HETEROFUNCTIONAL COCONDENSATION OF ACETOXYMETHYL-(PHENYL)SILANES WITH ORGANOSILICON COMPOUNDS CONTAINING SILICON-ATTACHED ETHOXY GROUPS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 9, pp. 1572-1577, September, 1962
Original article submitted February 14, 1962

In presence of catalysts, alkoxyalkyl(aryl)silanes undergo stagewise condensation with acetoxyalkyl(aryl)-silanes [1, 2]. The products of the reaction are condensation products of low molecular weight (organosiloxanes of linear structure) and ethyl acetate. Ferric chloride, aluminum chloride, toluenesulfonic acid, and the sodium derivative of a silanol may be used as catalysts.

In the present investigation we studied the cocondensation of organosilicon compounds having silicon-attached ethoxy groups with acetoxymethyl(phenyl)silanes in presence of hydrochloric acid. Our investigations showed that in presence of hydrochloric acid various compounds containing silicon-attached ethoxy groups readily undergo co-condensation with acetoxytrimethylsilane, with acetoxydimethylphenylsilane, with acetoxymethyldiphenylsilane, and with acetoxytriphenylsilane. In the condensation of tetraethoxysilane with acetoxytrimethylsilane reaction proceeds as follows:

$$Si(OC_2H_5)_4 + 4CH_3COOSi(CH_3)_3 \rightarrow$$
$$\rightarrow Si[OSi(CH_3)_3]_4 + 4CH_3COOC_2H_5 .$$

Tetrakistrimethylsiloxysilane is formed in about 80% yield. According to the literature [3] the yield of tetrakistrimethylsiloxysilane obtained from silicon tetrachloride and sodium trimethylsiloxide is only 18%. Hexaethoxydisiloxane reacts with acetoxytrimethylsilane with formation of hexakistrimethylsiloxydisiloxane in accordance with the equation:

$$(C_2H_5O)_3Si - O - Si(OC_2H_5)_3 + 6CH_3COOSi(CH_3) \rightarrow$$

$$\rightarrow [(CH_3)_3SiO]_3Si - O - Si - [OSi(CH_3)_3]_3 + 6CH_3COOC_2H_5.$$

By the cocondensation of octamethyltrisiloxane with acetoxytrimethylsilane in accordance with the above scheme we obtained octakistrimethylsiloxytrisiloxane:

$$[(CH_3)_3SiO]_3SiO - \underset{\displaystyle OSi(CH_3)_3}{\overset{\displaystyle OSi(CH_3)_3}{\overset{|}{\underset{|}{SiO}}}} - Si[OSi(CH_3)_3]_3 .$$

In the investigation of the cocondensation of acetoxytrimethylsilane with 1,3-bischloromethyltetraethoxydisiloxane and with 1,3,5-trischloromethylpentaethoxytrisiloxane it was shown that the scheme of the reaction is analogous to the above, which was confirmed by the isolation of compounds of general formula

$$ClCH_2Si(OSi(CH_3)_3)_2 - (O - Si(OSi(CH_3)_3)(CH_2Cl))_n - O - Si(OSi(CH_3)_3)_2CH_2Cl$$

in which n = 0 and 1, and the formation of ethyl acetate in close to the theoretical amounts. The reaction between 1,3-bischloromethyltetraethoxydisiloxane with acetoxydimethylphenylsilane goes in the same way with formation of 1,3-bischloromethyltetrakis(dimethylphenylsiloxy)disiloxane.

Investigation of this cocondensation reaction for the synthesis of unsaturated compounds of the siloxane series having methacryloyloxy groupings in the hydrocarbon groups showed that ethoxy[(methacryloyloxy)methyl]methylsilanes react with acetoxytrimethyl-, acetoxydimethylphenyl-, acetoxymethyldiphenyl-, and acetoxytriphenylsilanes in accordance with the general scheme

$$CH_2=C(CH_3)COOCH_2Si(CH_3)_{3-n}(OC_2H_5)_n + n\,CH_3COOSi(R)_n(CH_3)_{3-n} \rightarrow$$
$$\rightarrow CH_2=C(CH_3)COOCH_2Si(CH_3)_{3-n}[OSi(CH_3)_{3-n}]_n + n\,CH_3COOC_2H_5$$

in which R = CH_3-, C_6H_5-, n = 1, 2, 3.

