Journal of Organometallic Chemistry, 406 (1991) 119–122
Elsevier Sequoia S.A., Lausanne
JOM 21538

Reduction of 2,3-bis(bromomethyl)-1,4-dibromo-2-butene in the presence of organosilicon and organogermanium dihalides

Pierre Mazerolles and Christian Laurent

Laboratoire des Organométalliques (URA 477), Université Paul-Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex (France)

(Received October 16th, 1990)

Abstract

Reduction of a mixture of 2,3-bis(bromomethyl)-1,4-dibromo-2-butene (**1**) and dimethyldichlorosilane (or germane) with alkali metals (Li, Na, K) yields 1,2,3,4,5,6-hexahydro-2,2,5,5-tetramethyl-2,5-disila (or digerma) pentalene.

Reduction of a mixture of **1** and dimethyldichlorosilane with activated zinc or the zinc–copper couple in THF gives 3,4-bis(methylene)-1,1-dimethyl-1-silacyclopentane together with a new conjugated diene: 4,5-bis(methylene)-1,1,2,2-tetramethyl-1,2-disilacyclohexane, which is best prepared starting from 1,1,2,2-tetramethyl-1,2-dichlorodisilane. 3,4-Bis(methylene)-1,1-dimethyl-1-germacyclopentane was obtained similarly.

Introduction

2,3-Bis(bromomethyl)-1,4-dibromo-2-butene (**1**) readily obtained by reaction of bromine with 2,3-dimethyl-3-butanol [1,2] or better, in two steps from 2,3-dimethyl-1,3-butadiene [3] (1,4-addition of bromine, followed by radical bromination of the dibromide with NBS), is a good starting material for synthesis of cyclic species because of the position of the four allylic bromine atoms in the molecule. We therefore thought it of interest to examine its reduction in the presence of organosilicon or organogermanium dihalides in order to form disila (or digerma) bicyclic compounds.

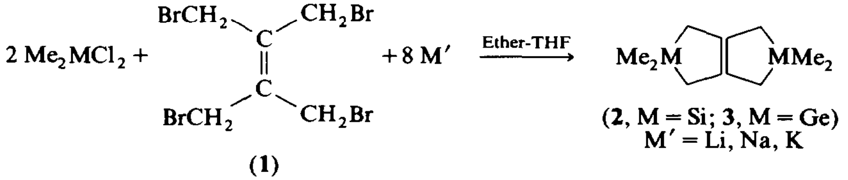
Reduction of dimethyldichlorosilane with alkali metals in the presence of 1,3-dienes leads to different compounds depending on the nature of the metal and the solvent used; cyclization occurs with lithium in ether, whereas with sodium, tetrahydrofuran must be used [4]. On the other hand, the formation of rings by reduction of 1,1,2,2-tetramethyl-1,2-dichlorodigermane in the presence of butadiene, isoprene and dimethylbutadiene, is dependent on the nature of the solvent, best results being obtained with a mixture of ether and tetrahydrofuran [5]. Similarly, the formation of 5-germaspiro[4,4]nonadienes by reduction of 1,1-dihalogermacyclopent-3-enes in the presence of dienes was found to depend on the nature of the halogen bound to

0022-328X/91/$03.50

germanium, on the reducing metal used, and on the solvent; the best results were obtained with lithium in ether–tetrahydrofuran (80 : 20) mixture or activated magnesium in THF [6,7].

Results

Reduction of a mixture of tetrabromide **1** and Me_2SiCl_2 (1 : 2 ratio) with finely cut lithium in ether–THF occurs at room temperature. The exothermic reaction gives the expected 1,2,3,4,5,6-hexahydro-2,2,5,5-tetramethyl-2,5-disilapentalene (**2**). When dimethylgermanium dichloride is used, the corresponding bicyclic digermane **3** is similarly formed:

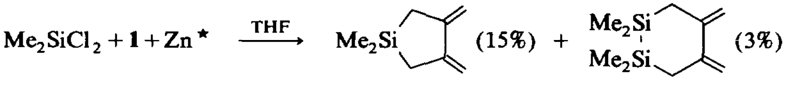


(**1**)

(**2**, M = Si; **3**, M = Ge)
M′ = Li, Na, K

With powdered sodium in tetrahydrofuran, the reaction, also exothermic, gives a dark-blue mixture containing the same bicyclic compounds but in lower yield because of the formation of a large amount of polymers; when potassium is used, the formation of polymers predominates.

