

solution. The ether layer was washed with saturated sodium bicarbonate solution, dried over "Drierite," and fractionated to yield 291 g. of carbinol, b. p. 121–122°. An additional 38 g. of carbinol was obtained by re-working the fore-run fractions; total yield was 76%.

**Catalytic Reduction with Raney Nickel.**—Five moles of methyl cyclopropyl ketone, 200 ml. of ethanol and approximately 25 g. of Raney nickel were sealed in a 1.25-l. rocking autoclave, and hydrogen was admitted to 1200 p. s. i. at room temperature. The reactants were gradually heated to 90° at which temperature hydrogenation began. Maximum temperature reached was 125°. The hydrogenation was stopped when the theoretical amount of hydrogen had been consumed. The product was fractionated to yield 46 g. of unconverted ketone, 131 g. of pentanol-2, and 145 g., 34% yield, of methylcyclopropylcarbinol, b. p. 120–122°.

**Catalytic Reduction with Copper Chromite.**—Three hydrogenations were run in essentially the same manner as follows with the exception of a difference in temperature: Five moles of methyl cyclopropyl ketone and 42 g. of a commercial barium-promoted copper chromite catalyst<sup>6</sup> were sealed into the previously mentioned hydrogenation vessel, and hydrogen was admitted to 1750 p. s. i. at room temperature. The reactants were heated to 100°, and after an induction period of about five hours, hydrogenation began. The reaction was completed within about four hours as indicated by the hydrogen consumption dropping to virtually nothing. With the exceptions of about 20 g. of fore-run the product consisted of 390 g., 90% yield of methylcyclopropylcarbinol, b. p. 121–122° (uncor.). *Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub>: N, 10.00. Found: N, 9.86.

When the hydrogenation was carried out at 120°, the yield of carbinol was 374 g., or 87%. At 150° the yield was 326 g., 76% yield of carbinol, b. p. 118–120°. From the refractive index it was evident that a close-boiling impurity of lower index than methylcyclopropylcarbinol was present. The impurity was assumed to be pentanol-2.

(6) E. I. du Pont de Nemours, Ammonia Division, Wilmington, Delaware.

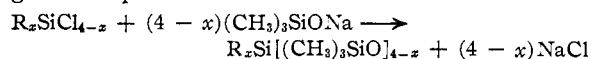
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS  
LEWIS FLIGHT PROPULSION LABORATORY  
CLEVELAND, OHIO RECEIVED MAY 7, 1949

### Preparation of Organopolysiloxanes from Sodium Trimethylsilanolate<sup>1,2</sup>

BY LEO H. SOMMER, LARRY Q. GREEN AND FRANK C. WHITMORE

The availability of trimethylsilanol in good yield and high purity from the controlled hydrolysis of trimethylfluorosilane, and its rapid and complete reaction with sodium to give sodium trimethylsilanolate,<sup>3</sup> led to a study of the latter as an intermediate for further synthesis.

In the present work sodium trimethylsilanolate was found to readily undergo Williamson type reactions with diethyldichlorosilane, ethyltrichlorosilane and silicon tetrachloride, according to the general equation

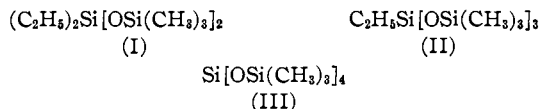


(1) XXIV in a series on organosilicon chemistry. For Paper XXIII see *THIS JOURNAL*, **71**, 3056 (1949).

(2) Taken in part from a thesis submitted by L. Q. Green to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the M.S. degree.

(3) Sommer, Pietrusza and Whitmore, *THIS JOURNAL*, **68**, 2282 (1946).

By this method there were synthesized diethyldi-(trimethylsiloxy)-silane (I), ethyltri-(trimethylsiloxy)-silane (II), and tetra-(trimethylsiloxy)-silane (III). Alternate names by the siloxane nomenclature are somewhat more cumbersome, *i. e.*, 1,1,1,5,5,5-hexamethyl-3,3-diethyltrisiloxane (I).



Compounds I and II are new organopolysiloxanes of a type not readily obtained in good yields by other methods which comprise cohydrolysis of the appropriate pair of monomers. Compound III was previously prepared in 27% yield by the cohydrolysis of ethyl orthosilicate and trimethyl-ethoxysilane with aqueous sodium hydroxide.<sup>4</sup>

In the present work compound III was also prepared by reaction of trimethylsilanol with ethyl orthosilicate in the presence of a small amount of sodium.

