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ORGANOSILICON CHEMISTRY
I. OCTAARYLSPIRO[5.5]PENTASILOXANES

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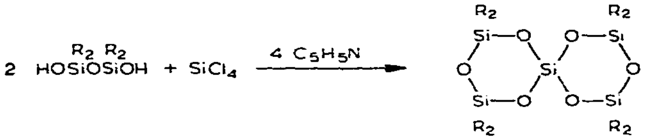
INTRODUCTION

Many polysiloxanes have been made by the rearrangement of cyclosiloxanes in the presence of a catalyst, but very little is known about polysiloxanes formed by rearranging spirobicyclosiloxanes. We have prepared some such spirobicyclic compounds and their polymers containing phenyl and tolyl groups and studied their structures by means of proton magnetic resonance techniques.

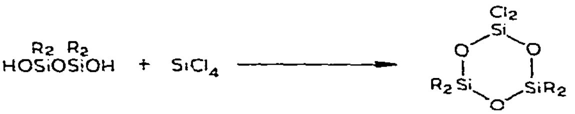
Octamethylspiro[5.5]pentasiloxane (I, R = methyl) was first prepared in less than 1 % yield by Scott[1] from the thermal rearrangement of the cohydrolysis product of dichlorodimethylsilane and silicon tetrachloride. Mayo[2] obtained an 8 % yield of this compound by treating tetramethyldisiloxane-1,3-diol with silicon tetrachloride in the presence of pyridine.

It was found that octaarylspiro[5.5]pentasiloxanes (I, R = phenyl, *m*-tolyl or *p*-tolyl) can be synthesized in good yields by using a procedure similar to that of Mayo's. When a tetraaryldisiloxane-1,3-diol was treated with silicon tetrachloride in the presence of pyridine as an acid acceptor the corresponding octaarylspiro[5.5]-pentasiloxane (I) was formed as the chief product (eqn. 1). However, in the absence



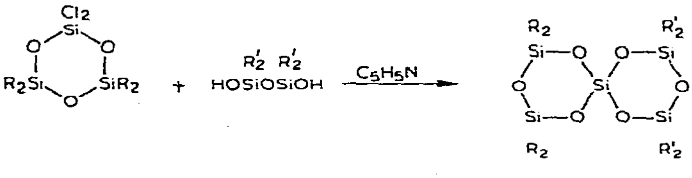
(1)

(I)



(2)

(II)



(3)

(III)

R and R' = C_6H_5, m-C_7H_7, or p-C_7H_7

of pyridine the main product obtained was 2,2-dichloro-4,4,6,6-tetraarylcyclotrisiloxane (eqn. 2). Compound (II) can be treated further with another tetraaryldisiloxane-1,3-diol in the presence of pyridine to give a mixed spiropentasiloxane (III) containing two kinds of aryl groups (eqn. 3).

Tetraaryldisiloxane-1,3-diols were prepared from the partial hydrolysis of dichlorodiarylsilanes, followed by treatment with sodium bicarbonate.

$$2\,R_2SiCl_2 \xrightarrow{H_2O} Cl\overset{R_2}{Si}O\overset{R_2}{Si}Cl \xrightarrow{NaHCO_3} HO\overset{R_2}{Si}O\overset{R_2}{Si}OH \qquad (4)$$

All six simple and mixed spiropentasiloxanes containing phenyl, *m*-tolyl and *p*-tolyl groups have been prepared and identified. They were polymerized in bulk and in solution in the presence of a basic catalyst to form polymers. These polymers are soluble in solvents such as toluene and chloroform. Possible polymer structures for these spiro bicyclic compounds are discussed on the basis of proton magnetic resonance (PMR) data.

EXPERIMENTAL

Dichlorodi-m-tolylsilane

Freshly prepared *m*-tolylmagnesium chloride (4.33 moles) in THF was treated with 367.8 g (2.17 moles) of $SiCl_4$ under dry nitrogen at the reflux. The mixture was filtered and the filtrate was evaporated. The residue was extracted with toluene and filtered. Removal of toluene from the filtrate produced a liquid which was fractionated to give 399.7 g (66 %) of dichlorodi-*m*-tolylsilane boiling at 144–146°/2 mm. (Found: Cl, 24.90. $C_{14}H_{14}Cl_2Si$ calcd.: Cl, 25.22 %.)

