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5-GERMASPIRO[4.4]NONA-2,7-DIENES

PIERRE MAZEROLLES and FABIENNE GREGOIRE

Laboratoire des Organométalliques, U.A. 477, Université Paul-Sabatier 118, route de Narbonne, 31062 Toulouse cedex (France)

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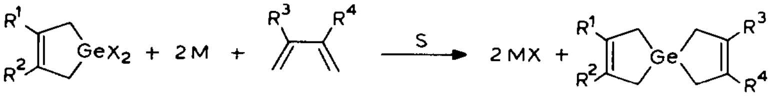
Summary

A novel series of bicyclic organogermanium derivatives: 5-germaspiro[4.4]nona-2,7-dienes have been prepared by reaction of 1,1-dihalogermacyclopent-3-enes with the appropriate conjugated diene and an alkali metal in a suitable organic solvent. The best results were obtained by using 1,1-dichlorogermacyclopentenes with isoprene or 2,3-dimethylbutadiene and lithium in 5/1 ether/tetrahydrofuran. Except for 2,3,7,8-tetramethyl-5-germaspiro[4.4]nona-2,7-diene, which is crystalline, the 5-germaspirononadienes are colourless liquids, which distil without decomposition under reduced pressure but which slowly polymerize on standing. In the mass spectra of all the spiradienes, the main peak corresponds to the loss of one ring, the less substituted in the case of unsymmetrical molecules. Attempts to obtain 5-germaspiro[4.4]nona-2,7-diene were unsuccessful.

Introduction

Three symmetrical silaspirononadienes, 5-silaspiro[4.4]nona-2,7-diene [1–3,5], 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene [2,4] and 2,3,7,8-tetramethyl-5-silaspiro-[4.4]nona-2,7-diene [6] have been described previously. Such compounds are commonly obtained by reaction of tetrachlorosilane [1,3] or a dialkoxydichlorosilane [2,4] with magnesium and a suitable conjugated diene in tetrahydrofuran [1,2,4] or toluene [3], but 5-silaspiro[4.4]nona-2,7-diene has also been made by the reaction, of 1-sila-3-cyclopentene-1-ylidene with butadiene and by co-condensation of the latter diene with silicon vapour [5]. 2,3,7,8-Tetramethyl-5-silaspiro[4.4]nona-2,7-diene has been obtained by trapping with 2,3-dimethylbutadiene of the silylene produced by thermolysis of 1-methoxy-1-trimethylsilyl-1-sila-3,4-dimethyl-3-cyclopentene [6].

In germanium series, the first germaspironona-2,7-diene, 2,7-dimethyl-5-germaspiro[4.4]nona-2,7-diene, was made by reaction of 1,1-dichloro-3-methyl-1-germa-3-cyclopentene with an alkali metal and isoprene [7], and we have extented this method to the other members of the series, symmetrical and unsymmetrical, by varying the nature of the alkali metal, the halogen atoms bounded to germanium, and the solvent in order to find the best conditions for cyclization.

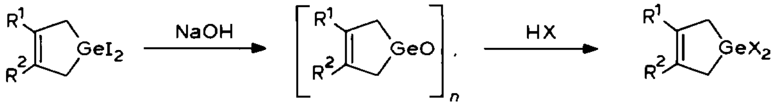


(1)

(X = F, Cl, Br, I; M = Na, Li; R^n = H, CH_3; S = Et_2O, THF or Et_2O/THF mixture)

Results and discussion

Starting compounds. 1,1-Dihalogeno-1-germacyclopent-3-enes are easily obtained in excellent yield by reaction of germanium diiodide with a suitable conjugated diene in the absence of solvent ($R^1 = H$, $R^2 = CH_3$; $R^1 = R^2 = CH_3$) or in pentane solution in a sealed tube ($R^1 = R^2 = H$) [8]. Thus 1,1-dichloro and 1,1-dibromo derivatives ($X = Cl$, Br), previously made by reaction of the corresponding diiodo with a silver halide in boiling heptane [8] or that of trichlorogermane with dienes ($X = Cl$) [9,10], have now been prepared more easily by hydrolysis of the diiodide followed by treatment of the oxide obtained with an excess of concentrated aqueous solution of the hydrogen halide at room temperature. This method can also be used for the synthesis of 1,1-difluorogermacyclopentenes (eq. 2).



