THE ADDITION OF CYCLIC SILOXANES CONTAINING Si-H BONDS TO UNSATURATED COMPOUNDS

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S. N. Borisov, V. V. Vinogradova, I. N. Lyashenko,
N. S. Nametkin, and T. I. Chernysheva

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences, USSR, and All-Union Research Institute of Synthetic Rubber

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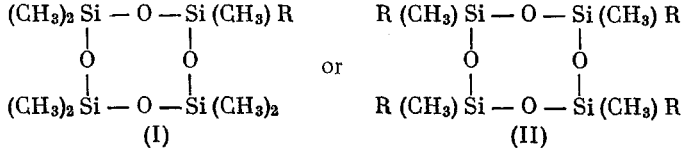
The preparation of modified polymers by use of the products of addition of cyclosiloxanes containing Si-H bonds to unsaturated compounds is practically unstudied. We know only the work of Ryan and Speier [1] who obtained methyl-(2-phenyl-propyl)cyclosiloxane by addition of $(CH_3SiHO)_{4-5}$ to α-methylstyrene in the presence of chloroplatinic acid, and the patent [2] on addition of $(CH_3SiHO)_5$ to the monoepoxy derivative of vinyl cyclohexene.

In the course of obtaining types of silico-organic elastomers we studied the addition of heptamethyl cyclotetrasiloxane to α-methylstyrene, 1-nonene, methylmethacrylate, and allyl amine, and also of sym-tetramethyl cyclotetrasiloxane to methylmethacrylate. We showed that, in the presence of chloroplatinic acid, addition in all cases, independent of the nature of the unsaturated compound, occurs according to the Farmer rule with retention of the cyclic structure and formation in each case of one compound of the type



(I) or (II)

The structures of the resulting compounds were confirmed by infrared spectra and NMR spectra. The conditions of the experiments and properties of the resulting compounds are given in the table.

EXPERIMENTAL

Heptamethyl cyclotetrasiloxane was isolated from the products of simultaneous hydrolysis of dimethyl dichlorosilane and methyl dichlorosilane. B.p. 63-65° (18 mm), n_D^{20} 1.3924, mol. wt. (cryoscopic) 282.6, 283 (282.6); % H (Si) 0.356; 0.358 (0.356).

Tetramethyl cyclotetrasiloxane was isolated from the products of hydrolysis of methyl dichlorosilane: b.p. 46° (20 mm); n_D^{20} 1.3875; d_4^{20} 0.9917. 1-Nonene, methylstyrene, allyl amine, and methylmethacrylate were standard pure products.

Method of carrying out the experiments. To 6.7 g of heptamethyl cyclotetrasiloxane in the presence of 0.2 ml of 10% solution of chloroplatinic acid in absolute isopropyl alcohol we added dropwise 2.9 g of 1-nonene. The reaction temperature rose to 139°; the reaction mixture was heated for one hour at 164°. We obtained 2 g (yield 20.8%) of addition product; b.p. 166° (22 mm); n_D^{20} 1.4208; d_4^{20} = 0.9292. Found: MR 111.291. Calculated: MR 111.60.

By an analogous method we carried out addition of heptamethyl cyclotetrasiloxane to α-methylstyrene, methylmethacrylate, and allyl amine; and also of sym-tetramethyl cyclotetrsiloxane to methylmethacrylate. The properties are given in the table.

Products of Addition of Cyclosiloxanes Containing Si-H Bonds to Unsaturated Compounds

Type of compound	R	Conditions of experiment: Reac. temp., °C	Conditions of experiment: Mole ratio of cyclosiloxane: unsatu. comp.	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	Found, %: C	Found, %: H	Found, %: Si	Found, %: N	Calculated, %: C	Calculated, %: H	Calculated, %: Si	Calculated, %: N
I	$-(CH_2)_8CH_3$	164	1 : 1	166 (2)	1,4208	0,9292	111,29	111,60	46,81; 47,18	9,66; 9,72	27,76; 28,14	—	47,05	9,80	27,45	—
I	$-CH_2CH(CH_3)C_6H_5$	60	1 : 2	126,5—127 (2,5)	1,4579	1,0047	108,84	108,06	48,20; 48,47	7,93; 8,04	27,24; 27,72	—	47,95	8,05	28,03	—
I	$-CH_2CH_2CH_2NH_2$	100	1 : 1	112 (18)	1,4224	0,9967	86,46	87,30	35,74; 35,95	8,73; 8,78	32,66; 32,33	4,80; 4,71	35,87	7,9	33,03	4,15
I	$-CH_2CH(CH_3)COOCH_3$	60—80	1 : 2	123,5 (10)	1,4175	1,0190	94,56	94,70	38,3 *	8,55*	29,5 *	—	37,65	7,9	29,35	—
II	$-CH_2CH(CH_3)COOCH_3$ **	60—80	1 : 6—8	219 (2,5)	1,4492	1,1149	154,17	155,72	45,1 *	7,68*	17,3 *	—	44,99	7,49	17,49	—

* Average of four determinations.

** Literature [3] gives b.p. 256 (7 mm), n_D^{25} 1.4482; d_4^{25} 1.114.

SUMMARY

We have obtained four new addition products of cyclic siloxanes containing the Si-H bond to unsaturated compounds of different classes. In the presence of chloroplatinic acid addition takes place according to the Farmer rule with formation of one adduct in each case.

LITERATURE CITED

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2. Milland Silicones Ltd. English patent 834326 (1960); Chem. Abstrs, 54, 25967f (1960).
3. J. L. Speier, J. Amer. Chem. Soc., 79, 974 (1957).