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THE REACTIONS OF CYCLIC SILOXANES WITH ACIDIC AND BASIC REAGENTS

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SUMMARY

Some ring opening reactions of cyclic siloxanes in organic solvents have been investigated. By the action of potassium hydroxide, hexaphenylcyclotrisiloxane and *cis*- and *trans*-trimethyltriphenylcyclotrisiloxane may all be converted into cyclotetrasiloxanes in good yield and, in the case of the latter two compounds, with a high degree of stereospecificity. By the action of hydrochloric acid, hexamethylcyclotrisiloxane is rapidly converted into octamethylcyclotetrasiloxane. The trimethyltriphenylcyclotrisiloxanes are much more resistant to the action of acids and conversion into cyclic tetramer is low.

INTRODUCTION

On treatment with acid or base oligomeric cyclic siloxanes can be polymerised to high molecular weight materials. It has been shown[1] that poly(methylphenylsiloxanes) with some degree of stereoregularity can be prepared by polymerisation of methylphenylcyclosiloxanes. The highest stereoregularity is obtained when the intermediate silanolates are covalent in character. It has also been shown by Sommer[2] that disiloxanes react with potassium hydroxide with retention of configuration at both silicon atoms. In the present work the initial stage in the reaction of some cyclic siloxanes with acid or base has been investigated. It was hoped that it would be possible, because of the mild conditions used in our experiments to investigate the initial ring opening process separately, and that the stereochemistry of the products might provide some information about the initial stages in the polymerisation process.

RESULTS AND DISCUSSION

When a dilute solution of hexamethylcyclotrisiloxane in benzene or ether was shaken with powdered potassium hydroxide at 20° the siloxane slowly reacted, being almost all consumed after 24 hours. A slight amount of octamethylcyclotetrasiloxane was formed, but the main product appeared to be linear polysiloxane. Under the same conditions hexaphenylcyclotrisiloxane reacted slowly to give a considerable conversion into octaphenylcyclotetrasiloxane. Under favourable conditions a 49% conversion of trimer into tetramer was observed. The reactions of *cis*- and *trans*-

TABLE 1

THE REACTION OF THE TRIMETHYLTRIPHENYLCYCLOTRISILOXANES WITH POTASSIUM HYDROXIDE

Reaction number	*Cyclo-trisiloxane isomer used*	*Solvent*	*Volume of solvent to 1 mmole of siloxane, (ml)*	*Temp. (°C)*	*Approx. time T for trimer to react (min)*	*Yield of cyclic siloxanes after time T (%)*
1	*cis*	*p*-Xylene	10	50	8	77
2	*trans*	*p*-Xylene	10	50	20	78
3	*cis*	*p*-Xylene	10	20	90	46
4	*trans*	*p*-Xylene	10	20	180	88
5	*cis*	Ether	10	20	20	91
6	*trans*	Ether	10	20	40	99
7	*cis*	Ether	2	20	3	20
8	*trans*	Ether	2	20	6	57
9	*cis*	THF	10	20	0.75	40
10	*trans*	THF	10	20	1.5	50

TABLE 2

THE REACTION OF THE TRIMETHYLTRIPHENYLCYCLOTRISILOXANES WITH POTASSIUM HYDROXIDE

Reaction number	*Proportions of tetramer isomers in the reaction products*							
	(I)		*(II)*		*(III)*		*(IV)*	
	GLC	*NMR*	*GLC*	*NMR*	*GLC*	*NMR*	*GLC*	*NMR*
1	30	32	58	52	9	13	3	3
2	8	6	66	55	18	33	8	6
3		30		59		8		3
4		3		58		28		11
5	28	29	56	56	10	12	6	3
6	9	10	70	60	14	20	7	10
7	39	42	55	51	6	6	0	1
8	1	1	55	54	34	33	10	12
9	13	15	52	54	26	22	9	9
10	9	7	54	56	22	25	15	12

Tetramer isomers (I), (II), (III) and (IV) are designated as isomers III, IV, V and VI, respectively, in the original publication[3] describing their isolation.