(2)

(Ib; IIa-IIc; IIIa, IIIb)

(Ib: $R^1 = R^2 = H$; $X = Cl$, 63%;

IIa: $R^1 = H$; $R^2 = CH_3$; $X = F$, 52%;

IIb: $R^1 = H$; $R^2 = CH_3$; $X = Cl$ 87%;

IIc: $R^1 = H$; $R^2 = CH_3$; $X = Br$ 70%;

IIIa: $R^1 = R^2 = CH_3$; $X = F$ 51%;

IIIb: $R^1 = R^2 = CH_3$; $X = Cl$ 74% yields, with respect to GeI_2)

Cyclization reaction. Since 1,4-disilylation of isoprene mainly gives the *cis*-isomer when used with sodium in tetrahydrofuran [11], we expected that under similar conditions the ring closure shown in eq. 1 would occur.

1,1-Diiodo-3-methylgermacyclopentene (IIb) was found to react exothermically with a mixture of isoprene and finely-divided sodium in tetrahydrofuran; the metal rapidly disappears but only polymers are obtained. With the corresponding 1,1-dichloro compound (IIb) the reaction goes more slowly; the reaction again gives mainly polymers, but traces of the expected 5-germaspirononadiene were detected. When lithium was used in ether the dichloride (IIb) was found to react slowly: a white precipitate of lithium chloride was formed progressively and the germaspiradiene was isolated in less than 5% yield. When tetrahydrofuran was used in place of the ether, the reaction was rapid and exothermic but the yield of germaspiradiene was still low.

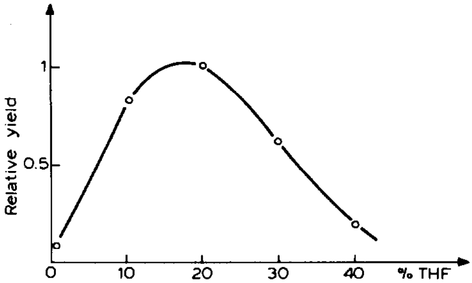
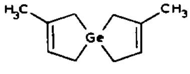
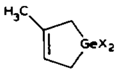


Fig. 1. Variation of the relative yield of 2,7-dimethyl-5-germaspiro[4.4]nona-2,7-diene with the proportion of THF in the Et_2O/THF solvent.

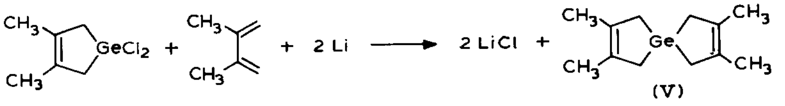
In order to determine the influence of the nature of the solvent on the yield of reaction 1 a series of experiments was carried out with constant amounts of dichloride (IIb), lithium and isoprene, but with an increasing proportion of tetrahydrofuran in the tetrahydrofuran/ether solvent. The results (Fig. 1) show that the yield of 5-germaspiradiene depends, markedly on the nature of the solvent, the best yield being obtained with a 5/1 ether/THF ratio.

To study the effect of the substituents on germanium, experiments were carried out with various groups X, for solutions of isoprene and lithium in 5/1 ether/tetrahydrofuran:

Starting compound	 yield %	
	X = F	~6%
	X = Cl	26%
	X = Br	19%
	X = I	traces
	X = OCH_3	~5%
$GeCl_4$		traces
$Cl_2Ge(OC_2H_5)_2$		~4%

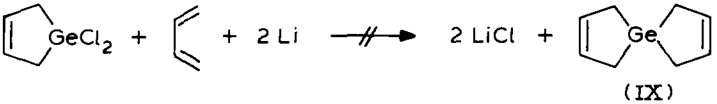
The yields are low (20–25%) for X = Cl and Br, and even lower for other substituents, especially for X = I and $GeCl_4$.