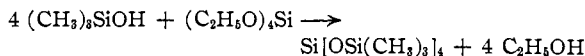


TABLE I  
PHYSICAL PROPERTIES

Compound no.	I	II	III <sup>a,b</sup>
Calcd. mol. wt.	264.5	324.5	384.7
B. p., °C. (733 mm.)	187	206	220
Ref. index, <i>n</i> <sub>D</sub> <sup>20</sup>	1.4005	1.3944	1.3895
Density			
{ 0°	0.8751	0.8756	0.8854
{ 20°	.8399	.8582	.8677
{ 60°	.8035	.8209	.8298
Mol. ref., found <sup>c</sup>	76.43	90.54	105.09
Mol. ref., calcd. <sup>d</sup>	76.90	90.75	104.80
Viscosity,			
{ 0°	2.020	2.723	4.235
{ 20°	1.441	1.896	2.868
{ 60°	0.841	1.067	1.503

<sup>a</sup> Melting point, *ca.* -60°. <sup>b</sup> Constants reported previously for compd. III (ref. 4) are *n*<sub>D</sub><sup>20</sup> 1.3865, b. p. 91° (9 mm.). In a private communication Dr. M. J. Hunter informs us that the density given in ref. 4 should be changed to *d*<sub>25</sub><sup>25</sup> 0.8630. <sup>c</sup> Calculated by the Lorentz-Lorenz equation. <sup>d</sup> Calculated by the method of Warrick, *THIS JOURNAL*, **68**, 2455 (1946).

In Table I are listed the three organopolysiloxanes and some of their physical properties.

Comparison of compounds I and II with the previously reported octamethyltrisiloxane and methyl-(trimethylsiloxy)-silane,<sup>5</sup> respectively, shows that boiling points, densities and refractive indices are greater in compounds I and II by amounts approximating those to be expected from the substitution of ethyl for methyl.

A more interesting comparison is given by the highly-branched compound III and its linear isomer, dodecamethylpentasiloxane.<sup>5</sup> In compound III, boiling point, refractive index and density are

(4) Wright and Hunter, *ibid.*, **69**, 803 (1947).

(5) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

lower, and the melting point is higher. The differences are: b. p., 9°;  $n_D^{20}$  0.0030;  $d_4^{20}$  0.0078; m. p. 24°.

Viscosity measurements were similar to those of other organopolysiloxanes with respect to the temperature dependence of viscosity.

#### Experimental

**Syntheses with Sodium Trimethylsilanolate.**—The synthesis of tetra-(trimethylsiloxy)-silane will be described as representative of the procedure employed. In a 1-liter round-bottomed flask fitted with a reflux condenser there were placed 500 cc. of dry benzene and 110 g. (1.2 moles) of trimethylsilanol.<sup>3</sup> To this was added 30.1 g. (1.3 moles) of sodium cut into small pieces. Immediate reaction occurred, accompanied by evolution of hydrogen. Since a good deal of heat was evolved, the reaction flask was cooled externally in order to prevent the reaction from becoming too violent. After reaction had slackened heat was applied for two hours, causing a gentle reflux of benzene, in order to insure complete reaction. At this point the solution was slightly opalescent, but no sodium trimethylsilanolate separated. After cooling, the solution was decanted from the excess sodium into the flask in which the siloxane preparation was to be carried out. The remaining sodium was washed twice with small portions of benzene and the washings added to the bulk of the silanolate solution. The unreacted sodium weighed 2.3 g., indicating that the theoretical quantity, 27.8 g., had reacted with the silanol.

Reaction of the benzene solution of sodium trimethylsilanolate with silicon tetrachloride was performed in a 1-liter three-necked flask fitted with an efficient stirrer, reflux condenser and dropping funnel. The silicon tetrachloride, 42.5 g. (0.25 mole) was distilled directly into the dropping funnel, care being taken to exclude moisture. It was added to the silanolate during forty-five minutes while cooling the reaction flask in an ice-bath. After completion of the addition, the mixture was heated to reflux temperature for forty hours resulting in the separation of a considerable amount of sodium chloride. Sufficient water was then added to dissolve all solid material, the benzene layer separated, and the aqueous layer extracted with two 100-cc. portions of benzene. The benzene solution of the product was dried over anhydrous potassium carbonate and the benzene removed by distillation. Fractional distillation of the residue in a glass-helix packed column of about twelve theoretical plates gave 36.3 g. (0.095 mole) of tetra-(trimethylsiloxy)-silane, b. p. 96° (13 mm.), a yield of 38%. Table II gives pertinent data for the three syntheses.

