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A CONVENIENT SYNTHESIS OF GERMACYCLOBUTANES

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Summary

The reaction of the di-Grignard reagents $BrMgCH_2CR_2CH_2MgBr$ (**2a**: R = H; **2b**: R = Me) with dichlorodimethylgermane gave 1,1-dimethylgermacyclobutane (**1a**) and its 3,3-dimethyl derivative **1b**, respectively, in more than 95% yield.

Introduction

Germacyclobutanes have been prepared by a number of methods [1,2]. All of them have certain drawbacks; they either involve multistep syntheses [3], give low yields of germacyclobutanes together with other products [3], are limited to special structural classes [4], or require expensive reagents [5]. We describe below a simple route to germacyclobutanes which gives high yields of pure compounds, as demonstrated for 1,1-dimethylgermacyclobutane (**1a**) and 1,1,3,3-tetramethylgermacyclobutane (**1b**).

Results and discussion

Starting materials for our syntheses are the 1,3-di-Grignard reagents **2a** [6] and **2b** [7]. It was advantageous to purify **2a** as obtained from the reaction of 1,3-dibromopropane with magnesium via formation of the (oligomeric) magnesacyclobutane and regeneration of **2a** by addition of 1 molar equivalent of magnesium bromide, as previously described ([6]; see Experimental); **2b** could be used directly. The reaction of **2a** or **2b** with dichlorodimethylgermane gave the germacyclobutanes **1a** and **1b** both in 96% yield and high purity (Scheme 1); special dilution techniques were not required, but in the case of **1b** reaction in a sealed vacuum system gave better results than the usual technique under nitrogen. Isolation was by hydrolysis with water, followed by separation and drying ($MgSO_4$) of the ethereal layer, and

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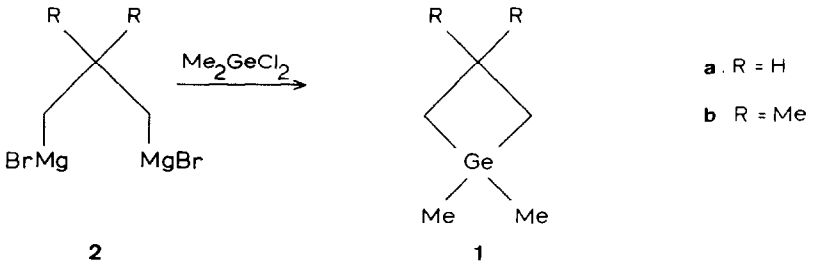
careful removal of the ether by fractional distillation. The residue was practically pure **1**, according to GLC and ^{1}H NMR analysis. Residual traces of diethyl ether were difficult to remove due to the high volatility of **1**. As in previous preparations [1,2], completely pure **1b** was therefore obtained by preparative gas chromatography.



SCHEME 1

The identity of **1a**, a known compound [5], was established from its ^{1}H NMR [2] and ^{13}C NMR spectrum and in particular from its characteristic mass spectrum, which was identical with that in the literature [8]. To our knowledge, **1b** has not been described previously; it is a highly volatile colourless liquid of boiling point 118°C and was fully characterized from its spectral data (see Experimental).

The ease of formation of germacyclobutanes by the di-Grignard route deserves some comment. While the thermodynamic stability of Group IVA four-membered rings decreases from carbon and silicon gradually via germanium [2] and rapidly for tin [9], the tendency to form such rings reaches a maximum for germanium. This is illustrated by the yields obtained from di-Grignard reagents with Group IVA electrophiles (Table 1); in this comparison, CO_2 is not strictly comparable as an electrophile to the other three electrophiles.

The high yields obtained for germacyclobutanes reflect not only the increasing polarity of the element–halogen bond, resulting in faster substitution by the alkyl anion, but probably also a fortuitous balance between two opposite thermodynamic effects: for the higher row elements, the increasing element–carbon bond length leads to higher ring strain due to the acute bond angle introduced at the hetero atom of the four-membered ring; this is in part compensated by the increasing polarizability of the higher row elements. It should be kept in mind, however, that in terms of ground or transition state energies, the observed differences in yield are small.

