Preparation of tribromogermylcyclopropanes by insertion of dibromogermylene into the C—Br bonds of 1,1-dibromo-2-trimethylsilylcyclopropane

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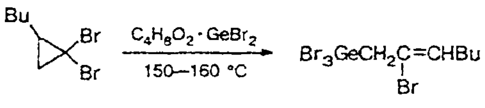
The reaction of 1,1-dibromo-2-trimethylsilylcyclopropane with dibromogermylene generated from its dioxane complex made it possible to obtain for the first time the products of insertion of dibromogermylene into one or both C—Br bonds of the dibromocyclopropane. Under similar conditions, alkyl-substituted *gem*-dibromocyclopropanes give only alkenylgermanes resulting from isomerization of the corresponding cyclopropyl-substituted tribromogermanes.

Key words: cyclopropylgermanes; dibromogermylene, dioxane complex; 1,1-dibromo-2-trimethylsilylcyclopropane; vinylgermanes.

Cyclopropylgermanes have been little investigated, although simple representatives of this class were prepared more than 30 years ago.[1,2] Virtually all the existing methods for the synthesis of these compounds are based on cyclopropanation of vinylgermanes;[3—5] the yields of final products in these reactions normally do not exceed 30%. The insertion of germylenes into the C—Hal bonds of easily available halocyclopropanes could serve as an alternative method for the preparation of cyclopropylgermanes. However, the high electrophilicity of germylenes hampers this process, and opening of the cyclopropane ring (CPR) may become the major reaction pathway. In fact, the previously described[6] insertion of the dibromogermylene generated from its dioxane complex ($C_4H_8O_2 \cdot GeBr_2$) at 140—160 °C into the C—Br bond of 2-bromo-1-butylcyclopropane was accompanied by opening of the CPR giving the corresponding alkenylgermane.

In this work we have shown that the reaction of $C_4H_8O_2 \cdot GeBr_2$ with *gem*-dibromocyclopropanes is also accompanied by cleavage of the three-membered ring. Thus the reactions of 2,2-dibromo-1-butylcyclopropane and 7,7-dibromonorcarane with the dibromogermylene generated from $C_4H_8O_2 \cdot GeBr_2$ at 140—160 °C is accompanied by the opening of the CPR in the insertion products and affords alkenylgermanes, *viz.*, 2-bromo-1-tribromogermylhept-2-ene (**1**) and 1-bromo-7-tribromogermylcycloheptene (**2**) (yields 52 and 53%, respectively).



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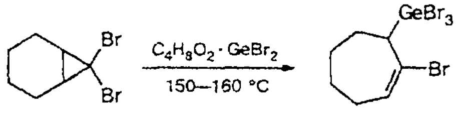

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It should be noted that these reactions give products of insertion into only one C—Br bond. In addition, among the products of the reaction of 7,7-dibromonorcarane with $C_4H_8O_2 \cdot GeBr_2$, compounds resulting from condensation of the initial dibromonorcarane with the main reaction products were detected by NMR spectroscopy and mass spectrometry; however, we were not able to identify and separate these compounds.

Based on the published data[7] indicating that an $SiMe_3$ group in a cyclopropane ring exerts a stabilizing effect in electrophilic reactions, it may be expected that in the case of 1,1-dibromo-2-trimethylsilylcyclopropane, the reaction would occur with the retention of CPR. In fact, unlike alkyl-substituted *gem*-dibromocyclopropanes, 1,1-dibromo-2-trimethylsilylcyclopropane smoothly reacts with dibromogermylene under similar conditions to give only products of insertion of $GeBr_2$ into the C—Br

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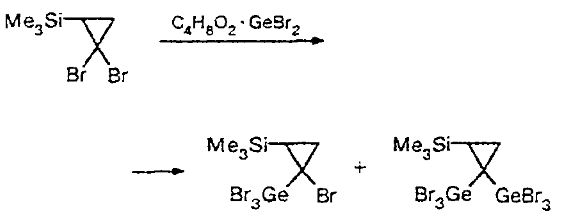
bonds of the starting dibromide, the CPR remaining intact. This made it possible to obtain for the first time the products resulting from insertion of $GeBr_2$ into one and both C—Br bonds of the starting dibromocyclopropane, namely, 1-bromo-1-tribromogermyl-2-trimethylsilylcyclopropane (**3**) and 1,1-bis(tribromogermyl)-2-trimethylsilylcyclopropane (**4**) (yields 40 and 50%, respectively).



3 **4**

The experiments were carried out at 150—160 °C (0.5 h) at a $C_4H_8O_2 \cdot GeBr_2$/dibromocyclopropane ratio of 1 : 1; the liberated dioxane was distilled off during the process.

An increase in the duration of heating (to 3 h) or an increase in the reaction temperature (to 180 °C) decreases the yields of products **3** and **4** due to an increase in the proportion of resinified products. When the $C_4H_8O_2 \cdot GeBr_2$/dibromocyclopropane ratio is 2 : 1 or larger, both the initial cyclopropane and $C_4H_8O_2 \cdot GeBr_2$ decompose almost completely over a period of 3 h at 180 °C, and compound **4** is formed in a yield of only 6%.

