SYNTHESIS AND PROPERTIES OF SILICON- AND GERMANIUM-CONTAINING HYDROCARBONS OF THE CYCLOPROPANE SERIES

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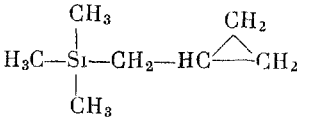
We obtained Si- and Ge-containing hydrocarbons of the cyclopropane series by Simmons and Smith's method [1], i e , by the reaction of trimethylallylsilane, trimethylallylgermane, trimethylvinylsilane, and triethylvinylsilane with methylene iodide in the presence of a zinc-copper couple prepared by an improved Shank and Shechter method [2]. Whether the double bond was α- or β-to the silicon or germanium atom in the initial compound, the yield of the cyclopropane derivative was about 30% When methylene iodide reacted with the hydrocarbon analog of trimethylallylsilane and trimethylallylgermane, 4,4-dimethylpentene-1, neopentylcyclopropane was also obtained in a yield of only 5% This showed that the element in the β-position to the double bond in trimethylallylsilane, trimethylallylgermane, and 4,4-dimethylpentene-1 does not have an important effect on the yield of the hydrocarbons with the threemembered ring The Raman spectra of all the products were obtained, and it was seen by examining the spectra that only in the case of trimethylgermylmethylcyclopropane was a noteworthy amount of an unsaturated compound produced that could not be separated by distillation. Evidently the unsaturated compound was produced by rearrangement of trimethylgermylmethylcyclopropane, so that it had the same composition

EXPERIMENTAL SECTION

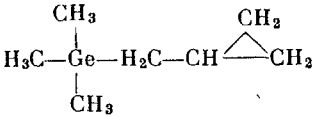
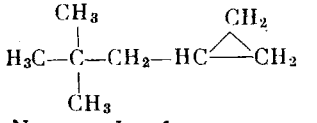
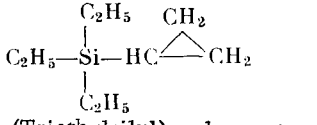
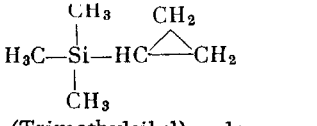
Trimethylallylsilane was synthesized from trimethylchlorosilane and allylmagnesium bromide, b.p 85-86° (760 mm), d_4^{20} 0.7170, n_D^{20} 1 4070 Literature data [3]. b.p 85 4° (752 mm), d_4^{25} 0.7195, n_D^{20} 1.4075. Trimethylvinylsilane was obtained from vinyltrichlorosilane and methylmagnesium bromide, b.p. 55.5° (755 mm) d_4^{20} 0.6897, n_D^{20} 1.3906. Literature data [3] b.p. 54.6° (744 mm); d_4^{20} 0.6903, n_D^{20} 1.3910. Triethylvinylsilane was obtained from vinyltrichlorosilane and ethylmagnesium bromide, yield 90%, b.p. 171-172° (760 mm), d_4^{20} 0.7870, n_D^{20} 1.4438. Literature data [3] b.p. 170-172° (753 mm), d_4^{20} 0.7873, n_D^{20} 1.4445. Trimethylallylgermane was obtained from allyltrichlorogermane and methylmagnesium bromide. b.p. 100° (757 mm), d_4^{20} 0.9930, n_D^{20} 1.4327. Literature data [4] b.p. 101° (764 mm), d_4^{20} 0.9952, n_D^{20} 1.4333. 4,4-Dimethylpentene-1 was prepared from allyl bromide and tert butylmagnesium chloride b.p. 71.6° (756 mm), d_4^{20} 0.6821, n_D^{20} 1.3916. Literature data [5] b.p. 72.1° (760 mm), d_4^{20} 0.6827, n_D^{20} 1.3918.

(Trimethylsilylmethyl)cyclopropane



A mixture of 53.6 g methylene iodide, 0 15 g iodine, 16 3 g zinc-copper couple, and 165 ml ether was heated for 30 min in a flask fitted with a reflux condenser and a stirrer. Then 34 g of trimethylallylsilane was added and the heating continued for 30 h The mixture was filtered and the filtrate washed with 5% HCl (3.50 ml), 50 ml of saturated soda solution, 50 ml of saturated NaCl solution, dried with calcium chloride, the ether removed, and the residue distilled. Trimethylsilylmethylcyclopropane was obtained in a yield of 38% (10 g), b.p. 113-114.5° (740 mm), d_4^{20} 0.7594, n_D^{20} 1.4168. Found C 65.67, 65.48, H 12.60, 12 51, Si 21 80, 21.84% MR 42.47. $C_7H_{16}Si$. Calculated C 65 54, H 12.57, Si 21.88%, MR 42.66.

