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First Synthesis of the Three Isomeric Parent Disilacyclohexanes. An Improved Preparation of Methylene Di-Grignard

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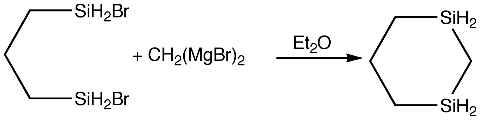
ABSTRACT



Ring closure of 1,5-dibromo-1,5-disilapentane with methylene di-Grignard was the key step in the preparation of the parent 1,3-disilacyclohexane. For that purpose, the preparation of methylene di-Grignard has been improved and simplified. The successful synthesis of the isomeric 1,2- and 1,4-disilacyclohexanes is also reported.

Saturated six-membered ring systems in which one or more CH_2 units in cyclohexane have been replaced by SiH_2 units are of general interest because they provide good examples to compare cyclohexane with its closest analogues. Known examples are 1-silacyclohexane,[1] 1,3,5-trisilacyclohexane,[2] and cyclohexasilane.[3] The parent disilacyclohexanes have not been described in the literature so far; however, a number of substituted derivatives of 1,2-disilacyclohexane,[4] 1,3-disilacyclohexane,[5] and 1,4-disilacyclohexane[6] have been reported. Because the Si−H bond has a higher reactivity than Si−alkyl or Si−aryl bonds, it is more convenient to prepare and work with substituted disilacyclohexanes. This may be a reason why the unsubstituted rings have remained a missing link in the field of silacyclohexanes for decades.

In recent years, the stereochemistry of six-membered silicon-containing ring systems has been of special interest in our group. In particular, we have studied the conformational energy surface of silacyclohexane[7] and the conformational properties of some of its monosubstituted derivatives.[8] Furthermore, we have investigated the gas-phase structure of 1,3,5-trisilacyclohexane,[9] its conformational surface, and the conformational behavior of its mono-, di-, and trisubstituted alkyl derivatives as deduced from NMR

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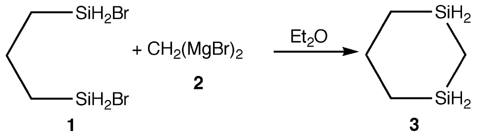
spectra[10] as well as from quantum chemical calculations.[11] The 1,3-disilacyclohexane is an intermediate between the former two ring systems, and it was of interest to explore its chemistry.

One possible way to achieve its preparation is shown in Scheme 1. Compound **1** may be prepared in a three-step procedure from allyltrichlorosilane;[12] the methylene di-Grignard **2**, however, has not been readily available. In fact, **2** has been known since as early as 1926, when it was first prepared by Emschwiller from methylene bromide and magnesium in diethyl ether.[13] The yields of **2** were originally low and unreliable, and its synthetic use was limited because of CH_3MgBr contamination but its preparation has been improved in several steps.[14] These include the use of magnesium amalgam instead of magnesium metal[15] and the use of diisopropyl ether as the reaction medium in which **2** does not dissolve. After the reaction, the diisopropyl ether can be decanted and the crude product dissolved in a 1:1 diethyl ether/benzene mixture from which the di-Grignard can be isolated. In this way, the contamination of CH_3MgBr, which will interfere with further reactions of **2**, is greatly diminished.[16] However, this last improvement as described by Bickelhaupt et al. requires the use of twice-sublimed magnesium, which is not commercially available, and an evacuated whole-glass manifold with break-seals. Most likely, these are the main reasons why Bickelhaupt's method has not found a common use.

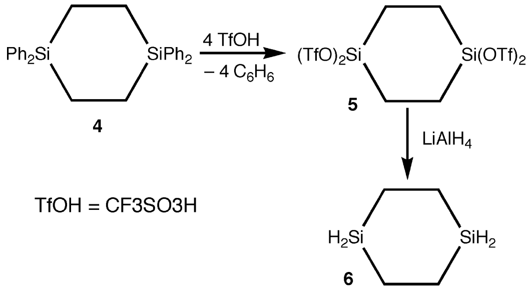
We have been able to simplify this process considerably, thereby keeping its main features unchanged. We have found that commercial Mg powder (−50 mesh, 99+%) may be used instead of twice-sublimed magnesium. Although our yields are, on the average, only 40% (compared with 80% according to Bickelhaupt), we found on the other hand that the amount of dibromomethane may be scaled up by a factor 4 (using the same amounts of solvents) without affecting the percentage yield of **2**. Thus, the amount of product per run can be doubled. Using a special reaction flask, the entire process can be carried out employing standard Schlenk techniques and commercially available starting materials. One such run can be completed in 2 days. A detailed experimental procedure for the methylene di-Grignard is given in the Supporting Information.

