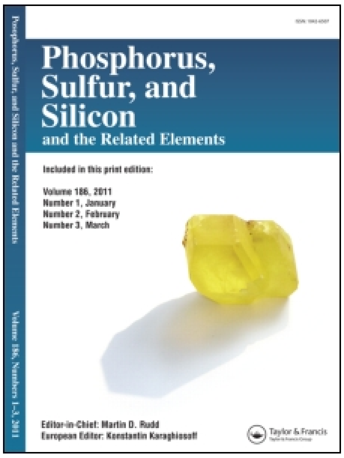
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Syntheses and Structures of Tetraazadisilacyclo-Hexanes

Jiliang He[a]; John F. Harrod[a]
[a] Chemistry Department, McGill University, Montreal, QC, Canada

To cite this Article He, Jiliang and Harrod, John F.(1994) 'Syntheses and Structures of Tetraazadisilacyclo-Hexanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 349 — 350

To link to this Article: DOI: 10.1080/10426509408021851

URL: http://dx.doi.org/10.1080/10426509408021851

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 349–350
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESES AND STRUCTURES OF TETRAAZADISILACYCLOHEXANES

JILIANG HE and JOHN F. HARROD
Chemistry Department, McGill University, Montreal, QC, Canada H3A 2K6

Abstract Several tetraazadisilacyclohexanes, with general formula $R_2Si(NHNR')_2SiR_2$ (R = Me or Ph, R' = H or Me), have been synthesized by a dehydrocoupling methodology. Structural study showed that planar and pyramidal coordinations about nitrogen atoms exist in these molecules.

INTRODUCTION

Cyclic silylhydrazine compounds, containing the Si-N-N unit, constitute an important family of cyclic silicon-nitrogen compounds. The conventional synthetic method for the preparation of these molecules is the intermolecular reaction of a hydrazine with a dihalosilane, with the elimination of hydrogen halide. However, the application of this method has its limitation when some dihalosilanes are too reactive towards hydrazines and side-reaction occurs. The dehydrocoupling of organosilanes with hydrazines provides a new and more efficient route to cyclic and acyclic silylhydrazine compounds.[1] In the presence of a dimethyltitanocene catalyst, diphenylsilane reacts with hydrazine to give 1,2,4,5-tetraaza-3,3,6,6-tetraphenyl-3,6-disilacyclohexane (**1**). The reaction of diphenylsilane with methylhydrazine afforded bis(2-methylhydrazino)diphenylsilane (**2**) in high yield. **2** was subsequently cyclized to two isolatable six-membered ring isomers, namely, 1,2,4,5-tetraaza-1,4-dimethyl-3,3,6,6-tetraphenyl-3,6-disilacyclohexanes (**3**) and 1,2,4,5-tetraaza-1,5-dimethyl-3,3,6,6- tetraphenyl-3,6-disilacyclohexanes (**4**), by the reaction with MeI, HCl or Ph_2SiCl_2, or by thermolysis at 250 - 300 °C,[2] or by the reaction with *n*-BuLi and Ph_2SiCl_2 followed by anionic rearrangement.[3]

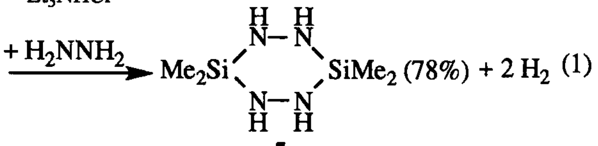
Structural study of tetraazadisilacyclohexanes reveals some striking features. The crystal structures of **1** and **3** show that **1** adopts a chair conformation of the Si_2N_4 ring,[1] while **3** adopts a twist-boat conformation.[3] Two geometries about nitrogens are found in each -N(R)- N(H)- unit (R = H for **1**; Me for **3**), *i.e.*, planar at N(R), and pyramidal at N(H). The driving force of the structural preference still remains unknown.

In the development of cyclic silylhydrazine chemistry, 1,2,4,5-tetraaza-3,3,6,6-tetramethyl-3,6-disilacyclohexane may play an important role as a building block for interesting polymeric materials due to its simple structure and NH functionality. However, its synthesis has not been reported. In this paper, we will describe its synthesis and characterization.

SYNTHESIS AND CHARACTERIZATION OF 1,2,4,5-TETRAAZA-3,3,6,6-TETRAMETHYL-3,6-DISILACYCLOHEXANE

In the absence of solvent, the dehydrocoupling reaction of 1,2-bis(dimethylsilyl)hydrazine with hydrazine took place spontaneously to form 1,2,4,5-tetraaza-3,3,6,6-tetramethyl-3,6-disilacyclohexane (5) in 78% yield. In the ^{1}H-NMR spectrum of 5, two resonances at 2.35 ppm and 0.10 ppm in 1:3 ratio are assigned to N-H and Si-CH_3, respectively. The ^{29}Si-NMR spectrum exibits a single resonance at -3.71 ppm. The identification of 5 was further confirmed by EI-MS (molecular ion: m/e = 176). 5 is a crystalline solid at ambient temperature. It can be purified by sublimation at 65°C under vacuum (0.01 mmHg). Equation (1) shows its synthesis starting from dimethylchlorosilane and hydrazine.

$$2\ Me_2HSiCl + H_2NNH_2 \xrightarrow[-\ Et_3NHCl]{Et_3N/Et_2O} MeH_2Si\text{-}NHNH\text{-}SiHMe_2\ (60\%)$$



5

In a comparative experiment, only 15% of 5 was obtained by the conventional method, *i.e.*, the reaction of dimethyldichlorosilane with hydrazine (1:1 ratio, at the presence of Et_3N). Again, this result demonstrates the efficiency of the dehydrocoupling method in the synthesis of this class of molecules.

REFERENCES

1. J. He, H.-Q. Liu, J.F. Harrod and R. Hynes, Organometallics, 13, 336(1994).
2. J. He and J.F. Harrod, Can. J. Chem., to be published in 72(1994).
3. J. He and J.F. Harrod, Heteroatom Chemistry, in press (1994).