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The Preparation and Polymerization of Fluorine-containing Siloxanes

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Silanes and cyclosiloxanes containing $\overline{\mathrm{CFClCF_2CH_2CH}}\mathrm{Si}-$ groups were prepared by the reaction of vinyl-substituted silicon compounds with chlorotrifluoroethylene. Polymerization of the cyclosiloxanes, using sulfuric acid catalysis, gave high molecular weight linear polysiloxanes.

Introduction

A convenient method for the synthesis of halogen-containing organosilicon compounds is the reaction of a vinylsilane or siloxane with a halogenated alkene or alkane. The free-radical addition of perhaloalkanes to vinylsilanes has been previously reported.[1-3] In this Laboratory, the reaction of a perhaloalkene with vinyl-substituted silicon compounds[4] was utilized to prepare silanes and cyclosiloxanes containing halogenated cyclobutyl groups. Compounds of this type were desired as precursors to solvent-resistant silicone elastomers.

Chlorotrifluoroethylene was treated with methylvinyldichlorosilane under autogenous pressure at 200° to give (2-chloro-2,3,3-trifluorocyclobutyl)-methyldichlorosilane (I) in 79% yield. A second product, 3,4-dichloro-1,1,2,2,3,4-hexafluorocyclobutane, resulting from the dimerization of chlorotrifluoroethylene, was formed in 17% yield. Confirmation of the silane structure was obtained through failure to react with chlorine, indicating the absence of a double bond, by elemental analyses and by nuclear magnetic resonance spectroscopy which showed the presence of only the one isomer described.

Conversion of (I) to linear polymers *via* a base-catalyzed polymerization of a cyclosiloxane intermediate[5,6] was not applicable due to the instability of the (chlorotrifluorocyclobutyl) grouping to alkali. In addition, separation of the cyclosiloxanes, obtained by hydrolysis of (I), from the reaction mixture was extremely difficult due to their high boiling points and thermal instability.

An alternative route to the preparation of cyclosiloxanes containing the (chlorotrifluorocyclobutyl) grouping was found in the reaction of chlorotrifluoroethylene with either vinylheptamethylcyclotetrasiloxane or divinylhexamethylcyclotetrasiloxane to form the corresponding (chlorotrifluorocyclobutyl) derivatives in good yield. Purification of these materials was effected easily by distillation.

Reaction of the cyclosiloxanes with small amounts of concentrated sulfuric acid and water under precisely controlled conditions gave high molecular weight linear polymers which, on removal of the residual acid, furnished materials suitable for use as elastomers.

Experimental

Preparation of (2-Chloro-2,3,3-trifluorocyclobutyl)-methyldichlorosilane (I).—Methylvinyldichlorosilane (5.1 moles, 719.4 g.) and chlorotrifluoroethylene (3.4 moles, 396.1 g.) were charged to a 2.4-l. steel, gas-heated autoclave. The autoclave was heated rapidly to 200° and maintained at that temperature for 8 hr. At the end of that time the autoclave was cooled rapidly with cold water, vented to a Dry-Ice-cooled trap to relieve residual pressure, then discharged into a Dry-Ice-cooled distillation flask. The flask then was fitted with a reflux condenser attached to a Dry-Ice-cooled trap. The crude reaction product was refluxed 16 hr. to remove dissolved chlorotrifluoroethylene. A total of 6.6 g. (0.04 mole) of unreacted chlorotrifluoroethylene was recovered.

Fractional distillation gave (I) (2.67 moles, 687.8 g.), b.p. 168°, n^{25}_{D} 1.4239, a 79% yield; and 3,4-dichloro-1,1,2,2,3,4-hexafluorocyclobutane (0.33 mole representing 0.66 mole $CF_2{=}CFCl$, 76.9 g.), b.p. 59.5°.

Anal. Calcd. for $C_5H_6Cl_3F_3Si$: Si, 10.9; C, 23.3; F, 22.2; Cl, 41.4; Cl (SiCl), 27.5. Found: Si, 11.3; C, 22.5; F, 23.2; Cl, 41.7; Cl (SiCl), 27.3.

Chlorination of (I).—Treatment of (I) with chlorine for several hours gave no evidence of reaction, indicating the absence of carbon–carbon unsaturation.

Hydrolysis of (I).—(I) (2.5 moles, 642 g.) was added dropwise, with stirring, to a mixture of toluene (518 g.) and water (730 g.). The mixture was stirred an additional hour, separated and washed with fresh water.

A 200-g. portion of the hydrolyzate–toluene solution was mixed with 0.95 g. of powdered potassium hydroxide in a flask fitted with a Dean–Stark trap and heated to reflux. After refluxing for 4 hr. the reaction mixture was found to be neutral and to contain small gel particles.