The influence of the nature of the diene was also investigated (with Li, X = Cl and the same solvent). With dimethylbutadiene the solid 2,3,7,8-tetramethyl-5-germaspiro[4.4]nona-2,7-diene (m.p. 92°C) was obtained in 33.2% yield (eq. 3):



(3)

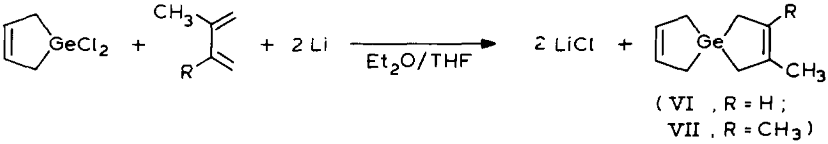
On the other hand, with butadiene, the expected unsubstituted germaspiradiene was not obtained; the lithium was attacked but only an undistillable polymer was formed. Similar results were obtained for X = I (eq. 4).



(4)

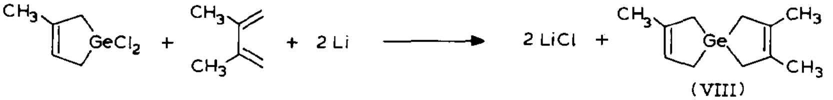
The syntheses of unsymmetrical spiranes were based on the results described above.

Thus spiranes containing one unsubstituted ring were made by the reaction of 1,1-dichloro-1-germacyclopent-3-ene with isoprene or 2,3-dimethylbutadiene and lithium (eq. 5).



(5)

The trisubstituted germaspirane was obtained from the reaction of 3-methyl-1,1-dichloro-1-germacyclopent-3-ene with 2,3-dimethylbutadiene (eq. 6).



(6)

Except for the tetramethyl-substituted compound the germaspiradienes are colourless liquids, which distil without decomposition under reduced pressure but which slowly polymerize on standing.

Their mass spectra (Fig. 2) are characteristic. The main peak corresponds to the fragment resulting from the loss of one ring of the molecule, which is the less-substituted in the case of unsymmetrical germaspiradienes.

Experimental

NMR spectra were recorded on Varian EM 360A and Bruker 250 spectrometers, mass spectra on coupled Pye Unicam-AEI MS20 spectrometer, and IR spectra on Perkin–Elmer 457 spectrophotometer.

Starting materials

1,1-Diiodo-3,4-dimethyl-1-germacyclopent-3-ene (IIId) was obtained in almost quantitative yield by shaking a mixture of germanium diiodide with a slight excess of 2,3-dimethylbutadiene (exothermic reaction). The 1,1-diiodo-3-methyl-1-germacyclopent-3-ene (IId) was made similarly but with gentle heating. 1,1-Diiodo-1-germacyclopent-3-ene (Id) was obtained in 94.4% yield by keeping a mixture of germanium diiodide (53 g), butadiene (30 ml) and pentane (80 ml) for two days at 100°C, with occasional shaking, in a 250 ml stainless steel autoclave.

1,1-Dichloro-1-germacyclopent-3-ene (Ib)

The diiodide Id (116.6 g) was treated with a solution of 60 g of sodium hydroxide in 300 ml of water. Neutralisation with dilute hydrochloric acid precipitated the corresponding oxide which was washed with ether. The solvent was removed from the residue, which was then shaken with a large excess of a concentrated hydrochlo-

