The iodide crystallized as trihydrate of almost black color, very soluble in water.

Anal. Calcd. for $FeI_2(C_4H_8N_2)_3 \cdot 3H_2O$: H_2O, 8.77. Found: H_2O, 8.45. Dried over calcium chloride *in vacuo* to constant weight.

Anal. Calcd. for $FeI_2(C_4H_8N_2)_3$: Fe, 9.94; I, 45.15; N, 14.95. Found: Fe, 10.08, 10.05; I, 45.0, 45.2; N, 14.55, 14.7.

Absorption Spectra.—The absorption spectra were determined with a Unicam Spectrophotometer. 5×10^{-5} to 10^{-4} molar solutions of the diimine complexes at an optical depth of 10 mm. were used. Measurements were reproducible within ±1%.

For the ultraviolet measurements the iodides were transformed to the chlorides by shaking the 10^{-3} *m* aqueous solutions of the former with silver chloride. The concentration of the chloride solutions was checked by comparison of the visible absorption with that of the pure iodide.

The photometric measurements on the very unstable complexes of the biacetyl-bis-anil were made in the following way: 2 ml. of a 0.01 *m* solution of the bis-anil[6] in absolute ethanol was mixed in an absorption cell of 5 mm. optical depth with 0.5 ml. of a solution prepared by dilution of 0.1 ml. of a 2.5 *m* aqueous solution of ferrous chloride with 25 ml. of absolute ethanol and the absorption measured within 10 to 15 seconds after the mixing. Fresh solutions were prepared for measurements at different wave lengths.

For the continuous variation measurements the 10^{-2} *m* alcoholic solutions of the bis-anil and of ferrous chloride, were mixed in variable proportions and the extinction measured at 600 mμ. The reproducibility of these measurements was about ±3%.

SÃO PAULO, BRAZIL

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNING GLASS WORKS AND THE DOW CORNING CORPORATION]

Silanol Derivatives of the Dimethyl Substituted Organosilicon Compounds

BY J. F. HYDE

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Dimethylsilanediol and the next member of the series, tetramethyldisiloxane-1,3-diol, have been isolated and characterized. They are relatively stable materials in the absence of acidic or alkaline dehydration catalysts.

One of the striking contrasts between organosilicon chemistry and organic chemistry has been the existence of compounds in which two hydroxyl groups are attached to a single silicon atom. The relatively stable character of such compositions was demonstrated by Kipping's extensive studies of diphenylsilanediol and its condensation products.[1]

These same studies further emphasized the polymeric character of the condensation products and disclosed the apparent inability of silicon–oxygen double bonds to form from the hydroxy-compounds by loss of water.

More recently a number of dialkylsilanediols have been reported.[2]

During the preparation of this manuscript a note by Lucas and Martin has appeared describing the tetramethyldisiloxane-1,3-diol, and its preparation by another method.[3]

The dimethylsilanediol had become increasingly conspicuous by its absence from the literature. It holds a position of some general interest from both a theoretical and a practical point of view, since it is the monomeric parent of a whole series of industrially important polymeric products.

The ready isolation of the dimethylsilanediol, and its behavior suggest that it is inherently no less stable under normal conditions than the diphenylsilanediol. It does appear to be more sensitive to the catalytic effect of traces of acid or base in causing dehydration, and these catalysts must be strictly excluded for a successful preparation.

The indications are that the dimeric diol is more stable toward dehydration than the monomeric diol. This might be expected on the basis of a greater separation of the hydroxyl groups. It is possible also that an intermolecular association of the hydroxyl groups could add a further stabilizing effect in both compounds. In the case of the dimeric diol, intramolecular hydrogen bridging could produce a six-membered ring of added stability.

This relatively stable character of the diols indicates that other factors besides the nature of the attached groups are involved. Presumably the same fundamental factors which oppose any tendency to form doubly bonded oxygen structures would favor the formation of stable diols. One of these factors could be polarizing effects due to the over-all positive nature of the ($R_2Si<$) grouping.