The table gives the physical properties of the new compounds. Those containing methacryloyl groups, namely 1-[(methacryloyloxy)methyl]tetramethyl-3-phenyldisiloxane, 3-[(methacryloyloxy)methyl]pentamethyl-1,5-diphenyltrisiloxane, 1-[(methacryloyloxy)methyl]trimethyl-3,3-diphenyldisiloxane, and 1-[(methacryloyloxy)methyl]-dimethyl-3,3,3-triphenyldisiloxane, (like methacryloyl derivatives of the methylsiloxane series) readily polymerize in presence of benzoyl peroxide. The investigation of the polymerization of methacryloyl derivatives of the methylphenylsiloxane series will be described in a future paper.

EXPERIMENTAL

A three-necked round-bottomed flask fitted with mechanical stirrer, thermometer, and reflux condenser was charged with a weighed amount of the ethoxy derivative. The calculated amount (+5% excess) of the acetoxysilane was added. The mixture was stirred, and concentrated hydrochloric acid (10% by weight on the mixture of organosilicon reactants) was added.

When the hydrochloric acid was added, the temperature of the reaction mixture rose to 50-53°. After this addition stirring of the mixture was continued until its temperature reached that of the room.

The resulting reaction mixture was dissolved in diethyl ether. The ethereal solution was washed with sodium bicarbonate solution until neutral. The washed product was fractionated. First, ethyl acetate was distilled off at atmospheric pressure, and then the organosilicon products were vacuum-distilled off.

Hexakistrimethylsiloxydisiloxane and octakistrimethylsiloxytrisiloxane were purified by sublimation.

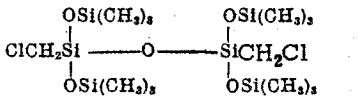
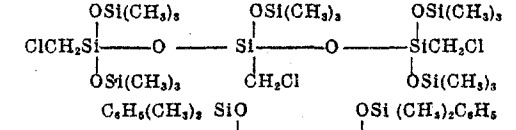
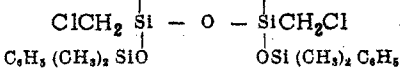
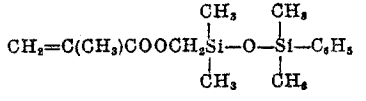
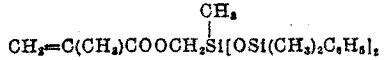
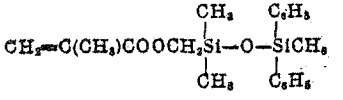
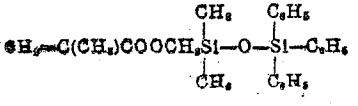
Tetrakistrimethylsiloxysilane $Si[OSi(CH_3)_3]_4$. From 20.8 g of tetraethoxysilane (b.p. 166°), 44.9 g of acetoxytrimethylsilane (b.p. 103°), and 6.5 g of 35% hydrochloric acid we obtained 31.5 g (82%) of products; b.p. 118-119° at 22 mm; n_D^{20} 1.3890; yield 82% of product.

Hexakistrimethylsiloxydisiloxane $[(CH_3)_3SiO]_3Si-O-Si[OSi(CH_3)_3]_3$. From 13.7 g of hexaethoxydisiloxane [b.p. 200° (13 mm); n_D^{20} 1.3902; d_4^{20} 0.9950], 32 g of acetoxytrimethylsilane, and 4.6 g of 35% hydrochloric acid we obtained 19 g (70%) of product; m.p. 96°. Found: C 35.50; H 8.62; Si 36.73%. $C_{18}H_{54}O_7Si_8$. Calculated: C 35.60; H 8.90; Si 37.03%.

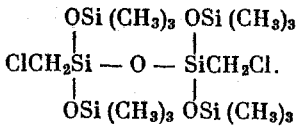
Octakistrimethylsiloxytrisiloxane

$$[(CH_3)_3SiO]_3Si-O-\underset{\displaystyle OSi(CH_3)_3}{\overset{\displaystyle OSi(CH_3)_3}{Si}}-O-Si[OSi(CH_3)_3]_3.$$

From 0.2 g of octaethoxytrisiloxane n_D^{20} 1.3965; d_4^{20} 1.0310; b.p. 224° (8 mm), 21.2 g of acetoxytrimethylsilane, and 3 g of 35% hydrochloric acid we obtained 11 g (66%) of product, m.p. 138°. Found: C 34.79; H 8.52; Si 36.98%. $C_{24}H_{72}O_{10}Si_{11}$. Calculated: C 34.75; H 8.68; 37.27%.

