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Abstract

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SYNTHESIS OF ORGANOSILICON COMPOUNDS CONTAINING A METHACRYLIC GROUP

In continuation of previously conducted investigations ([1]), the present communication describes the preparation of new organosilicon compounds containing a methacrylic group in the hydrocarbon radical at the silicon atom—methacrylatemethylalkoxysilanes and methacrylic compounds—tri-, tetra-, and pentasiloxanes. Methacrylatemethylalkoxysilanes were obtained according to the scheme:

$$\underset{(CH_3)_n}{ClCH_2Si(OR)_{3-n}} + CH_2=C(CH_3)COOK \xrightarrow{-KCl} \underset{(CH_3)_n}{CH_2=C(CH_3)COOCH_2Si(OR)_{3-n}},$$

where $R = C_2H_5$, C_4H_9, and $n = 2;\ 1;\ 0$.

The properties of the compounds obtained are presented in Table 1.

Table 1

Formulas	B.p. at 5 mm Hg, °C	d_4^{20}	n_D^{20}	MR found	MR calc.	Bromine number found	Bromine number calc.	Si, % found	Si, % calc.
$CH_2=C(CH_3)COOCH_2Si(OCH_3)_2C_4H_9$	72–73	0.9421	1.4310	55.19	55.38	78.8	79.2	13.55	13.80
$CH_2=C(CH_3)COOCH_2Si(OC_2H_5)_2CH_3$	97–98	0.9763	1.4260	60.88	60.94	68.7	69.2	11.91	12.07
$CH_2=C(CH_3)COOCH_2Si(OC_2H_5)_2C_4H_9$	86–87	0.9263	1.4340	64.75	64.43	69.3	96.6	12.11	12.15
$CH_2=C(CH_3)COOCH_2Si(OC_4H_9)_2CH_3$	126–127	0.9468	1.4345	79.40	79.38	54.8	55.6	10.14	9.72
$CH_2=C(CH_3)COOCH_2Si(OC_4H_9)_3$	144–145	0.9000	1.4370	94.05	94.28	45.9	46.2	8.32	8.09

To obtain methacrylic compounds of tri-, tetra-, and pentasiloxanes, the reaction of heterofunctional cocondensation of the above-mentioned alkoxysilanes with dimethyldiacetoxysilane and the products of its hydrolysis, as well as with trimethylacetoxysilane, was investigated according to the equations:

1) $$2CH_2=C(CH_3)COOCH_2Si(CH_3)_2OC_2H_5 + CH_3COOSi(CH_3)_2OCOCH_3 \rightarrow$$
$$\xrightarrow{C_2H_5OSO_3H} CH_2=C(CH_3)COOCH_2\underset{CH_3}{\overset{CH_3}{Si}}O\underset{CH_3}{\overset{CH_3}{Si}}O\underset{CH_3}{\overset{CH_3}{Si}}CH_2OCOC(CH_3)=CH_2 + 2CH_3COOC_2H_5$$

2) $$2CH_2=C(CH_3)COOCH_2Si(CH_3)_2OC_2H_5 + CH_3COOSi(CH_3)_2[OSi(CH_3)_2]_nOCOCH_3 \rightarrow$$
$$\xrightarrow{C_2H_5OSO_3H} CH_2=C(CH_3)COOCH_2Si(CH_3)_2[OSi(CH_3)_2]_mOSiCH_2OCOC(CH_3)=CH_2 + 2CH_3COOC_2$$

where $n = 1$ or 2, and $m = 2$ or 3.

3) $$CH_2=C(CH_3)COOCH_2Si(CH_3)(OC_2H_5)_2 + 2CH_3COOSi(CH_3)_3 \rightarrow$$
$$\xrightarrow{C_2H_5SO_3H} (CH_3)_3SiOSi(CH_3)OSi(CH_3)_3 + 2CH_3COOC_2H_5$$
$$CH_2OCOC(CH_3)=CH_2$$

In studying the heterofunctional cocondensation reaction it was found that the reaction proceeds readily with the formation of methacrylic compounds of siloxanes and the liberation of ethyl acetate at a temperature of ~20°, if ethylsulfuric acid containing not less than 2 wt.% water (calculated on the total amount of reacting organosilicon compounds) is used as the catalyst. The properties of the compounds obtained are presented in Table 2.

