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Synthesis and reactivity of 3-thia-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene and its selenium analog

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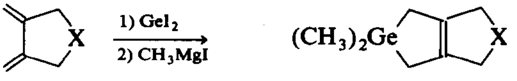
Abstract

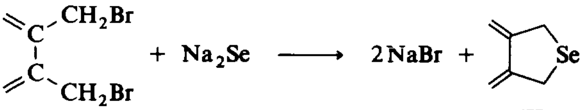
3-Thia-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene and its selenium analog, prepared by cycloaddition of a germylene to 3,4-bis(methylene)thiolane and selenolane, respectively, react with 2,3-dichloro-5,6-dicyanoquinone to give the corresponding substituted thiophene and selenophene Oxidation of the sulfur compound with metachloroperbenzoic acid leads to the germabicyclic sulfone, a precursor of 3,4-bis(methylene)germacyclopentane.

It was recently shown [1] that cycloaddition of germanium diiodide to 3,4-Bis(methylene)oxolane [2,3], thiolane [3] and phenylazolidine [3–6] leads to a new series of functional bicyclic organogermanium derivatives:



(X = O (Ia), S (Ib), N–Ph (Ic))

This reaction was extended to the synthesis of the selenium analog (X = Se). 3,4-bis(methylene)selenolane was obtained by reaction, at room temperature, of 2,3-bis(bromomethyl)-1,3-butadiene with sodium selenide in absolute alcohol under argon:



(II)

This reaction must be carried out in a gas-tight apparatus fitted with efficient traps in order to prevent escape of any of the *very toxic* hydrogen selenide *. This bis(methylene)selenolane, isolated by extraction with pentane and removal of al-

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* Hydrogen selenide is about one hundred times more toxic than hydrogen cyanide [7].

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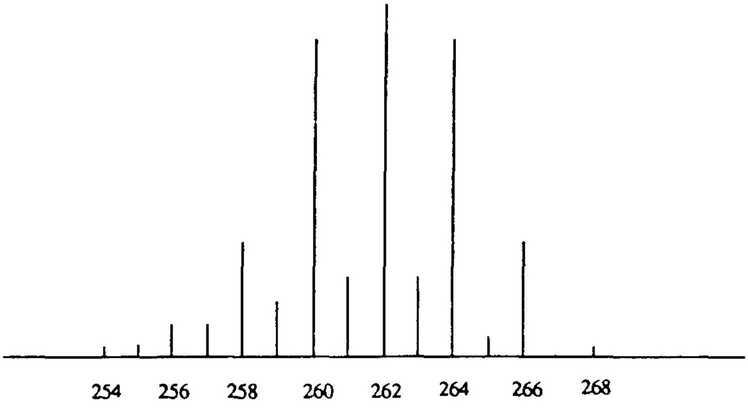
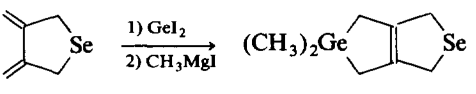


Fig. 1. Molecular ion of bicyclic compound Id.

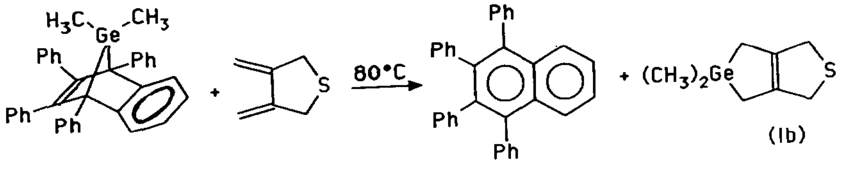
cohol by several washings, was used without further purification, after drying of the solution and distillation of the solvent:



(Id)

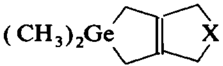
Pure Id was obtained in 60% yield by chromatography on silica. It is a thermally stable liquid having an unpleasant odor. Its mass spectrum is characterized, as that of the sulfur analog, by a large molecular ion pattern (rel. intensity 76.1%) consisting of 14 peaks resulting from the combination of the five germanium (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge) six selenium (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se) and carbon and hydrogen isotopes (Fig. 1).