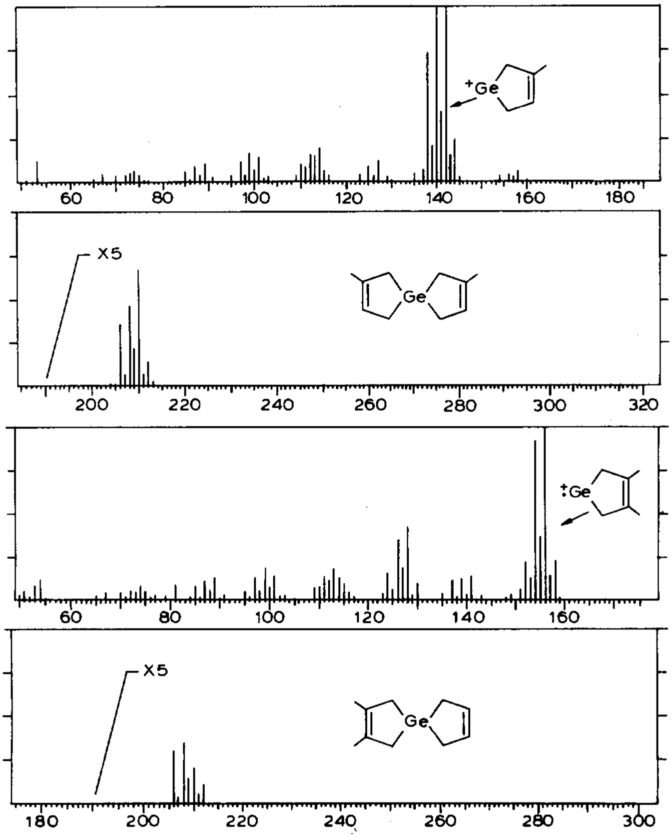


Fig. 2. Mass spectra of 2,7-dimethyl-5-germaspiro[4.4]nona-2,7-diene (a) and 2,3-dimethyl-5-germaspiro[4.4]nona-2,7-diene (b).

ric acid. The dichloride formed was extracted with pentane and the solution was dried over calcium chloride and distilled, to give 40.57 g of Ib (67% yield with respect to diiodide Id). Boiling point 67°C/20 mmHg; n_D^{20} 1.5208; (lit. [9] 66–67°C/17 mmHg; [14] 72–72.5°C/25 mmHg; n_D^{20} 1.5220).

1,1-Dichloro-3-methylgermacyclopent-3-ene (IIb)

This was made similarly from 65.32 g of germanium diiodide; 38.58 g of dichloride IIb were obtained (87.2% yield). Boiling point 81–83°C/15 mmHg (lit. [8] 98°C/34 mmHg; n_D^{20} 1.5128).

1,1-Dichloro-3,4-dimethylgermacyclopent-3-ene (IIIb)

From 32.66 g of germanium diiodide were obtained 16.70 g of the dichloride IIIb (74% yield). Boiling point 90°C/12 mmHg. (Lit. [8] 120°C/26 mmHg; n_D^{20} 1.5178).

1,1-Dibromo-3-methyl-1-germacyclopent-3-ene (IIc)

From 16.33 g of germanium diiodide were obtained 10.42 g of the dibromide IIc (70% yield). Boiling point 105–106°C/13 mmHg. (Lit. [8] 125°C/25 mmHg; n_D^{20} 1.5825).

1,1-Difluoro-3-methyl-1-germacyclopent-3-ene (IIa)

The oxide produced by hydrolysis of the diiodide IId (obtained by reaction of 32.66 g (0.1 mol) of germanium diiodide with 8.2 g (0.12 mol) of isoprene) was shaken in a plastic flask with 50 g of 40% hydrofluoric acid at 40°C (water bath). The fluoride was extracted with pentane and the solution dried over sodium sulfate. Distillation gave 9.31 g of the difluoride (52% yield). Boiling point 83–85°C/15 mmHg; n_D^{20} 1.4516; infrared spectrum (ν, cm^{-1}): 1625 (C=C); NMR (60 MHz, CCl_4, δ, ppm) 5.8 (CH=C); 1.9 (CH_2–C=); 1.75 (CH_3–C=); Anal. Found: C, 33.74; H, 4.76; F, 21.01, $C_5H_8GeF_2$; calcd.: C, 33.60; H, 4.51; F, 21.26%.