A 200-g. portion of the same hydrolyzate solution was refluxed with 9.5 g. of concentrated sulfuric acid. At the end of 4 hr., evolution of water had ceased. The mixture was washed, dried with $CaSO_4$ and freed of solvent. An attempt was made to distill the mixture. A small amount of product was obtained, b.p. 217° (4 mm.), n^{25}_{D} 1.4300. Decomposition was extensive and the distillation was stopped before completion. Infrared analysis indicated that the product was primarily the cyclotrisiloxane, contaminated with a small amount of a silanol-containing material.

Anal. Calcd. for $(C_5H_6F_3ClSiO)_x$: C, 29.7; Si, 13.9; Cl, 17.6; F, 28.2. Found: C, 30.4; Si, 14.3; Cl, 17.8; F, 25.7.

Dehydrochlorination of (I).—Quinoline (0.9 mole, 116.2 g.) was added slowly to (I) (1.0 mole, 257.5 g.). Heat was evolved and there was an immediate precipitation of quinoline hydrochloride. The mixture was stirred an additional hour and filtered to remove quinoline hydrochloride. Fractionation gave (2,3,3-trifluoro-1-cyclobutenyl)-methyldichlorosilane (0.63 mole, 139.8 g.), 70% yield. The product had these properties: b.p. 121.5°, n^{25}_{D} 1.4030, d^{25}_{4} 1.318.

Anal. Calcd. for $C_5H_5F_3Cl_2Si$: Si, 12.7; F, 25.8; C, 27.1; Cl, 32.1; Cl (SiCl), 32.1. Found: Si, 13.0; F, 25.3; C, 27.9; Cl (total), 31.0; Cl (SiCl), 31.3.

Mono-(2-chloro-2,3,3-trifluorocyclobutyl)-heptamethylcyclotetrasiloxane (II).—The reaction of chlorotrifluoroethylene (13.0 moles, 1514.5 g.) with monovinylheptamethylcyclotetrasiloxane (11.8 moles, 3645 g.) prepared as described elsewhere[7] was conducted in a 3.8-l. steel autoclave in a manner similar to that described for (I). A total of 4.0 moles (463 g.) of unreacted chlorotrifluoroethylene was

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(1) A. F. Gordon, U. S. Patent 2,715,113, August 9, 1955.

(2) R. N. Haszeldine and R. J. Marklow, 128th Meeting, American Chemical Society, Minneapolis, Minn., September, 1955.

(3) P. Tarrant and G. W. Dykes, 128th A.C.S. Meeting.

(4) A. F. Gordon, British Patents 760,201 and 802,358.

(5) J. F. Hyde, U. S. Patent 2,490,357, December 6, 1949.

(6) O. R. Pierce, G. W. Holbrook, O. K. Johannson and J. C. Saylor, 136th Meeting, American Chemical Society, Atlantic City, New Jersey, September, 1959.

(7) A. F. Gordon, U. S. Patent 2,884,432, April 28, 1959.

recovered. Fractional distillation gave (II) (8.3 moles, 3526 g.), b.p. 119° (10 mm.), $n^{25}D$ 1.4070, a 70% yield and 3,4-dichloro-1,1,2,2,3,4-hexafluorocyclobutane (0.3 mole, accounting for 0.6 mole $CF_2{=}CFCl$, 69.9 g.), a 4.6% yield.

Anal. Calcd. for $C_{11}H_{24}F_3ClO_4Si_4$: Si, 26.3; C, 31.1; F, 13.4. Found: Si, 26.7; C, 31.2; F, 12.1.

Bis-(2-chloro-2,3,3-trifluorocyclobutyl)-hexamethylcyclotetrasiloxane (III).—Chlorotrifluoroethylene (6.6 moles, 779 g.) and divinylhexamethylcyclotetrasiloxane[7] (3.0 moles, 960 g.) were charged to a 2.4-l. steel autoclave. The reaction was conducted as described previously.

Fractionation gave monovinylmono-(2-chloro-2,3,3-trifluorocyclobutyl)-hexamethylcyclotetrasiloxane (0.68 mole, 300 g.), b.p. 125° (10 mm.), $n^{25}D$ 1.4159, 28% yield; and (III) (0.83 mole, 475 g.), b.p. 167° (10 mm.), $n^{25}D$ 1.4159, 28% yield. Also, a 33% yield of 3,4-dichloro-1,1,2,2,3,4-hexafluorocyclobutane was obtained.

Anal. Calcd. for $C_{12}H_{24}F_3ClO_4Si_4$: Cl, 8.6; Si, 25.7. Found: Cl, 9.1; Si, 25.6.

