lower, and the melting point is higher. The differences are: b. p., 9°; n^{20}D 0.0030; d^{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.[3] 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,[a] %	Mol. wt. Calcd.	Mol. wt. Found[b]	Si, % Calcd.	Si, % 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

[a] Yields are based on the quantity of chlorosilane, sodium trimethylsilanolate being present in approximately 20% excess. [b] 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 sodium. 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^{20}D 1.3889, mol. wt., 391 (calcd., 384.7), d^{20} 0.868, a yield of 18%. Other fractions obtained, b. 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.[6] Densities were measured with pycnometers of about 5-cc. capacity. Viscosities were determined in Cannon–Fenske viscometers.[7]

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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Di-*t*-butyl-di-aminoalkyl Silicates[1]

BY PHILIP A. DI GIORGIO,[2] LEO H. SOMMER AND FRANK C. WHITMORE

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

$$(t\text{-BuO})_2Si(NH_2)_2 + 2HOCH_2CH_2NH_2 \longrightarrow (t\text{-BuO})_2Si(OCH_2CH_2NH_2)_2 + 2NH_3$$

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

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[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.

TABLE I

	Compound	Yield, %	B. p. uncor.[b] °C.	B. p. uncor.[b] mm.	n^{20}D[b]	d^{20}[b]	% Nitrogen Calcd.	% Nitrogen Obs.	Equivalent wt.[e] Calcd.	Equivalent wt.[e] Obs.	MRD[b] Calcd.	MRD[b] Obs.
I	$(t\text{-BuO})_2Si(OCH_2CH_2NH_2)_2$	63	144	16	1.4269	0.9731	9.52	9.47[c]	147	150	77.30	77.69
II	$(t\text{-BuO})_2Si(OCH_2CH_2NEt_2)_2$	43[a]	197	33	1.4272	.909	6.89	6.82[c]	203	206	115.02	114.9
III	$(t\text{-BuO})_2Si[O-CH(CH_3)CH_2NH_2]_2$	72	107	1	1.4264	.9548	8.69	8.52[d]	163	162	86.56	86.61
IV	$(t\text{-BuO})_2Si[O-CH_2CH(NH_2)CH_2CH_3]_2$	47	133	1	1.4266	.9462	7.99	7.96[d]	...	...	95.82	95.04
V	$(t\text{-BuO})_2Si[O-CH_2C(CH_3)(NH_2)CH_3]_2$	47	126	4	1.4246	.9328	7.99	7.92[d]	175	173	95.82	96.01
VI	$(t\text{-BuO})_2Si(OCH_2CH_2NHCH_2CH_2NH_2)_2$	41	187	3	1.4495	.9911	14.73	14.75[d]	...	...	103.10	103.10

[a] The 100% excess amino alcohol used was recovered and in later runs was shown to be unnecessary. In a run which was stopped before it went to completion, there was isolated 70 g. of material boiling at 130° at 12 mm., n^{20}D 1.4261, d^{20} 0.9180, *MR*D 85.56, equivalent weight 154. Theoretical values for di-*t*-butoxy-(2-diethylaminoethoxy)-aminosilane, $(t\text{-BuO})_2(Et_2NCH_2CH_2O)SiNH_2$ are: equivalent weight 153 and *MR*D 85.35. [b] These physical properties are those of a center fraction of the distillation flat which was taken as purified product. [c] Micro-Dumas by Mr. R. N. Walter. [d] Micro-Kjeldahl reported by Dr. P. M. Althouse as the average of three or more determinations with repeated cross-checks through tryptophan and urea standards. [e] A solution of the sample in aqueous methanol was titrated with 0.1 *N* hydrochloric acid to the methyl red end-point. [f] The calculated values were obtained by use of bond refractions given by Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by Warrick, THIS JOURNAL, **68**, 2455 (1946). Similar results may be obtained by use of the method of Sauer, *ibid.*, **68**, 954 (1946). The average deviation was 0.26 ml. when the sign was disregarded and 0.04 ml. when the sign was considered. Molecular refractions calculated for the alternate structure having the amino alcohol residue attached to silicon through nitrogen with the hydroxyl free showed an average deviation of 0.39 ml. when the sign was disregarded and 0.31 ml. when the sign was considered.

compounds prepared were sufficiently basic to be titrated completely with hydrochloric acid using methyl red indicator.

It is very improbable that the amino alcohol residues were attached to silicon through nitrogen rather than through oxygen. The structures involving attachment through oxygen were assigned for the following reasons: (1) 2-diethylaminoethanol, which contains no hydrogen atoms attached to nitrogen, reacted with the diaminosilane in a manner analogous to other amino alcohols containing unsubstituted amino groups; and the product obtained with 2-diethylaminoethanol had properties analogous to those of compounds obtained with amino alcohols possessing free amino groups; (2) if the nitrogen were attached to silicon, it is unlikely that it would be sufficiently basic to be titrated quickly and completely with hydrochloric acid using methyl red indicator; (3) the inertness of the di-*t*-butyl-di-(2-aminoethyl) silicate toward molten sodium indicates the absence of free hydroxyl groups.