The sulfur compound, usually obtained by cycloaddition of germanium diiodide to 3,4-bis(methylene)thiolane followed by alkylation, was also isolated by heating 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene [8,9] with the same diene in boiling benzene:



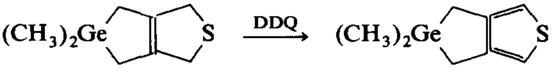
(Ib)

Dehydrogenation of bicyclic compounds



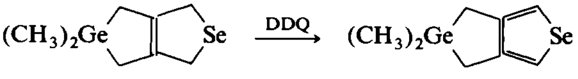
(X = S, Se)

The sulfur compound Ib reacts with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in dioxane at room temperature. This exothermic reaction gives the corresponding thiophene in almost quantitative yield within a few minutes:



(III)

The selenium compound (Id) also reacts, but with a stoichiometric amount of DDQ, the expected selenophene is only obtained in low yield:



(IV)

Oxidation of the sulfur compound (Ib)

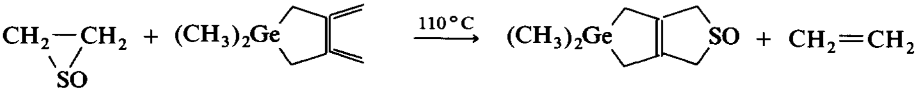
Thiagermabicyclooctene (Ib) reacts easily with metachloroperbenzoïc acid (MCPBA); the nature of compounds formed depends on the experimental conditions (Fig. 2):

(i) With the reagents in equimolecular amounts in ether at 0 °C, the expected sulfoxide is formed together with some sulfone, while some starting sulfur derivative Ib remains unchanged; oxidation with the same peracid in methylene dichloride at −30 °C gives V in 88% yield.

(ii) In contrast with two-mole equivalents of MCPBA at room temperature, bicyclic sulfone VI is obtained in 70% yield as large needles melting at 70 °C.

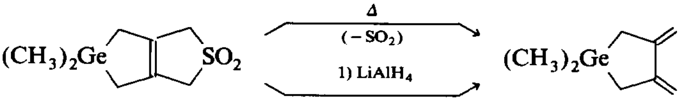
(iii) With an excess of peracid, the tricyclic compound VII is obtained.

Sulfoxide V, a viscous colourless liquid, was also formed in 13% yield by cycloaddition of sulfur monoxide [10–12] to 1,1-dimethyl-3,4-bis(methylene)germacyclopentane in boiling toluene:

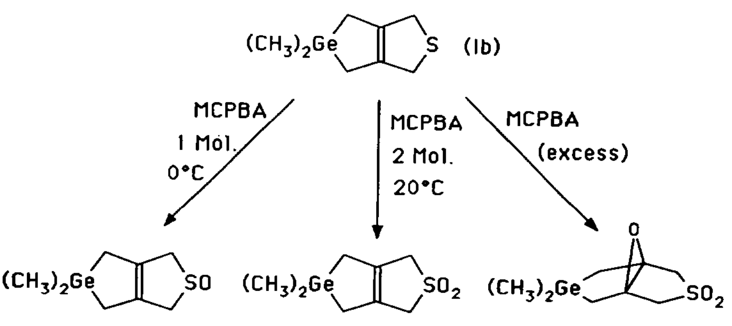


Oxidation of V with an equimolecular amount of MCPBA in ether at room temperature gives the expected sulfone (VI) in good yield.

Sulfone (VI), which is stable at room temperature, decomposes above 200 °C with evolution of sulfur dioxide and formation of 3,4-bis(methylene)germacyclopentane VIII, but some polymerization occurs at this temperature and VIII is prepared in better yield by reduction of VI with lithium aluminium hydride in ether:



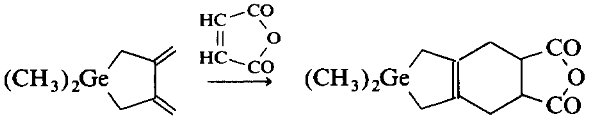
(VI) (VIII)



(V) (VI) (VII)

Fig. 2. Oxidation of thiagermabicyclooctene (Ib) with MCPBA.