1,3-*Dichloro*-1,1,3,3-*tetra-m-tolyldisiloxane*

A solution containing 7.2 ml (0.4 mole) of water and 11 ml (0.14 mole) of pyridine was added from a syringe in small droplets over a period of 3.5 h to 225 g (0.8 mole) of dichlorodi-*m*-tolylsilane dissolved in 100 ml of toluene at 85°. The mixture was filtered and the filtrate was evaporated. Fractionation of the residue produced 125 g (62 %) of distillate boiling at 234–235°/0.01 mm. (Found: Cl, 14.28. $C_{28}H_{28}Cl_2OSi_2$ calcd.: 13.97 %.)

1,3-*Dichloro*-1,1,3,3-*tetra-p-tolyldisiloxane*

This compound was prepared in a similar fashion in 54 % yield with a b.p. of 226–228°/0.01 mm and a m.p. of 76–79°. (Found: Cl, 14.13. $C_{28}H_{28}Cl_2OSi_2$ calcd.: 13.97 %.)

Tetra-m-tolyldisiloxane-1,3-*diol*

A solution containing 126.9 g. (0.25 mole) of 1,3-dichloro-1,1,3,3-tetra-*m*-tolyldisiloxane dissolved in 350 ml of ether was added with stirring over a period of 1.5 h to 127 g of sodium bicarbonate suspended in 700 ml of ether containing 2 ml of water. The slurry was stirred at room temperature until no more CO_2 was evolved. The filtrate of the reaction mixture was evaporated to give 115.5 g of residue melting at 60–68°. Two recrystallizations from petroleum ether gave 68.1 g (58 %) of crystals melting at 68.5–69.5°. (Found: C, 71.60; H, 6.62; Si, 11.82. $C_{28}H_{30}O_3Si_2$ calcd.: C, 71.42; H, 6.42; Si, 11.93%.)

Tetra-p-tolyldisiloxane-1,3-diol

This compound was prepared in the same fashion to give 78% yield of solids melting at 100.5–102.5°. (Found: C, 71.12; H, 6.34; Si, 12.08. $C_{28}H_{30}O_3Si_2$ calcd: C, 71.42; H, 6.42; Si, 11.93%.)

2,2-Dichloro-4,4,6,6-tetraphenylcyclotrisiloxane

Silicon tetrachloride (22.6 ml, 0.2 mole) was added rapidly to tetraphenyldisiloxane-1,3-diol (41.4 g, 0.1 mole) dissolved in 500 ml of benzene. The reaction mixture was stirred for 24 h while a slow stream of nitrogen was bubbled through to sweep away the HCl formed. Removal of benzene at reduced pressure produced a viscous residue. The latter was fractionated to give 31.4 g (61%) of product (b.p. 190–192°/0.06 mm, m.p. 83–85°). (Found: Cl, 13.58. $C_{24}H_{20}Cl_2O_3Si_3$ calcd.: Cl, 13.86%.)

2,2-Dichloro-4,4,6,6-tetra-m-tolylcyclotrisiloxane

This compound was prepared in a similar fashion as the corresponding phenyl compound, b.p. 244–248°/0.02 mm. (Found: Cl, 12.21. $C_{28}H_{28}Cl_2O_3Si_3$ calcd.: Cl, 12.49%.)

2,2-Dichloro-4,4,6,6-tetra-p-tolylcyclotrisiloxane

This compound was also prepared similarly as a liquid boiling at 232–235°/ 0.01 mm. (Found: Cl, 12.95. $C_{28}H_{28}Cl_2O_3Si_3$ calcd.: Cl, 12.49%.)

