1-(TRIORGANYLSILYL)-2-(TRIETHOXYSILYL)ETHANES

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The hydrosilylation reaction has found wide application in organosilicon synthesis [1]. In the present paper we studied the hydrosilylation of $CH_2=CHSi(OC_2H_5)_3$ (I) with triorganylsilanes in the presence of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol, which proceeds by the following scheme:

$$R^1R_2^2SiH + (I) \rightarrow R^1R_2^2SiCH_2CH_2Si(OC_2H_5)_3$$

The optimum conditions were found for the hydrosilylation of (I) with $(C_2H_5)_3SiH$ (III), which assured the maximum yield of 1-(triethylsilyl)-2-(triethoxysilyl)ethane (>90%): the gradual addition of (III) to a mixture of (I) and the catalyst or of (I) to a mixture of (III) and the catalyst. In both cases the optimum concentration of $H_2PtCl_6 \cdot 6H_2O$ is $(5.8\text{-}11.5) \cdot 10^{-2}$ mole % of (I). The addition of the catalyst to a mixture of (I) and (III), heated to 80°, causes a vigorous exothermic reaction. Above 110° the yield of the hydrosilylation product drops due to the reduction of the $H_2PtCl_6 \cdot 6H_2O$ to metallic Pt.

The optimum method was used to synthesize 27 new 1-(triorganylsilyl)-2-(triethoxysilyl)ethanes (Table 2). In addition, 1-(trimethylsilyl)-2-(triethoxysilyl)ethane was obtained by a similar method from $CH_2=CHSi(CH_3)_3$ and $(C_2H_5O)_3SiH$. The structure of the obtained products was confirmed by the NMR spectra: a singlet with τ 9.5 ppm (4H), representing the protons of the $-SiCH_2CH_2Si-$ fragment. Isomers of type $-SiCHSi-$ (with CH_3) are not formed. The stability of the obtained 1-(trialkylsilyl)-2-(triethoxysilyl)ethanes to hydrolysis increases noticeably with increase in either the length or branching of the alkyl radicals in the $R^1R_2^2Si$ group.

EXPERIMENTAL

The NMR spectra were obtained on a Tesla-487C spectrometer in CCl_4 solution at a frequency of 80 MHz, using cyclohexane as the internal standard. The triorganylsilanes were obtained from the corresponding

TABLE 1. Hydrosilylation of $CH_2=CHSi(OC_2H_5)_3$ (I) with Triethylsilane (III) [(III) : (I) mole ratio = 1.1 : 1]

$H_2PtCl_6 \cdot 6H_2O$, in mole % $\cdot 10^{-3}$ of (I)	Reaction conditions	Yield of $(C_2H_5)_3SiCH_2CH_2Si(OC_2H_5)_3$, %
0	A	0
19,3	B	78
57,9	B	92,1
115,8	B	92,8
19,3	C	77,8
57,9	C	91,7
115,8	C	92
57,9	D	60,8

Remarks. A) A mixture of (I) and (III) was heated from 20 to 110° in 10 min and then refluxed at 110° for 1440 min. B) (I) was added in 20 min to a mixture of the catalyst and (III) heated to 80°, after which the mixture was heated at 200° for 15 min. C) (III) was added in 20 min to a mixture of the catalyst and (I) heated to 80°, after which the mixture was heated at 200° for 15 min. D) The catalyst was added to a mixture of (I) and (III) heated to 80°. The temperature rose to 200° in 2 min.

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TABLE 2. Yields, Properties, and Analysis Data of $R^1R^2_2SiCH_2CH_2Si(OC_2H_5)_3$ (II)

