***m*-Nitrobenzophenone.** $Pd(OAc)_2$ (0.0022 g, 0.01 mmol, 1 mol.% Pd) was added in an atmosphere of argon to a mixture of Ph_4BNa (0.0922 g, 0.25 mmol), Na_2CO_3 (0.159 g, 1.5 mmol), and *m*-$NO_2C_6H_4COCl$ (0.1858 g, 1 mmol) in dry acetone (9 mL), and the mixture was stirred at 20 °C for 2.5 h. Then acetone was evaporated on a rotary evaporator, and the residue was diluted with water (10 mL), extracted with chloroform (3×5 mL), and dried with $MgSO_4$. After chloroform was removed on a rotary evaporator, *m*-nitrobenzophenone (0.149 g, 66%) was obtained, m.p. 96—97 C (*cf.* Ref. 8: m.p. 95 °C).

Chalcone was obtained similarly from Ph_4BNa and cinnamoyl chloride (yield 96%).

Thus, the catalytic reactions found occur under very mild conditions and can be used as a new efficient method for the synthesis of nonsymmetric ketones.

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1-(1-Trimethylsilylcyclopropyl)germatrane as the first representative of cyclopropylgermatranes

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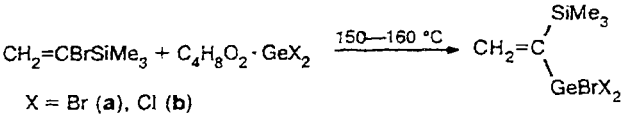
Virtually all germatranes exhibit physiological activities that largely depend on the substituents present in their molecules.[1] Therefore, it seemed of interest to prepare a germatrane molecule containing a cyclopropane fragment, whose presence accounts for the activity of some compounds, in particular, pyrethroids.[2]

In this study, we synthesized the first representative of cyclopropylgermatranes, *viz.*, 1-(1-trimethylsilylcyclopropyl)germatrane (**1**). As the first step, we prepared 1-tribromogermyl-1-trimethylsilylethylene[3] (**2a**) (yield 75%) and 1-bromodichlorogermyl-1-trimethylsilylethylene (**2b**) (yield 82%) by the reactions of 1-bromovinyltrimethylsilane with the dioxane complexes of dichloro- and dibromogermylene, respectively.[4]



2a,b

Subsequently 1-(trimethylsilyl)vinyltrihalogermanes **2** were converted into 1-trimethylsilyl-1-trimethoxygermylethylene (**3**) by treating them with methanol.

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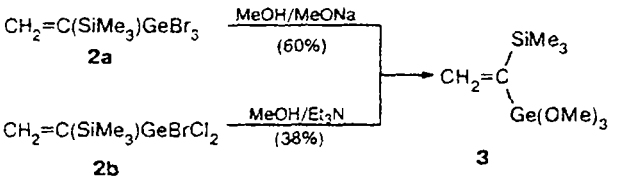
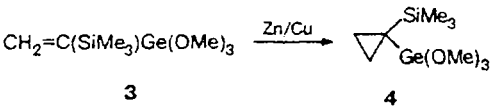
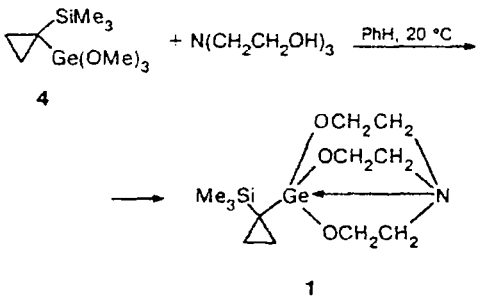


Cyclopropanation of compound **3** using a modified Simmons—Smith procedure[5] gave 1-trimethylsilyl-1-trimethoxygermylcyclopropane (**4**) in a yield of 33%.



Finally, the target germatrane, 1-(1-trimethylsilylcycloprpopyl)germatrane **1**, was obtained in 71% yield by transalkoxylation of compound **4** with triethanolamine.