Compound VIII, which is also formed though in low yield, by refluxing Ib with an excess of lithium aluminium hydride, readily undergoes typical cycloaddition reactions:



(VIII) (IX)

Experimental

3-Thia-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene (Ib)

(a) From germanium diiodide. To a stirred solution of 15.5 g (46.4 mmol) of 2,3-bis(iodomethyl)-1,3-butadiene in 400 ml refluxing ethanol was added a solution of 22.3 g (92.8 mmol) of sodium sulfide nonahydrate in 15 ml of water containing a small amount of hydroquinone. After 3 h reflux, 1.5 l of water was added; the organic layer was extracted with four portions of 70 : 30 ether–pentane then washed ten times with 100 ml portions of water. The extract was dried over calcium chloride, the solvent removed, and the residue chromatographed on 30 g of SiO_2 (eluent pentane), 2.70 g (24 mmol) or pure 3,4-bis(methylene)thiolane were isolated (52% yield). Germanium diiodide (7.84 g, 24.0 mmol) was added to a solution of this thiolane in 100 ml of benzene and the mixture refluxed for one hour to give in almost quantitative yield 3-thia-7,7-diiodo-7-germabicyclo[3.3.0]oct-1(5)-ene. NMR spectrum 80 MHz (δ ppm, C_6H_6–$CDCl_3$, TMS): 2.49 (s, 4H, CH_2Ge); 3.30 (s, 4H, CH_2S). After alkylation with an excess of methylmagnesium iodide and the usual work-up, 2.84 g (13.2 mmol, 55% yield) of 3-thia-7,7-dimethyl-7-germabicyclo[3.3.0] oct-1(5)-ene (Ib) were isolated, identical to the compound prepared from 2,3-bis(bromomethyl)-1,3-butadiene [1].

(b) From dimethylgermylene. A mixture of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene (1.00 g, 1.9 mmol), 3,4-bis(methylene)thiolane (0.38 g, 3.4 mmol) and 2 ml of benzene was heated. The liquid became turbid and a precipitate was formed. Heating was continued for 2 h and the precipitate then filtered off and washed with pentane. After removal of the solvent, the residue was chromatographed on 30 g of SiO_2 (eluant pentane) to give 0.080 g, (0.30 mmol) (16% yield) of pure Ib.

3,4-Bis(methylene)selenolane (II)

In a 300 ml Erlenmeyer fitted with a dropping funnel and a condenser connected to two traps cooled with liquid nitrogen and a bubbler containing iron sulfate solution, were placed 6.1 g (48.8 mmol) or anhydrous sodium selenide (Strem Chemicals) and 80 ml of absolute ethanol under argon. A solution of 7.05 g (29.4 mmol) of 2,3-bis(bromomethyl)-1,3-butadiene in 150 ml absolute ethanol was added dropwise during 1 h to the magnetically stirred mixture. After further stirring for 2 h, the red solution was extracted with pentane (five times 80 ml) and the organic layer washed with water (200 ml, then ten portions of 100 ml) in order to remove alcohol. After drying over sodium sulfate and elimination of the solvent under reduced pressure, 3.90 g of crude II (24.5 mmol, 83.4% yield) was obtained and was used without further purification.

3-Selena-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene (Id)

Reaction of II (3.90 g, 24.5 mmol) with 8.0 g (24.5 mmol) of germanium diiodide in 125 ml of boiling benzene was complete within 1 h. The resulting yellow solution was treated with an excess (0.1 mol) of methylmagnesium iodide. After 2 h refluxing the mixture was hydrolyzed and, after the usual treatment, the reddish residue distilled mainly at 108°C/2 mmHg (1.96 g, 7.49 mmol, 30.6% yield). The pure product was obtained by chromatography on silica (Merck 230–400 Mesh, 40 g, eluant pentane). NMR spectrum (300 MHz, δ ppm, $CDCl_3$): 0.37 (s, 6H, CH_3Ge); 1.40 (t, 4H, CH_2Ge); 3.59 (t, 4H, CH_2Se). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{72}Ge ^{80}Se, rel. intensity): 262, 76.1 (M^+), 247, 100.0 $(M - CH_3)^+$, 167, 69.8 $(CH_3GeSe)^+$, 99, 55.9 $(GeCH_3)^+$. Other peak 79, 65.6 $(C_6H_7)^+$.

