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Abstract

Full Text

CHEMISTRY

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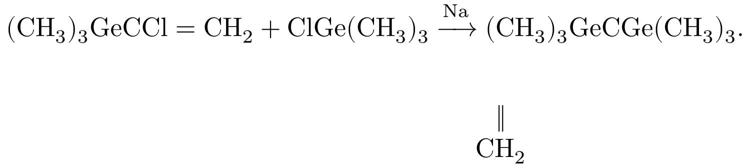
SYNTHESIS OF 1,1- AND 1,2-BIS(TRIMETHYLGERMYL)ETHY

The isomeric silicoolefins $(CH_3)_3SiCH=CHSi(CH_3)_3$ (I) and $[(CH_3)_3Si]_2C=CH_2$ (II) possess interesting physical and chemical properties. For example, compound I, in contrast to compound II, shows a greater exaltation of molecular refraction, an increased reactivity in ionic addition reactions, and a decreased reactivity in radical reactions ([1],[2]). In the Raman and infrared spectra of compounds I and II, various kinds of anomalies also appear in the positions of the characteristic frequencies and in their intensities ([3]).

The exceptional features noted for these compounds are probably due to d_π—p_π overlap of the π-electron shells of the multiple bond with the d-vacant orbitals of the silicon atom.

In order to study this effect in a series of analogous compounds of other group IVB elements, in the present work we obtained 1,1- and 1,2-bis(trimethylgermyl)ethylenes. The synthesis of these compounds was carried out according to the following schemes:

$$(CH_3)_3GeCH=CHCl+ClGe(CH_3)_3\xrightarrow{Na}(CH_3)_3GeCH=CHGe(CH_3)_3,$$



$$(CH_3)_3GeCCl=CH_2+ClGe(CH_3)_3\xrightarrow{Na}(CH_3)_3G e\underset{\underset{CH_2}{\|}}{C}Ge(CH_3)_3.$$

In addition, we attempted to obtain 1,2-bis(trimethylgermyl)ethylene by another route as well. However, it turned out that the addition of trichlorogermane to $(CH_3)_3GeC\equiv CH$, despite the precautions taken, proceeds mainly in the amount of two molecules, as a result of which, after methylation, tris(trimethylgermyl)ethane is formed preferentially.

$$(CH_3)_3GeC\equiv CH\xrightarrow{HGeCl_3}(CH_3)_3GeCH=CHGeCl_3(\sim 3\%)+$$

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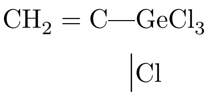
$$+ (CH_3)_3GeCH_2CH(GeCl_3)_2 (\sim 15\%) \xrightarrow{CH_3MgCl} (CH_3)_3GeCH = CHGe(CH_3)_3 +$$

$$+ (CH_3)_3GeCH_2CH[Ge(CH_3)_3]_2.$$

1,2-Bis(trimethylgermyl)ethylene, just like its silicon analogue, in contrast to 1,1-bis(trimethylgermyl)ethylene possesses a large (+0.8) exaltation of molecular refraction.

Experimental Part

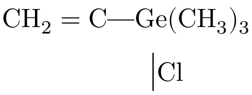
α-Chlorovinyltrichlorogermane



$$CH_2 = \underset{|\,Cl}{C}—GeCl_3$$

In a 150-ml flask with a reflux condenser were placed 140 g of $ClCH_2ClCHGeCl_3$ (^{4}) and 7 g of piperidine (pyridine may also be used). The contents of the flask were slowly ($\sim$ 2 hr) distilled at such a rate that the temperature of the escaping vapors did not rise above 150–160°. Distillation of the condensate on a column gave 30 g of $GeCl_4$, b.p. 83-85°, and 75 g of $Cl_3GeCCl = CH_2$, b.p. 152.5° (760); n_D^{20} 1.4990; d_4^{20} 1.7396; found MR_D 40.58; calculated MR_D 40.90; yield 61.5%. Literature data (^{4}): b.p. 151°, n_D^{20} 1.5002.

α-Chlorovinyltrimethylgermane



$$CH_2 = \underset{|\,Cl}{C}—Ge(CH_3)_3$$

To CH_3MgCl, prepared from 30.1 g of magnesium in 200 ml of ether, 75 g of α-chlorovinyltrichlorogermane was added. The contents of the flask were boiled for 4 hours and then treated with water. Distillation on a column of the dried $CaCl_2$ ether layer gave 45 g of

$$CH_2 = C(Cl) - Ge(CH_3)_3$$

with b.p. 120.5° (755), n_D^{20} 1.4517; d_4^{20} 1.1749; found MR_D 41.12, calculated MR_D 41.31; yield 80.5%. IR spectrum, see Fig. 1.

