

CHEMISTRY AND POLYMERIZATION OF 1, 1, 3, 3-TETRAMETHYL-1, 3-DISILA-2-OXAINDANE

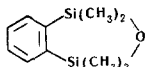
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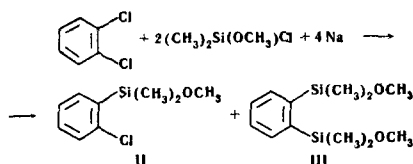
Reaction of *o*-dichlorobenzene with dimethylmethoxychlorosilane and sodium leads to the isolation of dimethyl(*o*-chlorophenyl) methoxysilane, *o*-bis(dimethylmethoxysilyl)benzene, 1, 1, 3, 3-tetramethyl-1, 3-disila-2-oxaindane, and 1, 1-dimethyl-1-silatribenzocycloheptatriene. When I is polymerized with H₂SO₄, the phenyl group is observed to split off.

It is of great interest to obtain polycarbosiloxanes with a regular distribution of elements along the molecule chain. One route to such polymers is polymerization of cyclic monomers. The present work aimed to prepare 1, 1, 3, 3-tetramethyl-1, 3-disila-2-

oxaindane,  (I), and to polymerize it.

For the synthesis of I we chose the reaction of *o*-dichlorobenzene with dimethylmethoxychlorosilane and sodium in toluene or tetrahydrofuran. When our work was started this compound had not been described in the literature, and it was only when we had characterized it that a publication appeared [1] on synthesizing it by reacting *o*-iodobromobenzene with (CH₃)₂SiCl(H) and magnesium, followed by esterification and hydrolysis.

Investigation showed the reaction product to be a complex mixture of compounds with a wide boiling range, 60° (40 mm) to 200° C (1 mm). Column distillation of the products of a few runs gave dimethyl (*o*-chlorophenyl)methoxysilane and *o*-bis(dimethylmethoxysilyl)benzene.

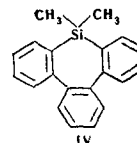


Material with bp 95°-97° C (40 mm) was also isolated. This is very close to the boiling point of II viz. 87°-90° (30 mm), but with almost twice the silicon content (23% instead of 13%), and more carbon (60% instead of 54%). The IR spectrum of this cut had an absorption band in the 930 cm⁻¹ region, characteristic of the Si-O-Si link in a 5-membered ring. After this cut had been treated with aqueous methanol at room temperature, two substances were isolated: 1) bp 91°-94° (20 mm), which crystallized on standing, and 2) bp 175°-180° C (25 mm). The IR spectrum of substance 1 showed (Fig. 1, a) absorption bands corresponding to the following groups: Si-O-Si at 655 or 697 and 933 cm⁻¹; Si-Me at 1255 cm⁻¹, symmetric deformation vibration, 2900 and 2960 cm⁻¹, valence vibrations of C-H; Si-C₆H₄

1120 cm⁻¹; C₆H₄ 750, 3017, 3042, 3090 cm⁻¹. The elementary analytical data, molecular weight found experimentally, and IR spectrum of the first substance identified it as I. Its physical constants were close to those given in the literature [1]. The second substance was a mixture of linear disiloxanes of the structure R'(R)₂SiOSi(R)₂R', where R and R' can be only Me, C₆H₅ and C₆H₄Cl. The IR spectrum (Fig. 1b) has absorption bands at 1060 and 550 cm⁻¹, belonging to ν_{as}(SiOSi) and ν_s(SiOSi); 1122, 3043, 3064, 3084 cm⁻¹ belonging to Si-C₆H₅, and 800 cm⁻¹ (rocking vibration), 1258 cm⁻¹ (symmetric deformation vibration), 2900 and 2960 cm⁻¹ (C-H valence vibrations) belonging to -Si-CH₃.

A chromatogram showed the 175°-180° C (25 mm) cut to contain two compounds.

