NOTES

The Synthesis of New Silicon-functional Silanols*

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Some years ago a new method¹⁾ for the preparation of diphenylsilanediol was applied to the synthesis of various organosilanols²⁾ and named as the "Silanolate method."³⁾ This procedure involves neutralization of sodium silanolate in an aqueous solution with hydrochloric acid to give silanol. Now it has been found that the above method can be extended to the preparation of silicon-functional silanols possessing both hydroxyl and alkoxyl groups on the silicon atom. The present paper describes the synthesis of such new silanols and their properties, reactions, and infrared absorptions. The synthetic route attempted to prepare various alkoxysilanols is indicated in the following scheme:

$$R_nSiCl_{4-n} + mR'OH + mC_5H_5N \rightarrow$$

$$R_nSi(OR')_mCl_{4-n-m} + mC_5H_5N\cdot HCl$$

$$R_nSi(OR')_mCl_{4-n-m} + \text{excess } 5\%\ NaOH_{aq} \rightarrow$$

$$R_nSi(OR')_m(ONa)_{4-n-m}$$

$$R_nSi(OR')_m(ONa)_{4-n-m} + (4-n-m)HCl_{aq} \rightarrow$$

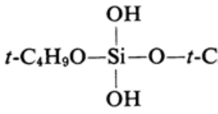
$$R_nSi(OR')_m(OH)_{4-n-m}$$

R: CH_3, $i\text{-}C_3H_7$, C_6H_{11}, $CH_2CH_2C_6H_5$, $CH_2C_6H_5$, C_6H_5, $1\text{-}C_{10}H_7$

R': CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $t\text{-}C_4H_9$, C_6H_{11}, C_6H_5, $CH_2CH_2NH_2$

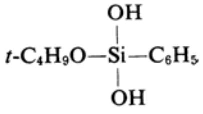
n: 0—2, m: 1—2

Thus, five new silicon-functional silanols containing a *t*-butoxyl group were obtained, these being di-*t*-butoxysilanediol (I), phenyl-*t*-butoxysilanediol (II), diphenyl-*t*-butoxysilanol (III), benzyl-*t*-butoxysilanediol (IV) and 1-naphthyl-*t*-butoxysilanediol (V).



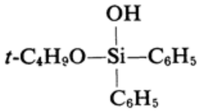
$$t\text{-}C_4H_9O-\overset{OH}{\underset{OH}{Si}}-O-t\text{-}C_4H_9$$

(I)



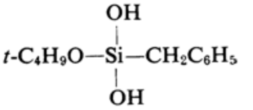
$$t\text{-}C_4H_9O-\overset{OH}{\underset{OH}{Si}}-C_6H_5$$

(II)



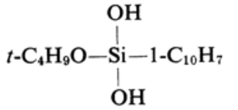
$$t\text{-}C_4H_9O-\overset{OH}{\underset{C_6H_5}{Si}}-C_6H_5$$

(III)



$$t\text{-}C_4H_9O-\overset{OH}{\underset{OH}{Si}}-CH_2C_6H_5$$

(IV)



$$t\text{-}C_4H_9O-\overset{OH}{\underset{OH}{Si}}-1\text{-}C_{10}H_7$$

(V)

I, in particular, derived from tetrachlorosilane is a unique silanol containing no silicon-bond; other similar organoalkoxysilanols could not be so obtained. In these cases, the corresponding siloxanes and alcohols were afforded by further condensation and hydrolysis. Grubb⁴⁾ suggested that base-catalyzed silanol condensation-reactions are sensitive to steric factors. The fact that only alkoxysilanols surrounded with bulky groups were isolated might support this suggestion. In spite of the fact that di-*t*-butoxysilanediol (I) was isolated in a good yield, isolation of di-*t*-butoxyorganosilanols was not successful, because the reaction products were all liquids and decomposed during distillation even at low pressure. Details of the synthesis of *t*-butoxysilanols, and their analyses, melting points, and crystal forms are shown in Table I.

The infrared spectra for all of the silanols obtained show a band at 1385—1395 cm^{-1} and a strong one at 1365 cm^{-1}; these are assigned to the *t*-butyl group.⁵⁾ Evidence for the presence of an OH group is provided by the existence of a band at 3350—3400 cm^{-1}, and for the Si-O grouping by a band at 1000—1100 cm^{-1}. In general, almost all organosilanols in the solid state have an OH absorption band

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1) S. Kohama, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1439 (1960).

2) S. Kohama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1760 (1960); ibid., **81**, 1874 (1960); ibid., **81**, 1889 (1960); ibid., **83**, 188 (1962).

3) S. Kohama, ibid. **82**, 69 (1961).

4) W. T. Grubb, *J. Am. Chem. Soc.*, **76**, 3408 (1954).

5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London (1958), p. 13.