$C_5H_{11}GeCl$. Found, %: C 33.27, 33.37; H 6.31, 6.57; Ge 40.43, 40.27
Calculated, %: C 33.51; H 6.18; Ge 40.51

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Fig. 1

Figure 1: Fig. 1

Raman spectrum ($\Delta\nu$, cm^{-1}) of $(CH_3)_3GeCCl = CH_2$. 147 (1); 190 (3 broad); 232 (2); 302 (2); 473 (1); 493 (7); 577 (10); 611 (6 broad); 740 (0); 1113 (0); 1153 (0); 1253 (2 broad); 1361 (2); 1409 (1 broad); 1601 (3); 2869 (0); 2912 (10); 2981 (3); 3005 (1); 3080 (1).

1,1-Bis(trimethylgermyl)ethylene

$$CH_2 = C(Ge(CH_3)_3)_2.$$

To 8 g of finely divided sodium were added 150 ml of ether, 23 g of $(CH_3)_3GeCl$, 1 ml of $CH_2 = C(Cl)Ge(CH_3)_3$, and ~ 0.5 ml of ethyl acetate. After the reaction had begun, the remaining 26 g of $CH_2 = C(Cl)Ge(CH_3)_3$ was added dropwise.

Fig. 1

After 5 hours' boiling, the contents of the flask were filtered from salts and distilled. There were obtained 8 g of $(CH_3)_3Ge—Ge(CH_3)_3$ with b.p. 136° and 26 g of

$$CH_2 = C(Ge(CH_3)_3)_2$$

with b.p. 72-73° (28); n_D^{20} 1.4655; d_4^{20} 1.1646; found MR_D 62.12; calculated MR_D 62.09; yield 68%.

$C_8H_{20}Ge_2$. Found, %: C 37.12, 37.04; H 7.89, 7.93; Ge 54.63, 54.65
Calculated, %: C 36.75; H 7.71; Ge 55.54

Raman spectrum ($\Delta\nu$, cm^{-1}) of $CH_2 = C[Ge(CH_3)_3]_2$. 150 (1); 173 (1); 195 (2 broad); 413 (6); 573 (10); 600 (8 broad); 1114 (0); 1147 (0); 1235 (2); 1250 (2); 1399 (1 broad); 1426 (1 broad); 1584 (1); 2906 (8); 2973 (4 broad); 3001 (1).

1,2-Bis(trimethylgermyl)ethylene

$$(CH_3)_3GeCH = CHGe(CH_3)_3.$$

Under the conditions of the preceding experiment, from 0.85 g of Na, 2.8 g of $ClGe(CH_3)_3$, and 2.5 g of $(CH_3)_3GeCH = CHCl^{(5)}$, 2.5 g of $(CH_3)_3GeCH = CHGe(CH_3)_3$ was obtained (yield 65.7%), b.p. 73° (29), n_D^{20} 1.4628; d_4^{20} 1.1444; found MR_D 62.90, calculated MR_D 62.09.

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$C_8H_{20}Ge_2$. Found, %: C 36.74, 36.49; H 7.81, 7.68; Ge 55.28, 55.25
Calculated, %: C 36.75; H 7.71; Ge 55.54

Raman spectrum ($\Delta\nu$, cm^{-1}) of $(CH_3)_3GeCH = CHGe(CH_3)_3$. 148 (1); 165 (1); 194 (1 broad); 230 (1); 273 (0); 572 (10); 602 (6); 1032 (0); 1150 (0); 1244 (2 broad); 1284 (2); 1329 (0); 1400 (0 broad); 1558 (1 broad); 2099 (0 broad); 2871 (1); 2907 (10); 2973 (7 broad).

The line 2099 belongs to an impurity of the compound $(CH_3)_3GeC{\equiv}CGe(CH_3)_3$, which, moreover, was identified in an amount of $\sim 1\%$ by gas-liquid chromatography, using an authentic sample of $(CH_3)_3GeC{\equiv}CGe(CH_3)_3$.