Table 2

Formula	B.p., °C (2 mm Hg)	d_4^{20}	n_D^{20}	MR, found	MR, calc.	Bromine number, found	Bromine number, calc.	Si, %, found	Si, %, calc.
$(CH_3)_3SiOSi(CH_3)OSi(CH_3)_2OCOC(CH_3)=CH_2$	91	0.9107	1.4150	87.30	87.46	49.1	50.0	26.00	26.23
$CH_2=C(CH_3)COOCH_2Si(CH_3)[OSi(CH_3)_2]_2OCOC(CH_3)=CH_2$	148	0.9862	1.4310	105.36	107.20	76.6	79.2	20.59	20.82
$CH_2=C(CH_3)COOCH_2Si(CH_3)[OSi(CH_3)_2]_3OCOC(CH_3)=CH_2$	163	0.9963	1.4310	125.46	127.84	66.5	67.0	23.52	23.43

Formula	B.p., °C (2 mm Hg)	d_4^{20}	n_D^{20}	MR, found	MR, calc.	Bromine number, found	Bromine number, calc.	Si, %, found	Si, %, calc.
$CH_2=C(CH_3)COOCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OOCC(CH_3)=CH_2$	177–178	0.9941	1.4310	104.30	104.48	57.3	57.9	11.5	11.10	25.36

A detailed description of the syntheses of the unsaturated organosilicon compounds obtained is presented in another article*. The synthesized methacrylic compounds are being studied with the aim of obtaining organosilicon polymers, as well as block copolymers.

Experimental Part

Preparation of methacrylatemethylalkoxysilanes

Into an autoclave of 150 ml capacity was charged a reaction mixture containing 0.26 mole of chloromethylalkoxysilanes: 38.1 g of chloromethyldimethylethoxysilane, 45.5 g of chloromethylmethyldiethoxysilane, 45.0 g of chloromethylmethylbutoxysilane, 59.6 g of chloromethylmethyldibutoxysilane, or 74.1 g of chloromethyltributoxysilane, 37.2 g (0.3 mole) of potassium methacrylate, 5 g of copper (as powder), and 0.3 g of hydroquinone. The autoclave, while rotating, was heated at 180° for 3.5 h. After cooling, the autoclave was opened; the reaction mixture was rapidly filtered to separate KCl and unreacted $CH_2=C(CH_3)COOK$, after which it was subjected to vacuum distillation. The fraction boiling within a 3° range (1° above and below the corresponding temperatures indicated in Table 1) was collected. Methacrylatemethylbutoxysilanes can also be obtained by heating under ordinary conditions at the boiling temperature of the reaction mixture for 2 h. Yield 30%.

Preparation of 1,3-dimethacrylatemethylhexamethyltrisiloxane, 1,4-dimethacrylatemethyloctamethyltetrasiloxane, 1,5-dimethacrylatemethyldecamethylpentasiloxan and 2-methacrylatemethylheptamethyltrisiloxane

A reaction mixture containing 12.1 g (0.06 mole) of methacrylatemethyldimethylethoxysilane and, respectively, 4.4 g of dimethyldiacetoxysilane, 6.25 g of 1,2-diacetoxytetramethyldisiloxane (d_4^{20} 1.0232, n_D^{20} 1.4010), or 8.1 g of 1,3-diacetoxyhexamethyltrisiloxane

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(d_4^{20} 1.0131, n_D^{20} 1.4030), or a reaction mixture containing 11.6 g (0.06 mole) of methacrylatemethylmethyldiethoxysilane and 28.8 g (0.12 mole) of trimethylacetoxysilane was placed in a round-bottom flask of 75 ml capacity, equipped with a mechanical stirrer, thermometer, dropping funnel, and condenser. With

stirring and cooling of the flask with water, ethylsulfuric acid containing 2 wt.% water was added dropwise to the mixture over 10–15 min, in an amount of 5 or 10 wt.% (for obtaining 2-methacrylatemethylheptamethyltrisiloxane). After addition of the ethylsulfuric acid had been completed, the reaction mixture separated into two layers; stirring was stopped and the mixture was left to stand for 48 h at a temperature of ~20°. After the holding period, the lower layer (ethylsulfuric acid) was separated by means of a separatory funnel. The ethereal layer was neutralized with $NaHCO_3$, after which it was subjected to distillation. First ethyl acetate was distilled off, and then the remaining product was distilled in vacuo. During distillation, fractions boiling at the temperatures indicated in Table 2 were collected. Yield 25–33%.

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REFERENCES

[1] K. A. Andrianov, N. S. Leznov, A. K. Dabagova, *Izv. AN SSSR, OKhN*, 1957, 459.

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