = CMe_2CHMe_2) with PCl_5 occurs *via* intramolecular rearrangement to form the dichloro derivative. The dihalo derivatives obtained are readily reduced by sodium to the initial octasilacubanes. Photochemical oxidation of octasilacubane (R = CMe_2CHMe_2) by dimethylsulfoxide has been studied, as a result of which monooxaoctasilahomocubane and dioxaoctasilabishomocubane have been formed, and its photolysis and photoluminescent properties have also been studied.

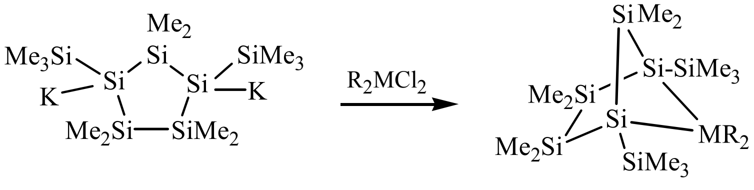
Cyclic silsesquioxanes $(RSiO_{1.5})_8$ with a vinyl group on the side chain have been obtained as a result of cross-metathesis (Ru=C) or silyl linkage (Ru–H, Ru–Si) reactions (Professor B. Marciniec, Adam Mickiewicz University, Poland).

Professor H. Stuger (Technical University of Graz, Austria) reported on a series of novel substituted cyclohexasilanes obtained by Austrian researchers. Their photoluminescent properties have been studied. It has been shown that in order to obtain the novel luminescent materials, the presence of a silacyclohexane ring and an oxygen-containing group on the side chain are needed.

Silacycles containing Si–P and Si–As bonds have been obtained by reaction of 2-(chlorodimethylsilyl)-1,3-dichloropentamethyltrisilane with phosphide and 2,3-bis(chlorodimethylsilyl)-1,4-dichlorohexamethyltetrasilane with Na/K arsenide, and their crystal structures have been studied (G. Tekautz, Technical University of Graz, Austria).

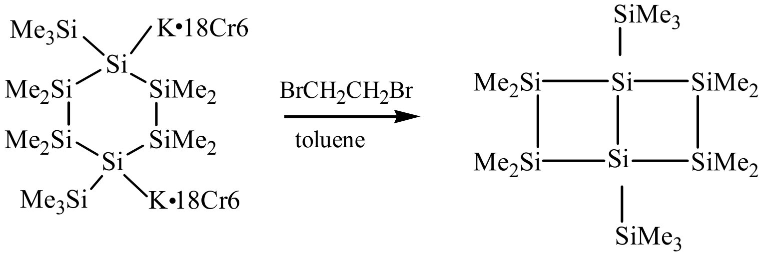
Rings containing the Si–Sn bond have been synthesized by the Wurtz reaction from the corresponding dichlorosilanes and dichlorostannanes. It is interesting to note that a 6-membered ring is formed as a result of reaction of dimethyldichlorosilane and diphenyldichlorostannane, while the same silane reacts with di(*tert*-butyl)dichlorostannane to form a 4-membered ring (Professor F. Uhlig, University of Dortmund, Germany).

Professor R. Fischer (Technical University of Graz, Austria) discussed the interesting transformations of 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane with potassium *tert*-butoxide, as a result of which cyclic mono- and dianions are obtained (**7**) that readily react with various dihalides to form novel compounds and bicyclic systems **8**.



