

3, 7, 11. Thymine was prepared by Dr. Marian Van Ess of the Golden State Co., and was measured in a 0.000193 *M* solution at *pH* 3, 7, 11. 5-Amino- and 5-nitouracil (Eastman) were purified by repeated precipitation from aqueous solution and were measured in 0.000238 *M* and 0.000112 *M* solutions, respectively, at *pH* 3, 7, 11.

Isobarbituric acid was obtained from Dr. F. F. Heyroth of the University of Cincinnati and was measured in a 0.0002 *M* solution at *pH* 4, 7.4, 11. 5-Carboxyuracil was prepared by Dr. Elizabeth Ballard and is the material reported by her.¹⁴

2-Aminopyrimidine was obtained through the courtesy of Dr. R. O. Roblin of the American Cyanamid Co., and was measured in a 0.000165 *M* solution at *pH* 3, 7, 11. 2-Amino-6-chloropyrimidine (m. p. 178–179°) and its isomer (m. p. 209–210°) were employed in 0.000325 and 0.000232 *M* solutions, respectively, at *pH* 3, 7, 11.

Isocytosine monohydrate¹⁵ (m. p. 275°) was used in a 0.0001185 *M* solution at *pH* 4, 5, 5.4, 6.4, 7.2, 7.4, 8, 9. Isocytosine-4-acetic acid was prepared by the late Dr. David E. Worrall and was described by him.¹⁶ It was measured at *pH* 3, 7, 11 in a 0.000115 *M* solution.

Cytosine monohydrate was prepared by the method of Hilbert and Johnson¹⁷ and was measured in a 0.000031 *M* solution at 0.1 *N* hydrochloric acid, *pH* 4, 5, 7.4, 9, 11.

(14) Ballard and Johnson, *THIS JOURNAL*, **64**, 794 (1942).

(15) Caldwell and Kline, *ibid.*, **62**, 2365 (1940).

(16) Worrall *ibid.*, **65**, 2053 (1943).

(17) Hilbert and Johnson, *ibid.*, **52**, 1152 (1930).

The 2-ethoxy-6-aminopyrimidine was obtained from the American Cyanamid Co., and was used in a 0.000103 *M* solution at *pH* 3, 7, 11. 2-Methyl-5-cyano-6-aminopyrimidine (m. p. 243–244°) was employed in a 0.000223 *M* solution with 0.1 *N* hydrochloric acid, 0.1 *N* sodium hydroxide and *pH* 7.4.

Except for the listed cases where either hydrochloric acid or sodium hydroxide were used all *pH* values were obtained with Kolthoff buffer tablets. In every case the comparison cells were filled with corresponding buffer, acid or base.

Summary

1. In the pyrimidines investigated, which have a plane of symmetry through the 2–5 positions, there is essentially no change in the position of λ_{\max} with change in *pH*.

2. 5-Uracil derivatives show an increase in λ_{\max} which may be related to the dipole moment of the substituent.

3. When the introduction of an auxochrome produces a symmetrical structure the introduction is not accompanied by the bathochromic shift usually met.

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Acetoxymethyl and Hydroxymethylsiloxanes

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As a continuation of the study of hydroxymethylsilicon compounds first reported by Speier, *et al.*,¹ who prepared trimethylsilylmethanol and studied its reactivity, acetoxymethyl and hydroxymethylsiloxanes have been synthesized. The esters, acetoxymethylpentamethylsiloxane and *sym*-bis-acetoxymethyltetramethylsiloxane were prepared and from the latter *sym*-bis-hydroxymethyltetramethylsiloxane was made by alcoholysis. The di-alcohol was found to be unstable, even at room temperature, but it could be handled, and a derivative was made with no noteworthy difficulty.

