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New series of functional bicyclic organogermanium compounds

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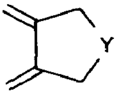
Abstract

1,4-Addition of germanium diiodide to 3,4-bis(methylene) oxolane, thiolane and phenylazolidine, leads to new series of functional bicyclic germanium derivatives, potentially valuable synthons for other organogermanium compounds.

Debromination of 1,4-dibromo-2,3-bis(bromomethyl)-2-butene (1) [1,2] by zinc–copper couple [3] in methylal/hexamethylphosphoramide or diethyl ether/HMPA (9 : 1), or by tin–copper couple in tetrahydrofuran [4] gives 2,3-bis(bromomethyl)-1,3-butadiene (2) in good yields [4–6]. This allylic bromide reacts readily with a series of sodium salts and amines to give bis(methylene) five-membered rings [5–7]:

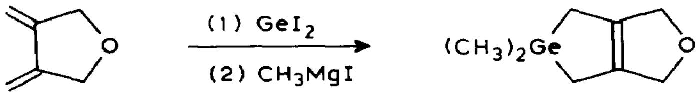


Y = O (**3a**) ; S (**3b**) ; N-R (**3c**)

(**3**)

Since these conjugated dienes are stable for some hours in solution, it was of interest to see if the 1,4-addition of germylenes, previously observed with linear [8–10] or cyclic [11–12] conjugated dienes, could also be achieved with these functional cyclic compounds.

3,4-Bis(methylene) oxolane (3a) was found to react with an equimolecular amount of germanium diiodide in boiling benzene, and subsequent alkylation did not affect the bicyclic structure:



(**3a**) (**5**)

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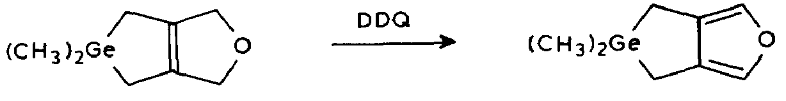
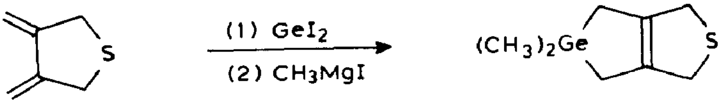
Dehydrogenation with 2,3-dichloro-5,6-dicyanoquinone (DDQ) gave a good yield of the corresponding substituted furan, a colourless liquid with a penetrating odor:



(5) (6)

This compound, less stable than the dihydro- derivative, polymerizes on standing, even under argon.

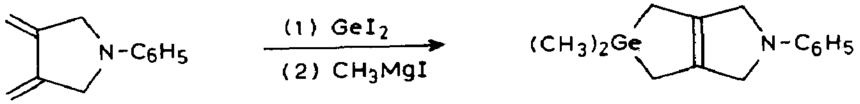
Similarly, 1,4-cyclization is observed with 3,4-bis (methylene) thiolane:



(3b) (7)

Pure bicyclic sulfide **7**, which is obtained by liquid chromatography (eluant pentane) is a stable compound characterized by an abundant molecular ion in the mass spectrum.

Germanium diiodide reacts with some decomposition with pure 3,4-bis(methylene)-*N*-phenyl azolidine (3c). However, in the presence of hydroquinone, addition occurs readily in benzene solution:



(3c) (8)

In contrast to the compounds containing oxygen and sulfur rings, this compound cannot be purified by column chromatography because it partially decomposes on silica; the pure product is obtained by crystallization from methanol.

Experimental

^1H NMR spectra were recorded on Bruker AM 300 WB and mass spectra on a coupled Girdel-Riber R 10-10 spectrometer. 1,4-Dibromo-2,3-bis(bromomethyl)-2-butene (**1**) was made as described in ref. 2 by addition at 0 °C of 160 g (1 mol) of bromine to 82 g (1 mol) of 2,3-dimethylbutadiene in CCl_4 followed by treatment with 356 g (2 mol) of *N*-bromosuccinimide in the presence of benzoyl peroxide. Yield 252 g (70%). 2,3-bis(bromomethyl)-1,3-butadiene (**2**) was prepared by reduction of 20 g (0.050 mol) samples of tetrabromide (**1**) with Zn–Cu couple in boiling diethyl ether-HMPA as describing ref. 6. Yield 8.5 to 9.2 g (70–75%).

