

Review

The chemistry of organo silanetriols

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Dedicated to Prof. Dr. Dr. h.c. mult. Herbert
W. Roesky on the occasion of his 80th
birthday.

ABSTRACT

The chemistry of organo silanetriols is reviewed covering the aspects of synthesis, structural chemistry, reactivity, properties and applications over the last 15 years. Besides relevant progress in established fields like supramolecular chemistry, surface modification and metallasiloxane formation, recent advances include structural investigations in liquid and gaseous states and studies concerning the

Abbreviations: AChE, acetylcholine esterase; AFM, atomic force microscopy; AKD, alkyl ketene dimer; APTES, 3-aminopropyltriethoxysilane; ASA, alkenyl succinic anhydride; aq., aqueous; BDE, bond dissociation enthalpy; bpy, 4,4'-bipyridine; BSA, bovine serum albumin; CES, sodium carboxyethylsilanetriolate; ChE, cholesterol esterase; ChOx, cholesterol oxidase; Cp, cyclopentadienyl; CVD, chemical vapor deposition; 2D, two dimensional; DABCO, 1,4-diazabicyclo[2.2.2]octane; DCC, dicyclohexylcarbodiimide; DFT, density functional theory; DMP, 2,6-Me₂C₆H₃; DMSO, dimethylsulfoxide; Et, ethyl; FET, field effect transistor; Fl, fluorenyl; GED, gas phase electron diffraction; GFP, green fluorescent protein; GPTMS, (3-glycidyloxypropyl)trimethoxysilane; HRMS, high resolution mass spectrometry; HSA, human serum albumin; IEP, isoelectric points; IR, infrared; ITO, indium tin oxide; *i*Pr, *iso*-propyl; MALDI-TOF, matrix assisted laser desorption/ionisation time of flight; MEMS, microelectromechanical systems; Me, methyl; Mes, mesityl (2,4,6-trimethylphenyl); MS, mass spectrometry; MST, methylsilanetriol; NEMS, nanoelectromechanical systems; NFC, nanofibrillar cellulose; NMR, nuclear magnetic resonance; NR, neutron reflectivity; OTS, octyltriethoxysilane; PEG, polyethyleneglycol; PFG-SSE, pulsed field gradient stimulated spin echo; PFOTMS, (pentafluorophenyl)trimethoxysilane; Ph, phenyl; pip, piperazine; POSS, oligomeric polyhedral silsesquioxane; SAM, self-assembled monolayer; SMS, synthesis mimetic simulation; TBAF, tetrabutylammonium fluoride; TBHP, *tert*-butyl hydroperoxide; *t*Bu, *tert*-butyl; TEM, transmission electron microscopy; Ter, 2,6-di(2,4,6-triisopropylphenyl)phenyl; THF, tetrahydrofuran; Tip, 2,4,6-triisopropylphenyl; TMEDA, N,N,N',N'-tetramethylethylenediamine; TMS, trimethylsilyl; trityl, triphenylmethyl; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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bio-activity of silanetriols. Based on irreversible condensation starting from silanetriols fascinating cage compounds and cerasomes have been reported as well as silanetriol-modified biopolymers and nanopatterning applications.