TABLE II

Cpd.	Yield, <sup>a</sup> %	Mol. wt.		Si. %	
		Calcd.	Found <sup>b</sup>	Calcd.	Found
I	52	264.5	264	31.8	31.8
II	44	324.5	327	34.6	34.3
III	38	384.7	386	36.5	36.2

<sup>a</sup> Yields are based on the quantity of chlorosilane, sodium trimethylsilanolate being present in approximately 20% excess. <sup>b</sup> Cryoscopically in benzene.

An attempted preparation of diethyldi-(trimethylsiloxy)-silane from the silanolate and diethyldichlorosilane in ethyl ether solution resulted in failure, thus indicating the need for a higher boiling solvent in these preparations.

**Tetra-(trimethylsiloxy)-silane from Trimethylsilanol and Ethyl Orthosilicate.**—A preliminary experiment indicated that ethanol and trimethylsilanol form an azeotropic mixture boiling in the range 62–70°. Since this would prevent the reaction from effectively being driven to completion by slow removal of ethanol, a large yield of tetra-(trimethylsiloxy)-silane was not expected.

In a 200-cc. round-bottomed flask were placed 41.7 g. (0.20 mole) of ethyl orthosilicate, 90 g. (1.00 mole) of trimethylsilanol, and a small amount (*ca.* 0.2 g.) of so-

dium. The mixture was heated at reflux temperature in a fractionating column for twenty-two hours. Fractionation in a glass-helix packed column of about twelve theoretical plates gave 14 g. of slightly impure tetra-(trimethylsiloxy)-silane, b. p. 215° at 732 mm. (uncor.),  $n_D^{20}$  1.3889, mol. wt., 391 (calcd., 384.7),  $d_4^{20}$  0.868, a yield of 18%. Other fractions obtained, b. p. 195–215°, 29.8 g., likely consist of products resulting from incomplete replacement of ethoxy groups by trimethylsiloxy groups.

**Physical Properties.**—Boiling points were determined in a modified Cottrell apparatus.<sup>6</sup> Densities were measured with pycnometers of about 5-cc. capacity. Viscosities were determined in Cannon-Fenske viscometers.<sup>7</sup>

**Acknowledgment.**—We thank Dr. F. Fischl of Standard Oil Development Co., Elizabeth, N. J., for the determination of the melting point of tetra-(trimethylsiloxy)-silane.

(6) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(7) Cannon and Fenske, *ibid.*, **10**, 297 (1938).

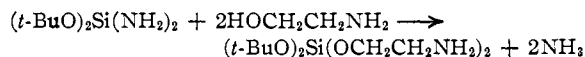
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RECEIVED FEBRUARY 25, 1949

### Di-*t*-butyl-di-aminoalkyl Silicates<sup>1</sup>

BY PHILIP A. DI GIORGIO,<sup>2</sup> LEO H. SOMMER AND FRANK C. WHITMORE

Di-*t*-butoxydiaminosilane<sup>3</sup> reacts with amino alcohols to yield di-*t*-butyl-di-aminoalkyl silicates.<sup>4</sup> The following equation is illustrative of the reaction.



By this method we have synthesized six new di-*t*-butyl-di-aminoalkyl silicates whose properties are listed in Table I.

For the syntheses, generally a solution of one mole of di-*t*-butoxydiaminosilane and two moles of amino alcohol was refluxed for one to three hours at approximately 150–200°. After the theoretical weight of ammonia had been evolved, the crude product was purified by distillation under reduced pressure. The yields of di-*t*-butyl-di-aminoalkyl silicates ranged from 40 to 70%.

The products were viscous, water-white liquids having little or no odor. The 2-aminoethyl and 2-(β-aminoethylamino)-ethyl compounds were found to be very soluble in water, but the other compounds were substantially insoluble. Di-*t*-butyl-di-(2-aminoethyl) silicate dissolved readily in ligroin, benzene, carbon tetrachloride, 95% ethanol, ether, acetone and pyridine. This silicate did not react with molten sodium. Most of the

(1) Paper XXV in a series on organic silicon compounds. For the preceding paper see *THIS JOURNAL*, **71**, 3253 (1949).

(2) Present address: Research Laboratory, General Electric Co., Schenectady, New York.

(3) Miner, Bryan, Holysz and Pedlow, *Ind. Eng. Chem.*, **39**, 1368 (1947).

(4) Private communication from Dr. C. S. Miner, Jr., who, with his co-workers, first prepared and characterized di-*t*-amyl-di-(2-aminobutyl) silicate from the reaction of 2-amino-1-butanol with di-*t*-amoxydichlorosilane and with di-*t*-amoxydiaminosilane.