TABLE I

ASYMMETRIC SYNTHESES OF *trans*-CYCLOPROPANE-1,2-DICARBOXYLIC ACID

Run	Solvent	Acid, % yield	$[\alpha]^{24}$D, H_2O	Optical yield	Dimethyl ester ester $[\alpha]^{24}$D EtOH
1	Toluene	60.0	−1.5°	1.8	−2.3°
2	Toluene	41.5	−1.9°	2.2	−2.8°
3	Toluene	40.1	−2.7°	3.1	−4.0°
4	DMF	46.0	+8.6°	10.2	+12.8°
5	DMF	46.0	+8.7°	10.3	+13.0°
6	DMF	51.0	+9.3°	10.9	+13.8°
7	Nitrobenzene	34.1	+0.25	0.3	+0.38°

investigation and will be the subject of a future publication.

INSTITUTE FOR CHEMICAL RESEARCH Y. INOUYE
KYOTO UNIVERSITY S. INAMASU
TAKATSUKI, JAPAN, AND M. OHNO
DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY T. SUGITA
TALLAHASSEE, FLORIDA H. M. WALBORSKY

RECEIVED MAY 22, 1961

METHYL-STANNO-SILOXANES AND METHYL-PLUMBO-SILOXANES

Sir:

A recent article[1] prompts us to report some results of our own studies in the field of alkylheterosiloxanes.

To gain some knowledge on the stability and properties of siloxanes, in which silicon atoms are partly replaced by other IVb elements (Ge, Sn, Pb), we have planned to synthesize heterosiloxanes of low molecular weight and definite composition. First we prepared some alkyl-germanosiloxanes,[2] *e.g.*, hexamethylgermanosilosane $Me_3SiOGMe_3$, by the reaction of $LiOSiMe_3$ with Me_3GeCl. We have found that this type of reaction furnishes also the synthesis of the corresponding tin and lead compounds.

Except for some studies on the tin-alkylsilanolates, compounds without alkyl groups attached to tin,[3,4,5a,5b,6] only few reports on real alkyl-stannosiloxanes have been published.[4,5c,7] Moreover these studies mainly dealt with polymeric materials whereas the first members of those series have not been described.

Okawara, *et al.*,[1] failed to obtain hexamethylstannosiloxane and bistrimethylsiloxy-dimethylstannane by method of transesterification and cohydrolysis. We were able to synthesize these compounds by a simple method: Lithium trimethylsilanolate reacts in anhydrous ethereal solution with trimethylchlorostannane forming insoluble LiCl and hexamethylstannosiloxane in very good yields according to

$$(CH_3)_3SiOLi + (CH_3)_3SnCl \rightarrow LiCl + (CH_3)_3SiOSn(CH_3)_3$$

Dimethyldichlorostannane and methyltrichlorostannane react under the same conditions forming LiCl and bis-trimethylsiloxy-dimethylstannane and tris-trimethylsiloxy-methylstannane, respectively

$$2\,(CH_3)_3SiOLi + (CH_3)_2SnCl_2 \rightarrow [(CH_3)_3SiO]_2Sn(CH_3)_2 + 2\,LiCl$$

$$3\,(CH_3)_3SiOLi + CH_3SnCl_3 \rightarrow [(CH_3)_3SiO]_3SnCH_3 + 3\,LiCl$$

Tatlock and Rochow[4] already had studied the reaction of Me_3SiOK and Me_2SnCl_2 in 1952, but reported only a few analytical data and physical constants of their reaction product. Table I shows the physical constants of the new methylstannosiloxanes.

Hexamethylstannosiloxane shows surprisingly high thermal stability. It may be distilled at atmospheric pressure without decomposition. Bistrimethylsiloxy-dimethylstannane, in contrast to the results of Okawara, *et al.*,[1] forms crystals melting at 48°. The melt is stable up to 150°. It may be vacuum distilled (b.p. (11 mm.) 74°), whereas the distillation under atmospheric pressure at 160° is accompanied by partial decomposition, hexamethyldisiloxane and dimethylpolystannoxane being formed

$$x[(CH_3)_3SiO]_2Sn(CH_3)_2 \rightarrow x(CH_3)_3SiOSi(CH_3)_3 + [(CH_3)_2SnO]_x$$

Under similar conditions tris-trimethylsiloxy-methylstannane undergoes thermal decomposition yielding hexamethyldisiloxane and polymeric methylpolystannoxane, which still contains trimethylsiloxy groups attached to tin.

