Reports of the Academy of Sciences of the USSR

CHEMISTRY

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Volume 118, No. 5

CHEMISTRY

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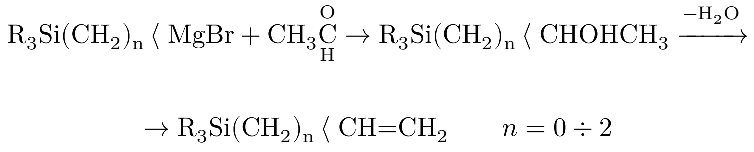
SYNTHESIS OF *p*-TRIALKYLSILYL- AND *p*-TRIALKYLSILYLALKYLSTYRENES

By the present time, methods have been developed for the synthesis of, and diverse properties have been studied for, a very large number of unsaturated organosilicon compounds (1,2). In particular, their ability to polymerize has been studied in considerable detail (3–5). As for the synthesis and study of styrenes substituted by silicon in the ring, only two patents have been devoted to this question; however, these give neither a detailed description of the synthesis nor the properties of the compounds obtained (6,7).

The aim of the present investigation was to develop methods for the synthesis of silicon-containing styrenes para-substituted in the ring. The general scheme for the synthesis of these compounds is as follows: by the Grignard reaction the corresponding alcohol was obtained, which was then dehydrated with formation of the silicon-substituted styrene:



$$R_3Si(CH_2)_n \langle MgBr + CH_3\overset{O}{\underset{H}{C}} \rightarrow R_3Si(CH_2)_n \langle CHOHCH_3 \xrightarrow{-H_2O}$$

$$\rightarrow R_3Si(CH_2)_n \langle CH{=}CH_2 \qquad n = 0 \div 2$$

The Grignard reaction of brominated *p*-trimethyl- and *p*-triethylsilylphenylmagnesium with acetaldehyde and acetone proceeded quite successfully, giving the corresponding alcohols in yields of 40-60%. Dehydration under mild conditions by boiling the alcohol over $KHSO_4$ did not lead to the desired results—the secondary alcohols were dehydrated only partially. Therefore we used the method of dehydrating alcohols over Al_2O_3 at 340–350° in vacuum at 150-160 mm Hg. This method gave satisfactory results, although in this case partial polymerization of the styrene formed took place. The styrenes were obtained in yields of 30-50%.

For synthesis by the same scheme of $R_3SiCH_2 \langle CH{=}CH_2$ and $R_3SiCH_2CH_2 \langle CH{=}CH_2$, it was necessary to develop methods for obtaining

$$Cl_3SiCH_2 \langle Br \quad \text{and} \quad Cl_3SiCH_2CH_2 \langle Br.$$

Yakubovich and Mosharev recently reported (8) the bromination of benzyltrichlorosilane with bromine; however, the proof of the structure of the compounds they obtained could not be considered strictly reliable. We likewise brominated benzyltrichlorosilane with bromine in the presence of Fe in the cold. Distillation on a column showed that only one product is formed. Under the same conditions β-phenylethyltrichlorosilane was brominated, and again only one product was isolated. Both substances obtained were subjected to spectral analysis. In a study (9) it was shown that the type of substitution—ortho, meta, or para—in a disubstituted benzene derivative can be identified from the 5–6 μ absorption region of the infrared spectrum. On an IKS-11 spectrograph with a NaCl prism, spectra in the 5–6 μ region were obtained.

Table 1

Starting organomagnesium bromide	Starting carbonyl compound	Alcohol obtained	Yield, %	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	OH, % found	OH, % calc.
$(CH_3)_3SiC_6H_4Br$	CH_3CHO	$(CH_3)_3SiC_6H_4CHOHCH_3$	47.1	91–92/2	1.5148	0.9611	8.72	8.45; 8.40
$(CH_3)_3SiC_6H_4Br$	CH_3COCH_3	$(CH_3)_3SiC_6H_4COH(CH_3)_2$	46	115–116/8	1.5130	0.9552	8.14	7.88; 8.00
$(C_2H_5)_3SiC_6H_4Br$	CH_3CHO	$(C_2H_5)_3SiC_6H_4CHOHCH_3$	57.6	136–137.5/3	1.5195	0.9624	7.16	6.82; 6.94
$(C_2H_5)_3SiC_6H_4Br$	CH_3COCH_3	$(C_2H_5)_3SiC_6H_4COH(CH_3)_2$	34.8	138–138.5/6	1.5213	0.9374	6.77	6.54; 6.60
$(C_2H_5)_3SiCH_2C_6H_4Br$	CH_3CHO	$(C_2H_5)_3SiCH_2C_6H_4CHOHCH_3$	13	137–138.5/4	1.5291	0.9544	6.42	6.14; 6.32
$(C_2H_5)_3SiCH_2CH_2C_6H_4Br$	CH_3CHO	$(C_2H_5)_3SiCH_2CH_2C_6H_4CHOHCH_3$	13	185–187/6.5	1.5172	0.9533	6.09	5.77; 5.60

the spectra of the above-mentioned bromides, which had first been ethylated. The spectra proved similar and contained only two bands (1775 and 1880 cm^{-1}), which, according to the cited work, characterize para isomers.