3-Thia-7,7-dimethyl-7-Germabicyclo[3.3.0]octa-1,4-diene (III)

A solution of thiagermabicyclooctene Ib (1.43 g, 6.65 mmol) in 2 ml of dioxane was added dropwise with stirring to 1.51 g (6.65 mmol) of dichlorodicyanoquinone in 10 ml of the same solvent. The exothermic reaction gave a dark mixture which lost its colour and gave a pink precipitate. After 1 h reflux, pentane (100 ml) was added, the solution filtered, and the filtrate washed five times with water (100 ml each). After drying of the solution over sodium sulfate and removal of the solvent, the residue was distilled under reduced pressure to give 1.03 g (4.84 mmol) of pure III (73% yield) b.p. 47°C/0.2 mmHg; $n_D^{20} = 1.5683$. NMR spectrum (300 MHz, δ ppm, $CDCl_3$): 0.43 (s, 6H, $GeCH_3$); 1.99 (s, 4H, CH_2Ge); 6.85 (s, 2H, =CHS). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{74}Ge, rel. intensity): 214, 38.6 (M^+); 199, 50.3 $(M - CH_3)^+$; 89, 29.4 $(GeCH_3)^+$. Other peaks at 110, 33.7; 91, 89.5 $(C_7H_7)^+$; 77, 100 $(C_6H_5)^+$. Anal. Found: C, 45.01; H, 5.69. $C_8H_{12}GeS$. calc.: C, 45.15; H, 5.68%.

3-Selena-7,7-dimethyl-7-germabicyclo[3.3.0]octa-1,4-diene (IV)

When a solution 1.05 g (4.01 mmol) of II in 1 ml of dioxane was added dropwise to 1.0 g (4.41 mmol) of DDQ in 3 ml of the same solvent, a black colour developed and then disappeared as a beige precipitate separated. After 1 h stirring, the precipitate was filtered off and washed with pentane, and the filtrate was washed with water until the dioxane had been completely removed. The solution was dried over sodium sulfate and the solvent removed. The residue, which contained a large amount of unchanged Id, was chromatographed on 30 g silica. Only a small amount of pure IV was isolated. NMR spectrum (300 MHz, δ ppm, $CDCl_3$): 0.43 (s, 6H, $GeCH_3$), 1.97 (d, 4H, CH_2Ge), $J = 0.9$ Hz; 7.49 (t, 2H, CHSe). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{72}Ge ^{80}Se, rel. intensity): 260, 60.0 (M^+), 245, 68.4 $(M - CH_3)^+$, 167, 15.7 $(CH_3GeSe)^+$, 89, 25.3 $(CH_3Ge)^+$. Other peaks at 91, 82.0 $(C_7H_7)^+$ and 77, 100.0 $(C_6H_5)^+$.

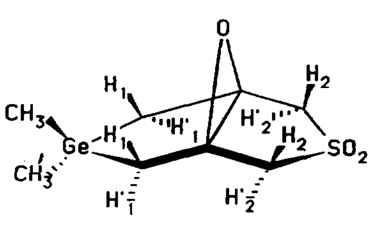
Oxidation of Ib with m*-chloroperbenzoic acid*

(a) With an equimolecular amount of MCPBA. (i) In diethyl ether at 0°C. Dropwise addition of a solution of 2.13 g (10.5 mmol) of 85% MCPBA in 30 ml of ether to 2.25 g (10.5 mmol) of sulfide Ib in the same solvent at 0°C gave a mixture containing mainly the expected sulfoxide V together with some sulfone VI and unchanged sulfide (Ib).

(ii) In methylene dichloride at low temperature. To a stirred solution of 1.09 g (5.1 mmol) of sulfide Ib in 40 ml of methylene dichloride at −30 °C, a solution of 1.03 g (5.1 mmol) of 85% MCPBA in 50 ml of the same solvent was added dropwise during 10 min. After 30 min additional stirring, dry NH_3 was introduced directly onto the surface of the mixture for several min. The excess of NH_3 was then removed by bubbling nitrogen in the solution, the solution was filtered, and the solvent evaporated under reduced pressure to give 1.25 g of crude V as a colourless viscous liquid. The pure product was obtained by chromatography on silica (eluent THF–pentane 70:30), which gave 1.04 g (88.2% yield), $n_D^{20} = 1.5515$. Infrared spectrum: strong absorption band at 1024 cm^{-1} for S–O bond (neat). NMR spectrum (80 MHz, δ ppm, $CDCl_3$): 0.27 (s, 3H, CH_3Ge); 0.30 (s, 3H, CH_3Ge); 1.37 (m, 4H, CH_2Ge); 3.09, 3.28, 3.58 and 3.79 (m, 4H, CH_2SO), $J_{AB} = 16$ Hz. Anal. Found: C, 42.02; H, 6.47. $C_8H_{14}GeOS$ calc.: C, 41.62; H, 6.11%.

