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Abstract

Full Text

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SYNTHESIS AND PROPERTIES OF DIMETHYLDI-(CYCLOPROPYLMETHYL)-, METHYLTRI-(CYCLOPROPYLMETHYL)-, AND TETRA-(CYCLOPROPYLMETHYL)-SILANES

(Presented by Academician A. A. Balandin, August 28, 1963)

Simmons and Smith (^{1}), by the interaction of methylene iodide in the presence of a zinc–copper couple with hexadiene-1,5, obtained 4-cyclopropylbutene-1 in 18% yield and 1,2-dicyclopropylethane in 36% yield. Nakhapetyan, Safonova, and Kazanskii (^{2}), by the reaction of methylene iodide with isoprene, obtained, along with alkenylcyclopropanes, 1-methyl-1-cyclopropylcyclopropane in low yield. These are the two examples known to us of the synthesis of dicyclopropane hydrocarbons by the reaction of dienes with methylene iodide. Earlier we (^{3}), and independently Seyferth (^{4}), showed that under the conditions of the Simmons–Smith reaction methylene iodide forms, with α- and β-monoalkenylsilanes, the corresponding silicon-containing cyclopropane derivatives in yields of about 30%.

In the present work we carried out the reaction of methylene iodide in the presence of a zinc–copper couple with organosilicon unconjugated di-, tri-, and tetraenes. In carrying out the reaction with dimethyldiallylsilane we obtained dimethyldi-(cyclopropylmethyl)-silane in 32% yield. It was not possible to isolate the product of the interaction of methylene iodide with only one double bond of dimethyldiallylsilane, namely dimethylallyl-(cyclopropylmethyl)-silane. By the reaction of methylene iodide under the same conditions with methyltriallylsilane, methyltri-(cyclopropylmethyl)-silane was obtained in 26% yield. This is the second (^{5}) of the known hydrocarbons containing three three-membered carbon rings, and the first hydrocarbon of this type containing a silicon atom. However, in the fraction isolated during rectification of the reaction mixture and boiling somewhat below the named hydrocarbon, according to the GLC spectrum, there was detected a certain (10–15%) impurity of an unsaturated hydrocarbon, which evidently was methylallyldi-(cyclopropylmethyl)- or methyldiallyl-(cyclopropylmethyl)-silane, or a mixture of them.

For the hydrocarbons obtained, G. K. Gaivoronskaya recorded GLC spectra; judging from these, these compounds contain no impurity of alkenyl- and cycloalkylalkenylsilanes.

In carrying out the reaction of methylene iodide in the presence of a zinc–

copper couple with tetraallylsilane, we obtained, in about 13% yield, a silicon hydrocarbon which, by its boiling point and elemental-analysis data, is evidently tetra-(cyclopropylmethyl)-silane.

Experimental Part*

Dimethyldiallylsilane was obtained in 73.5% yield from dimethyldichlorosilane and allyl bromide by the Grignard reaction, b.p. 135.5° (760 mm). Literature data (6): b.p. 136.8° (759 mm).

Methyltriallylsilane was synthesized from methyltrichlorosilane and allyl bromide by the Grignard reaction in 68% yield, b.p. 70–71° (24 mm), n_D^{20} 1.4645. Literature data (6): b.p. 180.3° (745 mm), n_D^{20} 1.4662.

Tetraallylsilane was obtained by the Grignard reaction from silicon tetrachloride and allyl bromide in 78% yield, b.p. 102° (13 mm), n_D^{20} 1.4860. Literature data (7): yield 37%, b.p. 90.5° (10 mm), n_D^{20} 1.4840.

* I. V. Vikha took part in the experimental work.

Dimethyl-di-(cyclopropylmethyl)-silane.

$$H_2C\triangle CH{-}CH_2{-}Si(CH_3)_2{-}H_2C{-}HC\triangle CH_2$$

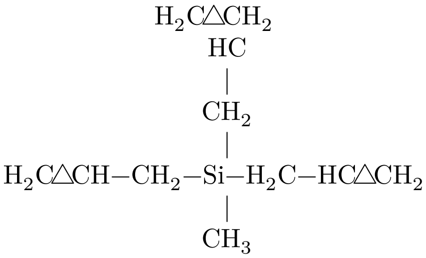
The reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel, and stirrer. To 51 g of freshly prepared zinc-copper couple and 200 ml of ether were added 188 g of methylene iodide and a catalytic amount of metallic iodine. The mixture was boiled for 30 min, after which 42 g of dimethyldiallylsilane was rapidly added dropwise, and heating was continued for 20 h. The liquid phase was then decanted, washed with 5% hydrochloric acid solution, saturated sodium bicarbonate solution, and dried over calcium chloride. After removal of the ether, rectification of the residue gave 16 g of dimethyl-di-(cyclopropylmethyl)-silane, yield 32%, b.p. 70.5–71° (25 mm), d_4^{20} 0.8268, n_D^{20} 1.4500.

