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1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE AND 1,1,3,3-TETRAMETHYL-1-SILA-3-GERMACYCLOBUTANE VIA ACTIVE METAL DERIVATIVES OF BIS(CHLOROMETHYL)DIMETHYLSILANE

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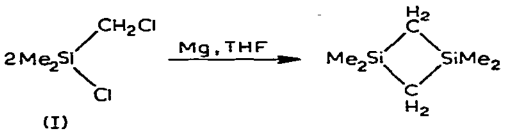
SUMMARY

The reaction of bis(lithiomethyl)dimethylsilane with dimethyldichlorosilane in diethyl ether has served in the preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in 24% yield and 1,1,3,3-tetramethyl-1-sila-3-germacyclobutane has been prepared in 21% yield by the Barbier reaction between bis(chloromethyl)dimethylsilane, dimethyldichlorogermane and magnesium in THF.

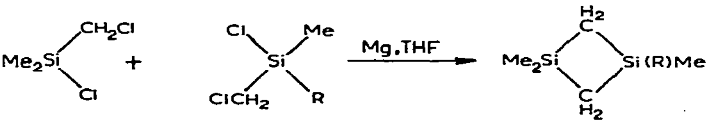
The usual procedure for the preparation of symmetrically substituted 1,3-disilacyclobutanes involves a double bimolecular condensation of compounds of type (I) (eqn. 1)[1]. In the preparation of compounds unsymmetrically substituted at silicon, yields of only *ca.* 20% were obtained by this method (eqn. 2) and an added complication was the presence of the two possible symmetrical species[2]. Such an approach is even less readily adaptable to the preparation of 1,3-dimetallocyclobutanes containing two different metals. One might conceive of a related procedure in which only a single condensation reaction of a preformed dimetal compound serves in the ring closure (eqn. 3). Indeed, such a procedure has been used to prepare 1,1,3,3-tetramethyl-1-sila-1-germacyclobutane[3]. However, the preparation of compounds of



(I)

(~50 %)

(1)



(2)

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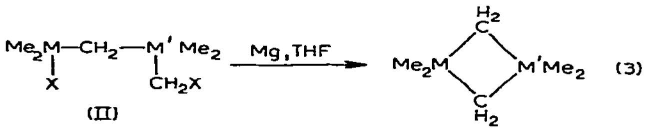
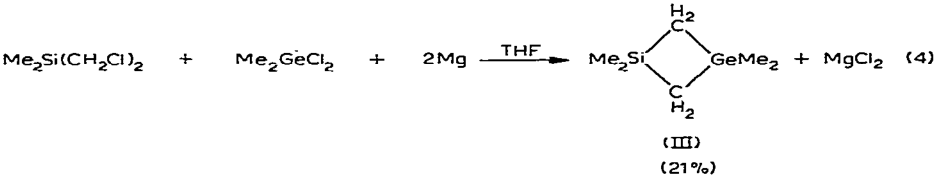


type (II) involves several steps, and a simpler and more direct route would be desirable even if the yields were lower than in reaction (3).

Bis(chloromethyl)dimethylsilane was shown some years ago to form a dilithium derivative in modest yield which reacted with trimethylchlorosilane to give $Me_3SiCH_2SiMe_2CH_2SiMe_3$ (37%)[4]. Thus a procedure based on the reaction of $Me_2Si(CH_2Li)_2$ with a diorganodihalo derivative of a Group IV element would have obvious advantages. Such a reaction with dimethyldichlorosilane was successful in preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in 24% yield. However, an analogous reaction with dimethyldichlorogermane was not successful. A large number of products was formed, but all were present in only very low yield. One of the products was 1,1,3,3-tetramethyl-1-sila-3- germacyclobutane, but the yield (2–3%) was unacceptably low.

A better procedure was found in a Barbier reaction in which bis(chloromethyl)-dimethylsilane was added to a well-stirred mixture of dimethyldichlorogermane and high purity magnesium in THF at 20° (eqn. 4). The product, (III), was characterized



by means of its elemental analysis, proton resonance spectrum and mass spectrum. A minor product (3–4%) was identified tentatively as 2,6-dichloro-2,4,4,6-tetramethyl-4-sila-2,6-digermaheptane, $(Me_2ClGeCH_2)_2SiMe_2$, on the basis of its NMR spectrum.

