STUDIES IN THE FIELD OF ALKOXYSILANES

XXIII. Spirocyclic Esters of Orthosilicic Acid*

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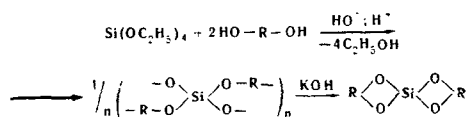
Spirocyclic glycolic esters of orthosilicic acid have been obtained by catalytic disproportionation of the corresponding polyesters formed during transesterification of tetraethoxysilane by glycols. The PMR spectra of these compounds were studied and their dipole moments were measured.

For a long time, attempts to synthesize spirocyclic esters of orthosilicic acid were unsuccessful [2—8]. However, recently these compounds have been obtained by the reaction between the corresponding glycols and silicon tetrachloride [9—15], and tetraacetoxysilane [16—20], and also by other methods [21—23]. Certain authors [24,25] have reported the formation of the above-mentioned spiroesters, although they have not confirmed their findings experimentally.

We have elaborated a method for synthesizing spirocyclic esters of orthosilicic acid of the aliphatic series, based on the catalytic disproportionation of polyesters formed during the transesterification of tetraethoxysilane by the corresponding glycols in the presence of traces of bases or acids [26].

After removing, by distillation, the alcohol formed during the reaction between tetraethoxysilane and glycol, the polyester formed may be converted into the monomeric spirocyclic compound by disproportionation catalyzed by KOH and forming during a controlled slow distillation or sublimation of the reaction mixture under reduced pressure. The reaction proceeds according to the scheme:

$$Si(OC_2H_5)_4 + 2HO-R-OH \xrightarrow[-4C_2H_5OH]{HO^-;H^+}$$

$$\longrightarrow \frac{1}{n}\left(\begin{array}{c} -O \\ -R-O \end{array} \right\rangle Si \left\langle \begin{array}{c} O-R- \\ O- \end{array} \right)_n \xrightarrow{KOH} R \left\langle \begin{array}{c} O \\ O \end{array} \right\rangle Si \left\langle \begin{array}{c} O \\ O \end{array} \right\rangle R$$

where R = divalent aliphatic radical.

*For part IX, see [1].

By this pathway, the following spiroesters were obtained (see Table 1):
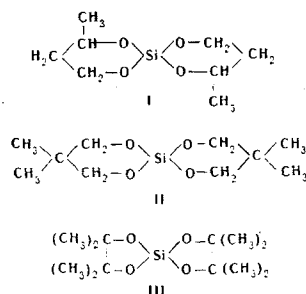
The ease of formation and stability of spirocyclic esters markedly increases with increase in the number of hydrocarbon substitutes (methyl groups) in the ring. Under the conditions examined, it was impossible to disproportionate polyesters obtained by an analogous pathway from tetraethoxysilane and ethanediol-1,2, propanediol-1,3, butanediol-1,4, or butanediol-2,3.

The spirocyclic esters of orthosilicic acid obtained are colorless liquid (I) or crystalline (II, III) compounds, readily soluble in the normal organic solvents. Even on storage they readily undergo polymerization. At normal temperatures, the viscosity of compound I markedly increases within 24 hr (to a honey-like consistency), and after 1 month this compound transforms into a solid glass-like polymer which is markedly less soluble in benzene and acetone than the original monomeric compound I. The polyester formed on storage may be reversibly polymerized into compound I when heated under vacuum in the presence of powdered KOH.

From the change in molecular weight and melting points of the monomeric spiroesters presented in Table 1 over a period of time (after 24 hr), it is possible to determine their comparative rates of polymerization.

Table 1
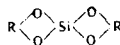
Spiroester	R	Mp, °C		M			Found, %			Calculated, %			Yield, %
		immediately after synthesis	after 24 hr	immediately after synthesis	after 24 hr	calculated	C	H	Si	C	H	Si	
I	—CH₂CH₂CH(CH₃)—*	—	—	212.3	326.8	204.3	48.53	8.02	13.93	47.03	7.89	13.75	89.2
II	—CH₂C(CH₃)₂CH₂—	141—142	No melt	247.2	384.4	232.3	51.27	8.42	12.29	51.69	8.68	12.08	86.2
III	—C(CH₃)₂C(CH₃)₂—	110—111	101—106	258.6	293.2**	260.4	54.90	9.41	10.97	55.35	9.29	10.79	81.2

*Bp 118° C (13 mm); d_4^{20} 1.1242; n_D^{20} 1.4421; MR_D 48.08; calc. MR_D 48.09.
**After boiling for 6 hr in benzene, M 298.3.