Experimental

^1H and ^{13}C NMR spectra were recorded for 3—15% solutions in $CDCl_3$ or C_6D_6 on Bruker CXP (200 MHz) and Bruker AM-360 (360 MHz) spectrometers. The GC/MS analysis was carried out on a Hewlett-Packard HP-5971 (70 eV) instrument using DB-5 quartz capillary column (0.32 mm×250 m); the temperature of the analysis was 280 °C. IR spectra were recorded on a Bruker-113 V FT spectrometer and on a Specord-80 spectrometer; liquids were analyzed in thin films (CsI window), and solids were analyzed as pellets with KBr or in vaseline oil.

Reaction of $C_4H_8O_2 \cdot GeBr_2$ with 1,1-dibromo-2-butylcyclopropane. A mixture of $C_4H_8O_2 \cdot GeBr_2$ (30.0 g, 93.6 mmol) and 1,1-dibromo-2-butylcyclopropane (24.0 g, 93.8 mmol) was refluxed for ~3.5 h at 150 °C, the dioxane liberated being distilled off. The reaction mixture was distilled and the fraction boiling at 114 °C (1 Torr) was collected. This gave 23.9 g (52.3%) of 2-bromo-1-tribromogermylhept-2-ene (**1**), n_D^{20} 1.5835. Found (%): C, 16.7; H, 2.5; Ge, 15.1. $C_7H_{12}Br_4Ge$. Calculated (%): C, 17.2; H, 2.3; Ge, 14.9. ^1H NMR ($CDCl_3$), δ: 0.93 (m, 3 H, CH_3); 1.50 (m, 4 H, CH_2); 2.16 (m, 2 H, CH_2C=); 3.57 (s, 2 H, CH_2Ge); 6.00 (m, 1 H, CH=).

Reaction of $C_4H_8O_2 \cdot GeBr_2$ with 7,7-dibromonorcarane. A mixture of $C_4H_8O_2 \cdot GeBr_2$ (24.4 g, 76.1 mmol) and 7,7-dibromonorcarane (19.3 g, 76.1 mmol) was heated for 2 h at 150—165 °C, the dioxane formed being distilled off. The residue was distilled *in vacuo* to give 18.8 g (52.8%) of 1-bromo-7-tribromogermylcycloheptene (**2**), b.p. 150—152 °C (1 Torr), n_D^{20} 1.6325. Found (%): C, 16.8; H, 2.3; Ge, 16.0. $C_7H_{12}Br_4Ge$. Calculated (%): C, 17.2; H, 2.3; Ge, 14.9. ^1H NMR ($CDCl_3$), δ: 1.25—2.50 (m, 10 H, CH_2); 4.17 (t, 1 H, CH_2Ge); 6.78 (t, 1 H, CH=). ^{13}C NMR, δ: 26.7, 26.8, 29.8, 30.2, 82.9, 118.1, 139.0.

Reaction of $C_4H_8O_2 \cdot GeBr_2$ with 2,2-dibromo-1-trimethylsilylcyclopropane. A mixture of $C_4H_8O_2 \cdot GeBr_2$ (32.2 g, 100 mmol) and 2,2-dibromo-1-trimethylsilylcyclopropane (27.5 g, 101 mmol) was refluxed for 0.5 h at ~150 °C. The hot solution was separated and distilled *in vacuo* to give 20.0 g (39.7%) of 1-bromo-1-tribromogermyl-2-trimethylsilylcyclopropane (**3**), b.p. 157—159 °C (13 Torr), n_D^{20} 1.5738, and 18.3 g (49.7%) of 1,1-bis(tribromogermyl)-2-trimethylsilylcyclopropane (**4**), b.p. 188 °C (1.5 Torr), n_D^{20} 1.6172.

Compound **3**. IR, ν/cm^{-1}: 2955 (C—H); 1250, 843 (Si—C); 937 (cyclopropane ring); 318 (Ge—Br_3). ^1H NMR ($CDCl_3$), δ: *trans*-**3**, 0.20 (s, 9 H, $SiMe_3$); 0.55 (m, 1 H, CH); 1.39, 1.68 (both m, 2 H, CH_2); *cis*-**3**, 0.24 (s, 9 H, $SiMe_3$); 1.03 (m, 1 H, CH); 1.45, 1.69 (both m, 2 H, CH_2). MS, *m/z*: 490 $[M-Me]^+$, 410 $[M-Me-Br]^+$, 352 $[M-Me_3SiBr]^+$, 272 $[M-Me_3SiBr-Br]^+$, 152 $[GeBr]^+$, 138 $[Me_2SiBr]^+$, 73 $[Me_3Si]^+$.

Compound **4**. IR, ν/cm^{-1}: 2955 (C—H); 1252; 841 (Si—C); 928 (cyclopropane ring); 320 (Ge—Br_3). ^1H NMR ($CDCl_3$), δ: 0.31 (s, 9 H, $SiMe_3$); 0.96 (t, 1 H, CH); 1.61 (m, 2 H, CH_2). MS, *m/z*: 721 $[M-Me]^+$, 656 $[M-Br]^+$, 583 $[M-Me_3SiBr]^+$, 351 $[M-Me_3SiBr-GeBr_2]^+$, 271 $[M-Me_3SiBr-GeBr_3]^+$, 152 $[GeBr]^+$, 138 $[Me_2SiBr]^+$, 73 $[Me_3Si]^+$.

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