1,1-Difluoro-3,4-dimethyl-1-germacyclopent-3-ene (IIIa)

Similarly from 65 g (0.2 mol) of germanium diiodide was obtained 19.56 g of IIIa (51% yield). Boiling point 74°C/14 mmHg; n_D^{20} 1.4591; NMR (60 MHz, CCl_4, δ, ppm) 1.85 (CH_3C=, CH_2C=). Anal. Found: C, 37.34; H, 5.16; F, 19.60. $C_6H_{10}GeF_2$ calcd.: C, 37.39; H, 5.23; F, 19.71%.

Reaction of 1,1-dichloro-3-methylgermacyclopent-3-ene with lithium in ether/tetrahydrofuran solution

Reactions of IIb (2.11 g, 0.01 mol) with lithium (0.14 g, 0.02 g atom) and an excess of isoprene (0.8 g) were carried out in 30 ml of a Et_2O/THF mixture, with these solvents present in 10/0, 9/1, 8/2, 7/3, and 6/4 ratio. In each case, the mixture was stirred overnight, unreacted lithium was filtered off, and water was added. The organic layer was dried over calcium chloride and concentrated to 20 ml. The relative proportions of 5-germaspiradiene in the various experiments were compared by GLC (SE 30 20%, 10 ft, 180°C) and the results are plotted in Fig. 1.

2,7-Dimethyl-5-germaspiro[4.4]nona-2,7-diene (IV)

A mixture of dichloride IIb (12.70 g, 0.06 mol) and isoprene (4.5 g, 0.066 mol) was added in one portion to a stirred suspension of finely cut lithium (1 g, 0.14 g atom) in ether (75 ml)/THF (15 ml) under argon. An exothermic reaction occurred, and external cooling was needed. The lithium, which takes on a gold-yellow colour, is attacked rapidly, and a white precipitate of lithium chloride is progressively formed. At the end of the reaction (5 to 6 h) the mixture is treated with water and the organic layer dried over calcium chloride and distilled. Germaspiradiene (IV, 3.26 g) is obtained (26% yield). Boiling point 106–107°C/13 mmHg; n_D^{20} 1.5316. Infrared spectrum (ν, cm^{-1}): 1635, s, (C=C). NMR spectrum (250 MHz, $CDCl_3$, δ, ppm) Enlarged singlets: 5.63 (2 H, =CH); 1.80 (6 H, CH_3); 1.71 (4 H, $GeCH_2CH$=); 1.61 (4 H, $GeCH_2C(CH_3)$=). Mass spectrum (Fig. 2a) m/e (rel. intensity). Characteristic Ge fragments for ^{74}Ge: 210 (M^+, 13.3); 142 ($M - C_5H_8$, 100). Anal. Found: C, 57.65; H, 7.97. $C_{10}H_{16}Ge$ calcd.: C, 57.52; H, 7.72%.

Synthesis of IV from IIa, IIc, IId, 1,1-dimethoxy-1-germacyclopent-3-ene, germanium tetrachloride or dichlorodiethoxygermane under similar conditions gave the following respective yields: 6, 19, traces, 5, traces, 4%.

2,3,7,8-Tetramethyl-5-germaspiro[4.4]-nona-2,7-diene (V)

Similarly reaction of a mixture of dichloride IIIb (13.47 g, 0.06 mol) and 2,3-dimethylbutadiene (6.0 g, 0.073 mol) gave 4.72 g of germaspirodiene V (33.2% yield). Melting point 92°C. Infrared spectrum (ν, cm^{-1}) 1642w, ($>C{=}C<$). NMR spectrum (250 MHz, $CDCl_3$, δ ppm) Enlarged singlets: 1.73 (12 H, CH_3); 1.70 (8 H, CH_2). Anal. Found: C, 60.76; H, 8.60. $C_{12}H_{20}Ge$ calcd.: C, 60.84; H, 8.51%.