The other hydrocarbons mentioned in the table were obtained in similar conditions.

Starting material	Product	Yield, (%)	b.p., °C (p, mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	C, % found	C, % calc.	H, % found	H, % calc.	Si, % found	Si, % calc.	Ge, % found	Ge, % calc.
Trimethyl-allylgermane	 (Trimethylgermylmethyl)cyclopropane	32,3	126 (745)	1,0290	1,4355	43,86	44,34							43,22 43,41	42,01
4,4-Dimethyl-pentene-1	 Neopentylcyclopropane	35,7	106—106,2 (760)	0,7376	1,4086	37,57	37,76	85,77 85,58	85,63	14,21 14,20	14,37				
Triethylvinyl-silane	 (Triethylsilyl)cyclopropane	29,2	173,3—174 (748)	0,8095	1,4444	51,34	51,95	69,44 69,30	69,15	12,86 12,70	12,89	17,99 17,90	17,95	—	—
Trimethylvinyl-silane	 (Trimethylsilyl)cyclopropane	—	90 (745)	0,7523	1,4093	37,56	38,01	62,47 62,28	63,08	12,36 12,14	12,35				

Raman spectra of the synthesized compounds, $\Delta\nu$ cm^{-1},

(Trimethylsilylmethyl)cyclopropane 182 (30b), 192 (35b), 228 (35 b), 332 (25), 533 (10), 595 (150), 690 (35), 768 (25), 811 (25), 896 (35), 960 (20), 1100 (10), 1192 (40b), 1211 (35), 1242 (5b), 1363 (20), 1401 (20), 1421 (15), 1456 (5), 2871 (40), 2900 (150), 2953 (130), 3008 (80), 3075 (15).

(Trimethylgermylmethyl)cyclopropane 183 (100b), 272 (5), 310 (20), 376 (5b), 468 (10b), 508 (10b), 520 (15b), 568 (150b), 602 (100b), 632 (20), 772 (10), 822 (10b), 900 (20), 960 (10), 1018 (5), 1140 (5), 1197 (30), 1220 (5), 1242 (35), 1301 (7), 1367 (10), 1422 (10b), 1610 (5), 1642 (15), 2852 (10), 2909 (130), 2980 (80), 3010 (60), 3075 (10).

Neopentylcyclopropane 292 (10), 315 (15), 340 (15), 500 (20), 738 (50), 776 (20), 800 (15), 822 (20), 872 (20b), 895 (30b), 932 (30 b), 982 (25), 1036 (10), 1107 (10), 1137 (15b), 1192 (40b), 1218 (10), 1252 (15), 1292 (5), 1320 (15), 1383 (25b), 1447 (30b), 2840 (20), 2865 (30), 2908 (120), 2962 (100), 3008 (130), 3075 (10).

(Triethylsilyl)cyclopropane 295 (10), 405 (10), 492 (10), 543 (100), 632 (15b), 653 (15b), 718 20b), 732 (20), 790 (10), 841 (50), 901 (30), 980 (30), 1018 (15b), 1035 (20), 1110 (15), 1128 (20), 1191 (100), 1242 (30), 1292 (10), 1377 (15), 1417 (30), 1467 (50), 2882 (120), 2917 (100), 2950 (20), 2960 (80), 3008 (100), 3075 (10).

SUMMARY

1. Hydrocarbons of the cyclopropane series containing silicon and germanium have been obtained for the first time and their properties described.

2. In the reaction of the unsaturated silicon-hydrocarbons studied with methylene iodide in the presence of a zinc-copper couple, neither the α- or β-position of the double bond relative to silicon (in the cases of the trimethyl- and trimethylvinyl-silane) nor the nature of the element in the β-position to the double bond (in the cases of trimethylallylsilane, trimethylallylgermane, and 4,4-dimethylpentene-1) showed a marked effect on the yield of the cyclopropane derivatives

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**