1-Bromodichlorogermyl-1-trimethylsilylethylene (2b). A mixture of $C_4H_8O_2 \cdot GeCl_2$ (46.0 g, 0.2 mol) and 1-bromovinyltrimethylsilane (36.0 g, 0.2 mol) was heated for 5 h at 150—160 °C, the dioxane liberated being removed. The residue was distilled *in vacuo* to give 57.5 g (75%) of compound **2b**, b.p. 60—112 °C (9 Torr).

1-Trimethylsilyl-1-trimethoxygermylethylene (3). *A.* 1-Tribromogermyl-1-trimethylsilylethylene (41.1 g, 0.1 mol)[3] was added with stirring to a solution of MeONa (prepared from sodium (6.9 g, 0.3 mol) and methanol (60 mL)); the mixture was stirred for ~1 h at 20 °C, filtered to remove the precipitate, and distilled *in vacuo* to give 16.2 g (60%) of compound **3**, b.p. 96—97 °C (19 Torr), n_D^{20} 1.4383.

B. Triethylamine (63.0 g, 0.621 mol) was added dropwise with stirring to a solution of compound **2b** (57.5 g, 0.150 mol) in hexane (270 mL) and methanol (20.0 g, 0.621 mol); the reaction mixture was stirred for 1 h at ~70 °C, cooled to 20 °C, and filtered from the precipitate. The precipitate was washed with hexane (2×50 mL), the filtrate and the eluent were combined, the solvent was evaporated under atmospheric pressure, and the residue was distilled *in vacuo*. The fraction boiling at 78—83 °C (10 Torr) was collected to give 20.3 g (54%) of product **3**, n_D^{20} 1.4430. Repeated distillation gave 15.0 g (38%) of product **3**, b.p. 86.5—87 °C (13 Torr), n_D^{20} 1.4446. ^{1}H NMR ($CDCl_3$), δ: 0.03 (s, 9 H, $SiMe_3$); 3.50 (s, 9 H, OCH_3); 6.38, 6.45 (both d, 2 H, CH_2=).

1-Trimethylsilyl-1-trimethoxygermylcyclopropane (4). Compound **3** (11.0 g, 0.042 mol) and CH_2I_2 (20.0 g, 0.075 mol) were added to a freshly prepared zinc—copper pair (5.6 g, 0.100 mol)[5] in ether (40 mL). The reaction mixture was stirred for ~20 h at 50 °C, the ether was evaporated under atmospheric pressure, and the residue was distilled *in vacuo* to give 3.9 g (33%) of compound **4**, b.p. 63—64 °C (1 Torr), n_D^{20} 1.4531. IR, ν/cm^{-1}: 1250, 843 ($SiMe_3$); 1069, 1045, 850 (GeOC); 912 (cyclopropane ring). ^{1}H NMR ($CDCl_3$), δ: 0.02 (s, 9 H, $SiMe_3$); 0.57 (m, 2 H, cyclopropane-ring CH); 0.91 (m, 2 H, cyclopropane-ring CH); 3.52 (s, 9 H, OCH_3).

1-(1-Trimethylsilylcyclopropyl)germatrane (1). Triethanolamine (0.7 g, 4.7 mmol) was added to a solution of compound **4** (1.2 g, 4.3 mmol) in benzene (5 mL). The mixture was stirred for ~15 min, and the benzene was evaporated. Recrystallization of the residue (chloroform—hexane, 1 : 1) afforded 1.0 g (71%) of germatrane **1**, m.p. 117—119 °C. IR, ν/cm^{-1}: 3071, 3045, 1097, 1078, 1049, 1020, 914. ^{1}H NMR ($CDCl_3$), δ: 0.02 (s, 9 H, $SiMe_3$); 0.57 (m, 2 H, cyclopropane ring); 0.91 (m, 2 H, cyclopropane ring); 2.80 (t, 6 H, CH_2N); 3.73 (t, 6 H, CH_2O).

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