

LETTERS
TO THE EDITOR

Synthesis of 1,1,5,5-Tetramethyl-3,3-diorganyltrisiloxanes

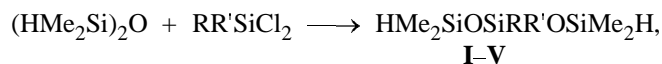
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Received April 15, 2002

1,5-Dihydrohexaorganyltrisiloxanes $(HR_2SiO)_2 \cdot SiR'R''$ are perspective monomers for the synthesis of polyorganylsiloxanes, organic, and organoelement compounds. A series of 1,1,3,5,5-pentamethyl-3-organyltrisiloxanes was previously prepared in 30–60% yields by co-hydrolysis of organyldichloromethylsilanes with excess chlorodimethylsilane at 2–4°C [1]. The by-products of this reactions were 1,1,3,3-tetramethyldisiloxane and 1,1,3,3,5,5-hexamethyltrisiloxane. The latter is also formed in a low yield by the reactions of octamethylcyclotetrasiloxane with 1,1,3,3-tetramethyldisiloxane, catalyzed by sulfuric acid [2]. The major product of this reaction is a complex mixture of α,ω -dihydrooligodimethylsiloxanes.

We have developed a method of synthesis of 1,1,5,5-tetramethyl-3,3-diorganyltrisiloxanes $HMe_2 \cdot SiOSiRR'OSiMe_2H$ (**I**) in yields of up to 94% by the reaction of 1,1,3,3-tetramethyldisiloxane with diorganyl-dichlorosilanes in a 2:1 ratio in the presence of catalytic amounts of water, by the following scheme.



R = R' = CH₃ (**I**), C₂H₅ (**II**); R = CH₃, R' = CH₂Cl (**III**), C₆H₅ (**IV**), CH=CH₂ (**V**).

With increased amounts of diorganyldichlorosilane, the yield of compound **I** decreases as a result of formation of a complex mixture of oligoorganylsiloxanes. In the absence of water, the reaction fails to occur even on prolonged boiling.

1,1,3,3,5,5-Hexamethyltrisiloxane (I). Water, 0.05 ml, was added to a mixture of 134 g of 1,1,3,3-tetramethyldisiloxane and 64.5 g of dichlorodimethylsilane, and the resulting mixture was left to stand at room temperature for 3 days, after which it was

washed with water, a solution of NaHCO₃, and again with water. The organic layer was separated and dried over sodium sulfate. Distillation gave 90.5 g (87%) of compound **I**, bp 125–127°C (720 mm), n_D^{20} 1.3822. ¹H NMR spectrum, δ , ppm: 0.07 s (6H, OSiMe₂O), 0.20 d (12H, Me₂SiO), 4.72 m (2H, SiH).

Compounds **II–V** were obtained in a similar way.

Compound II. Yield 82%, bp 80–82°C (34 mm), n_D^{20} 1.3993. ¹H NMR spectrum, δ , ppm: 0.20 d (12H, Me₂SiO), 0.46 q (4H, SiCH₂), 0.95 t (6H, SiCCH₃), 4.79 m (2H, SiH).

Compound III. Yield 94%, bp 100–102°C (40 mm), n_D^{20} 1.4083. ¹H NMR spectrum, δ , ppm: 0.15 m (15H, Me₂Si, OSiMeO), 2.48 s (2H, SiCH₂Cl), 4.89 m (2H, SiH).

Compound IV. Yield 80%, bp 81–83°C (4 mm), n_D^{20} 1.4542. ¹H NMR spectrum, δ , ppm: 0.30 d (12H, Me₂Si), 0.36 s (3H, OSiMeO), 4.88 m (2H, SiH), 7.4–7.6 m (5H, C₆H₅).

Compound V. Yield 89%, bp 70–76°C (76 mm), n_D^{20} 1.3699. ¹H NMR spectrum, δ , ppm: 0.16 s (3H, OSiMeO), 0.23 d (12H, Me₂SiO), 4.79 m (2H, SiH), 5.95 m (3H, CH=CH₂).

¹H NMR spectra were measured on a Bruker DPX-400 instrument for 5–10% solutions in CDCl₃, internal reference TMS.

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