Activated zinc powder and the zinc–copper couple [8] are known to reduce **1** to 2,3-bis(bromomethyl)-1,3-butadiene in ether or ether–HMPA [9]. Reduction of a mixture of dimethyldichlorosilane and **1** with activated zinc powder in tetrahydrofuran was fast and exothermic; two products were isolated by chromatography on silica (eluant pentane): 3,4-bis(methylene)-1,1-dimethyl-1-silacyclopentane (**4**) and a small amount of 4,5-bis(methylene)-1,1,2,2-tetramethyl-1,2-disilacyclohexane (**5**):

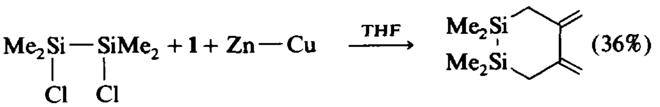


(**4**)

(**5**)

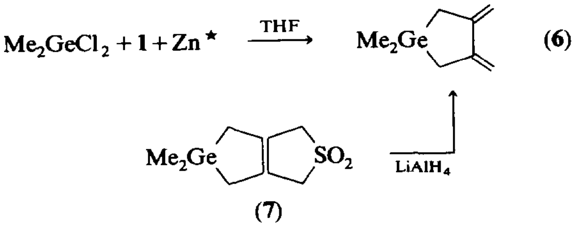
No formation of the bicyclic compound **2** was detected (VPC, NMR) in this reaction.

The compound **5** was obtained in better yield by reduction of **1** and 1,1,2,2-tetramethyl-1,2-dichlorodisilane by the zinc–copper couple in tetrahydrofuran:



(**5**)

Reduction of a mixture of dimethyldichlorogermane and **1** gave 3,4-bis(methylene)-1,1-dimethylgermacyclopentane (**6**), identical to the compound obtained by reduction of the bicyclic sulfone **7** [10]:



(**7**)

Experimental section

Reduction of a mixture of tetrabromide 1 and dimethyldichlorosilane by lithium in ether–tetrahydrofuran

A solution of **1** (4.0 g, 10 mmol) and 2.60 g (20 mmol) of dimethyldichlorosilane in 30 ml of an 80 : 20 ether–THF mixture was introduced in one portion into a 100 ml flask fitted with a reflux condenser containing 0.62 g (89 mmol) of finely cut lithium and 20 ml of the same solvent. The lithium was slowly attacked and a white precipitate of lithium halide was progressively formed. After 6 h stirring, 100 ml of pentane was added, the remaining lithium was removed by filtration through glass wool and the filtrate washed with water and dried over sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (Merck 60, 230–400 mesh, 30 g, eluant pentane) to give 0.70 g (3.6 mmol, 36% yield) of bicyclodisilane **2** as colourless crystals, m.p. 35 °C (Lit. [11] 33–35 °C). Infrared spectrum: no visible ν(C=C) absorption band in the range 1600–1650 cm^{-1}. ^{1}H NMR spectrum (80 MHz, $CDCl_3$, δ ppm): 0.15 (s, 12H, CH_3); 1.25 (s, 8H, CH_2). Lit. [11] (60 MHz, CCl_4, δ ppm): 0.16; 1.27. Anal. Found: C, 61.79; H, 10.09. $C_{10}H_{20}Si_2$ calc.: C, 61.14; H, 10.06%.

Reduction of a mixture of tetrabromide 1 and dimethyldichlorogermane by lithium in ether–tetrahydrofuran

Similar reduction of 4.0 g (10 mmol) of tetrabromide **1** and 3.48 g (20 mmol) of dimethyldichlorogermane by 0.57 g (82 mmol) of finely cut lithium in 50 ml of 80 : 20 ether–THF mixture, gave after 6 h stirring and the usual work-up 2.05 g of crude bicyclodigermane **3**. After purification by liquid chromatography, pure crystals of **3** (0.54 g, 19% yield) were isolated, m.p. 70–71 °C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ ppm): 0.304 (s, 12H, CH_3); 1.450 (s, 8H, CH_2). Anal. Found: C, 42.03; 7.16. $C_{10}H_{20}Ge_2$ calc.: C, 42.08; H, 7.06%.