TABLE I. TERTIARY

Reaction						Silanol
Chlorosilane		t-BuOH	Pyridine	5% NaOH	Ice	
	g.	g.	g.	ml.	g.	
$SiCl_4$	11	9.0	9.5	250	100	$(t\text{-}C_4H_9O)_2Si(OH)_2$
$C_6H_5SiCl_3$	10	7.5	8.0	200	100	$C_6H_5(t\text{-}C_4H_9O)Si(OH)_2$
$(C_6H_5)_2SiCl_2$	10	2.8	3.2	80	50	$(C_6H_5)_2(t\text{-}C_4H_9O)SiOH$
$C_6H_5CH_2SiCl_3$	12	4.0	4.2	200	100	$C_6H_5CH_2(t\text{-}C_4H_9O)Si(OH)_2$
$1\text{-}C_{10}H_7SiCl_3$	13	3.4	3.9	200	100	$1\text{-}C_{10}H_7(t\text{-}C_4H_9O)Si(OH)_2$

* All the melting points are uncorrected.

W: Water, B: Benzene, P: Petroleum ether. s: Soluble, p: Partially soluble, i: Insoluble.

near 3250 cm^{-1}.2,6-8) It is of interest that t-butoxysilanols show OH bands at frequences higher by about 100 cm^{-1} than those for ordinary organosilanols. The OH stretching absorption bands of t-butoxysilanols are listed in Table II, together with those of various organosilanols for comparison. The butoxysilanols obtained were stable in a desiccator but, on standing in the air, turned greasy. Treatment of these silanols with dilute sodium hydroxide solution gave a clear aqueous solution, from which the starting materials were recovered, together with a small quantity of oily matter, by neutralization. Diphenyl-t-butoxysilanol (III) in 90% aqueous acetone when hydrolyzed with a drop of aqueous hydrochloric acid at room temperature gave quantitatively diphenylsilanediol, in spite of the possibility of a silanol condensation taking place also.

$$(C_6H_5)_2Si(O\text{-}t\text{-}C_4H_9)OH \xrightarrow{H^+} (C_6H_5)_2Si(OH)_2 + t\text{-}C_4H_9OH$$

Under the same conditions, phenyl-t-butoxysilanediol (II) was converted into an oil which was soluble in almost all organic solvents but insoluble in dilute sodium hydroxide solution, and which exhibited a weak infrared band at 1365 cm^{-1}. Such a behavior of II towards acids is in accord with those of the previously reported silanols.2,3)

TABLE II. STRETCHING FREQUENCY OF O-H BOND IN VARIOUS SILANOLS (in Nujol)

Compound	(O-H) cm^{-1}	Literature
$(t\text{-}C_4H_9O)_2Si(OH)_2$	3400	
$C_6H_5(t\text{-}C_4H_9O)Si(OH)_2$	3350	
$(C_6H_5)_2(t\text{-}C_4H_9O)SiOH$	3400	
$C_6H_5CH_2(t\text{-}C_4H_9O)Si(OH)_2$	3350	
$1\text{-}C_{10}H_7(t\text{-}C_4H_9O)Si(OH)_2$	3300	
$(CH_3)_3SiOH$	3257	*1
$(CH_3)_2Si(OH)_2$	3125	*1
$HOSi(CH_3)_2OSi(CH_3)_2OH$	3247	*1
$(C_2H_5)_2Si(OH)_2$	3220	*2
$(C_6H_5)_3SiOH$	3260	*3
$(C_6H_5)_2Si(OH)_2$	3260	*3
$HO[Si(C_6H_5)_2O]_2H$	3260	*3
$HO[Si(C_6H_5)_2O]_3H$	3260	*3
$CH_3C_6H_5CH_2Si(OH)_2$	3250	*4
$CH_3(1\text{-}C_{10}H_7)Si(OH)_2$	3250	*4
$C_6H_5C_6H_5CH_2Si(OH)_2$	3250	*4
$C_6H_5(p\text{-}CH_3C_6H_4CH_2)Si(OH)_2$	3250	*4
$CH_3(p\text{-}CH_3C_6H_4)Si(OH)_2$	3250	*5
$CH_3(p\text{-}CH_3OC_6H_4)Si(OH)_2$	3200	*5
$CH_3(p\text{-}ClC_6H_4)Si(OH)_2$	3150	*5
$CH_3(p\text{-}BrC_6H_4)Si(OH)_2$	3150	*5
$CH_3(p\text{-}(CH_3)_2NC_6H_4)Si(OH)_2$	3250	*5
$CH_3(p\text{-}CH_2BrCHBrC_6H_4)Si(OH)_2$	3200	*6
$CH_3(p\text{-}CH_2{=}CHCH_2C_6H_4)Si(OH)_2$	3200	*6
$CH_3(p\text{-}CH_2{=}CHC_6H_4)Si(OH)_2$	3200	*6

[*1] S. W. Kantor, *J. Am. Chem. Soc.*, **75**, 2712 (1953).

[*2] M. Kakudo, *J. Chem. Phys.*, **21**, 1894 (1953).

[*3] R. E. Richards, H. E. Thompson, *J. Chem. Soc.*, **1949**, 125.

