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Abstract

Full Text

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ON THE ADDITION OF DIALKYL(PHENYL)SILANES TO ETHYLENIC HYDROCARBONS

The preparation of organosilicon compounds from unsaturated hydrocarbons was first described in 1947 ([1,2]). The authors showed that trichlorosilane and methyldichlorosilane add to unsaturated hydrocarbons in the presence of peroxide catalysts and under ultraviolet irradiation. In subsequent years, a number of papers and patents described the interaction of various silicon compounds containing the Si—H bond with unsaturated hydrocarbons and other unsaturated compounds; the effect of a number of catalysts on the reaction was also studied.

In 1954 Wagner ([3]) proposed using platinized carbon as a catalyst for the reaction of hydrosilanes with unsaturated compounds; it proved to be more active than the catalysts proposed earlier.

In a number of previous communications ([4–8]) we studied addition reactions of various silicon compounds containing the Si—H bond to unsaturated compounds.

In the present study, the addition reactions of diethylsilane, dibutylsilane, methylphenylsilane, and diphenylsilane to octene-1, nonene-1, and decene-1 were studied. The reactions were carried out in sealed ampoules in the presence of platinized carbon.

The addition of diethylsilane and dibutylsilane to octene-1 and nonene-1 at ratios of 1 : 2 proceeded only at one Si—H bond:

$$R_2SiH_2 + CH_2{=}CH(CH_2)_5CH_3 \text{arrow} R_2HSi{-}CH_2{-}CH_2(CH_2)_5CH_3$$

where R = C_2H_5; C_4H_9.

Under the same conditions and ratios of the starting substances, diphenylsilane added to decene-1, forming diphenyldecylsilane in 61% yield and diphenyldidecylsilane in 10% yield, according to the scheme:

$$[C_6H_5]_2SiH_2 + CH_2{=}CH(CH_2)_7CH_3 \text{arrow} (C_6H_5)_2SiHC_{10}H_{21} + [C_6H_5]_2Si[C_{10}H_{21}]_2$$

Dibutylsilane added to nonene-1 with formation of dibutylnonylsilane (yield 30.4%) and dibutyldinonylsilane (yield 6%) only at ratios of 1 : 4.

Diphenylsilane also added to decene-1 in the presence of benzoyl peroxide, whereas diethylsilane did not add to octene-1 in the presence of benzoyl peroxide under the same conditions.

As can be seen from Table 1, diethylsilane and dibutylsilane add to olefins in yields half as high as those of diphenylmethylsilane and diphenylsilane.

On the basis of the experimental data obtained by us, it may be concluded that the Si—H bond in dihydridosilanes containing phenyl radicals is more active in addition reactions to olefins than the Si—H bond in dihydridosilanes with alkyl radicals.

From dibutylnonylsilane and diphenyldecylsilane, by interaction with nonene-1, we obtained dibutyldinonylsilane and diphenylnonyldecylsilane.

Experimental Part

Dialkyl(phenyl)silanes were obtained by reduction of dialkyl(phenyl)dichlorosilanes with lithium aluminum hydride and, in their properties, corresponded to the literature data.

Diethylsilane, b.p. 54–56° at 754 mm; d_4^{20} 0.6834; n_D^{20} 1.3923

Dibutylsilane, b.p. 157–160° at 746 mm; d_4^{20} 0.7431; n_D^{20} 1.4219

Phenylmethylsilane, b.p. 140–143° at 751 mm; n_D^{20} 1.5046

Diphenylsilane, b.p. 100–101° at 3 mm; d_4^{20} 0.9964; n_D^{20} 1.5756

Experiments on the addition of dialkyl(phenyl)silanes to olefins in the presence of platinized carbon were carried out in sealed ampoules placed in a Carius-type furnace at 160–180° for 10 hr.

Diethyloctylsilane. From 20 g (0.18 mole) of octene-1 and 8 g (0.09 mole) of diethylsilane, in the presence of 0.1 g of platinized carbon, 3.7 g (yield 20.5%) of diethyloctylsilane was obtained, b.p. 107–109°/5 mm.

Found, %: C 72.21; 72.19; H 14.11; 14.13
$C_{12}H_{28}Si$. Calculated, %: C 72.00; H 14.00

Diethylnonylsilane. From 15 g (0.12 mole) of nonene-1 and 5 g (0.06 mole) of diethylsilane, in the presence of 0.1 g of platinized carbon, 2.7 g (yield 22.3%) of diethylnonylsilane was obtained, b.p. 110–112°/5 mm.

Found, %: C 72.44; 72.44; H 14.14; 14.02
$C_{13}H_{30}Si$. Calculated, %: C 72.34; H 14.10

Dibutylnonylsilane and dibutyldinonylsilane.
a) From 25 g (0.2 mole) of nonene-1 and 13 g (0.1 mole) of dibutylsilane, in the presence of 0.2 g of platinized carbon, 5.7 g (yield 23.4%) of dibutylnonylsilane was obtained, b.p. 142–144°/5 mm.

Found, %: C 75.55; 75.58; H 14.16; 14.15
$C_{17}H_{38}Si$. Calculated, %: C 75.44; H 14.11

b) From 52 g (0.41 mole) of nonene-1 and 14 g (0.1 mole) of dibutylsilane, in the presence of 0.2 g of platinized carbon, 8.2 g (yield 30.4%) of dibutylnonylsilane and 2.3 g (yield 6%) of dibutyldinonylsilane were obtained.

c) From 4 g (0.03 mole) of nonene-1 and 3.5 g (0.013 mole) of dibutylnonylsilane, in the presence of 0.1 g of platinized carbon, 3.7 g (yield 56.8%) of dibutyldinonylsilane was obtained. B.p. 215–218°/5 mm.

