

# Technical

## ✂ Oligosiloxanes from Betulinol

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### ABSTRACT

Oligosiloxanes were synthesized from betulinol and dimethyldichlorosilane. The reactions were carried out in solution, and the oligomers with molecular weights up to 3030 g/mol were obtained. The structure and thermal stability of the oligomers were determined by infrared spectroscopy and thermogravimetry, respectively.

### INTRODUCTION

The principal extraction component of birch bark is betulinol, which gives birch bark its white color. It is a triterpene alcohol, possessing two reactive hydroxyl groups. Our previous investigations show that it combines with diisocyanates, difunctional acid chlorides and acrylates to produce polyurethanes, oligoesters and polyacrylates, respectively (1-3). The object of this work was to provide more information about the reaction between betulinol and dimethyldichlorosilane.

### EXPERIMENTAL PART

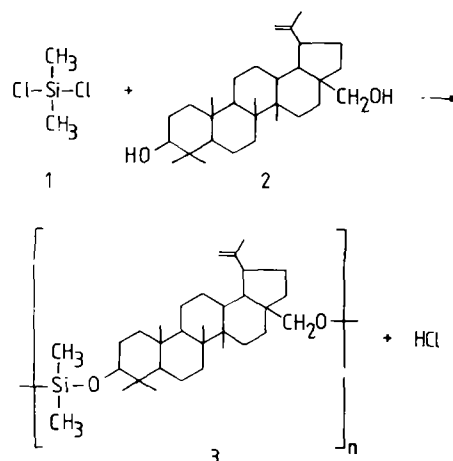
The crude betulinol, obtained as a byproduct from the commercial CSR process (4), was purified by crystallization in isopropanol. The melting point of the purified betulinol was 258 C, which is in accordance with literature values (5). The purity was checked by differential scanning calorimetry (DSC) and gas chromatography (GC) and was found to be 99.9%. Dimethyldichlorosilane for synthesis grade (bp 70 C, 98% purity by GC) from Merck was used as a reaction partner.

In a typical preparation of the reaction product (reaction 3, Table I), 4.4 g of betulinol was dissolved in the mixture of 20 cm<sup>3</sup> pyridine and 8 cm<sup>3</sup> toluene at 45 C in a three-necked flask equipped with a nitrogen inlet tube, a stirrer sealed with paraffin oil and a drying tube filled with CaCl<sub>2</sub>. Dimethyldichlorosilane (4.0 cm<sup>3</sup>) was added dropwise to the solution and heated for 6 hr at 60 C. After reaction the solution was cooled to room temperature and diluted with 50 cm<sup>3</sup> toluene, filtered and washed in separating funnel with dilute HCl and NaHCO<sub>3</sub> and finally with water. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was evaporated in a rotavapor and the remaining viscous mass was transferred to a glass plate and dried.

### RESULTS AND DISCUSSION

For the reaction between betulinol and dimethyldichlorosilane, based on the previously reported condensation between chlorosilane and an aromatic diol (6), the reaction shown in Scheme 1 is proposed.

Table I shows the results of the preparations under various conditions. In all reactions, white powdery substances were obtained, which were soluble in toluene, diethylether, tetrahydrofuran, methylenechloride, chloroform, *n*-hexane and cyclohexanone; and insoluble in water, ethyl alcohol, isopropanol, acetone and dimethylsulfoxide.



SCHEME 1

The IR spectrum of 2 shows typical absorption bands at 3400 (s), 3100, 2940 (s), 2880, 1650, 1450 (s), 1380 (s), 1190, 1100, 1020 (s) and 880 cm<sup>-1</sup>. The IR absorption bands of all reaction products were found at 3100, 2940 (s), 2880, 1650, 1450, 1380, 1370, 1350, 1250 (s), 1050 (s), 870 (s), 840 (s), and 780 cm<sup>-1</sup> (s). The disappearance of vibrations of OH groups at 3400 cm<sup>-1</sup> in all reaction products indicates the reaction between 1 and 2. The IR spectra of the reaction products have characteristic vibrations of siloxanes at 1050 and 840<sup>-1</sup>, indicating the presence of Si-O-C groups. The vibrations at 1250 and 780 cm<sup>-1</sup> are assigned to the methylene groups attached to Si.

