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LETTERS TO THE EDITOR

Reaction of Dimethyldichlorosilane with Hexamethyldisiloxane as a Source of Dimethylsilanone. A Route to Linear and Cyclic Polydimethylsiloxanes

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We have suggested in [1] a method for generating dimethylsilanone ($Me_2Si{=}O$) under mild conditions, based on the reaction of dimethyldichlorosilane with alkali metal and ammonium nitrates. In the course of these studies, we also found that the reaction affords, along with products of oligomerization of dimethyl- and methylchlorosilanones and their insertion into the starting Me_2SiCl_2 and into hexamethyldisiloxane formed in the process, also α-methyl-ω-chlorooligodimethylsiloxanes of the general formula $Me_3Si\cdot(OSiMe_2)_nCl$, n = 1, 2 (yield 1–3%). Their formation can be accounted for by participation of the released Me_3SiCl in the reaction.

It is known that organylchlorosilanes and $SiCl_4$ react with organosilicon compounds containing Si–O–Si or Si–O–C groups at elevated temperatures and pressures in the presence of a polar solvent or catalyst to give cyclic and linear polysiloxanes [2, 3]. It was reported that the reaction of Me_2SiCl_2 with hexamethyldisiloxane follows the scheme

$$Me_2SiCl_2 + Me_3Si^*OSiMe_3 \longrightarrow Me_3Si^*Cl + ClMe_2SiOSiMe_3 + Me_2Si(OSiMe_3)_2.$$

In the presence of $HClO_4$, Me_2SiCl_2 cleaves hexamethyldisiloxane even at 20°C to form unidentified polymethylsiloxanes and $Me_2Si(OSiMe_3)_2$ (yield 30%) [4].

Proceeding with these studies, we found that the reaction of Me_2SiCl_2 with hexamethyldisiloxane (molar ratio 1 : 1) at 60–65°C and ambient pressure under argon in the absence of catalyst and solvent gives Me_3SiCl (yield 51%) with generation of dimethylsilanone, which subsequently oligomerizes and is inserted into the Si–Cl bonds of the starting Me_2SiCl_2 and of Me_3SiCl formed in the process, and also into the Si–O bonds of hexamethyldisiloxane. The total conversion of Me_2SiCl_2 is 97%.

$$Me_2SiCl_2 + Me_3SiOSiMe_3 \xrightarrow[-Me_3SiCl]{} ClMe_2SiOSiMe_3 \longrightarrow Me_2Si{=}O + Me_3SiCl$$

$$(Me_2SiO)_n \leftarrow n\,Me_2Si{=}O \;(n = 3\text{–}7) \xrightarrow{Me_2SiCl_2} ClMe_2Si(OSiMe_2)_nCl, \quad n = 1\text{–}5$$

$$\xrightarrow{Me_3SiCl} Me_3Si(OSiMe_2)_nCl, \quad n = 1\text{–}3, 5$$

$$\xrightarrow{(Me_3Si)_2O} Me_3Si(OSiMe_2)_nOSiMe_3, \quad n = 1\text{–}5$$

According to gas chromatography–mass spectrometry, trace amounts of MeClSi=O and $Cl_2Si{=}O$ are also generated; these species were detected by their insertion products.

Reaction of dimethyldichlorosilane with hexamethyldisiloxane. The reaction was performed with freshly distilled Me_2SiCl_2 and hexamethyldisiloxane; the purity of the reactants was checked by GLC and by

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^{1}H and ^{29}Si NMR spectroscopy. The reaction was performed in a dry argon flow in a four-necked flask equipped with a stirrer (the stirrer was equipped with a hermetic liquid seal, and the stirrer rod was passed through a reflux condenser), a thermometer, a gas inlet tube, and a Vigreux column sealed in series with a reflux condenser and a descending condenser. The descending condenser was connected with a trap cooled with liquid nitrogen. A mixture of 10.96 g of Me_2SiCl_2 and 13.77 g of $(Me_3Si)_2O$ was stirred for 10 h at 60–65°C. From the reaction mixture we isolated 0.35 g of unchanged Me_2SiCl_2 [conversion 97%, δ 0.83 s (6H), δ_{Si} 32.12 ppm, s (1Si)]; 6.8 g of hexamethyldisiloxane [δ 0.04 s (18H), δ_{Si} 7.08 ppm, s (2Si)]; and 9.45 g of Me_3SiCl [yield 51% based on converted Me_2SiCl_2, content in the reaction mixture (minus unchanged starting reactants) 53 wt %; δ 0.43 s (9H), δ_{Si} 31.15 ppm, s (1Si)].

The remaining mixture (8 g, 47 wt %), according to GLC and gas chromatography–mass spectrometry (GC–MS), consisted of the following compounds [in braces are GC–MS data, *m/e* (*I*, %)]: 6.6 g (39%) of $Me_3Si(OSiMe_2)_nOSiMe_3$, n = 1–5; 24.7% of $Me_3SiOSiMe_2OSiMe_3$ {221 (100) $[M - 15]^+$}; 8.8% of $Me_3Si(OSiMe_2)_2OSiMe_3$ {295 (30) $[M - 15]^+$}; 3.5% of $Me_3Si(OSiMe_2)_3OSiMe_3$ {369 (17) $[M - 15]^+$}; 1.5% of $Me_3Si(OSiMe_2)_4OSiMe_3$ {443 (8) $[M - 15]^+$}; 0.4% of $Me_3Si(OSiMe_2)_5OSiMe_3$ {517 (8) $[M - 15]^+$}; 1.2 g (7.1%) of $Me_3Si(OSiMe_2)_nCl$, n = 1–3, 5, major component (6.5%) $Me_3SiOSiMe_2Cl$ {167 (100) $[M - 15]^+$}; 0.08 g (0.5%) of products of $Me_2Si{=}O$ insertion into the Me_2SiCl_2 molecule, major component (0.4%) $ClMe_2Si(OSiMe_2)_2Cl$ {261 (100) $[M - 15]^+$}; and 0.05 g (0.3%) of cyclic oligomers, major component $(Me_2SiO)_4$ {281 (100) $[M - 15]^+$}.

The composition of reaction products was determined by GLC on a Model 3700 chromatograph (thermal conductivity detector, 2000 × 2-mm column, stationary phase 5% SE-30 on Chromaton N-AW, carrier gas helium). The mass spectra were taken on a Hewlett–Packard HP-5971A mass spectrometer (electron impact, 70 eV, mass-selective detector) connected to an HP-5890 chromatography (25-m Ultra-2 column coated with phenylmethylsilicone, vaporizer temperature 250°C, column temperature 70–280°C, heating rate 20 deg min^{-1}). The ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz), solvent $CDCl_3$, internal reference cyclohexane.

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