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Abstract

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SYNTHESIS OF SILICON-, GERMANIUM-, AND TIN-CONTAINING *p*-SUBSTITUTED STYRENES AND α-METHYLSTYRENES

Unsaturated compounds containing elements of Group IVB of the periodic system in the molecule are attracting increasing attention from investigators. One of the most promising classes of monomers is element-containing styrenes. Compounds of this type are of interest because, unlike unsaturated aliphatic organoelement compounds, they polymerize more extensively, forming high-melting polymers ([1]-[3]). We have previously studied a method for the synthesis of silicon-containing styrenes and α-methylstyrenes by dehydration of the corresponding alcohols over $KHSO_4$ or, more conveniently, over Al_2O_3 at 300-340° in a tube furnace under a vacuum of 160-170 mm Hg ([4],[5]):

$$R_3Si|CH_2|_n-\langle C_6H_4\rangle-CHOHCH_3 \xrightarrow[-H_2O]{} R_3Si|CH_2|_n-\langle C_6H_4\rangle-CH{=}CH_2 \quad (n = 0;\ 2),$$

$$R_3Si|CH_2|_n-\langle C_6H_4\rangle-C(CH_3)OHCH_3 \xrightarrow[-H_2O]{} R_3Si(CH_2)_n-\langle C_6H_4\rangle-C|CH_3|{=}CH_2$$

$$(R = CH_3;\ C_6H_5).$$

The yields of silicon styrenes obtained by this method are 30-50%. This route to trimethyl- and triethylsilylstyrenes has also been used by other investigators ([6]-[8]). Another method for obtaining silicon-containing styrenes consists in the pyrolytic dehydrochlorination of chloroethylphenylsilanes or chloroisopropylphenylsilanes at 500° ([9]-[11]):

$$ClC_2H_4-\langle C_6H_4\rangle-SiCl_3 \xrightarrow[-HCl]{} CH_2{=}CH-\langle C_6H_4\rangle-SiCl_3,$$

$$ClC_3H_6-\langle C_6H_4\rangle-SiCl_3 \xrightarrow[-HCl]{} CH_2{=}C|CH_3|-\langle C_6H_4\rangle-SiCl_3.$$

The yields of trichlorosilylstyrene and trichlorosilyl-α-methylstyrene with this method of synthesis are 70–80%.

The ease of preparation and the high yields of the organomagnesium compound from p-chlorostyrene in tetrahydrofuran led to a third method for the synthesis of styryl and α-methylstyryl derivatives of silicon ([3],[8],[12],[13]), germanium ([3],[14]), tin ([3],[14]–[16]), and lead ([3],[14],[17],[19]).

$$R_3MHal + n\text{-}Cl{-}\langle C_6H_4\rangle{-}CH{=}CH_2 \xrightarrow[THF]{Mg} R_3M{-}\langle C_6H_4\rangle{-}CH{=}CH_2$$

$$(M = Si;\ Ge;\ Sn;\ Pb;\ R = CH_3;\ C_6H_5),$$

$$R_3MHal + n\text{-}Cl{-}\langle C_6H_4\rangle{-}C(CH_3){=}CH_2 \xrightarrow[THF]{Mg} R_3M{-}\langle C_6H_4\rangle{-}C|CH_3|{=}CH_2.$$

In the literature this method for preparing organomagnesium compounds, developed by Normant ([20]), as applied to the synthesis of element-containing styrenes has received the name of the Libbey and Ramsden method ([15]). The most extensive work on the synthesis of organoelement styrenes by this method belongs to Noltes, Bodding, and Van der Kerk ([3],[14]). They obtained trimethyl- and triphenylelement-substituted styrenes and α-methylstyrenes in yields of 60–80%.

The synthesis of silicon-, germanium-, and tin-containing styrenes by interaction

the interaction of vinyl bromide with bromophenyl derivatives of these elements according to the scheme ([23]):

$$R_3M\langle\ \rangle Br + CH_2{=}CHBr \xrightarrow[CoCl_2]{Mg} R_3M\langle\ \rangle CH{=}CH_2$$

proceeds in low yields and, as comparison of the properties of compounds obtained by this method and by the methods considered above shows, does not make it possible to obtain styrenes in the individual state.