The reaction of di-Grignard **2** with 1,5-disilapentane **1** in diethyl ether resulted in ring closure and formation of disilacyclohexane **3** in 17% yield (Scheme 1). Small amounts of 2,6-disilaheptane (detectable in the ^1H and ^{13}C NMR and MS spectra) are formed as a side product in this reaction, probably by reaction of traces of CH_3MgBr with **1**.

Scheme 1. Synthetic Route for 1,3-Disilacyclohexane **3**



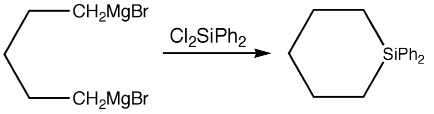
Scheme 2. Synthetic Route for 1,4-Disilacyclohexane **6**



Encouraged by the successful synthesis of 1,3-disilacyclohexane, we looked for possible reactions by which 1,4-disilacyclohexane might be prepared. Coupling reactions between 1,4-dibromo-1,4-disilabutane and 1,2-dibromoethane with lithium metal resulted in a complete reaction of the metal, but no traces of the desired product could be isolated. A second, more promising, synthetic route is shown in Scheme 2.

Kaszynski et al. have published a preparation of **4**.[17] Because it involves a tedious three-step synthesis, we decided first to prepare 1,1-diphenylsilacyclohexane as a model compound in order to test on it successive reactions with triflic acid and $LiAlH_4$.

Apparently, diphenylsilacyclohexane has not been described in the literature before. Its preparation went smoothly (eq 1); the reaction with 2 equiv of freshly distilled triflic acid turned it quantitatively into its triflic derivative, and a further reaction with $LiAlH_4$ resulted in the known silacyclohexane.



(1)

In a similar manner, **4** reacted with triflic acid to give **5**, which in turn was hydrogenated with $LiAlH_4$ to 1,4-disilacyclohexane **6**.

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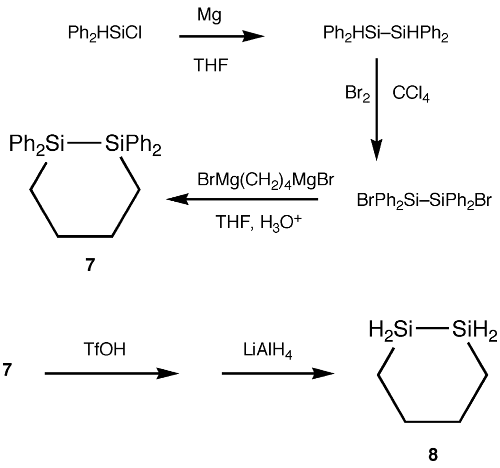
Scheme 3. Synthetic Route for 1,2-Disilacyclohexane **8**



We then turned to the last one of the isomeric disilacyclohexanes, the 1,2-disilacyclohexane. After several unsuccessful attempts, we came up with a similar strategy as in the case of 1,4-disilacyclohexane. 1,1,2,2-Tetraphenyl-1,2-disilacyclohexane **7** was prepared by well-known synthetic methods. Compound **7** was then converted to 1,2-disilacyclohexane **8** as outlined in Scheme 3.

All three disilacyclohexanes are colorless liquids at room temperature. Their syntheses should be carried out under inert atmosphere using standard Schlenk techniques. However, the products are not extremely air sensitive, and they can be exposed to dry air for a short time without decomposition.

In conclusion, we have been able to synthesize the three isomeric unsubstituted disilacyclohexanes for the first time. We have also improved considerably the synthesis of the simplest di-Grignard, $CH_2(MgBr)_2$. Additional investigations on the gas-phase molecular structures of the disilacyclohexanes, their potential energy surfaces, and ^1H NMR spectra analysis are currently underway.

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Supporting Information Available: Experimental procedures and spectral data for all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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