From ethereal solutions of trimethylbromoplumbane and sodium trimethylsilanolate NaBr precipitates and high yields of hexamethylplumbosiloxane are recovered[8])

$$(CH_3)_3SiONa + (CH_3)_3PbBr \rightarrow NaBr + (CH_3)_3SiOPb(CH_3)_3$$

This first member of the lead–siloxane series forms a colorless liquid of high vapor pressure and unexpected thermal stability. It may be transported in high vacuum even at room temperature and boils without decomposition at 172° under atmospheric pressure of dry nitrogen. At temperatures above 150° the vapor reacts with oxygen with explosion forming elementary lead. Under normal conditions the compound is stable against dry air and the influence of light.

TABLE I

MELTING AND BOILING POINTS OF METHYLSTANNOSILOXANES

Formula	Fp., °C.	B.p.			
		°C.	Mm.	°C.	Mm.
$(CH_3)_3SiOSn(CH_3)_3$	−59	141	720	38	11
$[(CH_3)_3SiO]_2Sn(CH_3)_2$	+48	160 dec.	720	75	11
$[(CH_3)_3SiO]_3SnCH_3$	+34	155 dec.	720	49	11

---

[1] R. Okawara, D. G. White, K. Fujitani and H. Sato, *J. Am. Chem. Soc.*, **83**, 1342 (1961).

[2] H. Schmidbaur and M. Schmidt, *Chem. Ber.*, **94**, 1138 (1961); **94**, 1349 (1961).

[3] W. I. Patnode and F. C. Schmidt, *J. Am. Chem. Soc.*, **67**, 2272 (1945).

[4] W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

[5] (a) K. A. Andrianov and A. A. Zhdanov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 779 (1958); *C.A.*, **52**, 19916 (1958); (b) K. A. Andrianov, A. A. Zhdanov and E. A. Kashutina, *Zhur. Priklad. Khim.*, **32**, 463 (1959); *C.A.*, **53**, 11079 (1959); (c) K. A. Andrianov, T. N. Gamina and E. N. Krushtaleva, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 798 (1956); *C.A.*, **51**, 3487 (1957).

[6] E. D. Hornbaker and F. Conrad, *J. Org. Chem.*, **24**, 1858 (1959).

[7] F. A. Henglein, R. Lang and L. Schmack, *Makromol. Chem.*, **22**, 103 (1957).

[8] $LiOSiMe_3$ under the same conditions does not form the plumbosiloxane with Me_3PbBr, because of the solubility of LiBr in diethyl ether, which prevents the metathetic reaction going to completion.

Hexamethylplumbosiloxane, as well as the tin compounds described above, are very sensitive to water. Even the moisture of the air leads to hydrolysis.

The infrared spectra of the new compounds are assigned easily to the structural units of the heterosiloxanes. Together with the analytical data and chemical reactions they unambiguously prove the composition. The wave length of the Si–O–X frequency (X = Si,Ge,Sn,Pb) seems to be of considerable interest. The comparison of the ν_{as} Si–O–X values of the hexamethylheterosiloxanes (Table II) demonstrates a systematic shift of this band to higher wave length in the sequence Si–Ge–Sn–Pb. Thermal stability as well as reactivity in heterolytic reactions decrease in the same order. The increasing mass, radii and decreasing electronegativity of the heteroatoms are the reasons for these observations. The new methylstanno- and methylplumbosiloxanes are characterized by extremely unpleasant odor. They all are highly toxic, mainly because of their good solubility in organic solvents (and in the lipoid) and their sensitivity against hydrolysis.

TABLE II

MELTING POINTS, BOILING POINTS AND SI–O–X FREQUENCIES IN THE INFRARED SPECTRA OF HEXAMETHYLHETEROSILOXANES

Formula	F.p. (°C.)	B.p. °C.	B.p. Mm.	ν_{as} Si–O–X (1/cm.)
$(CH_3)_3SiOC(CH_3)_3$	−91	103.5	760	1052
$(CH_3)_3SiOSi(CH_3)_3$	−57	100.5	760	1055
$(CH_3)_3SiOGe(CH_3)_3$	−68	117	725	990
$(CH_3)_3SiOSn(CH_3)_3$	−59	141	720	980
$(CH_3)_3SiOPb(CH_3)_3$	−1	172	720	959

INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MÜNCHEN
MÜNCHEN 2, MEISERSTRASSE 1
GERMANY
HUBERT SCHMIDBAUR
MAX SCHMIDT

RECEIVED MAY 8, 1961

IDENTITY OF NEOSAMINE C, "DIAMINOHEXOSE II" FROM ZYGOMYCIN A, AND 2,6-DIAMINO-2,6-DIDEOXY-D-GLUCOSE

Sir:

Neosamine C,[1] one of the four component fragments of neomycin C and a fragment wherein neomycin C differs stereochemically from neomycin B,[2] was shown earlier to be a 2,6-diamino-2,6-dideoxyhexose[3] and it was assigned D-glucose stereochemistry.[1]

Recently the antibiotic complex zygomycin A[4,5] was characterized. Hydrolysis of the complex gave a mixture of at least two diaminohexoses ("I" and "II"),[6,7] apparently resulting from a mixture of at least two isomeric zygomycins A. "Diaminohexose I" was shown[7] to be identical with neosamine B,[1] from neomycin B. The present report establishes the identity of "diaminohexose II" and neosamine C.