1-(Trimethylgermyl)-2,2-bis-(trichlorogermyl)ethane
$(CH_3)_3GeCH_2CH(GeCl_3)_2$. To 30 g of $(CH_3)_3GeC \equiv CH$, 37 g of $HGeCl_3$ was added dropwise with vigorous stirring. Distillation gave 15 g of $(CH_3)_3GeCl$, b.p. 94–95° (750); n_D^{21} 1.4340, 2 g of $(CH_3)_3GeCH = CHGeCl_3$, b.p. 100–103° (12 mm), and 16 g of $(CH_3)_3GeCH_2CH(GeCl_3)_2$, b.p. 138–139° (7); n_D^{20} 1.5570; d_4^{20} 1.8441. Found MR_D 88.41; calculated MR_D 87.35; yield 11%, m.p. 30–50°. The substance is prone to strong supercooling.

Raman spectrum ($\Delta\nu$, cm^{-1}) of $(CH_3)_3GeCH_2CH(GeCl_3)_2$. 148 (1 sh); 195 (0 sh); 240 (1); 267 (0 sh); 370 (0); 395 (1); 407 (10); 434 (2 sh); 487 (1); 574 (7); 611 (3 sh); 809 (2); 1193 (1); 257 (2 sh); 1292 (0); 1415 (1); 1519 (1 sh); 2873 (0 sh); 2913 (8 sh); 2981 (0 sh).

Tris-(trimethylgermyl)ethane
$(CH_3)_3GeCH_2CH[Ge(CH_3)_3]_2$. To CH_3MgCl, prepared from 12 g of Mg in 100 ml of ether, 14 g of $(CH_3)_3GeCH_2CH(GeCl_3)_2$ was added. After the usual work-up, 8.5 g of $(CH_3)_3GeCH_2CH[Ge(CH_3)_3]_2$ was isolated, b.p. 110° (12 mm); n_D^{20} 1.5018; d_4^{20} 1.2691; found MR_D 88.36; calculated MR_D 88.17; yield 65%.

Found, %: C 35.02, 34.91; H 7.83, 7.37; Ge 57.14, 57.47.
$C_{11}H_{30}Ge_3$. Calculated, %: C 34.74; H 7.95; Ge 57.28.

Raman spectrum ($\Delta\nu$, cm^{-1}) of $(CH_3)_3GeCH_2CH[Ge(CH_3)_3]_2$. 153 (1 sh); 175 (1); 201 (1 0sh); 227 (1); 275 (1); 407 (0); 441 (1); 462 (3); 575 (10); 597 (9 sh); 826 (1 sh); 1114 (0); 1146 (1 sh); 1238 (3); 1253 (3); 1299 (3); 1334 (0); 1412 (1 sh); 1513 (1); 2910 (10 sh); 2974 (7 sh).

1,2-Bis-(trimethylgermyl)ethylene
$(CH_3)_3GeCH = CHGe(CH_3)_3$. To CH_3MgCl, prepared from 2 g of Mg in 30 ml of ether, 2 g of $(CH_3)_3GeCH = CHGeCl_3$, b.p. 100–103° (12 mm), was added. After the usual work-up, 1 g of $(CH_3)_3GeCH = CHGe(CH_3)_3$ was obtained, b.p. 173° (760); n_D^{20} 1.4655; d_4^{20} 1.1756; MR_D 61.53; calculated MR_D 62.09; yield 61%.

Found, %: C 36.23, 36.44; H 7.67, 7.70; Ge 56.10, 55.70.
$C_8H_{20}Ge_2$. Calculated, %: C 36.75; H 7.71; Ge 55.54.

The Raman spectrum of this compound coincides with the preceding one. The spectral analysis was carried out by L. A. Leites.

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REFERENCES CITED

1. V. F. Mironov, *Bull. Soc. chim. Belgrade*, **23–24**, No. 1–2, 23 (1958–1959).
2. V. F. Mironov, *Chemistry and Practical Application of Organo-Silicon Compounds*, vol. 1, 1958, p. 129.
3. Yu. P. Egorov, L. A. Leites, V. F. Mironov, *Izv. AN SSSR, OKhN*, 1958, 510.
4. V. F. Mironov, N. G. Dzhurinskaya, A. D. Petrov, *DAN*, **131**, 98 (1960).
5. V. F. Mironov, N. G. Dzhurinskaya, *Izv. AN SSSR, OKhN*, 1963, 75.

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