METATHESIS OF ALKENYLGERMANES ON A RHENIUM OXIDE CATALYST

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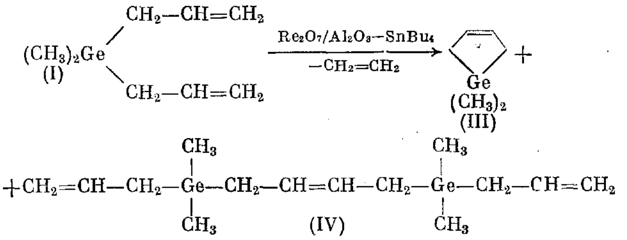
We have previously studied the metathesis of alkenyl derivatives of silicon [1-3]. In the case of the alkenyl derivatives of germanium, Nefedov et al. [4] have reported the polymerization of 1,1-dimethyl-1-germacyclopent-3-ene achieved by metathesis on a $(CO)_5W{:}C(OMe)Ph-TiCl_4$ system. In the present work, we studied the metathesis of alkenyl derivatives of germanium.

Dimethyldiallylgermane (I) and trimethylallylgermane (II) were used as the substrates. Ethylene liberation occurred upon the contact of (I) with a heterogeneous $Re_2O_7/Al_2O_3-SnBu_4$ system in n-heptane (the (I):heptane ratio was varied from 1:4 to 1:50) at 45°, which corresponded to a conversion of (I) from 20% to 50% (the total conversion of (I) varied from 25% to 65%). As in the case of dimethyldiallylsilane [2], the reaction proceeds by both possible pathways with the formation of 1,1-dimethyl-1-germacyclopent-3-ene (III) by an intramolecular mechanism and of 4,4,9,9-tetramethyl-4,9-digerma-1,6,11-dodecatriene (IV) by an intermolecular mechanism.



The structure of (III) was confirmed chromatographically and by comparison of its mass spectrum obtained in the chromato-mass spectral analysis of the reaction mixture with that of an authentic sample of (III) prepared according to Mironov and Gar [5]. The structure of (IV) was established by the analogy of the mass spectrum of (IV) and that of the previously studied silicon analog [2]. In both cases with the absence of a molecular ion peak, the peak with highest mass corresponded to $[M - C_3H_5]^+$ while the major peak corresponded to the $[All - EMe_2]^+$ (E = Si and Ge). The other ions present also correspond to analogous structural fragments. The yield of germacyclopentene (III) was 5-7% in the case of a 1:10 (I)/heptane ratio and 9-10% in the case of a 1:50 (I)/heptane ratio. The yield of the linear metathesis product (IV) varied from 10 to 25%.

In the metathesis of (II) with (II)/heptane ratio from 1:1 to 1:10 and 45°C contact temperature, the conversion relative to ethylene was 35-45% and the total conversion was 40-55%. The metathesis product in this case is 2,2,7,7-tetramethyl-2,7-digerma-4-octene (V)

$$2\underset{(II)}{(CH_3)_3Ge-CH_2-CH=CH_2}\xrightarrow[-CH_2=CH_2]{Re_2O_7/Al_2O_3-SnBu_4}\underset{(V)}{(CH_3)_3GeCH_2-CH=CH-CH_2-Ge(CH_3)_3}$$

Product (V) was isolated by fractional distillation in yields of about 30% and was characterized. The physical constants of this product are similar to literature values [6] and its mass spectrum was identical to that of an authentic sample prepared according to Gar et al. [6].

We should note that there is some discrepancy between the conversion relative to ethylene liberated and the total conversion (relative to unreacted starting material) in the metathesis of (II) (as in the case of (I)). This behavior is likely a consequence of condensation at the allyl groups without the liberation of ethylene. The chromato-mass spectral analysis of the reaction mixture showed the presence of dimer (II), whose mass spectrum contains a molecular ion with m/z 312 and a peak corresponding to $[M - CH_3]^+$.

