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Abstract

Full Text

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THERMAL TELOMERIZATION OF OLEFINS WITH SILANES CONTAINING AN Si–H BOND

As we have shown (^{1}), ethylene enters into a telomerization reaction with methyldichlorosilane and trichlorosilane at a temperature of 270-300° under pressure, under conditions ensuring an excess of ethylene, giving a mixture of substances of the structure $XSiCl_2(CH_2CH_2)_{nH}$, where $X = Cl,\ CH_3$. The reaction was carried out in steel autoclaves without the addition of catalysts or reaction initiators. Propylene with methyldichlorosilane also readily enters into the telomerization reaction under these conditions.

It was of interest to ascertain whether silanes not containing halogen also enter into this reaction, as well as silanes in which silicon is bonded to an aromatic nucleus, i.e., whether, for example, the following reactions are possible:

$$R_3SiH + n\,CH_2 = CH_2 \to R_3Si(CH_2CH_2)_{nH},$$

where $R = Alk;\ OAlk$;

$$ArSiCl_2H + n\,CH_2 = CH_2 \to ArSiCl_2(CH_2CH_2)_{nH}.$$

In the literature concerning the addition of silanes of this type to the double bond of olefins, it is stated that, in the presence of initiators of radical reactions, triethoxysilane generally does not add to the double bond (^{2})*; triethylsilane likewise does not react, or gives a small yield of an impure product (^{2,4}).

Phenyldichlorosilane, according to patent data (^{5}), reacts with ethylene at a temperature of 200-550° with formation of phenylethyldichlorosilane.

We have established that ethylene smoothly enters into a thermal telomerization reaction with phenyldichlorosilane. At 280° and 90 atm, compounds of the composition $C_6H_5SiCl_2(CH_2CH_2)_{nH}$, where $n = 1, 2, 3$, were obtained. The reaction of ethylene with triethylsilane was carried out at 300° and 200 atm. From the reaction products it was possible to isolate tetraethylsilane and triethyl-*n*-butylsilane. Fractions containing higher triethylalkylsilanes were also obtained.

In the case of the reaction of triethoxysilane with ethylene at 300°, a fall in pressure (from 100 to 35 atm) and absorption of ethylene (22 g per 75 g of charged triethoxysilane) were also observed. However, it was not possible to isolate individual alkyltriethoxysilanes, since under the reaction conditions a disproportionation reaction apparently takes place.

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* According to patent data (^{3}), triethoxysilane reacts with ethylene in the presence of platinized asbestos, giving ethyltriethoxysilane in 50% yield.

Experimental Part

Preparation of the starting silanes. $(C_2H_5)_3SiH$ was obtained from $C_2H_5SiCl_2H$ by the Grignard reaction, b.p. 108-109°; n_D^{20} 1.4115. Literature data: b.p. 107° (6); 103.5-104.5° (7); n_D^{20} 1.4117 (6); n_D^{20} 1.4100 (7).

Triethoxysilane was synthesized by the method of Havill et al. (8). The constants obtained for this compound coincided with the literature data.

Phenyldichlorosilane was synthesized from silicochloroform and phenylmagnesium bromide (9). The constants obtained coincide with the literature data.

Telomerization of ethylene with triethylsilane. The reaction was carried out in a steel autoclave of 0.5 l capacity. The autoclave was charged with 90 g of $(C_2H_5)_3SiH$ and, after purging with nitrogen, ethylene was introduced. The reaction mixture was heated to 300°, the pressure thereby rising to 200 atm. The reaction was conducted at 300-310° for 4 hr. In this time the ethylene pressure fell to 80 atm. Weight of the reaction product, 119 g. The product was fractionated on a 15 theoretical-plate column. The following was distilled:

a) 60 g of the starting triethylsilane, b.p. 108-109°; n_D^{20} 1.4112.

b) 15 g of tetraethylsilane, b.p. 153°; n_D^{20} 1.4246; d_4^{20} 0.7665; MR_{found} 48.30; MR_{calc} 48.78.

Found %: C 66.82; 66.59; H 13.96; 13.92
$C_8H_{20}Si$. Calculated %: C 66.56; H 13.97

Literature data (10): b.p. 153°; d_4^{20} 0.7662; n_D^{25} 1.4240.

b) 8 g of triethylbutylsilane, b.p. 89-93°/30 mm; n_D^{20} 1.4360; d_4^{20} 0.7810; MR_{found} 57.60; MR_{calc} 58.08.