Experimental

Intermediates. A. Amino Alcohols.—Sharples Co. 2-ethylaminoethanol and Eastman Kodak Co. 2-aminoethanol, 2-diethylaminoethanol, and 2-amino-2-methylpropanol were distilled before use. Commercial Solvents 2-aminobutanol, Dow 1-amino-2-propanol, and Eastman 2-(β-aminoethylamino)-ethanol were used as received. The properties of the intermediate known amino alcohols as used are listed below.

Compound	B. p., uncor. °C.	B. p., uncor. Mm.	n^{20}D	d^{20}
$NH_2CH_2CH_2OH$	83–86	21	1.455	1.016
$C_2H_5NHCH_2CH_2OH$	165	740	1.4411	0.9162
$(C_2H_5)_2NCH_2CH_2OH$	56–57	15	1.4412	0.8921
$CH_3C(CH_3)(NH_2)CH_2OH$	75	16	1.4482	
$CH_3CH_2CH(NH_2)CH_2OH$			1.4524	
$CH_3CH(OH)CH_2NH_2$			1.4479	
$NH_2CH_2CH_2NHCH_2CH_2OH$			1.486	

B. Di-*t*-butoxydiaminosilane.—This intermediate was used as received from the Minnesota Mining and Manufacturing Co. The material had equivalent weight 107, n^{20}D 1.4200 and d^{20} 0.9281. Distillation of a portion indicated over 95% purity. A center fraction had the following properties: b. p. 104° at 20 mm., n^{20}D 1.4199, d^{20} 0.9276. The observed *MR*D was 56.28 and the value calculated as indicated in Table I was 55.68.

Anal. Calcd. for $C_8H_{22}O_2N_2Si$: equivalent weight, 103; N, 13.58. Found: equivalent weight 106; N (Dumas), 13.58.

Synthesis of Di-*t*-butyl-di-aminoalkyl Silicates.—All six compounds were prepared in essentially the same manner. The following detailed description of the synthesis of di-*t*-butyl-di-(2-amino-1-methyl-ethyl) silicate (III) is representative of the method used. Yields, properties, and analyses of the six new compounds prepared may be found in Table I.

A solution of 231 g., 3.1 moles, of 1-amino-2-propanol and 309 g., 1.5 moles, of di-*t*-butoxydiaminosilane was refluxed for one hour in a two-liter, round-bottom flask equipped with water-cooled reflux condenser. Since at the end of this period the weight loss of the reactants corresponded to the theoretical weight of ammonia expected, the reaction was considered to have gone to completion. (Some of the other amino alcohols required a three-hour reflux period for completion of the reaction.) The equivalent weight of the crude product was 155, while the calculated equivalent weight of the expected product was 161. Distillation of the crude product at reduced pressure gave 345 g., 1.1 moles, of di-*t*-butyl-di-(2-amino-1-methyl-ethyl) silicate III.

Other compounds prepared by this method were: di-*t*-butyl-di-(2-aminoethyl) silicate I, di-*t*-butyl-di-(2-diethylaminoethyl) silicate II, di-*t*-butyl-di-(2-aminobutyl) silicate IV, di-*t*-butyl-di-(2-amino-2-methyl-propyl) silicate V, and di-*t*-butyl-di-[2-(β-aminoethylamino)-ethyl] silicate VI.

For a number of the syntheses the material balances on distillation were consistently low. In one run the volatile material lost was shown to be *t*-butyl alcohol by its melting point, boiling point, refractive index, water solubility, and conversion to *t*-butyl chloride with concentrated hydrochloric acid. Higher boiling fractions from a number of the syntheses had a high refractive index and low equivalent weight indicative of ester-interchange between *t*-butoxy groups and amino alcohol molecules.

The reaction of 2.0 moles of 2-ethylaminoethanol with 1.0 mole of di-*t*-butoxydiaminosilane repeatedly gave an anomalous result. The theoretical weight loss was attained in one and one-half hours; however, distillation of the crude product gave, as indicated by equivalent weights, an approximately equimolar mixture of di-*t*-butyl-di-(2-ethylaminoethyl) silicate, b. p. 165° at 16 mm. and n^{20}D 1.423, and *t*-butyl-tri-(2-ethylaminoethyl) silicate, b. p. 185° at 19 mm. and n^{20}D 1.435. The high refractive index of the higher boiling material precludes its being hexa-*t*-butoxydisilazane resulting from the condensation of di-*t*-

butoxy-diaminosilane. The presumed di-*t*-butyl-di-(2-ethylaminoethyl) silicate boiled at 285° at 740 mm. and did not decompose appreciably upon being refluxed at this temperature for one hour. Variation of conditions by adding the diaminosilane to the refluxing amino alcohol and *vice versa* appeared to give no improvement in eliminating or minimizing the formation of the side-product arising presumably by ester-interchange.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Solubility and Specific Rotation of *l*-Ascorbyl Palmitate and *l*-Ascorbyl Laurate