Experimental Part

Preparation of Dimethylsilanediol.—A 74.0-g. (0.5 mole) portion of $Me_2Si(OEt)_2$ (freshly distilled from potassium carbonate) was mixed with 34 g. (2 moles) of distilled H_2O in a Vycor brand erlenmeyer flask. After 24 hours at 25° with intermittent shaking, two liquid phases were still present. The mixture became homogeneous after 30 hours and the odor of ester was gone in 48 hours. After 8 hours on the water vacuum at 25° a semi-crystalline mass remained. Several hours on a Hyvac were necessary to remove the remaining water completely and leave 42.3 g. of a fluffy dry mass of flaky crystals (yield 92%). The density, determined by pycnometer with octamethylcyclotetrasiloxane as the immersion fluid, was found to be 1.097 ± 0.002.

Anal. Found: OH, 32.8 (Zerewitinoff); Si, 30.79. Calcd.: OH, 36.9; Si, 30.45.

Samples could be further purified by rinsing with low boiling petroleum ether, dissolving in benzene by heating to 60°, and cooling. The melting point of the platelets thus formed was 96–98°. The molecular weight determined cryoscopically in benzene was 94 (calcd. 92).

The diol is soluble in water to the extent of 245 g./100 g. of H_2O. The compound is sensitive to condensation

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(1) (a) W. Dilthey and F. Eduardoff, *Ber.*, **37**, 1139 (1904); (b) R. Robison and F. S. Kipping, *J. Chem. Soc.*, **93**, 439 (1908); (c) F. S. Kipping, *ibid.*, **101**, 2108 (1912); (d) **101**, 2125 (1912).

(2) (a) Diethylsilanediol. P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 344 (1946). (b) Organosilicon Compounds. Dialkylsilanediols. P. A. DiGiorgio, Abstract of a Paper presented at the Atlantic City Meeting of the American Chemical Society, April, 1946. (c) Di-*t*-butylsilanediol. Abstract of a Paper presented at the Atlantic City Meeting of the American Chemical Society, September, 1949, L. J. Tyler, L. H. Sommer and F. C. Whitmore.

(3) G. R. Lucas and R. W. Martin, THIS JOURNAL, **74**, 5225 (1952).

catalysts, and therefore an essential precaution in its preparation is avoidance of contact with traces of acidic or alkaline material. A sample of the diol stored in an acid-rinsed soda-lime sample bottle had become liquid in several months. The hydroxyl content of the resulting liquid was found to be 13% after having stood for three years, thus indicating the relatively less sensitive character of the higher members of the series of α,ω-diols toward dehydration catalysts.

Preparation of Tetramethyldisiloxane-1,3-diol.—This second member of the series can be prepared readily by another method. The corresponding alkali salt, 150 g. (0.5 mole) of the composition, NaO $(Me_2SiO)_2$ Na·5H_2O, was added in powder form in small portions with good stirring to a mixture of 1500 ml. of ethyl ether and 60 g. (1.0 mole) of gl. acetic acid. The added salt disappears and a precipitate of sodium acetate is formed. Tests with Alk-Acid paper were used to follow the course of the reaction to the neutral point. The solids were filtered and the ether filtrate concentrated on the water vacuum. This procedure yielded 54 g. of a mixture of oil and needle-like crystals. The needle-like crystals, freed from oil by washing with petroleum ether, had a melting point of 65–69°. The molecular weight, determined cryoscopically in glacial acetic acid, was 156 (calcd. for $HO(Me_2SiO)_2H$, 166). The density, determined by pycnometer, was 1.095 ± 0.008.

Anal. Found: OH, 20.8; Si, 34.0. Calcd.: OH, 20.5; Si, 33.8.

The solubility in water of the dimerdiol is approximately 11 g./100 g. of H_2O at 25°. Samples stored for approximately three years have become only slightly oily.