[*4] S. Kohama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1760 (1960).

[*5] S. Kohama, ibid., **82**, 69 (1961).

[*6] S. Kohama, ibid., **81**, 1889 (1960).

Experimental

Materials. — Methyltrichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane and tetrachlorosilane were all commercial products and were purified by redistillation, b. p. 65—66°C, 200—202°C, 160°C/10 mmHg, 57—58°C, respectively. Isopropyltrichlorosilane, cyclohexyltrichlorosilane, benzyltrichlorosilane, 2-phenylethyltrichlorosilane and 1-naphthyltrichlorosilane were prepared by the usual methods; b. p. 118—200°C, 195—199°C, 213—215°C 239—240°C and 181°C/30 mmHg, respectively. All alcohols used were purified by the ordinary way and redistilled before use.

General Procedure for the Synthesis of t-Butoxysilanols. — An organochlorosilane (about 10 g.) and 50 ml. of dry ether were placed in a 300 ml. three-necked flask. A solution of the appropriate amounts (equivalent in moles to chlorosilanes) of t-butanol and pyridine in 20 ml. of dry ether was added dropwise to the stirred contents

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6) S. W. Kantor, *J. Am. Chem. Soc.*, **75**, 2712 (1953).

7) M. Kakudo, *J. Chem. Phys.*, **21**, 1894 (1953).

8) R. E. Richards, H. E. Thompson, *J. Chem. Soc.*, **1949**, 125.

BUTOXYSILANOLS

Yield g. (%)	M. p.* °C	Solubility			Crystal from	Analysis			
						Si, %		OH, %	
		W	B	P		Calcd.	Obs.	Calcd.	Obs.
8.1 (60)	105—106	s	p	i	Needles	13.40	13.38	16.26	16.40
9.5 (75)	112—113	s	s	p	Needles	13.19	13.16	15.94	15.88
2.9 (27)	55— 56	p	s	s	Leaflets	10.29	10.31	6.23	6.12
9.1 (76)	79— 80	p	s	p	Needles	12.41	12.40	15.03	15.22
6.6 (51)	84— 86	p	p	i	Small leaflets	10.70	11.01	12.96	12.25

at room temperature over a period of 10 min. After the addition, the solution was warmed slightly to complete the reaction. Then the mixture was cooled in an ice bath and filtered from salts; the filter cake on a glass filter was washed with dry ether. The combined filtrate was poured cautiously with stirring into a mixture of excess 5% aqueous sodium hydroxide solution, ice and ether. The ether layer was separated and the aqueous layer was repeatedly extracted with small portions of ether totaling 50 ml. To the aqueous portion was added a small amount of ice so as to avoid further condensation of the silanol. Then the alkaline mixture was neutralized with aqueous hydrochloric acid (ca. 6%) using Brom-thymol Blue as an indicator. The solution was extracted with ether and the ethereal solution was dried over sodium sulfate. After the solvent had been removed in vacuo, the crude silanols obtained were recrystallized from hot benzene. Since diphenyl-*t*-butoxysilanol (III) is very soluble in petroleum ether, the extraction of III is conveniently carried out using this solvent. Analytical results and yields for the above *t*-butoxysilanols are given in Table I. All attempts to prepare other organoalkoxysilanols gave only tacky oils, which were insoluble in 5% aqueous sodium hydroxide solution and gradually changed into resins. These oils were assumed to be the corresponding siloxanes, from their silicon contents and infrared spectra.

The Hydrolysis of III.—Into a solution of III (5 g.) in 30 ml. of 90% aqueous acetone, a drop of concentrated hydrochloric acid (ca. 12 N) was added with stirring at room temperature; the mixture was further stirred for 10 min. and then allowed to stand for 1 hr. The precipitated crystals were filtered off. After the mother liquor had been repeatedly treated in the same manner as above, the aqueous acetone solution was evaporated to dryness. Recrystallization of the combined crystals from hot benzene afforded colorless needles (3.9 g.) melting at 165—167°C. This substance was identified as diphenylsilanediol by comparison of its infrared spectrum with that of an authentic sample[1] and by mixed melting point determination.

The Condensation of II with Hydrochloric Acid.—In the same treatment as described above, II (5 g.) gave only an oil. By removal of the solvent in vacuo, the oil was collected (3.9 g.). This was insoluble in 5% sodium hydroxide aqueous solution and, by heating in an electric heater at 150°C, 5 hr., gave a resin melting at 130°C.

Absorption Spectra. — Spectral measurements (Nujol mull) were performed with a Reiz infrared spectrophotometer at room temperature.

Analysis. — Silicon contents were determined gravimetrically by a simple digestion method,[9] and for active hydrogen the Zerewitinoff method[10] was used.

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9) S. Kohama, This Bulletin, 36, 830 (1963).

10) S. Siggia (Translated by Tsutomu Kuwata), "Quantitative Analysis via Functional Group," John Wiley and Sons, Inc., New York; Japanese Edition, Maruzen Co., Tokyo (1954), p. 74.