2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane with potassium hydroxide are summarised in Tables 1 and 2. With these compounds, between 20 and 99% of the original weight of trimer was recovered as tetramer, according to the conditions. It is seen that both the *cis* and *trans* trimer are converted to tetramer with potassium hydroxide in *p*-xylene, diethyl ether or tetrahydrofuran. Not surprisingly the *cis* isomer generally reacts more rapidly than the *trans* isomer. Polar solvents promote the reaction and in the polar ether tetrahydrofuran the reaction is extremely rapid. If the tetramers were left in contact with the potassium hydroxide in the solvents for times greater than those shown in Table 1 a further slow reaction took place and a more complex mixture of products was obtained.

Examination of the tetramer products by GLC and NMR spectroscopy showed that the formation of tetramer proceeded with a high degree of stereospecificity. The *cis* trimer gave predominantly tetramers (I), (II) and (III), whereas the *trans* trimer gave mainly (II) and (III) with lesser proportions of (I) and (IV), the stereospecificity increasing with concentration.

The shortest chain that can be formed by condensation of trimer molecules contains six siloxane units. Whether the tetramers are formed from this system or from some higher multiple of the trimer it would be expected that the *cis* trimer would yield the tetramers (I), (II) and (III), the yields being in the order $(\mathrm{I}) > (\mathrm{II}) \gg (\mathrm{III})$, whereas the *trans* trimer would give the tetramers (II), (III) and (IV), in the order $(\mathrm{II}) > (\mathrm{III}) \gg (\mathrm{IV})$.

When a solution of hexamethylcyclotrisiloxane in ether was shaken with 7.5 *M* hydrochloric acid at 20° the siloxane was progressively converted into octamethylcyclotetrasiloxane, this being the only volatile product detected. The half life of the trimer under these conditions was approximately 20 minutes. Over a period of 24 hours under these same conditions the concentration of octamethylcyclotetrasiloxane remained constant, indicating a much greater stability towards acid. The *cis*- and *trans*-trimethyltriphenylcyclotrisiloxanes remained unchanged when a solution in ether was shaken with 6 *M* hydrochloric acid at 20° for 24 hours. With acetone or tetrahydrofuran as solvent, under the same conditions, these compounds reacted progressively over a period of a few hours. A small proportion of a mixture of all four cyclic tetramers was obtained in each case but the major product appeared to be linear polysiloxanes. No differences in the reactivity of the two trimers were apparent under these conditions.

The results show that the order of reactivities of hexamethyl- and trimethyltriphenylcyclotrisiloxanes found with base catalysis is the reverse of that found with acid catalysis. This is to be expected on mechanistic grounds if we regard acid and base cleavage of the ring as commencing respectively with protonation of oxygen and nucleophilic attack on silicon. Protonation of oxygen will be inhibited by electron withdrawing groups such as phenyl on the silicon, whilst these same groups will facilitate nucleophilic attack. On this basis hexaphenyltrisiloxane would be expected to be the most reactive of all towards attack by base. The fact that this it is not so may possibly be due to steric hindrance by the bulky phenyl groups, particularly in view of the fact that under similar circumstances it has been shown[4] that the silanolate ion rather than the hydroxide ion is the attacking species.

EXPERIMENTAL

GLC analyses were carried out on a Pye series 104 chromatograph using a katharometer detector and a $9' \times \frac{1}{4}''$ o.d. column of 20% MS 2430 silicone gum on firebrick with hydrogen as carrier gas at a flow rate of 50 ml/min.

Column chromatography was carried out using silica gel MFC (Hopkin and

Williams) or silica gel SG (Whatman) as adsorbent and a 20/80 mixture of benzene and light petroleum (b.p. 60–80°) as eluent. Thin-layer chromatography was carried out on 6 × 6 in. glass plates with a 0.25 mm layer of silica gel G (Merck) as adsorbent and a 17/83 mixture of benzene and light petroleum (b.p. 60–80°) as developer. Components were located by spraying with a 2% solution of potassium permanganate in 20% sulphuric acid. Proton resonance spectra were obtained in carbon tetrachloride solution on a Perkin–Elmer R10 spectrometer operating at 60 MHz and 35° with tetramethylsilane as internal standard. IR spectra were recorded on a Perkin–Elmer Infracord 237 spectrometer.