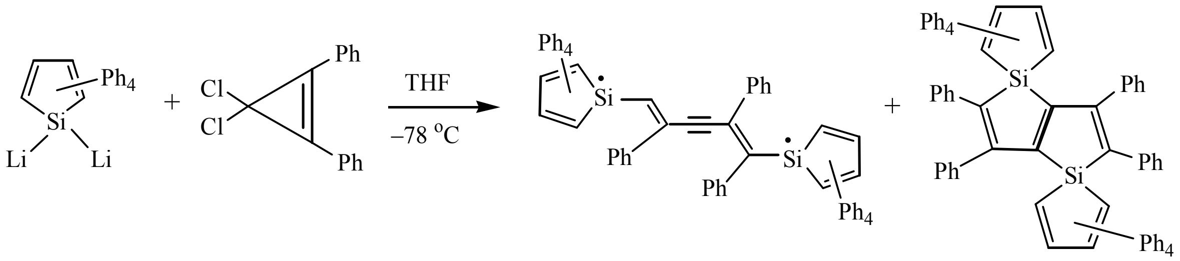
7 **8**

Cyclohexasilanyl 1,4-dipotassium **(9)** is a useful precursor of [2.2.n]oligosilanes and readily reacts with 1,2-dibromoethane to form the bicyclo derivative **10**. The reactions of the central Si–Si bond have been studied (A. Wallner, Technical University of Graz, Austria).



9 **10**

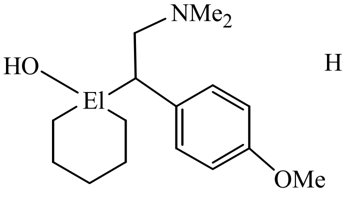
A lecture by Professor R. West (University of Wisconsin, USA) was devoted to the reaction of 1,1-dilithium-2,3,4,5-tetraphenylsilole with 1,1-dichloro-2,3-diphenylcyclopropene, which led to the diradical **11** as the major product and 1,4-disilapentalene **12** (25%), a novel delocalized silacycle. Diradical **11** is rather stable and inert: it does not react with water, alcohols, or chloroform and when heated is converted to compound **12**.



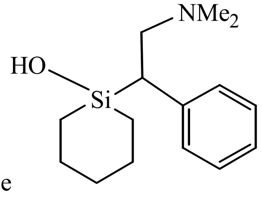
11 **12**

Latvian scientists (Professor E. Lukevics, L. Ignatovich, J. Popelis, Latvian Institute of Organic Synthesis, Latvia) reported on synthesis of a series of phenyl-, 2-furyl-, 2-(4,5-dihydrofuryl)-, and 2-thienylsilacyclopentanes and -silacyclohexanes by reaction of 1,1-dichloro-1-silacyclopentane or 1,1-dichloro-1-silacyclohexane with the corresponding lithium-containing heterocycles. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were studied and it was established that δ ^{29}Si depends substantially on the type of heterocycle. Thus in the silacyclopentane series, the ^{29}Si signal (from -9.72 to +9.23 ppm) is shifted downfield in the following order: 2-furyl-, 2-(4,5-dihydrofuryl)-, 2-thienyl-, and phenylsilacyclopentane. The spin–spin coupling constants $J^{29}\text{Si}–^{13}\text{C}_{(\text{Ar})}$ decrease in the same order.

A number of reports were devoted to the biological activity of organosilicon compounds containing silicon in the ring. The silicon analog **13b** of the drug venlafaxine **13a**, which has antidepressant properties, has been synthesized. A number of its modifications **14, 15** have been obtained and their pharmacological properties have been studied (Professor R. Tacke, University of Wurzburg, Germany, W. Bains, Amedis Pharmaceutical Ltd., UK).



13a,**b**



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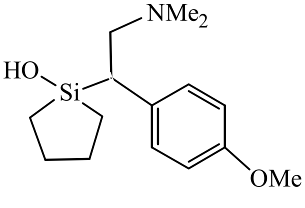

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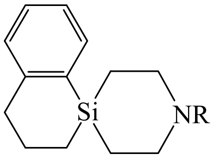
13 a El = C, **b** El = Si

Professor R. Tacke (University of Wurzburg, Germany) reported on synthesis of a series of biologically active derivatives of a novel heterocyclic system 1,4'-silaspiro[tetralin-1,4'-piperidine].



14–17

14 R = CH_2Ph; **15** R = 4-$CH_2C_6H_4OMe$; **16** R = $(CH_2)_2Ph$; **17** R = $CH_2CH{=}CMe_2$

According to established tradition, the Third European Conference on Silicon Chemistry will take place in Würzburg in 2005 and it will be combined with the 14th International Symposium on Organosilicon Chemistry.