Calcd. for $C_{14}H_{24}F_6Cl_2O_4Si_4$: C, 30.4; Si, 20.3; Cl, 12.9; F, 20.6. Found: C, 30.4; Si, 20.4; Cl, 13.1; F, 19.8.

Polymerization of (II).—(II) (100 g.) was vigorously stirred with a catalyst composed of 4 g. of concentrated sulfuric acid and an equal volume of octamethylcyclotetrasiloxane. Preliminary runs had shown that under these conditions the mixture polymerized to a viscosity of 300,000 centistokes in 45 minutes. Viscosity measurements were made with a Brookfield Viscometer. Since the mixture became warm from stirring, the viscosity figures are approximate. After stirring 45 minutes, water (0.04 mole, 0.72 g.) was stirred into the mixture. The viscosity increased rapidly to a high molecular weight polysiloxane.

Polymerization of (III).—The reaction was conducted using the same technique and proportions as in the previous run. The peak viscosity in this system had been previously determined to occur at 300,000 centistokes after 18 hr. The mixture was hydrolyzed with water (0.04 mole, 0.72 g.). The viscosity of the final polymer, as measured with a Brookfield Viscometer, was 2.8 × 10^6 centistokes.

Discussion

Rearrangement of siloxane bonds using sulfuric acid catalysis has been described previously.[8-10] In particular, the reaction intermediates proposed by Patnode and Wilcock[10] appear applicable to the present case. However, the reaction conditions are much more critical than in the case of octamethylcyclotetrasiloxane.

A study was made of various catalysts for the polymerization, which included concentrated sulfuric acid, fuming sulfuric acid (15% SO_3) and one composed of an equal volume mixture of concentrated sulfuric acid and octamethylcyclotetrasiloxane. This last catalyst was found to be the most active, probably due to its increased solubility in the fluorine-containing siloxane.

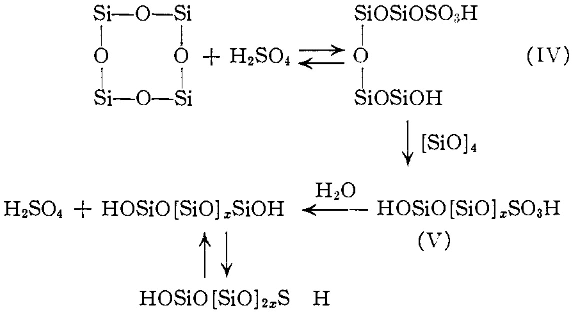
In the polymerization of both (II) and (III) it was found best to hydrolyze the mixture at the first viscosity peak. When the mixture was hydrolyzed before this maximum, the subsequent rate of polymerization was decreased and the resultant polymer was of lower molecular weight. Furthermore, the total time elapsed from cyclic to high polymer was longer when the mixture was hydrolyzed before peak viscosity (see Table I). If the initial reaction was allowed to continue beyond the viscosity maximum and then the mixture hydrolyzed, considerable depolymerization took place, resulting in low molecular weight products. In all cases, the use of stoichiometric amounts of water for hydrolysis was found to give maximum rates of polymerization and the highest molecular weight polymers.

TABLE I

EFFECT OF HYDROLYSIS BEFORE PEAK VISCOSITY

Initial stirring time, min.	Time from hydrolysis to polymer, min.	Total time, min.
$[CFClCF_2CH_2CH(CH_3)SiO]_1[(CH_3)_2SiO]_3$		
15	135	150
30	63	93
45	8	53
50	3	53
$[CFClCF_2CH_2CH(CH_3)SiO]_2[(CH_3)_2SiO]_2$		
135	1395	1530
390	960	1350
1080	20	1100

The polymerization reaction can be shown schematically



The principal difference between the above mechanism and that described previously[10] lies in the conversion of (IV) to (V). This step can be considered as an attack of (IV), probably as an ion, on unreacted starting material to form a linear polymer, (V). The maximum amount of (V) present is observed as the viscosity peak in the initial reaction. Unless hydrolysis is carried out at this point, side reactions, such as condensation to form sulfate-linked siloxane chains or cleavage of the chain by sulfuric acid, may occur and cause depolymerization. It can be seen that the amount of water used is critical, as too much will result in a regenerated acid of insufficient strength to promote further silanol condensation.

The great difference in rate of polymerization between (II) and (III) may be due to two factors. First, the solubility of sulfuric acid is much less in (III) and, second, the steric effects of the two cyclobutyl groups added to a possible inductive effect of the fluorine would tend to make the Si-O-Si linkage less susceptible to acid attack.

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(8) D. W. Scott, THIS JOURNAL, **68**, 2294 (1946).

(9) D. F. Wilcock, *ibid.*, **69**, 477 (1947).

(10) W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).