Analysis of the substances boiling above 100° (1 mm) indicates that reaction is complex. Addition of silyl groups was found to be accompanied by condensation of phenyl groups. In all the runs the 140°-200° (1 mm) cut gave on standing a white crystalline substance, mp 226°-227°. The elementary analysis, found molecular weight, and properties of this compound led to its being ascribed the structure 1, 1-dimethyl-1-silatribenzocycloheptatriene. X-ray analysis gave objective confirmation of the structure IV. * The



crystals (from dichloroethane) of this substance belonged to P_{bcn} space group, with parameters a = 14.61 ± 0.05, b = 15.21 ± 0.09, c = 6.89 ± 0.05 Å, with 4 molecules in the unit cell. The structure of the molecule, with a special position at symmetry axis 2, was found from electron density projections, and is characterized by ordinary bond lengths and valence angles. IR absorption spectra are not inconsistent with the assigned structure. IV had a very low solubility in ether, CHCl₃, and CCl₄, but was soluble in benzene, toluene, and tetrahydrofuran.

*The X-ray analysis was carried out by Yu. T. Struchkov, M. S., in the structure determination laboratory of the Institute for Heterocyclic Compounds, AS USSR.

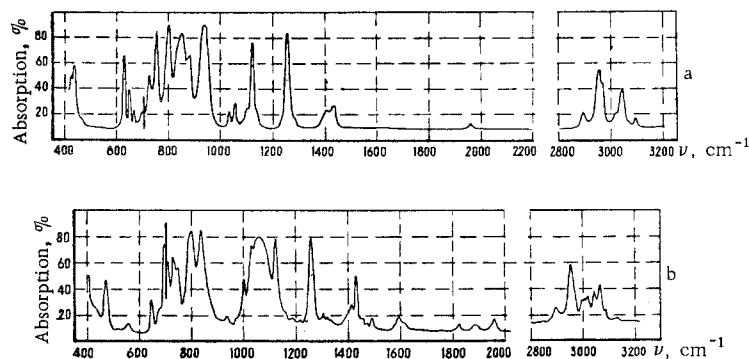


Fig. 1. IR absorption spectra: a) 1,1,3,3-tetramethyl-1,3-disila-2-oxaindane, spectrum determined with a thin layer of melt, using a UR-10 spectrophotometer with slit program 4; b) substance bp 175°–180° (25 mm), spectrum determined with a layer of suitable thickness.

I was polymerized with alkali and acid. Heating I with 1% KOH at 100°–140° C gave a liquid product, whose viscosity was practically unchanged on heating for 12 hours or by standing for 3 days at room temperature. H_2SO_4 polymerizes I both at room temperature (slowly) and on heating. However, elementary analysis of the polymer shows that the phenyl group is almost completely split off, and the IR spectra of the polymers resemble that of polydimethylsiloxane (Fig. 2).

EXPERIMENTAL

18.3 g (0.8 mole) Na was suspended in 150 ml toluene at 90°–110° C, then over a period of 2 hr 30 min a mixture of 29.5 g (0.2 mole) *o*- $Cl_2C_6H_4$ and 49.5 g (0.4 mole) $(CH_3)_2Si(OCH_3)Cl$ added, then the whole refluxed for a further 2 hr. Next day the precipitate was filtered off, washed with toluene (50 ml), then with ether. The filtrate was distilled to give the following cuts: 1) 60 g bp 85°–100° C, n_D^{20} 1.4540; 2) 19 g bp 60°–90° (60 mm), n_D^{20} 1.4880; 3) 10.5 g bp 49°–130° (1 mm), n_D^{20} 1.5030; 4) 9.5 g bp 130°–195° (1 mm), n_D^{20} 1.5470 and 5 g viscous residue in the distilling flask.

