

Reductive Coupling Reactions of Dihalogenogermanes with Magnesium and Magnesium Bromide: Simple Preparation of Cyclotrigermanes and Cyclotetragermanes

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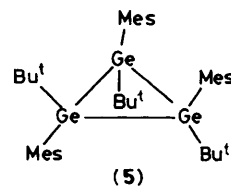
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The reactions of various dihalogenogermanes with Mg and MgBr₂ in tetrahydrofuran produce the corresponding cyclotrigermanes and cyclotetragermanes; the ring size of the products depends on the steric bulk of substituents on germanium.

Recently there has been considerable interest in the chemistry of small-ring compounds, because of their high reactivity resulting from strain energy, and some stable three-membered cyclogermanes have been synthesized.¹⁻⁴ Masamune *et al.* prepared stable cyclotrigermanes by treatment of dichlorobis-(2,6-dimethylphenyl)germane or dichlorobis-(2,6-diethylphenyl)germane with lithium naphthalenide.⁴ We report here a simple synthesis of cyclotrigermanes and cyclotetragermanes by reductive coupling of various dihalogenogermanes with Mg and MgBr₂ in tetrahydrofuran (THF).

The reactions were carried out under dry argon. Typically, to a mixture of Mg (220 mmol), MgBr₂[†] (60 mmol), and dry

THF in a small flask was added a solution of dichlorodimesitylgermane (57 mmol) [mesityl(Mes) = 2,4,6-trimethylphenyl] in THF by syringe, with stirring. The solution initially turned yellow, and then black after stirring for 2 h at room temperature. The mixture was hydrolysed with dilute hydrochloric acid, and extracted with ether. After evaporation, hexane was added to afford colourless crystals of

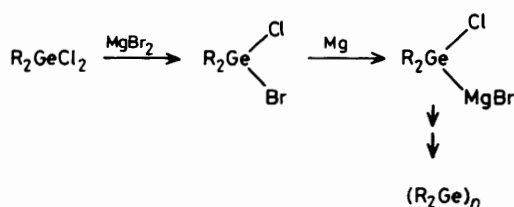


[†] Prepared *in situ* by the reaction of Mg and dibromoethane in THF; see ref. 5.

Table 1. Reductive coupling reactions of dihalogenogermanes by Mg and MgBr₂.
$$R_2GeX_2 + Mg + MgBr_2 \xrightarrow{THF} (R_2Ge)_n \quad X = Cl \text{ or } Br$$

Run	Starting material ^a	Reaction conditions	Products	Yields (%)
1	Ph ₂ GeCl ₂	Room temp.	(Ph ₂ Ge) ₄ (1) ^b	46
2	Mes ₂ GeCl ₂	Room temp.	(Mes ₂ Ge) ₃ (2)	54
3	Xy ₂ GeCl ₂	Room temp.	(Xy ₂ Ge) ₃ (3) ^c	62
4	Ar ₂ GeCl ₂	Reflux	(Ar ₂ Ge) ₃ (4) ^c	32
5	Mes(Bu ^t)GeCl ₂	Room temp.	[Mes(Bu ^t)Ge] ₃ (5)	10
6	Pr ₂ GeCl ₂	Reflux	(Pr ₂ Ge) ₄ (6) ^d	9
7	(Me ₃ SiCH ₂) ₂ GeCl ₂	Room temp.	[(Me ₃ SiCH ₂) ₂ Ge] ₄ (7) ^e	15
8	Ar ₂ GeBr ₂	Room temp.	(Ar ₂ Ge) ₃	15

^a Mes = 2,4,6-trimethylphenyl, Xy = 2,6-dimethylphenyl, Ar = 2,6-diethylphenyl. ^b Ref. 6. ^c Ref. 4. ^d M.p. 175–178°C; ¹H n.m.r. (CDCl₃) δ 1.32 (d, *J* 7 Hz, 48H) and 1.83 (sept, *J* 7 Hz, 8H); ¹³C n.m.r. (CDCl₃) δ 19.77 (d) and 23.35 (q); *m/z* 640 (*M*⁺). ^e M.p. 216–226°C; ¹H n.m.r. (CDCl₃) δ 0.10 (s, 72H) and 0.33 (s, 16H); ¹³C n.m.r. (C₆D₆) δ 2.83 (q) and 5.00 (t); *m/z* 992 (*M*⁺).



hexamesitylcyclotrimergermane (2) in 54% yield [m.p. 270–276°C; ¹H n.m.r. (CDCl₃) δ 2.02(s,36H), 2.17(s,18H), and 6.73(s,12H); ¹³C n.m.r. (CDCl₃) δ 20.78(q), 24.95(q), 128.11(d), 137.09(s), 142.43(s), and 142.96(s); *m/z* 624(*M*⁺ – Mes₂Ge)]. Various other cyclotrimergermanes and cyclotetramergermanes were synthesized similarly (Table 1). Reactions with dihalogenogermanes bearing bulky substituents afforded cyclotrimergermanes (runs 2–5, and 8), the less hindered dichlorogermanes gave cyclotetramergermanes (runs 1, 6 and 7). Only one of the two possible isomers was isolated in the reductive coupling of dichloro-(*t*-butyl)mesitylgermane (run 5), and was tentatively identified as *cis,trans* (5) [m.p. 201–203°C; ¹H n.m.r. (CDCl₃) δ 0.83 (s,9H), 1.26(s,18H), 2.23(s,6H), 2.27(s,3H), 2.47(s,6H), 2.71(s,6H), 2.76(s,6H), 6.77(s,2H), 6.83(s,2H), and 6.89(s,2H); ¹³C n.m.r. (CDCl₃) δ 20.86(q), 27.74(q), 27.90(q), 30.39(q), 32.78(q), 33.64(s), 33.91(s), 127.80(d), 127.91(d), 128.12(d), 137.01(s), 137.17(s), 138.14(s), 138.85(s), 143.40(s), 143.51(s), and 143.72(s); *m/z* 500(*M*⁺ – MesBu^tGe)].

For comparison, the reaction of dibromobis-(2,6-diethylphenyl)germane with Mg and MgBr₂ in THF was investigated. The reaction proceeded under milder conditions than that of the dichlorogermene, although the yield was low (run 8). However, the reaction of dichlorodimesitylsilane with Mg and MgBr₂ did not take place even under vigorous conditions.

The reaction probably proceeds through initial halogen exchange by MgBr₂ to produce bromochlorogermenes, which react reductively, giving cyclopolygermanes (Scheme 1).[‡] A similar mechanism has been postulated for the reaction of dichlorodiphenylsilane with Mg and MgBr₂.⁵

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[‡] During the reaction of dichlorodi-isopropylgermane with Mg and MgBr₂, bromochlorodi-isopropylgermane and dibromodi-isopropylgermane were detected by g.l.c.-mass spectrometry.