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Abstract

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ON THE ADDITION OF METHYLHYDRIDOSILICACYCLOALKANES AND THEIR OPEN-CHAIN ANALOGS TO ETHYLENE

The addition reaction of hydridosilanes to olefins, important from both the preparative and practical standpoints, has now been extensively investigated using examples of alkyl- (as well as chloro-, aryl-, alkenyl-) hydridosilanes ([1], [2]). In this reaction, in particular, the influence of various radicals attached to the Si—H group on the reactivity of hydridosilanes has been studied ([1]-[3]).

The aim of the present work was to determine the possibilities for synthesizing 1,1-substituted 1-silicacycloalkanes, using as an example the interaction of hydride derivatives of silicacycloalkanes with ethylene. It also seemed of interest to determine the comparative activity in this reaction of silicacycloalkanes of the series [$H(CH_3)Si(CH_2)_n$], with $n = 3; 4; 5$, as a function of ring size, and to compare it with the activity of open-chain analogs of the indicated silicacycloalkanes.

Table 1

Hydridosilane	Reaction temperature, °C	Percent addition to ethylene after 1 h	Percent addition to ethylene after 3 h	Percent addition to ethylene after 5 h
$H(CH_3)Si(CH_2)_3$	20	–	–	> 30
$H(CH_3)Si(C_2H_5)(CH_3)$	20	–	–	0
$H(CH_3)Si(CH_2)_4$	20	–	–	~ 5
$H(CH_3)Si(CH_2)_4$	45	38	> 97	–
$H(CH_3)Si(CH_2)_4$	70	65	> 97	–
$H(CH_3)Si(C_2H_5)_2$	45	8	30	60
$H(CH_3)Si(CH_2)_5$	70	35	> 90	–
$H(CH_3)Si(C_2H_5)(C_3H_7)$	70	10	20	38

In the literature ([4]), with regard to the question of interest to us, there were data only on the addition reaction of methylhydridosilicacyclopentane to cyano-containing olefins; the addition was carried out in the presence of chloroplatinic acid during boiling of the reagent mixture. In that work, the increased activity of 1-hydrido-1-methyl-1-silicacyclopentane in the reaction with 2-cyano-bicyclo-(2,2,2)-heptane was noted in comparison with other hydrides ($HSiCl_3$; $HSi(OC_2H_5)_3$; $H(CH_3)_2SiC_2H_5$, etc.).

We have established that the addition reaction of hydride derivatives of silicacycloalkanes to olefins can proceed at atmospheric pressure already at temperatures of 20-70°, even in the presence of platinized carbon (5% Pt), a catalyst less active than chloroplatinic acid. As a result of carrying out this part of the work, we found that the activity of 1-hydrido-1-methyl-1-silicacycloalkanes in the reaction with ethylene increases in the series:

$$H(CH_3)Si(CH_2)_5 < H(CH_3)Si(CH_2)_4 < H(CH_3)Si(CH_2)_3$$

This conclusion was made on the basis of studying both the two-component reaction—ethylene—methylhydridosilicacycloalkane (Table 1), and the investigation of three-component competition reactions (see, for example, Fig. 1).

Using both of the above-mentioned methods, we also established that methylhydridosilacycloalkanes are more active than their open-chain analogs:

$$\begin{aligned} H(CH_3)Si\overline{(CH2)3} &> H(CH_3)Si(CH_3)(C_2H_5), \\ H(CH_3)Si\overline{(CH2)4} &> H(CH_3)Si(C_2H_5)_2, \\ H(CH_3)Si\overline{(CH2)5} &> H(CH_3)Si(C_2H_5)(C_3H_7). \end{aligned}$$

In studying the comparative activity of methylhydridosilacycloalkanes in competing reactions with their open-chain analogs, it was found that the reaction of the open-chain hydrides with ethylene is actively inhibited until the overwhelming portion of the methylhydridosilacycloalkane has entered into reaction (compare Figs. 2 and 3 and Table 1). Only after this did the open-chain hydrides begin to interact actively with ethylene.

The reason for the inhibition of the catalytic addition reaction of open-chain hydrides to ethylene should possibly be sought in the greater ability of silacycloalkanes, in comparison with their open-chain models, to be adsorbed on the catalyst surface; the latter, however, requires experimental confirmation. A study of the regularities in the series of silacycloalkanes and their open-chain analogs as applied to the ability of these compounds to be adsorbed on the surface of platinum

Fig. 1. Chromatogram of a sample (after 2 hours) from an experiment on competing reactions of
$H(CH_3)Si\overline{(CH2)4}$ (*A*), $H(CH_3)Si\overline{(CH2)5}$ (*B*) at 70°;
$(C_2H_5)(CH_3)Si\overline{(CH2)4}$ (*C*);
$(C_2H_5)(CH_3)Si\overline{(CH2)5}$ (*D*)

Fig. 2. Chromatogram of a sample (after 5 h) from an experiment on competing reactions of

