and 25% ammonia did not lead to the isolation of any individual compound from among the reaction products.

EXPERIMENTAL

5-Bromomethylbenz-2, 1, 3-selenadiazole (II). A mixture of 5 g (0.025 mole) 5-methylbenz-2, 1, 3-selenadiazole (I) [2], 4.5 g (0.025 mole) bromosuccinimide, 0.05 g Br_2O_2 and 120 ml CCl_4 was refluxed for 7 hr. The succinimide which came out was filtered off, and the solvent distilled off. Yield 4.5 g (64%) yellow powder, mp 125°–126° (ex EtOH). Found: N 10.45; 10.55; Br 28.63; 29.02%, calculated for $C_7H_5BrN_2Se$: N 10.20; Br 29.00%.

5-(β, β-Dicarbethoxy-β-acetylamino)ethylbenz-2, 1, 3-selenadiazole (III). 1.3 g (0.0055 mole) acetylaminomalonic ester was added to a stirred solution of 0.125 g (0.0055 mole) Na in 20 ml absolute EtOH, the whole stirred for 1 hr at 20°, then a solution of 1.52 g (0.0055 mole) mole) II in 20 ml dry benzene was added gradually, and the mixture boiled for 3 hr. The NaBr was filtered off, and the filtrate evaporated to dryness. Yield 1.2 g (54%), mp 152°–153° (ex EtOH) Found: N 10.50; 10.08%, calculated for $C_{16}H_{19}N_3O_5Se$: N 10.20%.

1-(β, β-Dicarbethoxy-β-acetylamino) ethyl-3, 4-diaminobenzene (IV). H_2S was passed into a solution of 2 g III in 45 ml EtOH+10 ml 25% ammonia at 60°, for 1 hr 30 min. After cooling the precipitate was filtered off and the filtrate evaporated. The dry residue, 1.5 g (91%), was recrystalized from EtOH, white transparent plates, mp 182°, Found: N 12.77; 12.58%, calculated for $C_{16}H_{23}N_3O_5$: N 12.45%.

β-(3, 4-Diaminophenyl)-α-aminopropionic acid hydrochloride (V). A mixture of 5 g IV and 120 ml 20% HCl was heated on a steam bath for 4 hr. The solution was then vacuum evaporated to dryness, and a few volumes of water (about 5 ml) added. The oily residue was recrystallized from absolute EtOH and dry ether, yield 2.8 g (78%) while very hygroscopic product, mp 265°–267° (decomp.). Found: N 21.01; 21.07; Cl 25.83%, calculated for $C_9H_{13}N_3O_2 \cdot 2HCl$: N 21.50; Cl 25.50%; R_f 0.165.*

5-(β-Amino-β-carboxy)ethylbenz-2, 1, 3-selenadiazole (VI) hydrochloride. 1.2 g malonate III and 50 ml 20% HCl was refluxed for 10 hr, the products cooled, filtered, and the filtrate vacuum evaporated to dryness. The residue was recrystallized from absolute EtOH-ether. Yield 0.61 g (67%) grayish compound mp 275° (decomp.). Found: N 13.77; 13.75; Cl 12.18; 12.04%, calculated for $C_9H_8N_4O_4Se \cdot HCl$: N 13.71; Cl 11.65%.

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*The chromatographing was done on Leningrad Factory slow filter paper using n-BuOH:PrOH:0.1 N HCl in the ratios 2:1:1.

EFFECT OF SUBSTITUENT NATURE ON THE EQUILIBRIUM IN THE CATALYTIC REARRANGEMENT OF CYCLOSILOXANES IN SOLUTION

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Determinations are made of the polymer content of mixtures obtained by catalytic rearrangement of cyclosiloxanes with various substituents (CH_3, C_2H_5, n-C_3H_7, i-C_4H_9, C_6H_5, $CF_3CH_2CH_2$, $NCCH_2CH_2CH_2$) at the silicon, in methylethyl ketone and acetone. It is found that the equilibrium cyclosiloxane-polycyclosiloxane is shifted to the left as volumes, and in particular polarities, of substituents increase. The causes of this are considered.

When cyclosiloxanes are rearranged in solution in the presence of bases, the following equilibrium is established:

$$\text{cyclosiloxane} \rightleftharpoons \text{polycyclosiloxane} \qquad (1)$$

the position depends on solution concentration [1–3] but not on solvent nature [1, 2] or temperature. We showed [3, 4] that when mixed cyclosiloxanes containing the groups $(CH_3)_2SiO$ and $CF_3CH_2CH_2(CH_3)SiO$ (Φ) rearrange in acetone, the equilibrium concentration of polymer (P) decreases linearly with increase in mole fraction of Φ.