3-Oxa-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene (5). To a solution of 15.2 g (0.063 mol) of **2** in 40 ml of ether was added dropwise with stirring a solution of potassium hydroxide (12.5 g) in a mixture of DMSO (50 ml) and water (20 ml). After 3 h heating the mixture was cooled and 200 ml of pentane was added. The organic layer was decanted, washed ten times with water (50 ml portions), then dried over sodium sulfate. After removal of the solvent, the liquid residue (4.64 g, 0.048 mol, 75% yield), consisting mainly of 3,4-bis(methylene)oxolane, was heated for 15 min with 15.83 g (0.048 mol) of germanium diiodide in 100 ml of benzene. Alkylation with an excess (0.17 mol) of methylmagnesium iodide gave, after the usual treatment, 2.88 g (30%) of the expected dihydrofuran **5**. Boiling point 102–103 °C/24 Torr; n_D^{20} 1.5075. ^{1}H NMR ($CDCl_3$, δ ppm): 0.41 (s, 6H, Me_2Ge); 1.34 (s, 4H, CH_2Ge); 4.45 (s, 4H, OCH_2). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{74}Ge, rel. intensity): 200, 25.7, M^+; 185, 20.7, $(M-CH_3)^+$; 105, 30.7; 104, 36.0; 89, 100,0 $(GeCH_3)^+$. Other peaks at 95 (76.6), 91 (29.9) and 67 (31.0).

*3-Oxa-7,7-dimethyl-7-germabicyclo[3.3.0]octa-1,4-diene (**6**).* To a stirred solution of 1.50 g (0.0066 mol) of 2,3-dichloro-5,6-dicyanoquinone in 10 ml of dioxane, was slowly added a solution of 1.35 g (0.0066 mol) of **5** in 2 ml of the same solvent. The mixture turned black and then a turbid brown. The precipitate formed was filtered off, washed with pentane (80 ml), and the combined filtrate and washings were shaken 15 times with water to remove the dioxane and then dried over sodium sulfate. After removal of the solvent, the residue (0.63 g, 48% yield), purified by column chromatography, gave pure **6** as a colourless liquid. B.p. 78–79 °C/ 12 Torr; n_D^{20} 1.5148. ^{1}H NMR ($CDCl_3$, δ ppm): 0.43 (s, 6H, Me_2Ge); 1.79 (t, 4H, $GeCH_2$); 7.12 (t, 2H, =CH). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{74}Ge, rel. intensity): 198, 24.7 (M^+); 183, 26.5, $(M-CH_3)^+$; 89, 58.3 $(GeCH_3)^+$. Other peaks at 93 (100.0), 91 (88.7) and 77 (72.5).

3-Thia-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene (7). A solution of 23.67 g (0.099 mol) of dibromide **2** in ethanol (250 ml) was added with cooling to a solution of 0.173 g (0.025 mol) of powdered anhydrous sodium sulfide in 150 ml of the same solvent cooled in a water bath. The mixture was stirred for 3 h and 500 ml of pentane then added. Water (150 ml) was added and the organic layer was separated washed 10 times with water (100 ml each), and dried over sodium sulfate. After removal of the solvent, the residual crude 3,4-bis(methylene)thiolane (6.53 g, 0.058 mol) was heated with 19.0 g (0.058 mol) of germanium diiodide in 100 ml of benzene. Alkylation with an excess of methylmagnesium iodide gave 11.41 g of crude bicyclic sulfide **7**. Purification by column chromatography (silica gel Merck 230–400 mesh, 40 g; eluant pentane) gave pure **7** as a colourless liquid 6.76 g, 54% yield. B.p. 82 °C/0.8 Torr; n_D^{20} 1.5601. ^{1}H NMR ($CDCl_3$, δ ppm): 0.40 (s, 6H, Me_2Ge); 1.39 (s, 4H, CH_2Ge); 3.57 (s, 4H, SCH_2). Mass spectrum (70 eV), most important Ge-containing fragments (m/z for ^{74}Ge, rel. intensity): 216, 73.6, (M^+); 201, 71.8 $(M-CH_3)^+$, 121, 26.8; 89, 96.5 $(GeCH_3)^+$. Other peaks at 111 (100.0), 79 (84.0), 77 (56.5), 67 (24.4).

*3-Phenyl-3-aza-7,7-dimethyl-7-germabicyclo[3.3.0]oct-1(5)-ene (**8**).* To a stirred solution of 8.50 g (0.035 mol) of dibromide **2** in 50 ml of acetonitrile at room temperature was added a solution of 9.90 g (0.106 mol) of freshly distilled aniline in 25 ml of acetonitrile. The precipitate was filtered and washed with pentane. Concentration of the organic layer gave 4.01 g (0.029 mol) of solid azolidine **3c**. This was dissolved in 50 ml of benzene and the solution heated with 9.40 g (0.029 mol) of germanium diiodide in the presence of 20 mg of hydroquinone. The orange solution was then alkylated with methylmagnesium iodide (0.057 mol), to give, after the usual work-up, 4.38 g (55%) of crude **8**. Recrystallisation in methanol gave pure product m.p. 140 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.44 (s, 6H, Me_2Ge); 1.49 (s, 4H, CH_2Ge), 3.95 (s, 4H, CH_2N); 6.52, d; 6.65, t; 7.23, t (5H, C_6H_5). Anal. Found: C, 61.40; H, 6.98; N, 5.07. $C_{14}H_{19}GeN$ calcd.: C, 61.39; H, 6.99; N, 5.11%.

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