From $(C_2H_5)_3SiCH_2C_6H_4Br$ and $(C_2H_5)_3SiCH_2CH_2C_6H_4Br$ and acetaldehyde, the corresponding alcohols were obtained by the Grignard reaction, in only 13% yields. Considerable amounts of benzyltriethylsilane and β-phenylethyltriethylsilane, respectively, were isolated; these were formed during decomposition by water of the unreacted Grignard reagents. From the first alcohol, dehydration over Al_2O_3 gave the corresponding styrene in 50% yield. The second alcohol on dehydration also gave some amount of styrene, which, however, polymerized completely during distillation over Na. The polymerization of the styrenes obtained is being studied.

Bromination of benzyltrichlorosilane, prepared by the Grignard reaction from benzyl chloride and $SiCl_4$, was carried out in a three-necked flask equipped with a stirrer, dropping funnel, and reflux condenser. Into the flask were placed 580 g (2.59 moles) of benzyltrichlorosilane and 5 g of iron filings; with stirring over 10 h, 425 g (2.66 moles) of bromine was added. The temperature of the cooling bath was maintained within 10-20°. After completion of the addition of bromine, the mixture was heated for 20 min at 70°. Then for 5 h dry nitrogen was passed through the mixture to remove HBr. Vacuum distillation on a 30-plate column gave 485 g of *p*-bromobenzyltrichloro-

silane, yield 61.7%, b.p. 135°/12.5 mm, n_D^{20} 1.5600, d_4^{20} 1.6008, MR_D 61.51 (calc. 61.09). Under the same conditions, β-phenylethyltrichlorosilane, obtained by method [10], was brominated. From 700 g of β-phenylethyltrichlorosilane, 510.5 g of β-(n-bromophenyl)-ethyltrichlorosilane was obtained, yield 55%, b.p. 141°/7 mm, n_D^{20} 1.5481, d_4^{20} 1.5390, MR_D 65.75 (calc. 65.71).

Both bromides were ethylated with the aid of C_2H_5MgBr, giving n-bromobenzyltriethylsilane, yield 75%, b.p. 140.5-141°/5 mm, n_D^{20} 1.5324; d_4^{20} 1.1560, MR_D 76.52 (calc. 76.17), and β-(n-bromophenyl)-ethyltriethylsilane, yield 80.5%, b.p. 149°/4.5 mm, n_D^{20} 1.5248; d_4^{20} 1.1420, MR_D 80.21 (80.29).

n-α-Hydroxyethylphenyltrimethylsilane was prepared by the Grignard reaction in a three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. To the Grignard reagent prepared from 210 g (0.91 mole) of n-bromophenyltrimethylsilane, 80 g (1.8 moles) of acetaldehyde was slowly added. The temperature of the reaction mixture was maintained within 5-10° by cooling with an ice-water bath. After the addition of the aldehyde was complete, the mixture was stirred at room temperature for 3 hours and for another 3 hours at the boiling temperature. It was then decomposed in the usual way, and the organic layer was dried over anhydrous Na_2SO_4. Distillation gave 84.3 g of n-α-hydroxyethylphenyltrimethylsilane, yield 47.1%. The properties of the alcohol are presented in Table 1. All the remaining alcohols were synthesized under the same conditions. The results of the experiments are presented in Table 1.

Dehydration of the synthesized alcohols was carried out over ignited Al_2O_3 at 330-340° in an ordinary catalytic furnace. The alcohol was fed at a rate of 0.5 cm^3/min. The entire system was under a vacuum of 160-170 mm Hg, created by a water-jet pump. The product obtained was dried over Na_2SO_4 and distilled in vacuo. The properties and yields of the synthesized styrenes are presented in Table 2.

Table 2

Silicon-substituted styrene	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Calculated, % Si	Found, % C	Found, % H	Found, % Si
$(CH_3)_3Si{-}C_6H_4{-}CH{=}CH_2$	38.9	101–101.5/20	1.5221	0.8979	75.00	9.09	15.91	74.72 74.96	9.26 9.02	15.72 15.50
$(CH_3)_3Si{-}C_6H_4{-}C(CH_3){=}CH_2$	52.3	110–111/20	1.5188	0.8828	75.79	9.47	14.74	75.49 75.58	9.47 9.42	14.62 14.46
$(C_2H_5)_3Si{-}C_6H_4{-}CH{=}CH_2$	40.4	107–107.5/3	1.5205	0.9203	77.06	10.09	12.85	76.98 76.88	10.02 10.12	12.68 12.77
$(C_2H_5)_3Si{-}C_6H_4{-}C(CH_3){=}CH_2$	32.5	132–133/7.5	1.5218	0.9070	77.58	10.35	12.07	77.52 77.48	10.30 10.32	12.00 12.13
$(C_2H_5)_3SiCH_2{-}C_6H_4{-}CH{=}CH_2$	51.6	126–127/3.5	1.5237	0.9256	77.58	10.35	12.07	77.12 77.24	10.20 10.11	11.93 11.9

We express our deep gratitude to Yu. P. Egorov, who carried out the spectral analysis of the bromobenzyl- and bromophenylethyltriethylsilanes.

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Received
17 VII 1957

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