Octa-p-tolylspiro[5.5]pentasiloxane

A 250 ml benzene solution containing tetra-*p*-tolyldisiloxane-1,3-diol (23.5 g, 0.05 mole) and another 250 ml benzene solution containing $SiCl_4$ (5.1 g, 0.03 mole) were added simultaneously and at the same rate with stirring to 30 ml of pyridine dissolved in 400 ml of benzene at room temperature over a period of 2 h. The reaction mixture was stirred for a few hours and it was filtered to remove the solids. The filtrate was evaporated and extracted with toluene. Distillation of the filtered toluene extract gave 18.9 g of residue melting at 235–250°. Two recrystallizations from ethyl acetate gave 14.3 g (59%) of crystals melting at 248.5–250°. (Found: C, 69.83; H, 5.84; Si, 15.09. $C_{56}H_{56}O_6Si_5$ calcd.: C, 69.60; H, 5.84; Si, 14.53%.)

The PMR spectrum of the aromatic protons showed the expected A_2B_2 pattern characteristic of para substitution[3,4]. The spectrum showed no detectable impurities.

Octaphenylspiro[5.5]pentasiloxane

This compound (m.p. 257–258°) was prepared in a similar manner. (Found: C, 66.94; H, 4.60; Si, 16.43; mol. wt., 842. $C_{48}H_{40}O_6Si_5$ calcd.: C, 67.60; H, 4.73; Si, 16.48%; mol. wt. 853.)

Octa-m-tolylspiro[5.5]pentasiloxane

This compound (m.p. 120.5–121.5°) was also prepared in a similar way. (Found: C, 69.48; H, 5.96; Si, 14.73. $C_{56}H_{56}O_6Si_5$ calcd.: C, 69.60; H, 5.84; Si, 14.53%.) The PMR spectrum was consistent with the structure. No impurities were detected.

2,2,4,4-tetraphenyl-8,8,10,10-tetra-p-tolylspiro[5.5]pentasiloxane

A 50 ml benzene solution containing 2,2-dichloro-4,4,6,6-tetraphenylcyclotrisiloxane (5.1 g, 0.01 mole) and another 50 ml benzene solution containing tetra-*p*-tolyldisiloxane-1,3-diol (4.7 g, 0.01 mole) were added simultaneously and at the same rate with stirring to 50 ml of benzene and 3 ml of pyridine. The addition was carried out at room temperature over a period of 30 min while stirring was continued for 2 h. Using a work up procedure similar to that described for the simple spiro bicyclic compound above there was obtained a 36% yield of crystals melting at 213–214.5°. (Found: C, 68.98; H, 5.51; Si, 15.86. $C_{52}H_{48}O_6Si_5$ calcd.: C, 68.72; H, 5.33; Si, 15.44%.)

2,2,4,4-Tetraphenyl-8,8,10,10-tetra-m-tolylspiro[5.5]pentasiloxane

This compound (m.p. 123–124°) was prepared similarly from tetra-*m*-tolyldisiloxane-1,3-diol and 2,2-dichloro-4,4,6,6-tetraphenylcyclotrisiloxane. (Found: C, 68.21; H, 5.34; Si, 15.53. $C_{52}H_{48}O_6Si_5$ calcd.: C, 68.72; H, 5.33; Si, 15.44%.)

2,2,4,4-Tetra-p-tolyl-8,8,10,10-tetra-m-tolylspiro[5.5]pentasiloxane

This compound (m.p. 147–148°) was prepared similarly from 2,2-dichloro-4,4,6,6-tetra-*p*-tolylcyclotrisiloxane and tetra-*m*-tolyldisiloxane-1,3-diol. (Found: C, 69.36; H, 5.70; Si, 14.58. $C_{56}H_{56}O_6Si_5$ calcd.: C, 69.60; H, 5.84; Si, 14.53%.) The PMR spectrum of the aromatic region showed peaks characteristic of the *meta* and *para* patterns observed for the simple spirobicyclic compounds.

It should be pointed out that the infrared spectra of all these six simple and mixed octaarylspiro[5.5]pentasiloxanes are consistent with their structures. They all have a strong Si–O band at 1042 cm^{-1} but no indication of any silanol. The value 1042 cm^{-1} is interpreted as indicative of trimer rings although it is somewhat higher than normally observed for single trimer rings[5]. Another band was observed between 769–784 cm^{-1} in all six siloxanes and was not observed in the corresponding polymers. The origin of this band is not known but appears to be characteristic of the spirobicyclic structure.