Experimental

Preparation of Acetoxymethylsiloxanes.—Chloromethylpentamethylsiloxane^{2,3} was heated to reflux gently for twenty-four hours with a slight excess of anhydrous potassium acetate in a volume of glacial acetic acid equal to that of the siloxane. The chloromethyl compound was not noticeably soluble in the mixture, but dissolved after several hours as a large amount of potassium chloride precipitated. The mixture was finally washed thoroughly with distilled water, and the water insoluble material was distilled. Very nearly the following molar proportions of products resulted: hexamethylsiloxane⁴ 25 mole %, b. p. 98–99° at 735 mm., n_D^{25} 1.3748; acetoxymethylpentamethylsiloxane, 50 mole %, b. p. 180 at 735 mm., n_D^{25} 1.4040, d_4^{25} 0.902. *Anal.* Calcd. for

$\text{AcOCH}_2\text{SiMe}_2\text{OSiMe}_3$: Si, 25.5; sapon. equiv., 220; molar refr.,⁵ 59.82. Found: Si, 25.4; sapon. equiv., 219, 221; molar refr., 59.84; and *sym*-bis-acetoxymethyltetramethylsiloxane, 25 mole %, b. p. 250° at 730 mm., n_D^{25} 1.4215, d_4^{25} 0.993. *Anal.* Calcd. for $(\text{AcOCH}_2\text{Me}_2\text{Si})_2\text{O}$: Si, 21.2; sapon. equiv., 139.2; molar refr., 71.42. Found: Si, 21.1; sapon. equiv., 142, 141; molar refr., 71.2.

When *sym*-bis-chloromethyltetramethylsiloxane was similarly treated, a practically quantitative yield of this product resulted.

Cleavage of Acetoxymethylsiloxanes.—Both acetoxymethylpentamethylsiloxane and *sym*-bis-acetoxymethyltetramethylsiloxane were found to be resistant to acid hydrolysis. Neither ester was hydrolyzed to any appreciable extent after refluxing as long as 56 hours with 6 *N* sulfuric acid.

Both esters undergo rapid decomposition when treated with aqueous alkali. Cleavage of the Si–C bond occurred with the formation of methyl acetate and polysiloxanes. In one typical experiment, the diacetate ester was added quickly to boiling 2 *N* sodium hydroxide solution in 50% ethanol under a one-foot Vigreux column. Methyl acetate was distilled from the mixture as quickly as possible to minimize its saponification by the alkali. Two low boiling fractions were obtained: I, b. p. 53–58°, n_D^{25} 1.3551 had the odor of methyl acetate; sapon. equiv., calcd. 74; found, 78. This was the chief product. II, b. p. 58–67°, n_D^{25} 1.3361, yielded a 3,5-dinitrobenzoate, m. p. 106–107° and is thus identified as being largely methanol, b. p. 66°, n_D^{25} 1.3276, 3,5-dinitrobenzoate, m. p. 107°. This fraction also contained methyl acetate, judging by its odor and by the fact that it contained saponifiable material. When the distillate rose to a b. p. of 100°, the residue was cooled, acidified and extracted with benzene. The extract was distilled through the Vigreux column. Most of the silicon-containing product was obtained at 135–142°,

(1) Speier, Daubert and McGregor, *THIS JOURNAL*, **70**, 117 (1948).

(2) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

(3) Bluestein, *ibid.*, **70**, 3068 (1948).

(4) Hunter, Warrick, Hyde and Curry, *ibid.*, **68**, 2284 (1946).

(5) Warrick, *ibid.*, **68**, 2455 (1946).

leaving a small residue of high boiling oil which was apparently a dimethylpolysiloxane polymer. The distillate crystallized on standing and, after drying in a clay plate, melted at 58–61°. When mixed with an equal amount of authentic hexamethylcyclotrisiloxane a m. p. of 60–63° was obtained. Hexamethylcyclotrisiloxane has the properties,⁶ b. p. 133° at 760 mm., m. p. 64.5°.

Anal. Calcd. for $[(\text{CH}_3)_2\text{SiO}]_x$: Si, 37.8. Found: Si, 37.7, 37.8.