TABLE 1

YIELDS OF GROUP IVA FOUR-MEMBERED RINGS BY THE DI-GRIGNARD ROUTE

Electrophile	Reagent	Product	Yield [%]	Ref.
CO_2	**2a**	$\overline{CH_2CH_2CH_2C{=}O}$	33	[10]
Ph_2SiCl_2	**2a**	$\overline{CH_2CH_2CH_2SiPh_2}$	75	[11]
Me_2GeCl_2	**2a**	**1a**	96	This work
Me_2GeCl_2	**2b**	**1b**	98	This work
Me_2SnCl_2	**2b**	$\overline{CH_2CMe_2CH_2SnMe_2}$	48	[9]

Experimental

Magnesium was sublimed twice and used as a coarse crystalline powder. Solvents were distilled from sodium potassium alloy before use. The NMR spectra were measured in $CDCl_3$ with a Bruker WM 250 spectrometer at 250 MHz (^1H) or 62.89 MHz (^{13}C), respectively. Mass spectra were recorded on a Finnigan 4000 mass spectrometer.

1,1-Dimethylgermacyclobutane (**1a**)

A solution of 1,3-dibromopropane (3.42 g, 17 mmol) in diethyl ether (20 ml) was slowly added under nitrogen to magnesium (2.4 g, 100 mmol) in ether (150 ml). After completion of the reaction, the mixture was evaporated to dryness in vacuo and THF (40 ml) was added, and after 20 min stirring the residue was filtered off. This treatment of the residue was repeated four times. To 2.48 mmol of the magnesacyclobutane thus obtained, a solution of magnesium bromide (2.48 mmol) in diethyl ether (50 ml) was added; after stirring for 30 min, a clear solution of **2a** was formed. To this solution, dichlorodimethylgermane (0.432 g, 2.48 mmol) was rapidly added at room temperature. Stirring was continued for 1 h, then water was added; the ethereal layer was dried ($MgSO_4$), and the ether was removed by careful fractional distillation. The residue after removal of the ether was **1a** (96% yield; purity > 95% according to ^1H NMR spectroscopy and GC analysis (SE-30, room temperature). ^1H NMR, δ: 2.25 (quint., ^3J(HH) 8.2 Hz, 2H, $CH_2CH_2CH_2$), 1.46 (t, ^3J(HH) 8.2 Hz, 4H, $GeCH_2$), 0.48 ppm (s, 6H, Me). ^{13}C NMR, δ: 21.6 (tquint., ^1J(CH) 131 Hz, ^2J(CH) 4 Hz, $CH_2CH_2CH_2$), 20.3 (t, ^1J(CH) 132 Hz, $GeCH_2$), 0.07 ppm (q, ^1J(CH) 126 Hz, Me). Mass spectrum *m/z* (relative intensity), all peaks with expected isotope pattern: 146 (13) $\mathbf{1a}^{+\cdot}$, 131 (8) $[\mathbf{1a} - Me]^+$, 118 (100) $[\mathbf{1a} - C_2H_4]^{+\cdot}$ ($[Me_2Ge{=}CH_2]^{+\cdot}$ [8]), 103 (39), 89 (98).

1,1,3,3-Tetramethylgermacyclobutane (**1b**)

In an evacuated and fully sealed glass apparatus [12], dichlorodimethylgermane (11.02 mmol) was added in one portion to a solution of **2b** ([7], 11.02 mmol) in diethyl ether (1520 ml). After stirring for 2 d, water was added, and the organic layer was separated, dried ($MgSO_4$), and carefully fractionated to remove the ether. The yield in the residue was determined by weighing and subtracting the diethyl ether content as determined by ^1H NMR spectroscopy (98%) and by GLC with a pure sample of **1b** as standard (96%). Isolation of pure **1b** was achieved by preparative scale GLC (SE-30, room temperature); the isolated yield was 1.2 g (63%). Compound **1b** had b.p. 118°C, but was extremely volatile even at 40°C. ^1H NMR, δ: 1.35 (s, 4H, CH_2), 1.13 (s, 6H, C*Me*), 0.46 ppm (s, 6H, GeMe). ^{13}C NMR, δ: 36.8 (s, quaternary C), 34.2 (qquint., ^1J(CH) 128 Hz, ^3J(CH) 5 Hz, C*Me*), 34.1 (tm, ^1J(CH) 131 Hz, CH_2), 1.0 ppm (q, ^1J(CH) 127 Hz, GeMe). Mass spectrum *m/z* (relative intensity) (all the peaks had the expected isotope patterns): 174 (3) $\mathbf{1b}^{+\cdot}$, 159 (8) $[\mathbf{1b} - Me]^+$, 146 (3), 119 (74), 118 (100) $[Me_2Ge{=}CH_2]^{+\cdot}$ [8], 103 (44), 89 (87).

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