Found, %: C 71.36, 71.32; H 12.04, 12.07; Si 16.76, 16.88
$C_{10}H_{20}Si$. Calculated, %: C 71.35; H 11.97; Si 16.67

MR_D found 54.71, calculated 55.13.

Raman spectrum in cm^{-1}: 268(5), 330(35), 608(100), 690(25), 736(10), 775(40), 817(40), 902(60), 965(25), 989(10), 1105(10), 1135(15), 1196(broad), 1218(30sh), 1355(30), 1410(20), 1439(30), 1460(20), 2871(80), 2904(120), 2963(80), 3008(150), 3075(60sh).

Methyltri-(cyclopropylmethyl)-silane.



$$\begin{array}{c} \mathrm{H_2C\triangle CH_2} \\ \mathrm{HC} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{H_2C\triangle CH{-}CH_2{-}Si{-}H_2C{-}HC\triangle CH_2} \\ | \\ \mathrm{CH_3} \end{array}$$

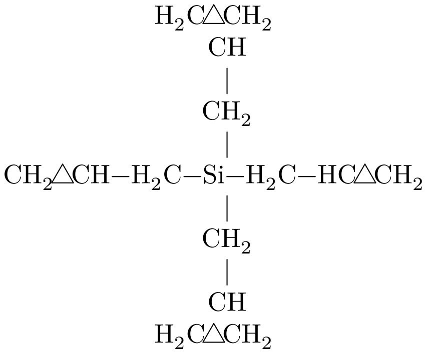
To 35 g of zinc-copper couple and 200 ml of absolute ether were added a catalytic amount of iodine and 150 g of distilled methylene iodide. The reaction mixture was boiled for 30 min, after which 24 g of methyltriallylsilane was rapidly added dropwise, and boiling was continued for a further 20 h. The mixture was then treated as in the synthesis of the preceding silicon hydrocarbon and distilled. There were obtained 8 g of methyltri-(cyclopropylmethyl)-silane, yield 26%, b.p. 110–113° (15 mm), d_4^{20} 0.8705, n_D^{20} 1.4718.

Found, %: C 75.16, 74.95; H 11.71, 11.62; Si 13.07, 13.17
$C_{13}H_{24}Si$. Calculated, %: C 74.92; H 11.60; Si 13.46

MR_D found 67.00, calculated 67.59.

Spectrum* of Raman scattering in cm^{-1}: 145(1), 312(2), 605(2), 667(0), 710(0), 767(2), 808(1sh), 896(3sh), 961(2), 1102(1sh), 1036(1sh), 1198(4), 1219(2), 1300(0), 1360(2), 1400(1), 1425(2), 1455(1), 2868(2sh), 2895(2sh), 2956(1), 3005(4), 3080.

Tetra-(cyclopropylmethyl)-silane.



$$\begin{array}{c} \mathrm{H_2C\triangle CH_2} \\ \mathrm{CH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2\triangle CH{-}H_2C{-}Si{-}H_2C{-}HC\triangle CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH} \\ \mathrm{H_2C\triangle CH_2} \end{array}$$

To 70 g of the zinc-copper couple, 200 ml of absolute ether, and several crystals of iodine were added 285 g of methyl iodide. The mixture was boiled for 30 min with stirring, after which 43 g of tetraallylsilane was added dropwise and heating was continued with stirring for 20 h. The reaction mixture was then worked up as in the preceding experiments, and the resulting mixture of silicon hydrocarbons was distilled in vacuo. A fraction with b.p. 130-132° (5 mm) was isolated in an amount of 7 g (12.9%); after redistillation over metallic sodium it had b.p. 120-121° (3 mm), d_4^{20} 0.9434, n_D^{20} 1.4795.

Found, %: Si 11.97, 12.13
$C_{16}H_{28}Si$. Calculated, %: Si 11.29

In addition, a fraction with b.p. 132-261° (3-5 mm) was obtained, which was evidently a mixture of products of the interaction of methyl iodide with tetraallylsilane and products of polymerization of the latter.

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Note: Figure translations are in progress. See original paper for figures.

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