2-Methyl-5-germaspiro[4.4]nona-2,7-diene (VI)

Use of a mixture of dichloride Ib (11.85 g, 0.06 mol) and isoprene (6.0 g, 0.088 mol) gave 0.93 g of germaspirodiene VI (7.95% yield). Boiling point 97°C/14 mmHg; n_D^{20} 1.5340. Infrared spectrum (ν, cm^{-1}) 1611s, (CH=CH); 1631w, (CH_3-C=C-CH_3). NMR spectrum: (250 MHz, $CDCl_3$, δ, ppm) Enlarged singlets: 6.00 (2 H, CH=CH); 5.64 (1 H, CH=C-CH_3); 1.80 (3 H, CH_3); 1.71 (2 H, CH_2CH=C-CH_3); 1.67 (4 H, CH_2CH=CH); 1.61 (2 H, $\mathit{CH}_2\overset{\|}{C}CH_3$). Anal. Found: C, 55.52; H, 7.24 $C_9H_{14}Ge$ calcd.: C, 55.94; H, 7.25%.

2,3-Dimethyl-5-germaspiro[4.4]nona-2,7-diene (VII)

Use of a mixture of dichloride Ib (11.85 g, 0.06 mol) and 2,3-dimethylbutadiene (6.0 g, 0.073 mol) gave 3.26 g of germaspirodiene VII (26% yield). Boiling point 112°C/15 mmHg; n_D^{20} 1.5350. Infrared spectrum (ν, cm^{-1}) 1610 s, (CH=CH); 1645w, (CH_3C=C-CH_3). NMR spectrum (250 MHz, $CDCl_3$, δ ppm), Enlarged singlets: 5.99 (2 H, =CH); 1.74 (10 H, CH_3, $\mathit{CH}_2\overset{\|}{C}CH_3$); 1.64 (4 H, CH_2CH=). Mass spectrum (Fig. 2b m/e (rel. intensity). Characteristic Ge fragments for ^{74}Ge: 210 (M^+, 4.0); 156 ($M-C_4H_6$, 100); 128 ($M-C_6H_{10}$, 42). Anal. Found: C, 56,52; H, 7.70. $C_{10}H_{16}Ge$ calcd.: C, 57.52; H, 7.72%.

2,3,7-Trimethyl-5-germaspiro[4.4]nona-2,7-diene (VIII)

Use of a mixture of dichloride IIb (12.94 g, 0.061 mol) and 2,3-dimethylbutadiene (6.0 g, 0.073 mol) gave 3.18 g of germaspirodiene VIII (23.8% yield). Boiling point 125°C/15 mmHg; n_D^{20} 1.5315. Infrared spectrum (ν, cm^{-1}) 1637m, (CH=CCH_3); 1645, w, sh, (CH_3C=C-CH_3). NMR spectrum (250 MHz, $CDCl_3$, δ, ppm): 5.61 (1 H, =CH); 1.79 (3 H, CH_3C=CH); 1.72 (10 H, $CH_2C(CH_3)CH_2$); 1.67 (2 H, CH_2CH=C(CH_3)); 1.57 (2 H, $\mathit{CH}_2C(CH_3)$=). Mass spectrum m/e (rel. intensity). Characteristic Ge fragments for ^{74}Ge: 224 (M^+, 11.8); 156 ($M-C_5H_8$, 100); 142 ($M-C_6H_{10}$, 55). Anal. Found: C, 60.37; H, 8.54. $C_{11}H_{18}Ge$ calcd.: C, 59.28; H, 8.14%.

5-Germaspiro[4.4]nonadiene (attempts) (IX)

The dichloride Ib (11.85 g, 0.06 mol) was brought into reaction with lithium (1.0 g, 0.14 g atom) in the presence of a large excess of butadiene at room temperature in 5/1 ether/THF. The alkali metal disappeared but, after usual treatment, the expected unsubstituted germaspirodiene was not isolated, only polymers being obtained.

Similarly, addition of an equimolecular mixture of *cis*-1,4-dibromo-2-butene and diiodide Id (or a half-molar amount of germanium tetrachloride) to a suspension of magnesium in tetrahydrofuran gave only polymers.

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