$H(CH_3)Si(C_2H_5)(C_3H_7)$ (*A*) and $H(CH_3)Si\overline{(CH2)5}$ (*B*) at 70°;
$(CH_3)Si(C_2H_5)_2(C_3H_7)$ (*C*);
$(C_2H_5)(CH_3)Si\overline{(CH2)5}$ (*D*)

Fig. 3. Chromatogram of a sample (4 hours) from an experiment on competing reactions of
$H(CH_3)Si(C_2H_5)_2$ (*A*) and $H(CH_3)Si\overline{(CH2)4}$ (*B*) at 45°;
$(C_2H_5)(CH_3)Si\overline{(CH2)4}$ (*C*)

Table 2

Hydridosilane	$T_{b.p.}$, °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$H(CH_3)Si(CH_2)_3$ —*	65.5	1.4328	0.7773	28.9	28.7
$H(CH_3)Si(C_2H_5)(CH_3)$	43–44	1.3792	0.6713	30.4	30.3
$H(CH_3)Si(CH_2)_4$ —	91	1.4405	0.8003	33.1	33.1
$H(CH_3)Si(C_2H_5)_2$	76	1.3972	0.7052	34.9	34.9
$H(CH_3)Si(CH_2)_5$ —**	118	1.4470	0.8160	37.6	37.4
$H(CH_3)Si(C_2H_5)(C_3H_7)$***	104–106	1.4069	0.7181	39.7	39.8

* Obtained from $Cl(CH_3)Si(CH_2)_3$—by reduction with $LiAlH_4$. Preparation of 95% purity.
** Obtained from $Cl(CH_3)Si(CH_2)_5$—by reduction with $LiAlH_4$.
*** Obtained from $ClHSi(CH_3)(C_2H_5)$ and n-C_3H_7MgBr.

Table 3

Standards of products of ethylation of hydridosilanes	$T_{b.p.}$, °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$(C_2H_5)(CH_3)Si(CH_2)_3$ —	65–66/160 mm Hg	1.4392	0.7920	37.8	37.9
$(CH_3)_2Si(C_2H_5)_2$	96	1.3981	0.7129	39.3	39.3
$(C_2H_5)(CH_3)Si(CH_2)_4$ —	131	1.4440	0.8106	41.9	42.1
$(CH_3)Si(C_2H_5)_3$	123	1.4155	0.7438	43.8	43.9

Standards of products of ethylation of hydridosilanes	$T_{\text{b.p.}}$, °C	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
$(C_2H_5)(CH_3)Si(CH_2)_3$ —	161–163	1.4520	0.8250	46.5	46.4
$(CH_3)Si(C_2H_5)_2(C_3H_7)$*	144	1.4212	0.7486	48.6	48.8

* Obtained from $(CH_3)SiCl_2(C_3H_7\text{-n})$ and C_2H_5MgBr.

of catalysts is the subject of our further study.

It is interesting to note that earlier, for open-chain hydridosilanes—one of which was active and the other inactive in two-component addition reactions to olefins catalyzed by platinized carbon—competing three-component reactions were also carried out ([1,3]). In this case, however, a phenomenon opposite to ours was observed. The "active" hydride accelerated the addition of the "inactive" hydride to the olefin. This observation was used as an argument in favor of a radical-chain mechanism for the reaction under consideration.

In the case of the ethylation reaction of methylhydridosilacyclopentane and methylhydridosilacyclohexane, as well as of all open-chain hydrides, addition to ethylene was practically the only process. In the case of methylhydridosilacyclobutane, the addition reaction was accompanied by formation of condensation products of the silacyclobutane derivative even at 20°. This is evidently the result of polymerization of silacyclobutanes ([5]) or telomeric transformations involving Si—H bonds ([6]).

Experimental Part

The addition of hydridosilanes to ethylene was carried out in a thermostated three-necked flask equipped with a thermometer, a tube for introducing ethylene, and two reflux condensers connected in series—one water-cooled and one with dry ice. As catalyst, Pt/C containing 5% Pt was used, taken in an amount of ~ 0.1 g per 0.08 g-equiv of silane hydride. Ethylene was supplied at a rate of ~ 9 ml per minute. The course of the reactions was monitored by sampling. In the case of two-component reactions, the composition of the mixture was judged from the change in n_D and, additionally, by gas-liquid chromatography. In three-component competition reactions, as well as in experiments on the interaction of ethylene with methylhydridosilacyclobutane, the composition of the mixture was judged from chromatograms. The analysis was carried out on an LKhM-5 instrument; the stationary phase was Inza brick + 20% polyphenylsiloxane oil No. 5; the carrier gas was helium. Depending on the boiling point of the hydridosilanes, the analysis was carried out at 80, 95, and 105°.

Table 1 presents the analytical data for two-component reactions—ethylene-hydridosilane. The properties of the hydridosilanes used in the reaction, obtained by ordinary organometallic methods, are presented in Table 2.

Table 3 gives the properties, also obtained by organometallic methods, of reference samples of the products of addition of hydridosilanes to ethylene. In all cases the reference samples were identical with the products of ethylation of the hydridosilanes. Figures 1–3 show typical examples of chromatograms of samples taken from experiments on competing reactions; samples were taken every hour for 8 hours.

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