

# Silylation of cellulose

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II: SILYLATION OF DI- AND TRIHYDROXY ALCOHOLS WITH 1:1:3:3-TETRAMETHYL-1:3-DICHLORODISILOXANE.

## SUMMARY

**E**THANE-1:2-diol and propane-1:3-diol react with 1:1:3:3-tetramethyl-1:3-dichlorodisiloxane forming the corresponding rings. However, no ring compounds could be traced through the reaction between butane-1:4-diol, glycerol and the dichlorodisiloxane respectively, where only polymeric compounds are formed. The silylation products of the di- and trihydroxy alcohols, as model compounds, has confirmed that the ring formation during silylation of cellulose with dichlorodisiloxane is uncertain.

## Introduction

Silylation of polyalcohols with trimethylchlorosilane and hexamethyldisilazane are well known and such silylated compounds are widely used in gas chromatography.

Silylation with difunctional reagents are not common. It seems that the silylated products are in the cyclic or polymeric forms. Kriehle and Burkhard<sup>1</sup> found that glycols react with  $\text{me}_2\text{SiCl}_2$ ,  $\text{me}_2\text{Si}(\text{Oet})_2$  and  $[(\text{etO})_2\text{me}_2\text{Si}]_2\text{O}$  and gives cyclic compounds. Wannagat<sup>2</sup> stated that the building

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of Si-N, containing inorganic ring system, is possible by condensation of  $\alpha$ -s difunctional building blocks. In addition to Si and N containing rings, the synthesis of rings with other hetero atoms is achieved e.g. tetra- and pentamethyldichlorodisilazanes react with glycol and yield cyclosiloxazanes. To obtain ring compounds, the condensation reaction must be carried out under high dilution; otherwise poly-condensation reactions predominate.

It is well known that silylation of numerous natural products has been reported<sup>3</sup> as patent, where some or all the hydroxyl protons of such compounds are replaced by silyl groups. The nature of the hydroxyl groups in cellulose suggests that any resistance to silylation may be due mostly to steric reasons and lack of solubility than to intrinsic chemical difficulties in displacing these particular protons by trimethylsilyl groups<sup>4</sup>. Silylation of carbohydrates was achieved through its fusion with N-trimethyl-silylacetamide<sup>5</sup>. Carrying out the silylation in the presence of a solvent e.g. pyridine, it seems that the secondary hydroxyl groups react preferably, as in case of glucose<sup>6</sup> and dextrin<sup>7</sup>.

Cellulose reacts with pure trimethylchlorosilane producing a soluble product. Higher chlorinated silanes e.g. dimethyldichlorosilane and methyltrichlorosilane cause cross linking of cellulosic chains giving insoluble products<sup>4</sup>. Such insoluble products are highly water-repellent; this is attributed to the presence of the silyl groups on/or near the surface of the individual fibres. Rebek *et al.*<sup>8</sup> suggested a mechanism

for graft polymerisation when dimethyldichlorosilane reacts with cellulose. They stated also that the dichloro compound may condense with two hydroxyl groups of the same cellulosic chain or with two hydroxyl groups of two different cellulosic chains, whereas the condensation may take place through ring formation or cross-linking.

In a previous investigation<sup>9</sup>, cellulose was silylated with 1:1:3:3-tetramethyl-1:3-dichlorodisiloxane, the silylated product is water-insoluble and also water-repellent. The present study was carried out to examine the possibility of ring formation through the reaction of the dichlorodisiloxane and the hydroxyl groups of C<sub>6</sub> atom of one glucose molecule and the hydroxyl groups of C<sub>2</sub> atom of another glucose molecule of the same cellulosic chain, where di- and trihydroxy alcohols as model compounds, are silylated with dichlorodisiloxane.

## EXPERIMENTAL

### 1 Materials used:

- (a) Ethane-1:2-diol, propane-1:3-diol, butane-1:4-diol and glycerol, pure grade, Merck, West Germany.
- (b) 1:1:3:3-tetramethyl-1:3-dichlorodisiloxane was supplied by Inorganic Institute, Technical University, Braunschweig, West Germany. This product was prepared according to the method described by Patnod and Donald<sup>10</sup>.