BY DANIEL SWERN

Renewed interest in *l*-ascorbyl palmitate,[2] resulting from its recently reported antiscorbutic activity,[3] non-toxicity[4] and commercial availability[5] has prompted us to determine its solubility at 25° in some typical organic solvents, water, and cottonseed and peanut oils. For purposes of comparison, we also determined the solubility of *l*-ascorbyl laurate[2] in the two vegetable oils. We have also determined the specific rotation of both *l*-ascorbyl palmitate and laurate. With the exception of water and petroleum naphtha, the temperature coefficient of solubility is high. Benzene and ethyl acetate are two of the best crystallizing solvents for purifying the esters.

Experimental

Solubility Determinations.[6]—Solubility in petroleum naphtha, boiling range 63–70°, and water was determined on saturated solutions obtained by shaking the solvent with excess solute until equilibrium, ascertained by analysis, was attained. With all the other solvents, equilibrium was approached from the solution side by allowing excess solute to crystallize. Dissolved ester was determined either by titration with 0.1 *N* sodium hydroxide[2] or by evaporation of solvent. At least two determinations were run; precision of duplicates was about five parts per thousand. Solubility of *l*-ascorbyl palmitate in glycerol could not be determined because the solution was a thick gel. Its solubility, however, appeared to be low. Results are summarized in Table I.

Specific Rotation.—Specific rotation was determined with a Bellingham and Stanley Glass Scale polarimeter that could be read directly to 0.01°. A 5–10% solution of the ester in 95% alcohol and a 4.00-dm. tube were employed.

TABLE I

SOLUBILITY AT 25 ± 0.10°: *l*-ASCORBYL ESTERS

Solvent	Sol.[a] g./100 g.	Solvent	Sol.[a] g./100 g.
Palmitate		Palmitate	
Water[b]	0.56	Ethyl acetate	4.9
Petroleum naphtha[c]	0.00	Ethyl cellosolve[e]	>33.9
Ethanol 95%[d]	23.5	Peanut oil	0.18
Benzene	0.45	Cottonseed oil	0.22
Ethylene glycol	0.18	Laurate	
1,2-Propylene glycol	6.6	Peanut oil	0.11
Dioxane	19.0	Cottonseed oil	0.08

[a] By titration. [b] Solubility by evaporation 0.31 g./100 g. Small and probably variable quantities of solute emulsified, thus accounting for the poor duplication between the results by titration and by evaporation. [c] B. p. range 63–70°. Solubility by evaporation 0.01 g./100. [d] Solubility by evaporation 23.4 g./100. [e] Insufficient material to complete determination.

l-Ascorbyl palmitate: $[\alpha]^{25.5}\text{D}$ + 23.3° (8.086 g. per 100 ml. of 95% ethanol solution). *l*-Ascorbyl laurate: $[\alpha]^{25.5}\text{D}$ + 26.6° (5.014 g. per 100 ml. of 95% ethanol solution).

PHILADELPHIA 18, PENNA.
RECEIVED JANUARY 26, 1949

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Swern, Stirton, Turer and Wells, *Oil and Soap*, **20**, 224 (1943).

[3] Ambrose and DeEds, *Arch. Biochem.*, **12**, 375 (1947).

[4] Fitzhugh and Nelson, *Proc. Soc. Exptl. Biol. Med.*, **61**, 195 (1946).

[5] Chas. Pfizer and Company, New York, N. Y.

[6] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, pp. 111 and 341.

Preparation of Fluorothiophene

BY ROBERT T. VANVLECK

Chloro- and bromothiophene are offered in the industrial market and iodothiophene is reported in the literature, but no reference has been made to fluorothiophene. This compound has been prepared in these Laboratories in small yields by the reaction of antimony trifluoride with iodothiophene in the presence of nitromethane as a solvent. The preparation of fluorothiophene from 2-iodothiophene indicates that the fluoro compound is the 2-isomer.

Nitroethane, nitropropane and *t*-butylthiophene were found not suitable as solvents for the reaction. Various other methods for preparing fluorothiophene proved unsuccessful; they include the reaction of antimony trifluoride with either chloro- or bromothiophene, the reaction of aluminum trifluoride with chlorothiophene, and the reaction of fluoboric acid with thiophene diazonium chloride. This last reaction was studied in an unsuccessful attempt to adapt Flood's synthesis of fluorobenzene[1] to the preparation of the thiophene analog. It is possible that the diazonium chloride was not obtained due to the instability of the aminothiophene.

Experimental

A mixture of 150 g. (0.72 mol) of iodothiophene and 43 g. (0.24 mole) of antimony trifluoride in 250 ml. of nitromethane was heated in a flask at reflux temperature (90–100°) for five hours; the product fluorothiophene distilled over through a small column as formed plus some

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[1] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 295.