Polymerization of octaarylspiro[5.5]pentasiloxane

All six octaarylspiro[5.5]pentasiloxane compounds described above have been polymerized in bulk and in toluene solution in the presence of a basic catalyst. In the bulk polymerization the molten compound was treated with a small amount of THF solution containing potassium naphthalene (equivalent to 40 ppm of KOH) under dry nitrogen for 15 min. The viscous polymer formed was dissolved in toluene containing some iodine and it was recovered by precipitating with an excess of methanol.

In the solution polymerization 2 g of the spirobicyclic compound dissolved in 1 ml of toluene at the reflux was treated with the same catalyst for 15 min. The solvent was evaporated and the polymer formed was treated in a similar way as that for the bulk polymer. The intrinsic viscosities of these polymers were determined in toluene solution at 25° and they ranged from 0.12 to 0.98 dl/g.

The polymers were fractionated by precipitating them twice from toluene solution with methanol. The fractionated polymers were washed with methanol and dried. The yields of fractionated polymers were 40–60%.

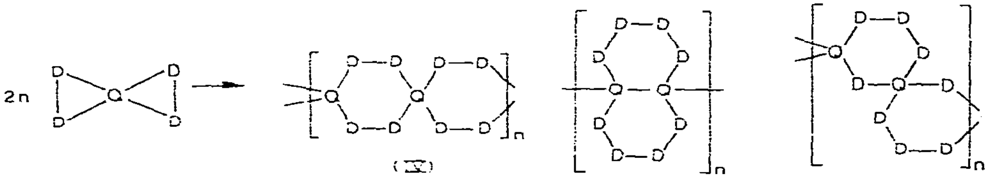
Proton magnetic resonance spectra

The PMR spectra were obtained from solutions of the polymers and monomers (octaarylspiro[5.5]pentasiloxane) dissolved in either carbon tetrachloride or deuterochloroform with concentrations ranging from 6–19% by weight. Spectra were measured by means of a Varian A-60 spectrometer at ambient temperature. The chemical shift values are reported as parts per million (ppm) downfield from internal tetramethylsilane with an estimated accuracy of ±0.05 ppm.

DISCUSSION

All polymers prepared from the octaarylspiro[5.5]pentasiloxanes are readily soluble in solvents like toluene and carbon tetrachloride. It is reasonable to assume that there is no significant amount of crosslinking. Additional evidence that crosslinking has not occurred is provided by the shape of the PMR peaks. For these polymers the observed peaks are rather sharp. It has been observed that crosslinking produces broad peaks and, if extensive, can prevent the observation of the spectrum[6].

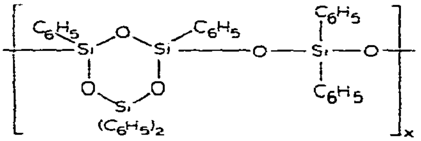
Three of the possible polymer structures are shown as follows:



(IV) (V) (VI)

Polymer structures with Q to D ratios other than substantially 0.25 were removed from consideration on the basis of elemental analysis data. Q and D represent the tetrafunctional and difunctional siloxane units[7], respectively. The elemental analysis data presented in Table 1 is consistent with polymer having a Q/D ratio of 0.25.

Polymer structures containing siloxane trimer rings were ruled out on the basis of infrared data. It has been well established that cyclic siloxane trimer structures have absorption bands in the 1010–1020 cm^{-1} region[5]. For example the polymer

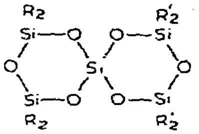


shows the trimer band at 1020 cm^{-1}. None of the polymers obtained from polymerization of the spirobicyclic monomers showed such absorption bands.

Data in Table 2 show that the aromatic methyl resonances in the polymers are shifted to higher field due to increased shielding from neighboring aromatic groups. The shielding is a result of the induced field caused by the ring current generated by the π electrons of the aromatic ring. The induced field opposes the applied laboratory

