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Abstract

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ISOMERIC SILAPENTANES AND NEW ROUTES FOR THEIR SYNTHESIS

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The known silicon hydrocarbons of the type R_nSiH_{4-n}, where R is alkyl and $n = 1, 2$, are few in number, and their properties have been studied quite insufficiently. Practically the only method for their preparation is the reduction of the corresponding alkylchlorosilanes with lithium aluminum hydride (^{1}):

$$R_nSiCl_{4-n} + (4-n)LiAlH_4 \rightarrow R_nSiH_{4-n} + (4-n)(LiCl + AlCl_3) \quad (1)$$

or the interaction of the corresponding halosilanes X_nSiH_{4-n} with organometallic compounds (^{2}). At the same time, alkylsilanes are of considerable interest both because of the specificity of their characteristic chemical reactions, due to the presence of several reactive Si–H bonds, and because of the abundance of structural isomers corresponding to a single empirical formula.

To elucidate the little-studied question of the influence of the position of the silicon atom in the silicon-carbon skeleton on the properties of alkylsilanes, we synthesized a series of silapentanes $C_4H_{12}Si$, which may be regarded as the corresponding pentanes in which one of the carbon atoms is replaced by silicon. To obtain isomeric silapentanes, new routes for their synthesis were developed, represented by the schemes:

$$2RR'SiHCl \xrightarrow{AlCl_3} RR'SiH_2 + RR'SiCl_2 \quad (2)$$

$$R = CH_3,\ C_2H_5; \quad R' = C_2H_5,\ n\text{-}C_3H_7,\ i\text{-}C_3H_7; \quad R + R' = C_4H_{10}$$

$$R_nSiX_{4-n} + (4-n)R'_3SiH \xrightarrow{AlCl_3} R_nSiH_{4-n} + (4-n)R'_3SiX \quad (3)$$

$$R = C_2H_5,\ C_4H_9 \text{ and others}; \quad R' = C_2H_5; \quad n = 1, 2; \quad X = Cl, Br$$

$$4CH_3(C_2H_5)_2SiH \xrightarrow{AlCl_3} 2C_2H_5(CH_3)_2SiH + (C_2H_5)_2SiH_2 + (C_2H_5)_4Si \quad (4)$$

Dialkylchlorosilanes, when heated in the presence of 8-10 mol. % $AlCl_3$, react according to scheme (2) to an extent of 65-70%, the yield of the very volatile dialkylsilanes being 45-60% of theory. The results of the catalytic reduction of alkylhalosilanes by triethylsilane (3), carried out during fractional distillation of a stoichiometric mixture of the reagents, are given in Table 1.

Table 1

Reduction of alkylhalosilanes by triethylsilane

Alkylhalosilane	Amount of catalyst, mol. %	Conversion of alkylhalosilane to alkylsilane, %	Reaction product	Yield based on reacted alkylhalosilane, %
$(C_2H_5)_2SiCl_2$	1.0	100	$(C_2H_5)_2SiH_2$	52.8
$(C_2H_5)_2SiBr_2$	1.5	100	Same	59.2
CH_3-n-$C_3H_7SiCl_2$	1.2	36.5	CH_3-n-$C_3H_7SiH_2$	61.8
Same	4.0	81.3	CH_3-iso-$C_3H_7SiH_2$(!)	47.0
n-$C_4H_9SiCl_3$	2.0	90.0	n-$C_4H_9SiH_3$	98.0
iso-$C_4H_9SiCl_3$	1.3	76.9	iso-$C_4H_9SiH_3$	98.2
sec-$C_4H_9SiCl_3$	1.4	72.3	sec-$C_4H_9SiH_3$	97.5

The data in Table 1 show that the degree of conversion of alkylhalosilanes into alkylsilanes, and the structure of the latter, are determined both by the structure of the initial halosilane and by the amount of catalyst—$AlCl_3$ (the reduction of methylpropyldichlorosilane may be accompanied by isomerization of the propyl radical).

Table 2

Properties of isomeric silapentanes and pentanes

Skeleton structure	b.p., °C (at 760 mm)	n_D^{20}	d_4^{20}	V^{20}	R_D^{20}	H(Si), %, found	H(Si), %, calc.
C–C –C– C–C	36.1	1.3575	0.6262	115.09	0.3502	–	–
C–C –C– Si– C*	53.6	1.3857	0.6738	130.94	0.3484	2.21	2.28
C–C –C– C–Si	54.1	1.3912	0.6756	130.59	0.3518	3.23	3.43
C–C –Si– C–C	55.6	1.3916	0.6837	129.04	0.3480	2.18	2.28
Si–C –C– C–Si	78.0	1.4235	0.7276	143.35	0.3504	–	–
C C– C– CC /	27.9	1.3536	0.6196	116.29	0.3505	–	–
C Si –C– CC /	45.7	1.3783	0.6681	132.06	0.3453	1.05	1.14
C C– Si– C*C /	49.4	1.3790	0.6650	132.67	0.3475	2.21	2.28
C C– C– SiC /	49.5	1.3890	0.6720	131.29	0.3519	3.05	3.43
Si C –C– C*C /	49.3	1.3898	0.6738	130.94	0.3517	3.10	3.43
Si C –C– SiC /	95(?)	–	–	–	–	–	–
· C C / CC / C	9.5	1.3513**	0.613**	117.7**	0.352**	–	–
C Si / CC / C	26.2	1.3588	0.6399	137.87	0.3439	–	–