In the present work a method previously described [4] was used to determine P in systems obtained by rearranging cyclosiloxanes at 20° in the presence of potassium polymethylsiloxandiolate. The concentration of siloxane groups in solution was 3.33 mole/l. The rearrangement of the rings $(RR'SiO)_m$ (table, **I–VIII**), was effected in methylethyl ketone, some of the polymers being insoluble in acetone. Mixed cyclosiloxanes (table, **VIII–XIII**) containing in addition to the group D $NCCH_2CH_2(CH_3)SiO$ (N), $NCCH_2CH_2CH_2(CH_3)SiO$ (C), and Φ, were rearranged in acetone. Special experiments confirmed (e.g. for I, VI, VII, and VIII) that change of solvent is practically without effect on the equilibrium. Attainment of equilibrium was checked for all rings by repeated keeping with increasing amounts of catalyst, and in the cases of siloxanes I, VI, and VII, it was confirmed that the same P values were obtained both by rearrangement of the rings and by destruction of the corresponding polymers.

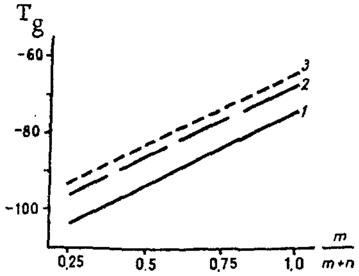

Fig. 1. Relationship between glass temperature T_g of siloxane polymers and their composition: 1) $(\Phi_mD_n)_x$; 2) $(N_mD_n)_x$; 3) $(C_mD_n)_x$; 1 and 2–authors' data; 3–A. I. Ponomarev's (VNIISK) data.

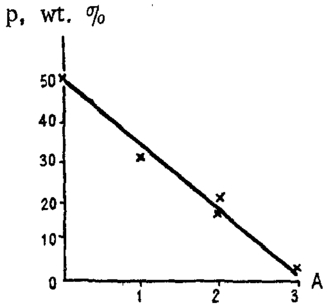

Fig. 2. Relationship between equilibrium content of polymer and number of C—C bonds in the siloxane group: A–Number of C—C bonds in the group.

Equilibrium Polymer Content

$(RR'SiO)_m$ in methylethyl ketone				Traces			
Cyclosiloxane			P, wt %*	Cyclosiloxane		Dipole moment	P, wt %*
Compound	R	R'		Compound	Symbol		
I	CH_3	CH_3	52.3	VIII	ΦD_3	2.76	45.3
II	CH_3	C_2H_5	32.2	IX	ND_3	3.45	3.8
III	CH_3	n-C_3H_7	21.1	X	CD_3	3.58	traces
IV	C_2H_5	C_2H_5	17.5	XI	Φ_2D_2	—	31.4
V	CH_3	i-C_4H_9	2.9	XII	N_2D_2	—	1.0
VI	CH_3	C_6H_5	3.0	XIII	C_2D_2	—	traces
VII	CH_3	$CF_3CH_2CH_2$	0				

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*From sum rings+polymer.

**V. F. Evdokimov (VNIISK) [= All Union Scientific Research Institute for Synthetic Rubber] assisted with the determinations of dipole moments.

It can be seen from the table (I–V) that the equilibrium (1) is displaced towards the left with increase in volume of substituents. Then for cyclosiloxanes with isomeric groups (III–IV) the value of P is almost the same. Polar radicals decrease P more powerfully than nonpolar ones (VII and V). The effect of polarity is especially prominent in the rearrangement of mixed rings. The dipole moments of the cyclosiloxanes VIII-X indicate increase in polarity of substituents in the order $CF_3(CH_2)_2 < NC(CH_2)_2 < NC(CH_2)_3$ (table). The value of P decreases in the same order for cyclosiloxanes VIII–X and XI–XIII. The less sterically voluminous by more polar β-cyanoethyl group shifts the equilibrium (1) rather more than does the 3,3,3-trifluoropropyl group (IX and VIII, XII and XI).

The position of the equilibrium (1) is known to be temperature-independent both in solution and for neat material [2, 5, 6], so that shift of the equilibrium towards the left is connected with relative decrease of polymer entropy. In the case of polar substituents this is probably brought about mainly by strengthening of interchain interaction and the corresponding decrease in mobility of segments of the polymeric chains. This is confirmed by the increase in glass point temperature T_g of polysiloxanes with increase in mole fraction of polar groups, and with increase in polarity of those groups (Fig. 1). According to [7] the values of the alkyl groups affect T_g of polysiloxanes but little, but increase their molecular volumes. Hence the relative decrease in entropy of polymers in the I–V series may be connected with disintegration of the molecular coil, and with difference in potential barriers to rotation around the C—C bonds in alkyl groups, present in the polymer and in the rings. Indirect support for the latter is the practically linear decrease in P with increase in number of C—C bonds in the siloxane chain (Fig. 2), and the closeness of the P values for III and IV.

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