Found %: C 70.37; 70.31; H 14.08; 14.08; Si 15.57; 15.57.
$C_{10}H_{24}Si$. Calculated %: C 70.24; H 14.03; Si 15.66

Literature data (10): b.p. 192°; n_D^{25} 1.4358; d_4^{20} 0.7786.

c) 18.5 g of fraction 70-110°/4 mm. It was not possible to isolate hexyl- and octyltriethylsilanes from it in pure form, evidently because of the presence of impurities of disproportionation-reaction products. Residue, 11 g.

Telomerization of ethylene with phenyldichlorosilane. The reaction was carried out in an autoclave of 0.15 l capacity made of steel ÉYa-1T. The autoclave was charged with 35 g of $C_6H_5SiCl_2H$ and, after purging with nitrogen, ethylene was introduced. The reaction mixture was heated to 280°, the pressure thereby rising to 90 atm. The reaction was conducted at 280-300° for 3 hr. In this time the ethylene pressure fell to 60 atm. A total of 43 g of product was obtained. The product was distilled on a 15 theoretical-plate column. The following fractions were isolated:

Fraction I: b.p. 104-107°/20 mm, weight 14 g, n_D^{20} 1.5170

Fraction II: b.p. 78-83°/3 mm, weight 4.7 g, n_D^{20} 1.5140

Fraction III: b.p. 98-104°/3 mm, weight 3 g, n_D^{20} 1.5100

Residue, 11 g.

On redistillation, phenylethyldichlorosilane, phenylbutyldichlorosilane, and phenylhexyldichlorosilane were isolated in individual form from fractions I, II, and III, respectively. These substances rapidly turn red in the light.

and are readily hydrolyzed in air. The properties and analyses of the compounds obtained are summarized in Table 1.

Table 1

Analysis and physical constants of $C_6H_5SiCl_2(CH_2CH_2)_{nH}$

n	n_D^{20}	d_4^{20}	MR, found	MR, calc.	B.p., °C/mm	C, %, calc.	C, %, found	H, %, calc.	H, %, found	Cl, %, calc.	Cl, %, found	Si, %, calc.	Si, %, found
1*	1.5180	1.1490	54.12	54.12	84/7	46.83	47.17 47.18	4.89	4.98 5.14	34.56	34.44 34.30	13.62	13.63 13.24
2	1.5140	1.1181	62.80	63.42	90–91/3	51.49	51.11 50.95	6.04	6.10 6.20	30.41	31.83 30.78	12.05	12.05 11.68
3	1.5100	1.0832	72.15	72.72	115–118/3	55.12	55.17 55.02	7.26	6.90 7.23	27.13	26.94 27.08	10.75	10.83 10.26

* Literature data: b.p. 134–135.5°/5 mm (^{4}), 225–235° (^{12}).

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CITED LITERATURE

[1] A. N. Nesmeyanov, R. Kh. Freidina, E. Ts. Chukovskaya, DAN, **112**, 271 (1957); **113**, 120 (1957).
[2] E. Pietrutza, L. Sommer, F. Whitmore, J. Am. Chem. Soc., **70**, 484 (1948).
[3] G. Wagner, C. Strother, English Patent 670617.
[4] D. Seyferth, E. Rochow, J. Org. Chem., **20**, 250 (1955).
[5] A. J. Barry, D. E. Hook, L. DePree, U.S. Patent 2510853; Chem. Abstr., **44**, 8933 c (1950); English Patent 632824, Chem. Abstr., **44**, 5378 (1950).
[6] F. Whitmore, E. Pietrutza, L. Sommer, J. Am. Chem. Soc., **69**, 2108 (1947).
[7] H. Gilman, R. Ingham, A. Smith, J. Org. Chem., **18**, 1743 (1953).
[8] M. Havill, J. Joffe, H. Post, J. Org. Chem., **13**, 280 (1948).
[9] A. J. Barry, English Patent 618403; Chem. Abstr., **43**, 5801 (1949).
[10] F. Whitmore, L. Sommer et al., J. Am. Chem. Soc., **68**, 475 (1946).
[11] R. F. Flemming, U.S. Patent 2386452; Chem. Abstr., **40**, 6039 (1946).

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

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