Skeleton structure	b.p., °C (at 760 mm)	n_D^{20}	d_4^{20}	V^{20}	R_D^{20}	H(Si), %, found	H(Si), %, calc.
C C / CC / Si	84.4	–	–	–	–	–	–

* New compound. ** At 0°.

Table 2 gives the properties of the 8 silapentanes obtained by us, as well as tert-butylsilane (2) and two disilapentanes—1,2- and 1,3-disilylpropanes (3,4)—in comparison with their hydrocarbon analogues, the isomeric pentanes (5).

It was noted earlier (4,6) that replacement of carbon atoms in hydrocarbons by silicon increases the polarizability of the molecule. This, together with the greater atomic weight of silicon and more significant intermolecular interaction, leads to an increase in molecular volume (by 14-16 ml/mole), boiling point (by 16-22°), specific gravity (by 0.04-0.06 g/ml), and refractive index (0.02-0.04). In the case of silapentanes it becomes obvious that such a change in physical properties is determined not only by the very fact of replacing a carbon atom in a given hydrocarbon by silicon, but also by the position of the silicon atom in the silicon-carbon skeleton, which is partly associated with the number of Si—H bonds. For this reason, it is hardly expedient to compare the properties of silicon hydrocarbons with those of hydrocarbons having a similar skeletal structure. Thus, for example, of the nine isomeric silapentanes, three are analogous in structure to *n*-pentane, four to isopentane, and two to neopentane. The formal nature of making such an analogy is obvious: chemically inert, because of the absence of reactive bonds at the silicon atom, nonpolar tetramethylsilane and polar tert-butylsilane, which possesses three reactive Si—H bonds, are structural analogues

neopentane. From a comparison of silicon hydrocarbons having the same skeletal structure with one another and with alkanes analogous to them in structure, it is difficult to find a general regularity in the change of physical properties. It is therefore more expedient to classify silicon hydrocarbons not from the standpoint of their analogy to hydrocarbons, but according to the electronic state of the silicon atom in them. In alkylsilanes silicon may possess four different "sets of bonds": a) 4 Si—C bonds (SiR_4); b) 3 Si—C bonds and 1 Si—H bond (R_3SiH); c) 2 Si—C bonds and 2 Si—H bonds (R_2SiH_2); d) 1 Si—C bond and Si—H bonds ($RSiH_3$). One may therefore speak of a primary, etc. (up to quaternary) silicon atom in alkylsilanes. This makes it possible to combine silicon hydrocarbons with the same "set of bonds" at the Si atom, but with a different structure of the silicon-carbon skeleton, which permits the regularities in the properties of alkylsilanes associated already with the "positional isomerism" of the silicon atom in the silicon-carbon skeleton and with "isomerism of the hydrocarbon radical" at the silicon atom to be revealed.

Fig. 1. Rate of hydrolysis of 0.001 g-mol of isomeric silapentanes with 20% aqueous NaOH at 750 mm and 18°. 1—(CH3)2C2H5SiH; 2—(C2H5)2SiH2; 3—CH3(n-C3H7)SiH2; 4—CH3(iso-C3H7)SiH2; 5—n-, iso- and sec-C4H9SiH3.

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1—$(CH_3)_2C_2H_5SiH$; 2—$(C_2H_5)_2SiH_2$; 3—$CH_3(n\text{-}C_3H_7)SiH_2$; 4—$CH_3(\text{iso-}C_3H_7)SiH_2$; 5—*n*-, iso- and sec-$C_4H_9SiH_3$.

The rate of the alkaline hydrolysis reaction of silapentanes decreases from $RSiH_3$ to R_3SiH (Fig. 1). In the same order the specific refraction also changes ($RSiH_3 > R_2SiH_2 > R_3SiH > R_4Si$). In decreasing mobility of the hydrogen atom at silicon, silapentanes with a secondary silicon atom are arranged, in turn, in the series:
$CH_3\text{-iso-}C_3H_7SiH_2 > CH_3\text{-}n\text{-}C_3H_7SiH_2 > (C_2H_5)_2SiH_2$*. In exactly the same order all the physical constants (b.p., d_4^{20}, n_D^{20}, R_D^{20}) of the indicated dialkylsilanes also increase.