The reaction shown in eqn. 4 has demonstrated the feasibility of our approach, and studies directed more generally to the preparation and investigation of mixed metal cyclobutanes are in progress.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Bis(chloromethyl)dimethylsilane was prepared by photochemical chlorination of dimethyl(chloromethyl)chlorosilane[5], followed by methylation with MeMgBr in ether of the $(ClCH_2)_2MeSiCl$ which was separated by fractional distillation.

Reaction of bis(lithiomethyl)dimethylsilane with dimethyldichlorosilane

A 150 ml three-necked flask equipped with high-speed stirring assembly, a pressure-equalizing dropping funnel and a condenser topped with a nitrogen inlet tube was charged with 1.96 g (0.28 g-atom) of lithium dispersion and 70 ml of dry diethyl ether. The contents were cooled to −10° and 7.81 g (49.7 mmoles) of bis(chloromethyl)dimethylsilane was added dropwise over a 1-h period with vigorous stirring. The resulting mixture was stirred at 10° for 30 min, cooled to −10° again, and 7.77 g (60.0 mmoles) of dimethyldichlorosilane (Dow Corning Corp.) was added dropwise during 1 h. After the reaction mixture had been stirred overnight at room temperature unconverted lithium and precipitated lithium salts were filtered and the filtrate was trap-to-trap distilled in vacuum into a receiver cooled to −78°. Two fractions were taken. The higher boiling one (10.5 g) was examined by gas–liquid partition chromatography (GLC) (20% General Electric Co. SE-30 silicone rubber gum on Chromosorb W) and found to contain one major product, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, in 24% yield. It had n_D^{25} 1.4388 (lit.[6] n_D^{27} 1.4380) and its infrared and NMR spectra agreed with those previously reported for this compound[7].

Barbier reaction of bis(chloromethyl)dimethylsilane, dimethyldichlorogermane and magnesium in THF

A 500-ml three-necked flask equipped with a stirrer, a reflux condenser topped with a nitrogen inlet tube and a pressure-equalizing dropping funnel was charged with 3.82 g (0.159 g-atom) of magnesium powder (Alfa Inorganics, Inc.) and 200 ml of dry THF under nitrogen. The magnesium was activated with a small quantity of ethyl iodide and then 6.10 g (38.8 mmoles) of the silane and 8.05 g (46.2 mmoles) of Me_2GeCl_2 in 50 ml of THF were added slowly during 1 h with rapid stirring. The resulting reaction mixture was stirred at room temperature for 4 h, then was heated at reflux overnight. Filtration was followed by high-vacuum trap-to-trap distillation of the filtrate. GLC analysis showed the presence of one major high boiling component which was identified as 1,1,3,3-tetramethyl-1-sila-3-germacyclobutane (21% yield), n_D^{25} 1.4612. (Found: C, 38.44; H, 8.50. $C_6H_{16}SiGe$ calcd.: C, 38.15; H, 8.55%.)

The proton resonance spectrum (Varian HA-60, in $CDCl_3$): singlets at 0.20 ppm downfield from internal TMS (6 H, Me_2Si), 0.32 ppm (4 H, $SiCH_2Ge$) and 0.42 ppm (6 H, Me_2Ge). These assignments are based on previously reported[8] NMR spectra of methyl-silicon and -germanium compounds in which the shift for MeGe consistently was observed to be *ca.* 0.2–0.3 ppm downfield from the corresponding MeSi resonance.

IR spectrum (liquid film): 2940s, 2890s, 2788m, 2439w, 1874m, 1795w, 1741m, 1590w, 1479m, 1410s, 1361s, 1340sh, 1252s, 1077w, 1050w, 948s, 925sh, 835s, 826s, 801s and 740m cm^{-1}.

The mass spectrum (Hitachi–Perkin–Elmer RMU 6E mass spectrometer, chamber voltage 80 V) showed fragments corresponding to the molecular ion, M; $(M-CH_3)^+$; Me_3Si^+, $MeSi^+$, Me_2HSi^+, Si^+, Me_3Ge^+, $MeGe^+$. The relative percentages of the isotopes in the molecular ion (observed and calculated) are given below.

m/e	186	188	189	190	192
Observed (%)	19	23	10	35	8
Calcd. (%)	18	25	9	34	9

A minor (3–4%) product of longer retention time was isolated by GLC and tentatively identified as 2,6-dichloro-2,4,4,6-tetramethyl-4-sila-2,6-digermaheptane on the basis of its NMR spectrum which showed singlets at −0.30 ppm (4 H, $SiCH_2$-

Ge), 0.20 ppm (6 H, Me_2Si) and 0.71 ppm (12 H, Me_2ClGe). Enough material for an analysis could not be obtained.

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