(b) With two-mole equivalent of MCPBA. A solution of 3.0 g (14.7 mmol) of 85% MCPBA in 100 ml of ether was added at 20 °C with stirring in 1 h. to 1.58 g (7.35 mmol) of bicyclic sulfide Ib. After 2 h standing at room temperature, 50 ml pentane was added followed by 5 % aqueous sodium hydroxide until the mixture was basic. The organic layer was washed five times with water and dried over calcium chloride. After removal of the solvent, the residue was recrystallized from pentane, to give 1.28 g (5.18 mmol) of large colourless needles of sulfone VI. F = 70 °C, (70.5% yield). Anal. Found: C, 38.90; H, 5.67; S, 12.80. $C_8H_{14}GeO_2S$ calcd.: C, 38.92; H, 5.72; S, 12,99%. IR spectrum (CH_2Cl_2): strong absorption bands $\nu(SO_2)$ at 1309 and 1124 cm^{-1}. NMR spectrum (300 MHz, δ ppm, $CDCl_3$): 0.43 (s, 6H, CH_3Ge); 1.61 (m, 4H, CH_2Ge); 3.72 (m, 4H, CH_2SO_2). Upon irradiation of the 3.72 ppm signal, the signal lying at 1.61 ppm became a singlet.

(c) With an excess of MCPBA. Addition (20 °C, 1 h) of a solution of 10.0 g (49.3 mmol) of 85% MCPBA in 100 ml of ether to 2.30 g (10.7 mmol) of the sulfide Ib gave after 2 h. stirring and usual treatment, 2.48 g of crude product. Sulfone VI (1.4 g) was removed by extraction with pentane and the part soluble in ether was chromatographed on 20 g SiO_2 (eluent ether) to give 0.67 g (2.55 mmol) of oxide VII. Yield 23.8%. Crystallisation by addition of pentane at 0 °C gave pure crystals melting at 143 °C. Anal. Found: C, 36.61; H, 5.38; S, 18.11. $C_8H_{14}GeO_3S$ calcd.: C, 36.55; H, 5.37; S, 18.26%. NMR spectrum (300 MHz, δ ppm, $CDCl_3$): 0.36 (s, 3H, $CH_3'Ge$); 0.40 (s, 3H, CH_3Ge); 1.18 and 1.23 (d, 2H, H_1'); 1.61 and 1.66 (d, 2H, H_1); 3.40 and 3.44 (d, 2H, H_2'); 3.50 and 3.54 (d, 2H, H_2).



Preparation of sulfoxide V (second process)

A mixture of bis(methylene)germacyclopentane (VIII) (0.65 g, 3.55 mmol) and ethylene episulfoxide (0.41 g, 5.39 mmol) in 3 ml toluene was refluxed for 1 h. Chromatography of the resulting mixture afforded 0.11 g (13.4% yield) of the expected pure sulfoxide V, having identical spectra to those of the sample obtained by the previous method.

Oxidation of sulfoxide V

To an ethereal solution of sulfoxide V (0.36 g, 1.56 mmol) was added a solution of 0.32 g (1.57 mmol) of 85% MCPBA at room temperature. After the usual treatment and purification by liquid chromatography, 0.28 g of pure sulfone VI was obtained (72.7% yield).

1,1-Dimethyl-3,4-bis(methylene)-1-germacyclopentane (VIII)

Reduction of 3.91 g (15.8 mmol) of sulfone VI with a large excess (5 g) of lithium aluminium hydride in 150 ml of boiling ether (2 h) gave, after hydrolysis and usual work-up, 1.50 g (8.2 mmol) of VIII. Yield 52%. B.p. 57 °C/13 mmHg. NMR (60 MHz, δ ppm, TMS): 0.37 (s, 6H, CH_3Ge); 1.73 (s, 4H, CH_2Ge); 4.68 and 5.10 (d, 2H, 2H, $=CH_2$). Ref. [14]: 0.32, 1.74, 4.70 and 5.12 ppm.

A mixture of VIII (0.21 g, 1.15 mmol) and maleic anhydride (0.10 g, 1.10 mmol) in 3 ml benzene was boiled. After removal of the solvent and recrystallization of the residue in hexane, the expected cycloadduct IX was obtained as white needles melting at 65 °C. NMR spectrum (δ ppm, TMS, CCl_4): 0.37 (s, 6H, CH_3Ge); 1.00 (s, 4H, CH_2Ge); 2.40 (m, 4H, $CH_2C=$); 3.25 (m, 2H, CHCO).

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