Found, %: C 78.73; 78.71; H 14.09; 14.11
$C_{26}H_{56}Si$. Calculated, %: C 78.78; H 14.14

Phenylmethyloctylsilane. From 15 g (0.13 mole) of octene-1 and 8 g (0.06 mole) of phenylmethylsilane, in the presence of 0.15 g of platinized carbon, 6.1 g (yield 40%) of phenylmethyloctylsilane was obtained. B.p. 154–156°/5 mm.

Found, %: C 71.87; 71.91; H 13.98; 14.01
$C_{15}H_{26}Si$. Calculated, %: C 72.00; H 14.00

Phenylmethylnonylsilane. From 10 g (0.08 mole) of nonene-1 and 5 g (0.04 mole) of phenylmethylsilane, in the presence of 0.1 g of platinized carbon, 5.9 g (yield 59.1%) of phenylmethylnonylsilane was obtained. B.p. 160–162°/5 mm.

Found, %: C 77.52; 77.50; H 11.32; 11.32
$C_{16}H_{28}Si$. Calculated, %: C 77.73; H 10.92

Diphenyldecylsilane and diphenyldidecylsilane.
a) From 14 g (0.1 mole) of decene-1 and 9 g (0.05 mole) of diphenylsilane, in the pres-

in the presence of 0.1 g of platinized charcoal, 9.8 g (yield 61.2%) of diphenyldecylsilane and 2.3 g (yield 10%) of diphenyldidecylsilane were obtained.

b) The reaction was carried out in a three-necked flask with a stirrer. For the reaction, 28 g (0.2 mole) of decene-1, 19 g (0.1 mole) of diphenylsilane, and 1 g of benzoyl peroxide were taken. The reaction mixture was heated for 16 hours at 80°. 13.2 g (yield 41.2%) of diphenyldecylsilane was obtained.

Diphenyldecylsilane, b.p. 194–196°/5 mm.

Found, %:	C 81.53; 81.35; H 9.74; 9.81
$C_{22}H_{32}Si$. Calculated, %:	C 81.48; H 9.87

Diphenyldidecylsilane, b.p. 259–260°/5 mm.

Found, %:	C 82.54; 82.64; H 10.87; 10.94
$C_{32}H_{52}Si$. Calculated, %:	C 82.76; H 11.20

Diphenylnonylsilane and diphenyldinonylsilane. From 12 g (0.09 mole) of nonene-1 and 7.4 g (0.04 mole) of diphenylsilane in the presence of 0.1 g of platinized charcoal, 7.5 g (yield 60.6%) of diphenylnonylsilane and 1.6 g (yield 9.1%) of diphenyldinonylsilane were obtained.

Diphenylnonylsilane, b.p. 206–207°/6 mm.

Found, %:	C 81.41; 81.07; H 9.42; 9.55
$C_{21}H_{30}Si$. Calculated, %:	C 81.29; H 9.67

Diphenyldinonylsilane, b.p. 256–260°/6 mm.

Found, %:	C 82.17; 82.17; H 11.01; 11.07
$C_{30}H_{48}Si$. Calculated, %:	C 82.56; H 11.01

Diphenylnonyldecylsilane. From 4 g (0.03 mole) of nonene-1 and 5 g (0.015 mole) of diphenyldecylsilane in the presence of 0.1 g of platinized charcoal, 4.4 g (yield 64.7%) of diphenylnonyldecylsilane was obtained. B.p. 255–257°/5 mm.

Found, %:	C 82.82; 83.00; H 10.92; 11.07
$C_{31}H_{50}Si$. Calculated, %:	C 82.66; H 11.11

Table 1

Name of substance	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Yield, %
Diethyloctylsilane	$(C_2H_5)_2SiHC_8H_{17}$	107/5	0.7822	1.4377	67.14	67.58	20.5
Diethylnonylsilane	$(C_2H_5)_2SiHC_9H_{19}$	112/5	0.7894	1.4400	71.62	72.21	22.3
Dibutylnonylsilane	$(C_4H_9)_2SiHC_9H_{19}$	144/5	0.8008	1.4463	90.09	90.73	23.4
Phenylmethyloctylsilane	$C_6H_5CH_3SiHC_8H_{17}$	158/5	0.8658	1.4892	78.06	77.99	40.1
Phenylmethylnonylsilane	$C_6H_5CH_3SiHC_9H_{19}$	162/5	0.8663	1.4898	82.54	82.52	59.0
Diphenylnonylsilane	$(C_6H_5)_2SiHC_9H_{19}$	207/5	0.9419	1.5328	101.84	102.21	60.6
Diphenyldecylsilane	$(C_6H_5)_2SiHC_{10}H_{21}$	196/3	0.9441	1.5332	106.75	106.92	61.2
Dibutyldinonylsilane	$(C_4H_9)_2Si(C_9H_{19})_2$	218/5	0.8182	1.4548	131.49	132.14	56.8

Name of substance	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Yield, %
Diphenyldi(cyclohexylmethyl)silane	$(C_6H_5)_2Si(C_7H_{13})_2$	257/6	0.9154	1.5176	144.05	143.62	9.1
Diphenyldi(decahydro-1-naphthylmethyl)silane	$(C_6H_5)_2Si(C_{11}H_{19})_2$	257/5	0.9189	1.5181	148.30	148.43	48.5
Diphenyldi(tetrahydro-1-naphthylmethyl)silane	$(C_6H_5)_2Si(C_{11}H_{13})_2$	266/5	0.9193	1.5187	153.38	152.88	10.0

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