TABLE 1

ELEMENTAL ANALYSIS OF POLYMERS FROM



Monomer			*Found*	*Calcd. for Q/D ratio*		
R	*R'*			0	0.25	0.5
C_6H_5	C_6H_5	C	66.50	73.16	67.60	63.12
		H	4.73	5.08	4.73	4.41
		Si	17.39	14.16	16.48	18.45
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	C	68.44	74.30	69.60	65.58
		H	5.96	6.23	5.84	5.50
		Si	14.73	12.40	14.53	16.43
C_6H_5	p-$CH_3C_6H_4$	C	67.97	73.50	68.72	64.42
		H	5.17	5.70	5.33	4.99
		Si	16.05	13.22	15.44	17.38
m-$CH_3C_6H_4$	m-$CH_3C_6H_4$	C	68.46	74.30	69.60	65.58
		H	5.69	6.23	5.84	5.50
		Si	14.51	12.40	14.53	16.43
C_6H_5	m-$CH_3C_6H_4$	C	68.53	73.50	68.72	64.42
		H	5.46	5.70	5.33	4.99
		Si	14.82	13.22	15.44	17.38
p-$CH_3C_6H_4$	m-$CH_3C_6H_4$	C	68.00	74.30	69.60	65.58
		H	5.89	6.23	5.84	5.50
		Si	14.70	12.40	14.53	16.43

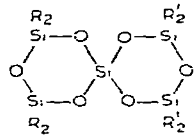
field above and below the plane of the aromatic ring. Hence protons in this environment experience a shielding effect and appear at higher field[8]. Protons nearest the center of the aromatic ring experience the greatest shielding. The methyl resonances for the *meta* isomer are shifted more than those in the *para* isomers. This is to be expected since in the *meta* isomers the methyl groups are closer to the plane of the neighboring aromatic ring.

The PMR spectra (Fig. 1) of all the polymers examined show more peaks than can be explained on basis of type of substituted phenyl group present. For example, the polymer prepared from the *meta* substituted spirobicyclic compound shows two well defined moderately sharp peaks. One might argue that these two peaks are due to the substituent groups located on silicon atoms in axial and equatorial positions. However, at ambient temperatures the rate of interconversion of the various conformations is too rapid to permit their detection. The PMR spectra of all the cyclic dimethylsiloxanes from D_4 thru D_7 are observed to have only one single sharp peak[9]. It is doubtful that even in polymers the restricted motion is sufficient to permit observation of the various conformations. Rochow and LeClair[10] have shown that molecular motion, principally due to methyl group rotation, exists in methyl silicones even at temperatures as low as 77°K. Honnold[11] *et al.* attribute the narrow proton resonance line for silicone oil at −50°C. to interchain rotation about the Si–O–Si axis.

These additional peaks are not likely due to low molecular weight material because the polymers have been fractionated. For example the molecular weight of

TABLE 2

CHEMICAL SHIFTS OF METHYL PROTONS IN



s = shoulder; p = predominant peak;
m = monomer

Monomer		Chemical shift δ (ppm from Me_4Si)		
R	R'	Monomer	Bulk polymer	Solution polymer
p-$CH_3C_6H_4$	p-$CH_3C_6H_5$	2.29	2.22 s 2.26 p	1.92 s 2.25 p
C_6H_5	p-$CH_3C_6H_4$	2.29	2.22 2.25	2.12 2.22
m-$CH_3C_6H_4$	m-$CH_3C_6H_4$	2.19	1.62 1.80	1.63 1.82
C_6H_5	m-$CH_3C_6H_4$	2.22	1.75 2.21 m	1.68 1.83 1.93
p-$CH_3C_6H_4$	m-$CH_3C_6H_4$	2.22 2.30	1.67 1.83 1.92 2.17	1.68 1.83 1.95 2.17

the polymer prepared from the meta substituted spirobicyclic compound was found to be approximately 6×10^4. The molecular weight of the polymer prepared from the mixed *meta* and *para* spirobicyclic compound is approximately 3.5×10^5.

It is our belief that the additional peaks are related to polymer structure rather than due to the type of substituted phenyl groups present. The PMR spectra of polymers obtained from the mixed spirobicyclics show peaks characteristic of each type of substituted phenyl group in addition to those due to polymer structure. In order to rigorously interpret the chemical shift of the aromatic methyl resonance in terms of the preceding structures it is necessary to have known model compounds containing the various structures. Unfortunately, these model compounds are not available. Nevertheless, some tentative conclusions may be given.