Table I shows the range of molecular weights obtained in various reactions. In reaction 3, it is seen that reaction time affects molecular weights. The prolonged heating in reaction 6 leads to lower molecular weights. On the basis of molecular weights it can be concluded that in all reactions oligomers were formed. The *n*-value of 6 in reaction 3 indicates the formation of hexamer while, in the other reactions with *n*-values varying between two and four, lower homologs such as dimers, trimers and tetramers were obtained. The found Si content of 5.0% in reaction 3 points to the reaction scheme proposed earlier. The steric hindrance of betulinol limits the possibility in obtaining higher molecular weights under the investigating conditions as was indicated previously (1,2).

Figure 1 presents the TG curves of the substances obtained from the reaction products 1,3 and 4. As can be seen from the curves the decomposition takes place in the temperature range of 400-500 C. The decomposition reactions were of first order as determined by Freeman and Carroll

TABLE I

## Results of the Reaction of Dimethyldichlorsilane with Betulinol

Reaction number	1	2	3	4	5	6
Amount of reactants:						
betulinol, in mM (g)	5.0 (2.2)	5.0 (2.2)	9.9 (4.4)	9.9 (4.4)	9.9 (4.4)	9.9 (4.4)
dimethyldichlorsilane in mM (g)	16.3 (2.1)	20.9 (2.7)	33.3 (4.3)	33.3 (4.3)	41.1 (5.3)	33.3 (4.3)
Volume of solvent:						
pyridine in cm <sup>3</sup>	10	10	20	20	20	20
toluene in cm <sup>3</sup>	4	4	8	8	8	8
Reaction conditions:						
temperature in C	60	80	60	80	62	60
time in hr	2.5	2.5	6	2.5	2.5	12
Yield in g	1.8	2.3	4.9	4.2	6.1	5.8
Calc. yield in g	2.8	2.8	5.7	5.7	5.7	5.7
Appearance	Powder	Powder	Powder	Powder	Powder	Powder
Mol. wt., M <sub>n</sub> <sup>a</sup>	1770	1615	3030	1190	1865	1545
Si % <sup>b</sup>	—	—	5.0	—	—	—

<sup>a</sup>M<sub>n</sub> was determined by a Perkin-Elmer Model 115 vapor pressure osmometer. The solvent was toluene, and benzil was used to calibrate the instrument.

<sup>b</sup>Si was determined by scanning electron microscope, type Cambridge Stereoscan 250, fitted with energy dispersive X-ray analysis (EDXA), type PGT 1030.

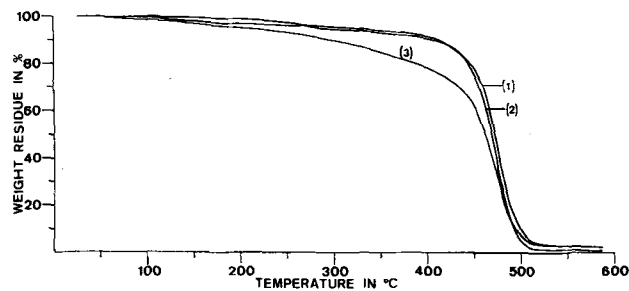


FIG. 1. TG-curves of the substances. (1) The substance obtained from the product of reaction 1. (2) The substance obtained from the product of reaction 3. (3) The substance obtained from the product of reaction 4 under nitrogen, heating rate 10 C/min.

(7) for curve 1. Then, the activation energies were obtained by a first-order Arrhenius plots according to Tang (8). The activation energies obtained from Figure 1 are 82 kJ/mol and 270 kJ/mol in the temperature ranges of 375-410 C

and 415-510 C, respectively, as determined according to Currie and Pathmanand (7).

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