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Thus, despite the well-known lability of the Ge−All bond relative to the Si−All bond in various reactions (for example, the Ge−All bond is cleaved by hydrogen halides even at −80°C [6]), its presence in mono- and dialkenylgermanes does not hinder their metathesis by the action of the $Re_2O_7/Al_2O_3-SnBu_4$ system.

In conclusion, we note that the purity of the substrates used plays an extremely important role in the success of the metathesis reaction of alkenyl derivatives of group IVB elements.

EXPERIMENTAL

The chromato-mass spectral analysis was carried out on an LKB-2091 instrument using an SE-30 column.

The sample of dimethyldiallylgermane (I) obtained by the methylation of diallylgermane had bp 145.5-146°C, d_4^{20} 1.035, and n_D^{20} 1.4641 [7]. This sample was purified by chromatography on an alumina column. The sample of trimethylallylgermane (II) synthesized according to Petrov et al. [7] had bp 100°, d_4^{20} 0.9935, n_D^{20} 1.4330 and was further purified by chromatography on an alumina column.

Metathesis of Dimethyldiallylgermane (I). The catalyst was prepared by our previous method. The metathesis was carried out for a solution of 5.25 g (0.03 mole) (I) in 45 ml heptane in the presence of 3 g $Re_2O_7/Al_2O_3-SnBu_4$. The catalysate was filtered and distilled. Chromato-mass spectroscopy showed that the catalysate contained 6% (III) and 27% (IV). A tarry product was obtained in about 30% yield in the residue. Mass spectrum of (III), m/z (%): 154* ($[M]^+$, 50), 139 ($[M-CH_3]^+$, 48), 100 ($[M-C_4H_6]^+$, 91), 85 (100), 71 (16.5), 70 (7), 69 (3.5), 57 (21), 56 (9.5), 55 (9), 44 (18), 43 (19), 42 (12), 41 (22.5), 40 (41.5). Mass spectrum of (IV), m/z(%): 295 ($[M-C_3H_5]^+$, 47), 267 (24.5), 257 (81), 241 (36), 217 (10.5), 201 (16), 153 (13), 141 ($[AllGeMe_2]^+$, 100), 139 (17), 115 ($[GeMe_3]^+$, 65), 101 (44.5), 100 ($[GeMe_2]^+$, 15.5), 85 (53).

2,2,7,7-Tetramethyl-2,7-digerma-4-octene (V). By analogy, the metathesis was carried for a solution of 6.3 g (0.04 mole) (II) in 60 ml heptane in the presence of 5 g $Re_2O_7/Al_2O_3-SnBu_4$. A sample of (V) with bp 80°C (9 mm), d_4^{20} 1.12, and n_D^{20} 1.4715 was obtained after filtration of the catalysate and removal of the solvent by vacuum distillation of the residue. A yield of about 15% condensation products was obtained in the final residue. Mass spectrum of (V), m/z(%): 284 ($[M]^+$, 8.5), 231 ($[M-C_4H_5]^+$, 1), 230 ($[M-C_4H_6]^+$, 1), 215 (1.5), 169 (2.5), 154 (17), 139 (6), 115 $[GeMe_3]^+$, 100), 100 ($[GeMe_2]^+$, 14), 85 (15.5), 71 (2.3), 70 (1.5).

The authors express their gratitude to T. K. Gar for providing authentic samples of 1,1-dimethyl-1-germacyclopent-3-ene and 2,2,7,7-tetramethyl-2,7-digerma-4-octene.

CONCLUSIONS

Feasibility was demonstrated for the metathesis of dimethyldiallylgermane on a rhenium oxide/alumina catalyst with the formation of dimethylgermacyclopentene and a linear product, 4,4,9,9-tetramethyl-4,9-digerma-1,6,11-dodecatriene. The metathesis of trimethylallylgermane leads to the quantitative preparation of 2,2,7,7-tetramethyl-2,7-digerma-4-octene.

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* In all cases, the mass spectral data are given for monoisotopic spectra for the ^{70}Ge isotope.