Next day cut 4 had given a white crystalline precipitate, to which 10 ml ether was added, the solid filtered off, twice washed with ether, yield of IV 0.05 g, mp 219°–222° C, after recrystallizing from benzene it had mp 226°–227°. Found: C 83.78; 84.05; H 6.44; 6.40; Si 9.80; 9.75%; M 286, 284 (Rast), 284 (X-ray analysis). Calculated for $C_{20}H_{18}Si$: C 83.87; H 6.32; Si 9.79%; M 286.

Column fractionation of 75 g of a cut bp 60°–120° C (40–60 mm) (from a number of runs) gave:

a) 10 g II, bp 87°–90° (30 mm), d_4^{20} 1.059, n_D^{20} 1.4978. Found: C 54.63; 54.70; H 6.19; 6.29; Si 13.63 Cl 17.26; 17.00%; M 178; MR_D 55.55. Calculated for $C_9H_{13}OClSi$: C 53.84; H 6.52; Si 13.99; Cl 17.66%; M 200.7; MR_D 55.96.

b) 21.5 g substance bp 95°–100° C (32 mm); d_4^{20} 0.9687, n_D^{20} 1.4905. Found: C 59.93; H 7.55; Si 23.11; Cl 1.31%.

c) 6 g III, bp 142°–145° C (20 mm); d_4^{20} 0.9841; n_D^{20} 1.4973. Found: C 56.30; 57.00; H 8.18; 8.35; Si 21.36; 21.33%; M 268.2; MR_D 75.715. Calculated

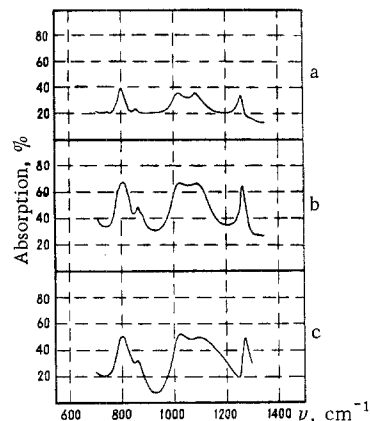


Fig. 2. IR absorption spectra; a) polydimethylsiloxane; b) and c) polymers prepared by H_2SO_4 polymerization of I at room temperature and by heating respectively.

for $C_{12}H_{22}O_2Si_2$: C 56.62; H 9.76; Si 22.08%; M 254, MR_D 75.79.

19.2 g cut b, bp 95°–100° (32 mm), 10 ml MeOH, and 6 ml water were stirred together at room temperature for 1 hr 30 min. 20 ml ether was added, the ether layer separated off, washed with water, dried for 10 min over $CaCl_2$, and then distilled to give:

1) 5.6 g I, bp 93°–99° C (22 mm), after repeated distillation it had bp 91°–94° (20 mm), d_4^{20} 0.9727, n_D^{20} 1.4950, and crystallized, mp 33°. Found: C 57.51; 57.45; H 7.51; 7.56; Si 27.24; 27.64%; M 198; MR_D 62.47. Calculated for $C_{10}H_{16}OSi_2$: C 57.63; H 7.72; Si 26.96%; M 208.4; MR_D 62.724.

2) 4 g cut bp 175°–180° C (25 mm); d_4^{20} 0.9843; n_D^{20} 1.5139. Found: C 66.09; H 8.8; Si 20.35; Cl 2.37; 2.80%.

Polymerization of I. a) A drop of H_2SO_4 was added to 0.5 g I, and the whole heated at 140° C for 2 hr. The liquid product was left overnight, and next day there

was a gelatinous polymer. Found: C 33.29; H 8.02; Si 33.42%.

b) A drop of H_2SO_4 was added to 0.5 g I, the mixture stirred, then left at room temperature. After 3 days the product was a mobile liquid, after 5 days the viscosity had increased considerably, and after 15 days a viscous polymer resulted. The IR spectrum of the latter was the same as the IR spectra of the previous polymer and polydimethylsiloxane. Found: Si 32.65, 33.0%.

REFERENCES

1. W. Piccoli, U. S. Patent no. 3050542, 1962; RZhKh 13N116, 1964.

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