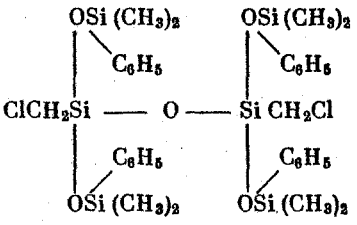
Compound	Formula	B.p., °C (p, mm)	d_4^{20}	n_D^{20}	*MR* Found	*MR* Calc.
1,3-Bichloromethyltetrakistrimethylsiloxydisiloxane		233—234 (40)	0,9944	1,4169	133,00	133,38
1,3,5-Trischloromethylpentakistrimethylsiloxytrisiloxane		245 (25)	1,0368	1,4230	174,23	173,92
1,3-Bischloromethyltetrakis(dimethylphenylsiloxy)disiloxane		302 (3)	1,1163	1,5185	210,73	210,94
1-[(Methacryloyloxy)methyl]tetramethyl-3-phenyldisiloxane		108—109 (1)	0,9913	1,4823	88,89	88,80
3-[(Methacryloyloxy)methyl]pentamethyl-1,5-diphenyltrisiloxane		165—166 (1)	1,0229	1,5028	128,12	127,73
1-[(Methacryloyloxy)methyl]trimethyl-3,3-diphenyldisiloxane		145—146 (1)	1,0471	1,5253	109,028	108,40
1-[(Methacryloyloxy)methyl]dimethyl-3,3,3-triphenyldisiloxane		163—167 (0,03)	1,0866	1,5630	129,10	129,18

1,3-Bischloromethyltetrakistrimethylsiloxydisiloxane



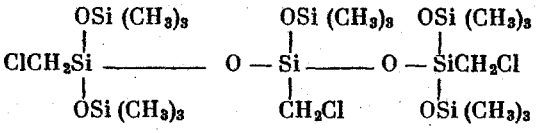
From 7 g of 1,2-bischloromethyltetraethoxydisilane [b.p. 172° (40 mm); d_4^{20} 1.1245; n_D^{20} 1.4250], 11.2 g of acetoxytrimethylsilane, and 1.8 g of 35% hydrochloric acid we obtained 5.65 g (53.6%) of product, b.p. 209-210° (20 mm). Found: C 31.58; H 7.60; Cl 13.61; Si 32.25%. $C_{14}H_{40}O_5Cl_2Si_6$. Calculated: C 31.84; H 7.58; Cl 13.45; Si 31.97%.

1,3-Bischloromethyltetrakis(dimethylphenylsiloxy)disiloxane



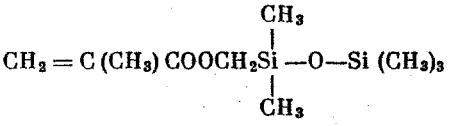
From 7 g of 1,2-bischloromethyltetraethoxydisiloxane, 16.2 g of acetoxydimethylphenylsilane [b.p. 126-128° (30 mm)], and 2 g of 35% hydrochloric acid we obtained 3 g (about 20%) of product. Found: C 51.93; H 6.24; Cl 9.18; Si 22.05%. $C_{34}H_{58}O_5Cl_2Si_6$. Calculated: C 52.60; H 6.18; Cl 9.15; Si 21.73%.

1,3,5-Trischloromethylpentakistrimethylsiloxytrisiloxane



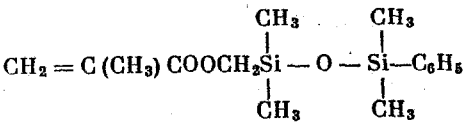
From 9.8 g of 1,3,5-trischloromethylpentaethoxytrisiloxane [b.p. 198° (17 mm); n_D^{20} 1.4320; d_D^{20} 1.1603], 13.7 g of acetoxytrimethylsilane, and 2.3 g of 35% hydrochloric acid we obtained 6.1 g (43%) of product. Found: C 30.15; H 7.02; Cl 14.27; Si 31.59%. $C_{18}H_{51}O_7Cl_3Si_8$. Calculated: C 30.45; H 7.17; Cl 14.41; Si 31.68%.