In structure (IV) all the aromatic methyl groups are magnetically equivalent so that the PMR spectra should show only one resonance. The observation of more than one aromatic methyl resonance therefore shows that structure (IV) cannot be the entire polymer structure. The choice between structures (V) and (VI) cannot be made on the basis of the PMR data alone until spectra of model compounds are available. The aromatic methyl groups in these structures are not magnetically equivalent. Therefore spectra of polymers containing either structure would be expected to show more than one aromatic methyl resonance.

However, structure (V) can be ruled out on the basis of steric hindrance. A polymer structure containing such a Q chain would be too crowded to exist. The molecular model of structure (V) cannot be made because of considerable crowding. In structure (VI) the D units containing aromatic methyl groups are located in three different environments. Furthermore, structure (VI) can be readily made from molecul-

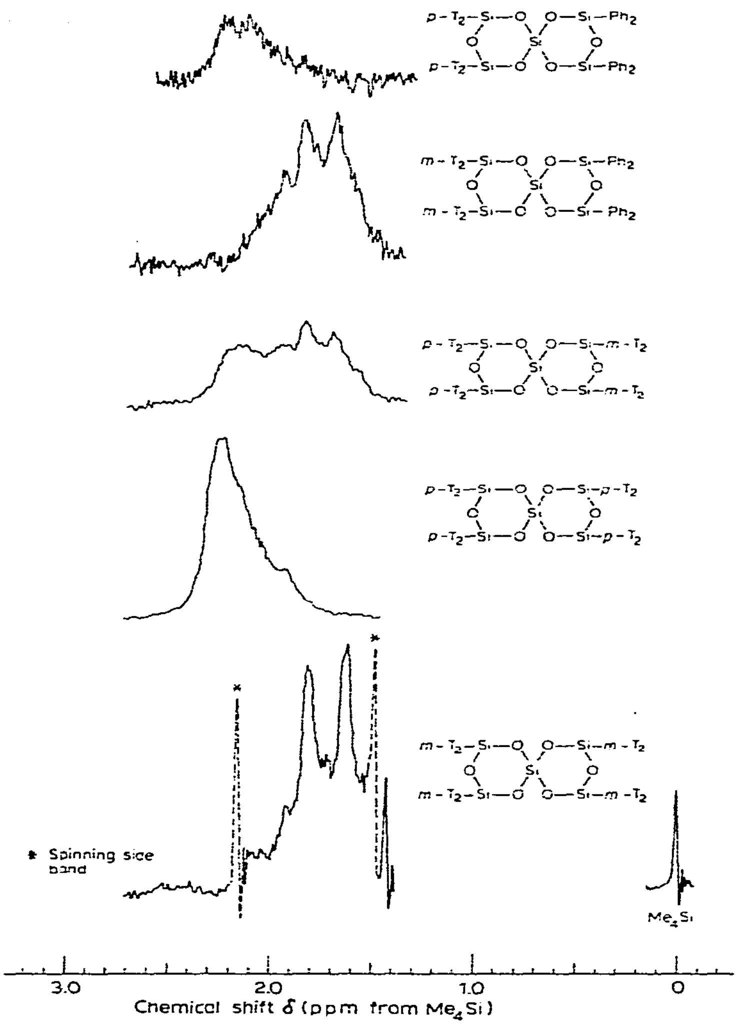


Fig. 1. PMR spectra of solution polymers from various monomers.

ar models without crowding. It is, therefore, believed that structure (VI) is the predominant structure although the possibility of having mixtures containing small amounts of structure (IV) cannot be ruled out.

It should be pointed out that only the methyl proton resonances are of interest for determining polymer structure in this discussion. The phenyl proton resonances (chemical shift between 6–7.5 ppm) are too complex to be interpreted because of the spin–spin coupling of adjacent protons.

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SUMMARY

A series of six octaarylspiro[5.5]pentasiloxanes containing phenyl, *m*-tolyl, and *p*-tolyl groups have been synthesized by treating a disiloxanediol with either $SiCl_4$ (for simple bicyclic) or with a dichlorocyclotrisiloxane (for mixed bicyclic). They can be rearranged into non-crosslinking polymers. The structures of these polymers have been proposed based on PMR studies and steric considerations.

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