Reduction of a mixture of 1 and dimethyldichlorosilane by sodium or potassium in tetrahydrofuran

Exothermic reduction of tetrabromide **1** (4.0 g, 10 mmol) and dimethyldichlorosilane (2.6 g, 20 mmol) with sodium (1.89 g, 82 mmol) or potassium (3.20 g, 82 mmol) in 50 ml of THF gave after 6 h stirring dark-blue mixtures containing the bicyclic disilane **2**. Yields, determined by VPC analysis, were 19 (Na), 7 (K)%.

Reduction of a mixture of tetrabromide 1 and dimethyldichlorosilane by activated zinc

A solution of 8.0 g (20 mmol) of tetrabromide **1** and 2.60 g (20 mmol) of dimethyldichlorosilane in 50 ml of THF was slowly added (1 h) to a stirred suspension of activated zinc (8 g) in 10 ml of THF. After 5 h stirring, 200 ml of pentane was added to the mixture which was then filtered through Celite. The filtrate was washed ten times with 200 ml portions of water, then dried and the solvent slowly distilled. The residue was chromatographed on 30 g silica gel (eluant pentane) to give 0.43 g (3.11 mmol, 15.5% yield) of pure 1,1-dimethyl-3,4-bis(methylene)-1-silacyclopentane, b.p. 47 °C/12 mmHg. ^{1}H NMR spectrum (60 MHz, CCl_4, δ ppm): 0.17 (s, 6H, CH_3); 1.53 (s, 4H, CH_2Si); 4.58 and 5.06 (m, 4H, $C{=}CH_2$). (Lit. [12]: 250 MHz, $CDCl_3$, δ ppm: 0.14, 1.61; 4.73; 5.21.) The second compound, isolated in small yield (0.12 g, 3.0%), was identified as 1,1,2,2-tetramethyl-4,5-bis(methylene)-1,2-disilacyclohexane (see below).

Reduction of a mixture of tetrabromide 1 and 1,1,2,2-tetramethyl-1,2-dichlorodisilane by zinc–copper couple in tetrahydrofuran

Similar reduction of 10.0 g (25 mmol) of tetrabromide **1** and 4.69 g (25 mmol) of tetramethyldichlorodisilane with an excess (10 g) of zinc–copper couple in 60 ml of THF gave, after the usual work-up, 1.78 g (9.05 mmol) of bis(methylene)disilacyclohexane **6** (36% yield), b.p. 91–92 °C/25 mmHg; $n_D^{20} = 1.5010$; ^{1}H NMR spectrum (80 MHz, $CDCl_3$, δ ppm): 0.09 (s, 12H, CH_3); 1.74 (d, 4H, CH_2Si); 4.55 and 4.85 (m, 4H, $C{=}CH_2$). Anal. Found: C, 61.05; H, 10.62. $C_{10}H_{20}Si_2$ calc.: C, 61.14; H, 10.26%.

Attempted reduction of a mixture of tetrabromide 1 and dimethyldichlorosilane by activated zinc in benzene

No apparent reduction was observed when a mixture of 4.0 g of tetrabromide **1**, 2.6 g of dimethyldichlorosilane and 8 g of activated zinc in 60 ml of benzene was boiled. The presence of the expected bis(methylene)silacyclopentane **4** was not detected after 3 h reflux.

Reduction of a mixture of tetrabromide 1 and dimethyldichlorogermane by activated zinc in tetrahydrofuran

Reduction of a mixture of tetrabromide **1** (4.0 g, 10 mmol) and dimethyldichlorogermane (3.48 g, 20 mmol) with a large excess of activated zinc (8 g) gave bis(methylene)dimethylgermacyclopentane (**6**) [12] in 9% yield, identical (VPC, NMR) to the compound obtained by reduction of the bicyclic sulfone **7** [10].

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