### 2 Silylation

Tetramethyldichlorodisiloxane (0.1 mole) and triethylamine (0.2 mole) were dissolved in 600 ml. absolutely dry tetrahydrofuran. The mixture was cooled to -20°C, with continuous and vigorous stirring; (0.1 mole) of the diol or glycerol which is dissolved in 100 ml tetrahydrofuran was added dropwise within ½ hour. The mixture was left for 24 hours under continuous stirring at room temperature. It should be noted that the reaction was carried out under nitrogen atmosphere

The precipitated triethylamine hydrochloride was filtered under nitrogen atmosphere. The product was obtained by removing most of the solvent, using reduced pressure. The product was freed from any salt traces by dissolving in 100 ml petroleum ether (60-78°C) and stored in a well-closed container in a deep freeze for 24 hours. The precipitated amine hydrochloride was filtered over anhydrous Na<sub>2</sub>SO<sub>4</sub> and under nitrogen atmosphere. The crude material was distilled using Vigreux-column under mild conditions.

It is worth noting that the above mentioned conditions are greatly similar to that used during the preparation of cyclosilazanes by Wannagat *et al.*<sup>11</sup>

## RESULTS AND DISCUSSION

The reaction product of ethane-1:2-diol with the dichlorodisiloxane gives a product with a boiling point 42°C at 11 mm Hg. Such compound is suggested to be 1:1:3:3-tetramethyl-1:3-disila-2:4:7-trioxa-cycloheptane (I).

The element analysis of the suggested molecule (C<sub>6</sub>H<sub>16</sub>O<sub>3</sub>Si<sub>2</sub>) was found to be as follows: C, 37.25%; H, 8.20%; and Si, 29.93%, where the calculated values are: C, 37.46%; H, 8.38%; and Si, 29.20%. The yield was found to be 36%, measured refractive index and density were: 1.4105 and 0.9927, respectively.

The reaction between propane-1:3-diol and the dichlorodisiloxane gives a product with a boiling point 27°C at 0.1 mm Hg; such a compound is suggested to be 1:1:3:3-tetramethyl-1:3-disila-2:4:8-trioxa-cyclooctane (II).

The element analysis of the suggested ring (C<sub>7</sub>H<sub>18</sub>O<sub>3</sub>Si<sub>2</sub>) was found to be as follows: C, 40.04%; H, 8.89%; and Si, 26.41% which agrees with the calculated one: C, 40.74%; H, 8.79%; and Si, 27.22%. The yield was about 24%, its refractive index and density were 1.4152 and 0.9811, respectively.

The mass spectra display peaks at masses 193 for (I) and 207 for (II) as the highest values, which correspond to the parent compound with increase of one mass unit. The second peaks following those for the parent compound reveal the loss of the mass 16(CH<sub>3</sub> + H) supporting that the increase of

the original mass arise from proton rupture, while the three preceding peaks correspond to the successive loss of the three remaining  $\text{CH}_3$  groups. The rupture of the four  $\text{CH}_3$  groups leaves the cyclic ring, which is characterised by the peaks at masses 133 (I) and 148 (II). These results support the given cyclic structure.

The fragmentation of the cyclic ring proceeds through the stepwise elimination of the  $\text{CH}_2$ -groups leaving the C-Si-O part with the mass 104. The fragmentation of this part takes place in different ways for the two compounds; however, the lowest mass 44 (I) or 43 (II) is almost the same and corresponds to the smallest fragment  $\text{SiO}$ , since the Si-O bond is the strongest linkage in the molecule.

These results are in conformity with other physical measurement analyses, which are under investigation.

Butane-1:4-diol reacts with the dichlorodisiloxane and after distilling the crude material, a fraction with 65-67°C at 0.05 mm pressure was obtained.

In the case of glycerol, a fraction of 55-62°C boiling range at 0.04-0.05 mm Hg was obtained. It has to be mentioned that during distilling the crude product, the material contained in the flask is solidified after foaming.

The presence of any ring structure in the reaction products was not traced as indicated from the mass spectrum analysis, where only polymeric structures were detected.

In the case of butane-1:4-diol, the formation of 9-membered ring may be hard due to the statistical difficulty encountered in bringing the two ends of the molecule to the proper reacting position and/or extremely unstable under the present experimental conditions.

In the case of glycerol, due to the presence of three hydroxyl groups, the reaction is complicated and polymeric structures were formed.

## Conclusion

It is well known that glucose unit in the cellulosic chain contains two secondary hydroxyl groups and one primary hydroxyl

group. According to this, and despite the very mild experimental conditions, it is observed that no ring could be formed from the reaction between butane-1:4-diol and dichlorodisiloxane. Also, no ring could be traced during the treatment of glycerol with dichlorodisiloxane. So, ring formation through the reaction of the dichlorodisiloxane and the hydroxyl groups of  $\text{C}_6$  atom of one glucose molecule and the hydroxyl groups of  $\text{C}_2$  atom of another glucose molecule of the same cellulosic chain seems to be uncertain.

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