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Preliminary communication

THE SYNTHESIS OF 1-METHYL-1-SILAADAMANTANE

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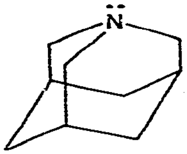
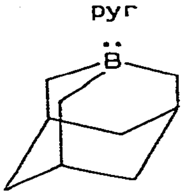
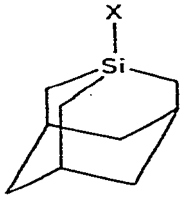
Summary

The synthesis of 1-methyl-1-silaadamantane from *cis*-1,3,5-tris(trimethylsilylmethyl)cyclohexane and $AlCl_3$ is described. 1-Chloro-1-silaadamantane was also isolated as a minor product.

Adamantane derivatives with one bridgehead carbon atom replaced by a heteroatom are rare. To date, only two analogs have been reported: the well-known 1-azaadamantane (I) first synthesized by Lukes, Galik, and Bauer [1] and the more recently prepared 1-boraadamantane obtained as the pyridine complex II by Mikhailov and Smirnov [2].


(I)


(II)


(IIIa) X = Me
(IIIb) X = Cl

The potential for new and interesting chemistry from organometallic compounds in which a metal atom is incorporated into the adamantane cage structure prompted us to initiate an investigation of a new class of compounds, 1-metalloadamantes. In this communication we wish to report the synthesis of the first member of this class, 1-methyl-1-silaadamantane (IIIa)*.

The success of aluminum chloride catalyzed redistribution reactions as a

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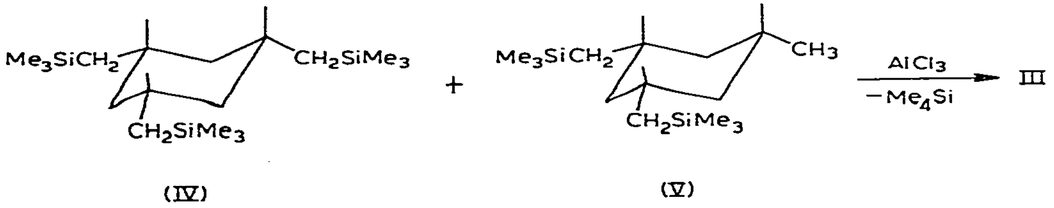
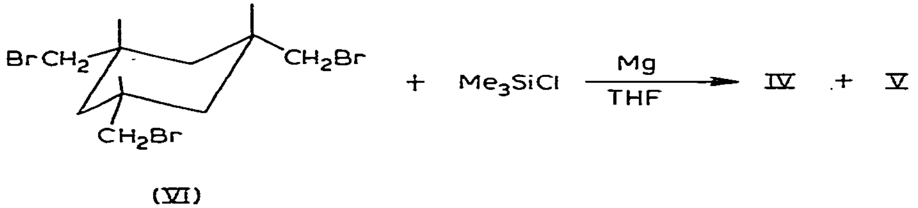
*1-Methyl-1-silatricyclo[3·3·1·$1^{3,7}$] decane according to IUPAC nomenclature.

route to otherwise inaccessible carbosilanes [3,4] led us to believe that that approach would be a good starting point for making compounds like III. This was the case, for we prepared IIIa from a mixture of *cis*-1,3,5-tris(trimethylsilylmethyl)cyclohexane (IV) and *cis*-3,5-bis(trimethylsilylmethyl)methylcyclohexane (V) and $AlCl_3$ in ~50% yield.

We obtained IV and V by adding *cis*-1,3,5-tris(bromomethyl)cyclohexane (VI) [1] to a mixture of magnesium turnings and trimethylchlorosilane in THF at 0°C followed by refluxing the mixture for 15 h. IV and V were obtained in 71 and 11% yields, respectively, and isolated by preparative gas chromatography*.





Our most successful preparation of IIIa was from a mixture of IV and V and $AlCl_3$ in the presence of benzene. A typical procedure is described below.

A mixture of 2.48 mmol of IV and 0.50 mmol of V in 5 ml benzene was heated to reflux under nitrogen with rapid stirring while 0.75 mmol of $AlCl_3$ (10 wt.%) was added. After 20 h, wet acetone was added and the solution washed with 10% HCl and H_2O. Drying over anhydrous $MgSO_4$, followed by concentration in vacuo gave a pale-yellow oil. Preparative gas chromatography was used to obtain analytically pure IIIa (1.5 mmol, 50% yield based on IV and V) as a colorless oil possessing an odor very similar to adamantane. Elemental analysis: Found: C, 72.08; H, 11.06; calcd.: C, 72.21; H, 10.91%; as well as mass spectral (*m/e* 166), NMR, and IR data support the proposed structure.

While the reaction conditions have not yet been optimized we did find that the neat reaction of IV and $AlCl_3$ gave IIIa in 15% yield whereas high dilution in benzene gave no detectable amounts of IIIa. A 40 wt.% loading of $AlCl_3$ under the conditions described above gave IIIa and solid 1-chloro-1-silaadamantane (IIIb) as identified by NMR, IR and mass spectrometry.

Our interest in silaadamantanes is two-fold: the unique geometry of the bridgehead silicon should provide an interesting reaction site for mechanistic

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*Structures IV and V are supported by elemental analysis, NMR, IR, and mass spectral data.

studies and this cage system will serve as a basis for developing silicon analogues to known effective antiviral and anti-Parkinson's disease agents such as amantidine (1-aminoadamantane) and its derivatives [5].

Acknowledgement

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References

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