In the present investigation, for the synthesis of silicon-, germanium-, and tin-substituted styrenes we used both the method of organomagnesium synthesis (Normant–Ramsden) and a new method developed by us for the high-temperature condensation of p-chlorostyrene with silicon hydrides.

On repeating the syntheses, p-trimethylsilyl- and p-trimethylstannylstyrenes were obtained in yields of 76 and 62%, respectively, i.e., approximately the same yields as in work ([3]).

For the first time by this method there were obtained: *p*-triethylsilyl-, *p*-triethylgermyl-, and *p*-triethylstannylstyrenes. The yields of these compounds were somewhat lower and amounted to 35–40%. Under insufficiently deep vacuum, a considerable part of the styrene formed polymerizes in the distillation flask.

However, of still greater interest than the trialkylelement-substituted compounds should be the element-substituted and, first of all, silicon-substituted styrenes with functional groups at the atom of the element (halogens or alkoxy groups).

Such monomers can be converted into polymers both by polymerization at the double bond and by hydrolysis at the M—Hal (—OR) bonds, followed by polycondensation. Monomers of this type before the present investigation had been synthesized only by pyrolysis of chloroalkylphenylchlorosilanes ([9,11]). It proved that styrylchlorosilanes can also be obtained by the interaction of chloro *p*-vinylphenylmagnesium with silicon tetrachloride, methyltrichlorosilane, and dimethyldichlorosilane in yields exceeding 50%. The formulas, properties, and analyses of the element-containing styrenes synthesized by the indicated Mg-organic method are given in Table 1.

By the procedure of the recently developed reaction of high-temperature condensation ([21,22]) of chlorosilicon hydrides with chlorinated aryls, using *p*-chlorostyrene or *p*-chloro-α-methylstyrene as the aromatic component, in the present investigation we obtained a series of chlorosilylstyrenes and α-methylchlorosilylstyrenes:

$$Cl_3SiH + Cl\langle\ \rangle CH{=}CH_2 \xrightarrow{500\text{–}600^\circ} HCl + Cl_3Si\langle\ \rangle CH{=}CH_2.$$

The results of experiments on the synthesis of chlorosilylstyrenes and α-methylchlorosilylstyrenes by the method of high-temperature condensation are presented in Table 2.

It is interesting to note that in the case of the interaction of trichlorosilane and methyldichlorosilane with *p*-chlorostyrene and with *p*-chloro-α-methylstyrene, we were unable to isolate from the reaction mixture either silicon tetrachloride or methyltrichlorosilane, nor any reduction products of styrene or α-methylstyrene. Probably, the high-temperature interaction here proceeds mainly by a condensation reaction, and not by reduction.

Experimental part

Preparation of *p*-trimethylsilylstyrene

The reaction was carried out in a nitrogen atmosphere in a three-necked flask equipped with a stirrer, dropping funnel, thermometer, and reflux condenser. To 15 g of Mg (0.6 mole) were added 2–3 ml of ethyl bromide in 7–8 ml of tetrahydrofuran (THF). To the magnesium thus activated, 70 ml of THF was added. After the addition of 50 g (0.6 mole) of *p*-chlorostyrene in 70 ml of THF had been completed (over 2 h), the reaction mixture was stirred at 30–40° for another 45 min (until complete dissolution of the magnesium). To the resulting Grignard ···

reagent over 2 hr. At 25° there was added 38.8 g (0.35 mole) of trimethylchlorosilane dissolved in 100 ml of THF. The reaction mixture was then heated at 40° for 2 hr; 0.01 g of picric acid was added, and the mixture was decomposed with 5% HCl solution. After the usual work-up and drying over $CaCl_2$, the mixture was distilled. THF was distilled off at 10–20°C with a water-jet pump, and the residue was distilled in vacuum (0.1–0.4 mm Hg). There was obtained 39 g of *p*-trimethylsilylstyrene in 76% yield. Its properties, as well as the yields and properties of other trialkylelement-substituted styrenes obtained in an analogous manner, are given in Table 1.

