GEOMETRIC ISOMERS OF ALKENYL COMPOUNDS OF GERMANIUM

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Abstract

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GEOMETRIC ISOMERS OF ALKENYL COMPOUNDS OF GERMANIUM

In previous communications we described the synthesis and properties of the cis-trans isomers of propenyl derivatives of phosphorus (^{1}), arsenic (^{2}), antimony (^{3}), bismuth (^{4}), mercury (^{1,5}), and tin (^{1}). Recently Seifert described certain propenyl derivatives of silicon, tin, and germanium (^{6}).

The present work was undertaken with the aim of synthesizing and investigating the properties of stereoisomeric propenyl derivatives of germanium, as well as germanium derivatives containing an isopropenyl group, which have not previously been described in the chemical literature. We synthesized tetra-cis-propenylgermane and tetra-trans-propenylgermane, starting from cis-propenyllithium and, respectively, trans-propenyllithium and germanium tetrachloride.

$$4CH_3CH{=}CHLi + GeCl_4 \rightarrow (CH_3CH{=}CH)_4Ge + 4LiCl.$$

Isopropenyllithium with germanium tetrachloride gives tetraisopropenylgermane. The cis- and trans-isomers of triethylpropenylgermane were obtained by the interaction of triethylgermanium bromide with cis-propenyllithium and, respectively, trans-propenyllithium,

$$CH_3CH{=}CHLi + (C_2H_5)_3GeBr \rightarrow CH_3CH{=}CHGe(C_2H_5)_3 + LiBr,$$

and the reaction of triethylgermanium bromide with isopropenyllithium led to triethylisopropenylgermane.

The configurations of the obtained isomers of tetrapropenylgermane and triethylpropenylgermane were established with the aid of IR absorption spectra. Tetrapropenylgermane, obtained from trans-propenyllithium and germanium tetrachloride, has absorption bands in the region of the C=C bond at 1620 and 975 cm^{-1} for the out-of-plane vibration of $= C - H$, whereas its stereoisomer, obtained from cis-propenyllithium and germanium tetrachloride, has bands at 1605, 925, and 970 cm^{-1} (weak)$*$ (^{7}). On this basis the former was assigned the trans-configuration, and the latter the cis-configuration. Triethylpropenylgermane, synthesized from triethylgermanium bromide and trans-propenyllithium, has an absorption band in the region of the C=C bond at 1615 cm^{-1}, whereas its stereoisomer, obtained from triethylgermanium bromide and cis-propenyllithium, has an absorption band at 1605 cm^{-1}. This allowed the first to be regarded as the trans-isomer and the second as the cis-isomer. Thus, as was to be expected on the basis of the rule established by us in 1948 (^{8}), these exchange reactions proceed with retention of the configuration of the propenyl radical.

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* The vibration frequency 970 cm^{-1} indicates a small impurity of the trans-isomer, which may have formed during synthesis from the trans-propenyllithium present as an impurity.

Table 1

Physical constants of propenylgermanium derivatives

No.	Compound	B.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calculated
1	$\left(\begin{smallmatrix}CH_3\\ H\end{smallmatrix}C{=}C\begin{smallmatrix}H\\ \ \end{smallmatrix}\right)_4Ge$	64–66/1	1.4930	1.0074	68.33	67.20
2	$\left(\begin{smallmatrix}H\\ CH_3\end{smallmatrix}C{=}C\begin{smallmatrix}H\\ \ \end{smallmatrix}\right)_4Ge$	77.5–78.5/4	1.5040	1.0377	67.60	67.20
3	$\begin{smallmatrix}CH_3\\ H\end{smallmatrix}C{=}C\begin{smallmatrix}H\\ Ge(C_2H_5)_3\end{smallmatrix}$	60–62/10	1.4590	1.0108	54.33	54.72
4	$\begin{smallmatrix}H\\ CH_3\end{smallmatrix}C{=}C\begin{smallmatrix}H\\ Ge(C_2H_5)_3\end{smallmatrix}$	58–60/10	1.4625	1.0342	53.44	54.72
5	$[CH_2{=}C(CH_3)]_4Ge$	60–62/2	1.4935	1.0245	67.24	67.20
6	$CH_2{=}C(CH_3)Ge(C_2H_5)_3$	55–56/10	1.4581	—	—	—

Comparison of the molecular refractions of identical pairs of trans- and cis-isomers of tetrapropenylgermanium (Nos. 1, 2, Table 1) and triethylpropenylgermanium (^{3,4}) shows that in both cases the trans-isomers have a greater molecular refraction than their cis-isomers. We previously observed this phenomenon for propenyl cis-trans isomers of antimony (^{9}), mercury (^{9}), bismuth (^{4}), and also for β-chlorovinyl isomers of antimony (^{9}). The same has also been described for β-chlorovinyl compounds of arsenic (^{10}).

Experimental part

Tetra-cis-propenylgermanium. To cis-propenyllithium (^{11}), obtained from 30 g of cis-propenyl bromide and 3 g of lithium in 200 ml of dry ether, 7 g of germanium tetrachloride in 7 ml of ether was slowly added at 0–5°.