As was to be expected, the influence of radical isomerism on the course of change in the physical constants of butylsilanes is of the same character as, for example, in the case of isomeric butyl alcohols. The structure of the radical in $C_4H_9SiH_3$ is little reflected in the mobility of the Si—H bond (the rate of hydrolysis of the three isomeric butylsilanes is almost identical). Among isomers with the same skeletal structure, alkylsilanes $RSiH_3$ possess the highest values of boiling point, refractive index, and refraction, while tri- and tetraalkylsilanes R_3SiH and R_4Si possess the lowest. At the same time dialkylsilanes R_2SiH_2 have the greatest volatility. Comparison of the properties of silapentanes and disilapentanes makes it evident that the b.p. of 1,2-disilylpropane (95°) reported in the literature (3) is not correct. It should be expected that $H_3SiCH_2CH(CH_3)SiH_3$ has a b.p. of about 73°.

Experimental Part

The synthesis of alkylsilanes according to schemes (2) and (3) was carried out under identical conditions. We give the most characteristic examples.

Diethylsilane. 30.9 g (0.25 g-mol) of diethyldichlorosilane was slowly distilled over 3.1 g (0.023 g-mol; 9.2 mol. %) of $AlCl_3$. On repeated distillation—

* The greater reactivity of methylisopropylsilane is due to the maximal $+I$-effect of the substituents (isopropyl group), causing polarization of the bond

$$\overset{\delta+}{Si} - \overset{\delta-}{H}.$$

In the distillate, 3.8 g of diethylsilane with b.p. 54-57° (44.2%); 7.0 g of unreacted $(C_2H_5)_2SiHCl$ (22.7% of the initial amount), and 12.3 g of diethyldichlorosilane with b.p. 127-129° (80.4% of theory, calculated on reacted diethylchlorosilane) were obtained. Conversion of $(C_2H_5)_2SiHCl$: 77.3%.

Butylsilane. On distillation in a rectification column of a mixture consisting of 26.6 g (0.14 g-mol) of n-$C_4H_9SiCl_3$, 48.5 g (0.42 g-mol) of $(C_2H_5)_3SiH$, and 1.5 g (0.011 g-mol; 2 mole %) of $AlCl_3$, the following fractions were obtained: I (52-56°), 10.8 g (butylsilane); II (56-143°), 2.2 g; III (143-147°), 55.7 g (Cl 25.0%, which corresponds to a mixture containing 95.2% $(C_2H_5)_3SiCl$ and 4.8% $C_4H_9SiCl_3$); IV (above 147°), 6.1 g. Ninety percent of the initial n-$C_4H_9SiCl_3$ reacted. The yield of butylsilane was 98%, calculated on reacted n-$C_4H_9SiCl_3$.

Methylisopropylsilane. On fractionation of a mixture consisting of 20.6 g (0.13 g-mol) of methyl-n-propyldichlorosilane, 30.6 g (0.26 g-mol) of triethylsilane, and 2.1 g (0.016 g-mol; 4 mole %) of $AlCl_3$, 4.4 g of methylisopropylsilane with b.p. 48-52° (47%), 4.4 g of unreacted triethylsilane (14.3% of the initial amount), 3.9 g of unreacted $CH_3(C_3H_7)SiCl_2$ (18.7% of the initial amount), and 30.1 g of triethylchlorosilane (93.5%, calculated on methyl-n-propyldichlorosilane that entered into the reaction) were obtained. Conversion of $CH_3(C_3H_7)SiCl_2$: 81.3%. When the reaction was carried out with 1 mole % $AlCl_3$, the reduction proceeded normally and methyl-n-propylsilane was formed in 62% yield.

Dimethylethylsilane. A mixture consisting of 30.6 g (0.3 g-mol) of methyldiethylsilane and 1.5 g (0.0113 g-mol; 3.8 mole %) of $AlCl_3$ was boiled in the flask of a rectification column for 3 hours; during this time the temperature of the reflux decreased from 75 to 44°. On taking off the distillate, 9.8 g of dimethylethylsilane with b.p. 44-48° (81.2%), 4.0 g of diethylsilane with b.p. 53-58° (66.2%), 2.7 g of unreacted methyldiethylsilane (8.8% of the initial amount), and 7.7 g of tetraethylsilane with b.p. 149-151° (n_D^{20} 1.4267; d_4^{20} 0.7729; 77.9%) were obtained. Conversion of methyldiethylsilane: 91.2%.

All the silapentanes investigated are colorless, mobile, volatile liquids with a sharp hydrocarbon odor, not self-igniting in air.

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