Reaction of hexamethylcyclotrisiloxane with potassium hydroxide

A small quantity (approx. 0.001 mole) of A.R. potassium hydroxide was weighed accurately in a closed container and then powdered under dry solvent in a pestle and mortar. The resultant suspension was transferred to a 10 ml flask containing an equimolecular quantity of hexamethylcyclotrisiloxane and sufficient solvent to make the cyclosiloxane concentration 0.02 *M*. The solution was shaken at 20° and samples (0.4 ml) were withdrawn at intervals over 24 h. These samples were filtered through a small plug of cotton wool and sealed in small tubes. At the end of each experiment the samples were examined by GLC (column temp. 100°) with standard solutions of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane as reference materials. With benzene as solvent the trimer reacted slowly, about 25% being consumed after 4 h and 95% after 24 h. At the same time a small amount of tetramer was formed. In ether the reaction was somewhat more rapid and only a slight trace of trimer remained after 24 h. The amount of tetramer formed was still small, although slightly more than in benzene.

Reaction of hexaphenylcyclotrisiloxane with potassium hydroxide

The reaction was carried out as above, but in this case the course of the reaction was followed by TLC. During development linear polysiloxanes remain at the base line but hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane have R_f values sufficiently different to be distinguished. With *p*-xylene as solvent at a temperature of 20° no reaction was observed after 40 min but after 24 h the trimer had almost completely reacted and a component with the same R_f value as octaphenylcyclotetrasiloxane had been formed. When the reaction was carried out at 50° this conversion was complete after 2 h. This reaction at 50° was repeated using a larger quantity (0.813 g) of siloxane and the reaction product was worked up by column chromatography on silica gel. A solid fraction (0.400 g) was obtained, which was recrystallised to give a product with m.p. 196° and an IR spectrum identical with that of an authentic sample of octamethylcyclotetrasiloxane (m.p. 200°)[5].

Reaction of the trimethyltriphenylcyclotrisiloxanes with potassium hydroxide

The procedure was similar to that described above. Individual trimer isomers (about 0.2 g, 0.0005 mole) were shaken with an equimolecular amount of powdered potassium hydroxide and solvent (5 ml). The reactions were followed by TLC and the times taken for the trimer to react were determined. Each experiment was then repeated on a large scale (about 1 g trimer) under the conditions found for complete reaction and the product worked up by column chromatography on silica gel. The products were colourless viscous oils, some of which partially crystallised on standing. In one case (*trans* trimer in *p*-xylene at 50°) the crystals were separated, pressed between filter papers and recrystallised from methanol to give a product with m.p. 99° and a proton resonance spectrum identical with that of tetramer isomer (III) (m.p. 99°). In each case portions of the oils (before any crystallisation had taken place) were analysed by GLC (benzene solution, column temperature 265°) and NMR spectroscopy. The relative proportions of the tetramer components were determined independently from the peak areas of the gas chromatogram and from the intensities of the methyl proton resonances in the NMR spectrum. The results are shown in Table 2.

Reaction of hexamethylcyclotrisiloxane with hydrochloric acid

Hexamethylcyclotrisiloxane (1.00 g) dissolved in diethyl ether (60 ml) was stirred with 7.5 *M* hydrochloric acid (25 ml) at 20°. Portions (5 ml) of the ether layer were withdrawn at 20 min intervals over 2 h and finally after 24 h. Each sample was immediately washed with water until free of acid, dried over calcium chloride and the ether distilled off. The residues were examined by GLC (column temperature 100°) against standard solutions of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane as reference materials.

Reaction time (min)	0	20	40	60	80	100	120
Unreacted trimer %	100	54.5	18.2	10.9	10.9	10.9	7.2

After 24 h no trimer could be detected. The concentration of tetramer did not change appreciably after the first two hours reaction time. The cyclic trimer and tetramer were the only volatile products detected.

Reaction of the trimethyltriphenylcyclotrisiloxanes with hydrochloric acid

The trimer (0.1 g) dissolved in solvent (6 ml) was shaken with 6 *M* hydrochloric acid (2 ml) at 20°. Portions of the ether layer were withdrawn at intervals, washed with water until neutral and the solution spotted onto a TLC plate. When acetone or tetrahydrofuran was used as solvent the samples withdrawn were neutralised with ammonia, the solvent evaporated off, and the residue extracted with ether. The ether was distilled off from these extracts and the residue dissolved in benzene and examined by GLC (column temperature 265°) against solutions of the two trimers as reference materials.

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