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1. Introduction

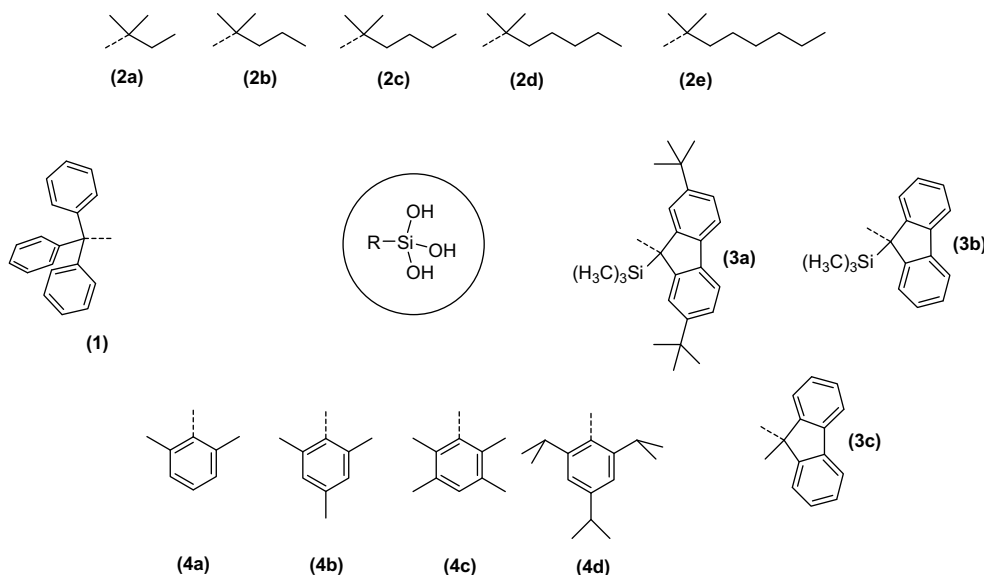
Silanetriols with the general formula $\text{RSi}(\text{OH})_3$ (R = organic substituent) comprise a unique class of compounds which combines properties of silicic acid with those of organosilicon compounds. In fact, organo silanetriols are isoelectronic to the corresponding phosphonic and sulfonic acid derivatives which have widespread applications. Compared to the latter compounds the chemistry of silanetriols is, however, more delicate owing to their propensity to undergo condensation reactions with formation of siloxane bonds. Therefore, silanetriols are frequently quoted in the literature as formal monomers in the formation of polymers even though they do not necessarily occur as actual intermediates in the condensation of trifunctional halosilane and alkoxy silane precursors under hydrolytic conditions. Since the initial preparation of a stable silanetriol in 1959 by Takiguchi et al. [1], numerous examples of this compound class have been prepared and isolated. One of the salient features of silanetriols is their tendency to form hydrogen bonded networks taking advantage of the presence of three donor and acceptor sites in close proximity for which the strong polarity of the Si–O bond is beneficial. Comprehensive review articles dealing with the preparation and solid state structures of silanols and also silanetriols cover the literature until 2000 [2–4]. In addition, reviews focusing on important derivatives of silanetriols like metallasiloxanes [5,6] and oligomeric polyhedral silsesquioxanes (POSS) [7] are available and therefore these topics will not be explicitly covered in this article. Owing to the sometimes quite flexible use of the term silanetriol, we restrict ourselves to molecular compounds with one C–Si bond and three silanol units at the same silicon atom which excludes silicic esters and POSS trisilanols *etc.* However, we included deprotonated silanetriols in our selection, since silanetriols as weak acids are inherently accompanied by

these species being their conjugate acids. Moreover, closely related examples of organosilanetriols where bulky organic substituents are connected to silicon *via* nitrogen, silicon, or transition metals have been included for comparison, because the reactivity of the bond connecting the substituent to the silanetriol unit is negligible in these special cases owing to the unique steric situation.

This review aims at covering the literature from 2000 until 2015. The available information was divided into different sections dealing with the aspects of synthesis, structure, reactivity, properties and applications. Moreover, the authors distinguish between silanetriols that have been prepared and isolated and those that were claimed without isolation and characterization.

2. Synthesis

The controlled hydrolysis of suitable trihalosilanes is frequently employed in the preparation of silanetriols. Among the available methods, it is the most straightforward synthetic route, especially, if sterically demanding substituents prevent the resulting silanetriol from further condensation. Following this methodology, several new silanetriols have been synthesized (Scheme 1). Thus (triphenylmethyl)silanetriol (**1**) was obtained in good yield by the hydrolysis of (triphenylmethyl)trichlorosilane, which was prepared starting from (trichloromethyl)trichlorosilane [8,9]. This silanetriol forms adducts with solvent molecules in the solid state which have been characterized by X-ray crystallography for [1·THF] and [1·acetone] (for details see Section 3). A series of silanetriols (**2a–e**), $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{CSi}(\text{OH})_3$ ($n = 1–5$), with tertiary alkyl substituents at silicon has been prepared *via* the corresponding trihalosilanes. The chain length of the substituents has been varied systematically which influences their surfactant properties as well as their solid-state sheet structures [10]. For the smallest



Scheme 1. Survey of synthesized silanetriols **1–4** with the connection site of the respective substituent drawn with a broken line.

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