Table 2

Parameters of the PMR Spectra of Spirocyclic Esters of
Orthosilicic Acid

Spiroester	Chemical displacements, ppm*			
	τ_{CH_3}	τ_{C-CH_2-C}	τ_{OCH_2}	τ_{OCH}
I**	8.76 (d)	8.30 (qu)	6.00 (tr)	5.83 (quint)
II	9.04 (s)	—	6.31 (s)	—
III	8.78 (s)	—	—	—

*s, singlet; d, doublet; tr, triplet; qu, quadruplet; quint, quintet.
**KCCB of vicinal protons in ♥[3] $J_{H-H} \approx 6.5$ Hz.

Spirocyclic esters of orthosilicic acid are very
readily hydrolyzed, even by the moisture of the air.
On standing in air, the crystalline compounds II and
III dissolve into a viscous rubber-like mass within
several hours and the original glycol may be isolated
from the products of hydrolysis.

In order to reveal the structure and conformation
of the spirocyclic esters obtained, the PMR spectra
of these compounds were studied and their dipole mo-
ments were measured.

The PMR spectrum of spiroester I is analogous to
the spectrum of butanediol-1,3 [27], and can be dis-
tinguished only by the small paramagnetic displace-
ment of all lines of resonance absorption. The PMR
spectra of compounds II and III consist of two and one
singlets, respectively, the position of which is ex-
tremely characteristic for the resonance of the meth-
ylene and methyl protons.

Thus, the multiplicity of the lines in the PMR spec-
tra (see Table 2) indicate the high rate of conforma-
tion transitions in molecules I—III at room tempera-
ture.

A study of the Brigleb-Stuart model showed that for
spiroester II, because of the large size of the methyl
groups, the existence of six-membered rings in the
form of a "bath" is sterically impossible. The dipole
moment of compound II, calculated for the conforma-
tion of both rings in the form of an "armchair," is
equivalent to 2.6 D, which is in agreement with the
experimentally determined value of 2.88 D. The dipole
moment of compound I is equivalent to 2.27 D, i. e.,
in comparison with the dipole moment of compound II
is reduced by 0.5 D. This is probably due to low steric
hindrances in the molecule of compound I. Thus, the
values of the dipole moments and PMR spectra of

compounds I and II indicate the presence of rapid arm-
chair-armchair conformation transitions in these mol-
ecules. The dipole moment of compound III, both
five-membered rings of which are apparently almost
planar, does not differ from 0 within the limits of
error of the measurements, which confirms the non-
polar symmetrical structure of this compound with the
silicon atom in the center of symmetry.

EXPERIMENTAL

Preparation of Spirocyclic Esters of Orthosilicic Acid. The alcohol
formed during transesterification was slowly removed by distillation
from a mixture of 20.8 g (0.1 mole) tetraethoxysilane, 0.2 mole of
the corresponding glycol, and 0.2 g n-toluenesulfonic acid. Normally,
the theoretical quantity is isolated (22.5 ml). To the polyester thus
obtained was added 0.5 g of powdered KOH and the mixture was heated
under vacuum. As a result, the spirocyclic ester was slowly removed
by distillation or sublimation. The latter was purified by means of re-
peated distillation or sublimation under vacuum.

Physical constants and data of the analysis and yields of the ob-
tained spirocyclic esters are presented in Table 1. Physical constants
of the spiroesters were determined immediately after preparation and
also 24 hr after preparation.

PMR Spectra. PMR spectra were obtained in the YaMR-5535TsLA
spectrophotometer (40 MHz). Spiroesters I and II were studied in the
form of 15% (by volume) solutions in CCl_4 and compound III was
studied in $HCCl_3$. Cyclohexane ($\tau_{C_6H_{12}}$ = 8.56 ppm) was used as an
internal standard. The values of the chemical displacements were
determined by the method of lateral bands with an accuracy of ± 0.01
ppm.

Dipole Moments. Dipole moments were measured by the method
of heterodyne pulsations (frequency of 1 MHz) in benzene solutions
at 25° C. The results of the measurements were extrapolated to in-
finite dilution by the method of Gederstrand.

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Table 3

Experimental Data Concerning the Determination of Dipole
Moments

Spiro-ester	c, mole fraction	ε	d	$P_{total},$ cm^3	MR_D, cm^3	P_{or}, cm^3	μ, D
I	0.004085	2.3102	0.8764	157.70	47.95	107.35	2.27
	0.002919	2.2970	0.8754				
	0.001954	2.2938	0.8751				
II	0.002213	2.2966	0.8752	232.53	57.15	172.53	2.88
	0.001529	2.2954	0.8751				
	0.001174	2.2921	0.8749				
III	0.003371	2.3071	0.8751	220.82	66.54	150.95	2.69
	0.002330	2.2966	0.8750				
	0.001887	2.2916	0.8750				
	0.000000	2.2740	0.8742				

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