Preparation of Tetramethyldisiloxane-1,3-diol Sodium Salt.—To 296 g. (1 mole) of octamethylcyclotetrasiloxane was added 320 g. of 50% aqueous NaOH (4 moles). After adding approximately 100 ml. of methanol the mixture was stirred and gradually heated to boiling. More methanol was added in small amounts during this time until the reaction mixture became homogeneous. After cooling somewhat the water suction was applied to remove the solvent, and any uncombined water. The remaining powdery mass represented essentially a quantitative yield of the hydrate. The product was readily recrystallized from hot acetone giving a neut. equiv. value of 151 (calcd. for $NaO(Me_2SiO)_2$-Na·5H_2O, 150).

Further Physical Measurements for Characterization and Identification. A. X-Ray Diffraction Data.—For rapid identification, powder diffraction data may be used. The following data were obtained by standard procedures on samples prepared by triturating with mineral oil.

TABLE I

PRINCIPAL LINES

Dimethylsilanediol		Tetramethyldisiloxane-1,3-diol			
d	*I/I*$_1$	*d*	*I/I*$_1$	*d*	*I/I*$_1$
11.3	0.534	9.5	0.197	2.03	0.102
8.55	0.647	7.75	1.00	1.98	.094
4.50	1.00	5.00	0.564	1.95	.094
4.26	0.193	4.55	.718	1.81	.077
4.10	.181	4.36	.290	1.74	.077
3.76	.091	3.92	.256		
3.16	.136	3.40	.154		
3.00	.193	3.08	.265		
2.71	.125	2.62	.085		
2.21	.148	2.49	.077		
1.90	.102	2.12	.059		

B. **Microscopic Data.**—Examination of the dimethylsilanediol at a magnification of 40× showed its characteristic crystal habit to be flat elongated octahedral plates. The tetramethyldisiloxane-1,3-diol at a magnification of 100× was found to be in the form of long needles. Both were entirely homogeneous showing no signs of the presence of one in the other.

The dimeric diol crystals, on crushing, showed a marked cleavage tendency parallel to the long direction and the fragments had a fibrous appearance with curved and distorted ends indicating flexibility.

The following additional microscopic data were obtained. *Monomer:* refractive indices (5893 Å., 25°): n_1 = 1.454 ± 0.002, n_2 = 1.446 ± 0.002; extinction: parallel. *Dimer:* refractive indices (5893 Å., 25°): n_1 = 1.459 ± 0.002, n_2 = 1.464 ± 0.002; extinction: parallel; sign of elongation: positive.

C. **Infrared Measurements.**—Patterns of solid films of the two compounds formed on sodium chloride plates using a Baird instrument are well defined and unique.

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MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Electrical Effects of Substituent Groups in Saturated Systems. Reactivities of 4-Substituted Bicyclo[2.2.2]octane-1-carboxylic Acids[1]

BY JOHN D. ROBERTS AND WALTER T. MORELAND, JR.[2]

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The reactivities of a series of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and esters with X = –H, –OH, $-CO_2C_2H_5$, –Br and –C≡N have been determined. The apparent ionization constants of the acids in 50% aqueous ethanol at 25°, the reactivities of the acids toward diphenyldiazomethane in ethanol at 30°, and the saponification rates of the ethyl esters were measured and found to parallel one another throughout the series. The order of reactivities with the various substituents at the 4-position was –C≡N > –Br > $-CO_2C_2H_5$ > –OH > –H. Although transmission of electrical effects of substituent groups through the bicyclo[2.2.2]octane ring system is not possible by resonance interaction involving conjugated unsaturation, the magnitudes of the substituent influences were found to be comparable to those observed in *m*- and *p*-substituted benzene derivatives. The Kirkwood–Westheimer ellipsoidal cavity model for calculation of electrostatic effects of polar substituent groups on reactivity gives qualitative agreement with the experimental results.

Introduction

One of the important problems in the theoretical treatment of the relation of structure to reactivity of organic compounds is elucidation of the mechanisms of transmission of electrical effects of substituent groups in aromatic systems. Of the so-called "static" or ground-state electrical influences, the resonance (mesomeric), inductive and direct electrostatic (or field) effects appear to be most clearly recognized. The latter two influences have to a great extent resisted disentanglement and are very frequently treated together as a composite effect. In this and succeeding papers, we plan to recognize

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(1) Presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1952.

(2) U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1952.