R^1	R^2	Yield, %	bp, °C (p, mm on Hg)	d_4^{20}	n_D^{20}	Found			Empirical formula	Calculated		
						MR	mol.wt.*	Si, %		MR	mol.wt.	Si, %
CH_3	CH_3	98,6	74(4)	0,8850	1,4150	74,84	263,5	21,30	$C_{11}H_{28}O_3Si_2$	74,73	264,52	21,24
C_2H_5	C_2H_5	92,1	119,5(5,5)	0,8949	1,4304	88,62	306,8	18,26	$C_{14}H_{34}O_3Si_2$	88,65	306,60	18,32
CH_3	n-C_3H_7	88,6	119,5—120(4)	0,8851	1,4300	93,57	321,3	17,51	$C_{15}H_{36}O_3Si_2$	93,32	320,63	17,52
CH_3	i-C_3H_7	87,5	115,5(4)	0,8891	1,4305	93,24	318,4	17,39	$C_{15}H_{36}O_3Si_2$	93,32	320,63	17,52
C_6H_5	CH_3	87,1	135(3,5)	0,9606	1,4700	94,89	320,5	17,01	$C_{18}H_{30}O_3Si_2$	94,62	326,59	17,20
i-C_3H_7	n-C_3H_7	85,4	129—130(4)	0,8919	1,4333	101,67	347,4	16,12	$C_{17}H_{40}O_3Si_2$	102,62	348,68	16,11
CH_3	n-C_4H_9	86,5	134,5(5,5)	0,8865	1,4330	102,22	346,6	15,94	$C_{17}H_{40}O_3Si_2$	102,62	348,68	16,11
CH_3	i-C_4H_9	85	128—128,5(4,2)	0,8932	1,4332	101,50	346,8	15,95	$C_{17}H_{40}O_3Si_2$	102,62	348,68	16,11
C_2H_5	n-C_4H_9	86	138,5—139(3,5)	0,8914	1,4365	106,51	360,2	15,40	$C_{18}H_{42}O_3Si_2$	107,27	362,71	15,49
C_2H_5	i-C_4H_9	82,5	134,5—135,5 (3,5)	0,8951	1,4357	105,87	363,9	15,41	$C_{18}H_{42}O_3Si_2$	107,27	362,71	15,49
n-C_9H_{19}	CH_3	87	155—156(3,5)	0,8807	1,4355	111,72	372,5	14,96	$C_{19}H_{44}O_3Si_2$	111,92	376,74	14,91
n-C_4H_9	n-C_4H_9	86,1	160—161(4)	0,8841	1,4402	116,55	388,9	14,40	$C_{20}H_{46}O_3Si_2$	116,56	390,76	14,38
i-C_4H_9	i-C_4H_9	82,3	160—162(7)	0,8879	1,4375	115,92	391,6	14,31	$C_{20}H_{46}O_3Si_2$	116,56	390,76	14,38
n-$C_{10}H_{21}$	CH_3	90	168(3,5)	0,8774	1,4370	116,69	387,5	14,34	$C_{20}H_{46}O_3Si_2$	116,56	390,76	14,38
C_2H_5	n-C_5H_{11}	86,1	160(4)	0,8844	1,4400	116,47	388,5	14,32	$C_{20}H_{46}O_3Si_2$	116,56	390,76	14,38
C_2H_5	i-C_5H_{11}	89	154—155(4)	0,8792	1,4398	117,10	391,2	14,32	$C_{20}H_{46}O_3Si_2$	116,56	390,76	14,38
CH_3	C_6H_5	89,6	193(5,5)	1,0230	1,5173	114,98	390,3	14,35	$C_{21}H_{32}O_3Si_2$	114,51	388,66	14,45
CH_3	n-C_6H_{13}	91	172(3,6)	0,8793	1,4390	121,08	405,2	13,82	$C_{21}H_{48}O_3Si_2$	121,21	404,79	13,88
C_2H_5	C_6H_5	90,8	212,5(6,5)	1,0208	1,5133	119,59	401,6	14,03	$C_{22}H_{34}O_3Si_2$	119,16	402,69	13,95
C_2H_5	n-C_6H_{13}	83,5	117,5—118,5(4)	0,8840	1,4412	125,17	414,2	13,31	$C_{22}H_{50}O_3Si_2$	125,86	418,82	13,41
n-C_5H_{11}	n-C_5H_{11}	84,2	176(3)	0,8807	1,4430	130,53	432,6	12,98	$C_{23}H_{52}O_3Si_2$	130,61	432,85	12,98
i-C_5H_{11}	i-C_5H_{11}	83,5	168—169(3,5)	0,8775	1,4408	130,22	433,3	13,03	$C_{23}H_{52}O_3Si_2$	130,61	432,85	12,98
CH_3	n-C_7H_{15}	88,1	187(4)	0,8777	1,4418	130,44	433,1	12,99	$C_{23}H_{52}O_3Si_2$	130,61	432,85	12,98
C_6H_5	C_6H_5	86,5	229(4) ,mp 63—65°	—	1,5492	—	451,3	12,36	$C_{26}H_{34}O_3Si_2$	134,40	450,73	12,46
n-C_6H_{13}	n-C_6H_{13}	88,9	204—205(5)	0,8793	1,4455	143,90	472,8	11,86	$C_{26}H_{58}O_3Si_2$	144,45	474,93	11,83
C_2H_5	n-C_8H_{17}	87	194—195(4,2)	0,8800	1,4442	144,40	472,2	11,73	$C_{26}H_{58}O_3Si_2$	144,45	474,93	11,83
n-C_7H_{15}	n-C_7H_{15}	88,5	225—226(6)	0,8773	1,4492	158,11	517,4	10,85	$C_{29}H_{64}O_3Si_2$	158,40	517,01	10,87
CH_3	n-$C_{10}H_{21}$	89,7	233—234(4)	0,8731	1,4476	158,40	517,9	10,86	$C_{29}H_{64}O_3Si_2$	158,40	517,01	10,87