Preparation of *sym*-bis-Hydroxymethyltetramethyldisiloxane.—*sym*-bis-Acetoxyethyltetramethyldisiloxane was dissolved in about a fifteen-fold excess of absolute methanol and acidified with hydrogen chloride. After twenty-four hours at room temperature, about 90% of the theoretically possible amount of methanol-methyl acetate azeotrope, b. p. 53° at 740 mm., was removed by distillation through a still of about 50 theoretical plates. The mixture was cooled and made up to its original volume with absolute methanol. After an additional twenty-four hours, all volatile material was removed at 25° and 20 mm. pressure with a stream of dried air bubbling through the liquid. The non-volatile residue was *sym*-bis-hydroxymethyltetramethyldisiloxane, n_D^{25} 1.4358, d_4^{25} 0.979; m. p. -7.5 to -5°; viscosity: 9.1 cs. at 56°; 32.6 cs. at 21°; *Anal.* Calcd. for $\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_2$: Si, 28.87; OH, 17.5; mol. wt., 194; molar refr., 52.0. Found: Si, 28.55; 28.83; OH, 17.1, 17.1; mol. wt. (ebullioscopically in ethanol), 187; molar refr., 51.7.

The compound formed a di-3,5-dinitrobenzoate readily, m. p. after recrystallization from ethanol, 118.5–119°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_{13}\text{Si}_2$: Si, 9.63. Found: Si, 9.72.

As the material aged, its constants changed and the viscosity at 56° increased appreciably during one-half hour at this temperature. When heated for distillation at about 5 mm. pressure, water was eliminated and a complex resinous mass resulted which became quite fluid on exposure to water. This resinous material was not further characterized.

Discussion

The chloromethylidisiloxanes react with potassium acetate in glacial acetate acid at a far more rapid rate than does chloromethyltrimethylsilane. A similar difference was found in reactivity by Sommer, *et al.*,⁷ to apply to α -chloroethyl-diethylsilanol, α -chloroethyl-trialkylsilanes, and α -chloroethyl-diethylphenylsilane, the first being about 12-fold more reactive than the last and about 170-fold more reactive than the α -chloroethyl-trialkyl-

(6) Hunter, Hyde, Warrick and Fletcher, *THIS JOURNAL*, **68**, 667 (1946).

(7) Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946).

silanes. This may be analogous to the enhanced activity displayed by beta oxygenated organic halides under similar circumstances

The formation of two acetate esters from the mono chlorinated disiloxane resulted through the rearrangement of the siloxane structures in the acetic acid solution. Similar rearrangements have been described in previous publications.^{8,9,10} The products were statistically distributed, indicating that the acetoxy group on the methyl substituent had no detectable effect upon the silicon oxygen bonds as an influence upon their ability to rearrange.

The acetoxyethyl group was cleaved very readily with the formation of methyl acetate and a siloxane bond. This cleavage is thus the same as that found by Krieble and Elliott² for the chloromethyl group. The formation of methyl acetate rather than methanol in the alkaline medium indicates that the cleavage reaction occurs at a rate faster than that of the saponification of the ester.

The instability of the hydroxymethylsiloxane structure is in complete contrast with the great stability displayed by trimethylsilyl-methanol.¹ The reason for this instability cannot be confidently stated until the structure of the polymer formed has been established.

Summary

Chloromethylpentamethyldisiloxane was found to react readily with potassium acetate in acetic acid to form a statistical distribution of hexamethyldisiloxane, acetoxyethylpentamethyldisiloxane, and *sym*-bis-acetoxyethyltetramethyldisiloxane. The acetoxyethyl group was cleaved by aqueous alkali to form methyl acetate and hexamethylcyclotrisiloxane as the chief products. *sym*-bis-Hydroxymethyltetramethyldisiloxane was prepared by methanolysis of the corresponding diacetate.

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(8) Scott, *ibid.*, **68**, 2294 (1946).

(9) Wilcock, paper presented at 110th meeting of the American Chemical Society, Chicago, Ill., September 1946.

(10) Speier, *THIS JOURNAL*, **71**, 273 (1949).