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SHORT COMMUNICATIONS

Synthesis of Silicon-Containing Monomers with Aldehyde Groups

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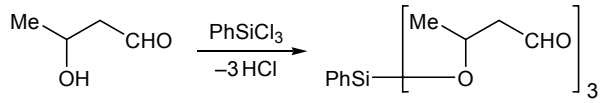
Silicon-containing monomers with different functional groups are used in the synthesis of heat and corrosion resistant polymers, as well as modifiers for various polymers to improve their operational characteristics [1–3]. The goal of the present work was to synthesize silicon-containing monomers functionalized with aldehyde groups, which may be used for the preparation of polymers with enhanced heat and frost resistance and tensile strength as compared to carboxy-containing polymers [3].

The procedure developed by us for the synthesis of such monomers is based on the reaction of trichloro(phenyl)silane with hydroxy aldehydes. The reaction of trichloro(phenyl)silane with β-hydroxybutyraldehyde gave tris-butanal **I** (Scheme 1).

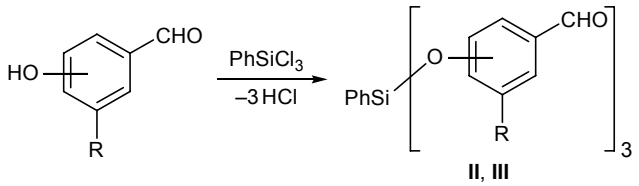
Scheme 1.



I

Under analogous conditions, from aromatic hydroxy aldehydes (salicylaldehyde and vanillin) we obtained trialdehydes **II** and **III**, respectively (Scheme 2).

Scheme 2.



II, **III**

II, 2-PhSiO, R = H; **III**, 4-PhSiO, R = MeO.

The products were isolated as light yellow powders which are readily soluble in aromatic hydrocarbons, alcohols, ketones, and ethers and insoluble in aliphatic hydrocarbons and water.

3,3′,3″-[Phenylsilanetriyltris(oxy)]tributanal (I). A solution of 17.0 mL (0.1 mol) of trichloro(phenyl)-silane in 10 mL of toluene was added in small portions in a nitrogen atmosphere to a solution of 36.6 g (0.32 mol) of β-hydroxybutyraldehyde and 37 mL (0.3 mol) of triethylamine in 20 mL of toluene. The progress of the reaction was monitored by IR spectroscopy, following disappearance of the OH absorption band. When the reaction was complete (after 2–3 h), the precipitate was filtered off, the filtrate was evaporated under reduced pressure to a volume of 5 mL, and 10 mL of hexane was added. The jelly-like material was dried under reduced pressure at 50°C. Yield 46.6 g (87%), mp 112°C. IR spectrum, ν, cm^{-1}: 3080–3030 (C–H), 1090–1020 (Si–O–C), 1715–1696 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.32 m (9H, CH_3), 2.67 m (6H, CH_2), 3.62 m (3H, CH), 7.23 m (5H, H_{arom}), 9.70 s (3H, CHO). Mass spectrum: *m*/*z* 366 (I_{rel} 25%). Found, %: C 58.99; H 7.15; O 26.19; Si 7.66. $C_{18}H_{26}O_6Si$. Calculated, %: C 58.75; H 7.07; O 26.36; Si 7.72. *M* 366.49.

2,2′,2″-[Phenylsilanetriyltris(oxy)]tribenzaldehyde (II) was synthesized in a similar way. Yield 81%, mp 129°C. IR spectrum, ν, cm^{-1}: 3080–3030 (C–H), 1090–1020 (Si–O–C), 1715–1696 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.88 m (6H, H_{arom}), 7.23 m (5H, H_{arom}), 7.37 m (3H, CH), 7.64 m (3H, CH), 10.24 s (3H, CHO). Mass spectrum: *m*/*z* 468 (I_{rel} 20%). Found, %: C 69.21; H 4.30; O 20.49; Si 5.99. $C_{27}H_{20}O_6Si$. Calculated, %: C 69.05; H 4.25; O 20.75; Si 5.85. *M* 468.54.

4,4′,4″-[Phenylsilanetriyltris(oxy)]tris(3-methoxybenzaldehyde) (III). Yield 78%, mp 137°C. IR spectrum, ν, cm^{-1}: 3080–3030 (C–H), 1090–1020 (Si–O–C), 1715–1696 (C=O). ^{1}H NMR spectrum, δ,

ppm: 3.73 m (3H, CH_3), 6.81 m (3H, CH), 7.20 m (1H, Ph), 7.20 m (6H, H_{arom}), 9.87 s (3H, CHO). Mass spectrum: *m*/z 558 (I_{rel} 25%). Found, %: C 64.50; H 4.69; O 25.78; Si 5.03. $C_{30}H_{26}O_6Si$. Calculated, %: C 64.30; H 4.55; O 25.95; Si 5.19. *M* 558.61.

The purity of the isolated compounds was checked by TLC on Silufol UV-254 plates; spots were visualized under UV light, by treatment with iodine vapor, or by thermal treatment. The IR spectra were recorded on an FSM 1201 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Bruker AM-500 spectrometer at 500.13 MHz from solutions in DMSO-d_6. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS 50 instrument.

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