*The molecular weight was determined cryoscopically in benzene.

organylmagnesium halides by reaction with $HSiCl_3$, $(CH_3)_2SiHCl$, $CH_3Si(H)Cl_2$, and $C_2H_5Si(H)Cl_2$, cf. [2-5]. $(CH_3)_3SiCH=CH_2$, $(C_2H_5O)_3SiCH=CH_2$, and $(C_2H_5O)_3SiH$ were purified by distillation through a column immediately before use in the reaction. The (I) products were synthesized in a dry argon atmosphere. Their properties were determined taking all of the necessary precautions to prevent the entrance of traces of moisture.

1-(Triethylsilyl)-2-(triethoxysilyl)ethane. To a mixture of 9.5 g (0.05 mole) of $(C_2H_5O)_3SiCH=CH_2$ and 0.1 ml of a 1.5% solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol ($28.9 \cdot 10^{-4}$ mole %), heated to 80°, was added 7 g (0.06 mole) of Et_3SiH in 20 min, after which the mixture was heated for another 15 min (here the temperature rose from 80 to 200°). Distillation of the mixture gave 14 g (91.7%) of 1-(triethylsilyl)-2-(triethoxysilyl)ethane with bp 119-120° (5.5 mm). In Table 2 are given the properties and analysis data that were obtained for the product after purification by repeated distillation over Na.

1-(Trimethylsilyl)-2-(triethoxysilyl)ethane. To a mixture of 5 g (0.05 mole) of $(CH_3)_3SiCH=CH_2$ and 0.1 ml of a 1.5% solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol ($28.9 \cdot 10^{-4}$ mole %), heated to 50°, was added 9.8 g of $(EtO)_3SiH$ in 20 min, after which the mixture was heated for another 15 min, and here the temperature rose from 50 to 193°. Distillation of the mixture gave 12.5 g (98.6%) of 1-(trimethylsilyl)-2-(triethoxysilyl)ethane with bp 73.5-74.3° (4 mm) (see Table 2).

The other 1-(triorganylsilyl)-2-(triethoxysilyl)ethanes were obtained in a similar manner (see Table 2).

NMR spectrum (τ, ppm): $(CH_3)_3SiCH_2CH_2Si(OC_2H_5)_3$; 9.99 s (9H, CH_3); 9.54 s (4H, $SiCH_2CH_2Si$); 8.79 t (9H, CH_3CO, ^3J = 7.5 Hz); 6.23 q (6H, CH_2O). $(C_2H_5)_3SiCH_2Si(OC_2H_5)_3$; 9.59 s (4H, $SiCH_2CH_2Si$); 9.55 m (6H, $CH_3\underline{CH_2}$); 9.09 m (9H, $\underline{CH_3}CH_2$); 8.86 h (9H, CH_3CO, ^3J = 7.5 Hz).

CONCLUSIONS

The conditions were found for the hydrosilylation of $CH_2=CHSi(OC_2H_5)_3$ with triorganylsilanes in the presence of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol, which assured a high yield (>90%) of the 1-(triorganylsilyl)-2-(triethoxysilyl)ethanes. These conditions were used to synthesize 27 new 1-(triorganylsilyl)-2-(triethoxysilyl)-ethanes.

The addition of $(C_2H_5O)_3SiH$ to $(CH_2=CHSi(CH_3)_3$ in the presence of the same catalyst gave 1-(trimethylsilyl)-2-(triethoxysilyl)ethane in 98.6% yield.

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