After two hours of stirring, the reaction mixture was treated with 200 ml of saturated ammonium chloride solution at 5-10°. The ether layer was separated, and the aqueous layer was extracted with 50 ml of ether. The combined ether solution was dried over calcium chloride. After three quarters of the solvent had been distilled off using a water-jet pump, the reaction product was treated with dry ammonia (^{12}); the precipitate thus formed was filtered off, ether was removed from the filtrate, and the residue was distilled in vacuo. The following fractions were collected:

I. 77.5°/4 mm, 0.94 g, n_D^{20} 1.5004.
II. 77.5-78.5°/4 mm, 2.16 g, n_D^{20} 1.5040, d_4^{20} 1.0347. Yield 28%.
III. 78.5-155°/4 mm, 1.67 g, n_D^{20} 1.5419.
Residue 1.50 g.

For the second fraction, MR found 67.60, MR calculated 67.20*.

Found, %: C 60.67; 60.64; H 8.41; 8.43
$C_{12}H_{20}Ge$. Calculated, %: C 60.84; H 8.51

* Calculated from the refractions of the C–H, C–C, C=C, C–Ge bonds (^{13}).

Tetra-trans-propenylgermane. Under the conditions described for cis-tetrapropenylgermane, from 30 g of trans-propenyl bromide, 3 g of lithium, and 7 g of germanium tetrachloride, the following fractions were obtained by distillation of the residue:

I. 50-64°/1 mm, 0.69 g, n_D^{20} 1.4906.
II. 64-66°/1 mm, 2.55 g, n_D^{20} 1.4930, d_4^{20} 1.0074. Yield 33%.
III. 66-140°/1 mm, 1.73 g, n_D^{20} 1.5150.
Residue 1.00 g.
For fraction II, MR found 68.33, MR calculated 67.20.

Found %: C 61.07; 60.94; H 8.55; 8.54
$C_{12}H_{20}Ge$. Calculated %: C 60.84; H 8.51

Tetra-isopropenylgermane. Under the conditions described for cis-tetrapropenylgermane, from 30 g of isopropenyl bromide, 3 g of lithium, and 7 g of germanium tetrachloride, the following fractions were obtained by distillation:

I. 54-60°/2 mm, 0.63 g, n_D^{20} 1.4878.
II. 60-62°/2 mm, 2.80 g, n_D^{20} 1.4935, d_4^{20} 1.0245. Yield 36%.
III. 62-100°/2 mm, 0.20 g, n_D^{20} 1.4990.
Residue 1.31 g.
For fraction II, MR found 67.24, MR calculated 67.20.

Found %: C 61.09; 61.10; H 8.90; 8.84
$C_{12}H_{20}Ge$. Calculated %: C 60.84; H 8.51

Triethyl-cis-propenylgermane. To cis-propenyllithium, obtained from 5.16 g of cis-propenyl bromide and 0.59 g of lithium in 40 ml of ether, a solution of 10 g of triethylgermanium bromide (2) in 10 ml of ether was added dropwise over 30 min at 0–5°. On the second day the reaction products were decomposed with 70 ml of saturated ammonium chloride solution at 5–10°. The ethereal solution was separated, and the aqueous layer was extracted twice (with 25 ml each time) with ether. The ethereal solutions were combined and dried over calcium chloride.

After removal of the ether, the residue was fractionated. The following fractions were collected:

I. Up to 58°/11 mm, 0.57 g, n_D^{20} 1.4615.
II. 58–60°/11 mm, 6.39 g, n_D^{20} 1.4625, d_4^{20} 1.0342. Yield 77%.
Residue 0.26 g.
For fraction II, MR found 53.44, MR calculated 54.72.

Found %: C 52.71; H 9.63; Ge 35.03
$C_9H_{20}Ge$. Calculated %: C 53.82; H 10.04; Ge 36.15

Triethyl-trans-propenylgermane. Under the conditions described for triethyl-cis-propenylgermane, by reaction of trans-propenyllithium, obtained from 5.16 g of trans-propenyl bromide and 0.59 g of lithium, with 10 g of triethylgermanium bromide, the following fractions were obtained by distillation of the residue:

I. Up to 60°/10 mm, 1.2 g, n_D^{20} 1.4590. Yield 10.4%.
II. 60–62°/10 mm, 5.12 g, n_D^{20} 1.4590, d_4^{20} 1.0108. Yield 61%.
Residue 0.50 g, n_D^{20} 1.4685.
For fraction II, MR found 54.33, MR calculated 54.72.

Found %: C 52.69; H 9.93; Ge 35.87
$C_9H_{20}Ge$. Calculated %: C 53.82; H 10.04; Ge 36.15

Triethyl-isopropenylgermane. Under the conditions described for triethyl-cis-propenylgermane, from 5.16 g of isopropenyl bromide, 0.59 g of lithium, and 10 g of triethylgermanium bromide, after the appropriate treatments and fractionation, the following fractions were obtained:

I. Up to 55°/11 mm, 0.93 g, n_D^{20} 1.4580. Yield 10%.
II. 55–56°/11 mm, 5.45 g, n_D^{20} 1.4581. Yield 66%.
Residue 0.85 g, n_D^{20} 1.4660.

For fraction II

$$C_9H_{20}Ge.$$

Found, %: C 54.29; H 10.13; Ge 35.08
Calculated, %: C 53.88; H 10.04; Ge 36.15

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