Preparation of *p*-trichlorosilylstyrene. The Grignard reagent, prepared from 28 g (0.2 mole) of *p*-chlorostyrene by the method described above, was treated over 2 hr, at a reaction-mixture temperature of −50°, with 102 g (0.6 mole) of silicon tetrachloride. After completion of the addition of the Grignard reagent, the contents of the flask were heated to 30–40° (over 1 hr). After separation of the precipitate, the mixture was distilled; THF and $SiCl_4$ were distilled off at room temperature with a water-jet pump. The remaining portion was distilled in vacuum (0.4–0.5 mm Hg). There was obtained 25 g of *p*-trichlorosilylstyrene, i.e., 55% of the theoretical yield.

Preparation of *p*-trichlorosilylstyrene by the method of high-temperature condensation. The reaction was carried out in the presence of

Table 1

Compound obtained	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % M	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % M	Calculated, % Cl
p-$(CH_3)_3SiC_6H_4CH{=}CH_2$	76	56/0.5	1.5250	0.8913	75.76; 75.56	8.89; 8.85	15.30; 15.15	–	75.72	9.20	15.08	–
p-$(CH_3)_3SnC_6H_4CH{=}CH_2$	62	68/0.5	1.5643	1.2990	49.30; 49.33	5.06; 5.00	44.24; 44.56	–	49.30	6.10	44.60	–
p-$(C_2H_5)_3SiC_6H_4CH{=}CH_2$	35	69/0.4	1.5290	0.9107	76.98; 76.99	10.30; 10.22	12.72; 12.96	–	76.88	10.19	12.93	–
p-$(C_2H_5)_3GeC_6H_4CH{=}CH_2$	35	85/0.3	1.5472	1.0740	63.97; 63.70	8.44; 8.21	27.57; 27.80	–	63.96	8.43	27.61	–
p-$(C_2H_5)_3SnC_6H_4CH{=}CH_2$	40	101/0.5	1.5530	1.2556	54.01	7.17	37.54	–	54.40	7.35	38.25	–
p-$Cl_3SiC_6H_4CH{=}CH_2$	55	71/0.4	1.5570	1.2570	–	–	44.61	–	–	–	–	44.80

Compound obtained	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % M	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % M	Calculated, % Cl
p-$Cl_3SiC_6H_4C(CH_3)=CH_2$	50	47/0.4	1.5415	1.8570	–	–	32.35	–	–	–	–	32.71
p-$ClSi(CH_3)_2C_6H_4CH=CH_2$	50	52.5/0.34	1.5370	1.0410	–	–	18.12	–	–	–	–	18.34

Table 2

Styrene obtained	Reaction-zone temp., °C	Duration of contact of reagents, sec	Yield, %, based on starting chlorostyrene	Yield, %, based on converted silicon hydride	Properties of styrene b.p., °C/mm Hg	Properties of styrene: n_D^{20}	Properties of styrene: d_4^{20}	Cl content, %, found	Cl content, %, calculated
n-$Cl_3Si-C_6H_4-CH=CH_2$	570	30	30	65	64/0.44	1.5570	1.2570	44.6	44.8
n-$Cl_3Si-C_6H_4-C(CH_3)=CH_2$	550	40	19	35	67/0.52	1.5500	1.4060	41.95	42.21
n-$Cl_2Si(CH_3)-C_6H_4-CH=CH_2$	570	30	34	61.5	47/0.44	1.5459	1.1817	32.40	32.71
n-$Cl_2Si(CH_3)-C_6H_4-C(CH_3)=CH_2$	550	40	23	53.5	57/0.4	1.5484	1.1417	30.4	30.8

apparatus described in [23]. For the reaction, 33.8 g (0.25 mole) of trichlorosilane and 27.7 g (0.2 mole) of *p*-chlorostyrene were taken. Experimental conditions: temperature 550°, duration of contact of the reagents in the reaction zone 30 sec.

As a result of the reaction, upon distillation we isolated: 7 g of $HSiCl_3$, i.e., 20.7% of the $HSiCl_3$ taken into the reaction; 6 g of *p*-chlorostyrene, i.e., 21.7% of the *p*-chlorostyrene taken into the reaction; and 12.5 g of *p*-trichlorosilylstyrene, which amounts to 30% of the theoretical yield of *p*-trichlorosilylstyrene, or 65% based on converted silicon hydride.

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