[(Methacryloyloxy)methyl]pentamethyldisiloxane



From 10.1 g of ethoxy[(methacryloyloxy)methyl]dimethylsilane (n_D^{20} 1.4300; d_4^{20} 0.9421), 6.7 g of acetoxytrimethylsilane, and 1.6 g of 35% hydrochloric acid we obtained 9.6 g (56%) of product d_4^{20} 0.910; n_D^{20} 1.4200).

1-[(Methacryloyloxy)methyl]tetramethyl-3-phenyldisiloxane



From 0.02 mole of ethoxy[(methacryloyloxy)methyl]dimethylsilane, 0.025 mole of acetoxydimethylphenylsilane, and 0.7 g of 35% hydrochloric acid we obtained 3.7 g (60%) of product. Found: C 57.74; H 7.79; Si 18.35%. $C_{15}H_{24}O_3Si$. Calculated: C 58.40; H 7.78; Si 18.23%.

3-[(Methacryloyloxy)methyl]heptamethyltrisiloxane

$$CH_2=C(CH_3)COOCH_2\overset{CH_3}{\underset{|}{Si}}-[OSi(CH_3)_3]_2.$$

From 7 g of diethoxy[(methacryloyloxy)methyl]methylsilane (n_D^{20} 1.4260; d_4^{20} 0.9753), 8.3 g of acetoxytrimethylsilane, and 1.5 g of hydrochloric acid we obtained 6.8 g (71%) of product.

1-[(Methacryloyloxy)methyl]trimethyl-3,3-diphenyldisiloxane

$$CH_2=C(CH_3)COOCH_2Si(CH_3)_2-O-Si(C_6H_5)_2CH_3.$$

From 0.02 mole of ethoxy[(methacryloyloxy)methyl]dimethylsilane, 0.021 mole of acetoxymethyldiphenylsilane [b.p. 194-198° (25 mm), acetate value 22.9], and 0.78 g of 3% hydrochloric acid we obtained 2 g (33%) of product; b.p. 174-178°. Found: C 64.47; H 6.95; Si 15.30%. $C_{20}H_{26}O_3Si_2$. Calculated: C 64.83; H 7.00; Si 15.17%.

1-[(Methacryloyloxy)methyl-dimethyl-3,3,3-triphenyldisiloxane

$$CH_2=C(H_3)-COOCH_2Si(CH_3)_2-O-Si(C_6H_5)_3.$$

From 16.2 g of ethoxy[(methacryloyloxy)methyl]dimethylsilane, 26.8 g of acetoxytriphenylsilane [b.p. 230-240° (12 mm); acetate value 16.9], and 3.17 g of 35% hydrochloric acid we obtained 5.2 g (20%) of product, b.p. 167° (0.03 mm). Found: C 70.88; H 6.60; Si 12.21%. $C_{25}H_{28}O_3Si_2$. Calculated: C 69.5; H 6.71; Si 12.95%.

3-[(Methacryloyloxy)methyl]pentamethyl-1,5-diphenyltrisiloxane

$$CH_2-C(CH_3)-COOCH_2Si(CH_3)[OSi(CH_3)_2C_6H_5]_2.$$

From 7 g of diethoxy[(methacryloyloxy)methyl-methylsilane, 12.2 g of acetoxydimethylphenylsilane, and 1.9 g of 35% hydrochloric acid we obtained 2.9 g (22%) of distilled product. Found: C 59.82; H 7.18; Si 19.56%. $C_{21}H_{32}O_4Si_3$. Calculated: C 59.72; H 7.21; Si 18.95%.

SUMMARY

1. An investigation was made of the cocondensation of various organosilicon compounds containing silicon-attached ethoxy groups with acetoxymethyl(phenyl)silanes in presence of hydrochloric acid. The process leads to the formation of cocondensation products and ethyl acetate.

2. The following new organosilicon compounds were prepared by this reaction: 1,3-bischloromethyltetrakistrimethylsiloxydisiloxane, 1,3-bischloromethyltetrakis(dimethylphenylsiloxy)disiloxane, 1,3,5-trischloromethylpentakistrimethylsiloxytrisiloxane, 1-[(methacryloyloxy)methyl]tetramethyl-3-phenyldisiloxane, 1-[(methacryloyloxy)methyl[trimethyl-3,3-diphenyldisiloxane, 1-[(methacryloyloxy)methyl-dimethyl-3,3,3-triphenyldisiloxane, and 3-[(methacryloyloxy)methyl]pentamethyl-1,5-diphenyltrisiloxane.

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