Neosamine C and "diaminohexose II" were converted separately to their N,N′-diacetyl derivatives, the former by a modification of the method employed earlier for the neomycins[8] and the latter[7] by the method of Roseman and Ludowieg.[9] Comparison of the physical properties of the N-acetylated derivatives (needles from acetone) establishes their identity (*cf.* Table I).

TABLE I

PHYSICAL PROPERTIES OF 2,6-DIACETAMIDO-2,6-DIDEOXY-D-GLUCOSE SAMPLES

N,N′-Diacetyl-	M.p., °C.	Mix. m.p.[a]	$[\alpha]^{25}D$[e]	R_{NAG}[b]
Neosamine C	209–215	...	35.6	1.33
"Diaminohexose II"	211–216	209–213	37.2	1.32
Synthetic[c]	207–212	207–215	35.8	1.32
Synthetic[d]	209–213	209–217	36.8	1.32

[a] Mixture m.p. with N,N′-diacetylneosamine C. [b] R_f (sample)/R_f (N-acetylglucosamine); BAW 415. [c] Present sample. [d] Diaminoglucose sample of Weidmann and Zimmermann,[12] acetylated by the standard method.[8] [e] Equilibrium values.

In connection with this work an authentic sample of 2,6-diamino-2,6-dideoxy-D-glucose has been prepared, starting with the known methyl N-acetyl-D-glucosaminide (I).[10] Treatment of I with *p*-toluenesulfonyl chloride in pyridine gave the amorphous methyl N-acetyl-6-O-tosyl-α-D-glucosaminide (II), R_f 0.90 (PEAW:122 = pyridine: ethyl acetate:water, 1:2:2) [*Anal.* Found: C, 49.21; H, 6.16; N, 3.45; S, 8.11]. The tosylate (II) was heated for 24 hr. at 105° in saturated methanolic ammonia to give the crude 6-amino compound, which was purified by means of its crystalline N-acetyl derivative (needles from methanol), methyl 2,6-diacetamido-2,6-dideoxy-α-D-glucosaminide (III), R_f 0.77 (BAW 221),[11] m.p. 240–242°, $[\alpha]^{26}D + 119°$ (c 0.42, water), [*Anal.* Found: N, 10.13]. Hydrolysis[11] of III gave 2,6-diamino-2,6-dideoxy-D-glucose dihydrochloride, $[\alpha]^{27}D + 61.5°$ (c 0.96, water), R_f 0.17 (BAW 221)[11]; corresponding physical constants for authentic neosamine C dihydrochloride are $[\alpha]^{23}D + 69°$ (c 0.87, water), R_f 0.17 (BAW 221).[11] The synthetic diamine was N-acetylated[9]; identity of the synthetic material and the antibiotic degradation fragments is established by the data of the table.[12]

Further confirmation of the identity of the four samples was provided by their nearly superimposable n.m.r. spectra, a physical property which has

[1] K. L. Rinehart, Jr., P. W. K. Woo, and A. D. Argoudelis, *J. Am. Chem. Soc.*, **80**, 6461 (1958).

[2] K. L. Rinehart, Jr., A. D. Argoudelis, T. P. Culbertson, W. S. Chilton, and K. Striegler, *ibid.*, **82**, 2970 (1960).

[3] K. L. Rinehart, Jr., and P. W. K. Woo, *ibid.*, **80**, 6463 (1958).

[4] M. Shibata, E. Higashide, T. Kanzaki, H. Yamamoto, and K. Nakazawa, *Agr. Biol. Chem. Japan*, **25**, 171, 176 (1961).

[5] J. Hitomi, S. Horii, T. Yamaguchi, M. Imanishi, and A. Miyake, *J. Antibiotics (Japan), Ser. A*, **14**, 63 (1961).

[6] H. Hitomi, S. Horii, T. Yamaguchi, and A. Miyake, *Chem. Pharm. Bull. Japan*, in press.

[7] (a) S. Horii, T. Yamaguchi, H. Hitomi, and A. Miyake, *ibid.*, [4], **9**, 340 (1961); (b) S. Horii, *J. Antibiotics (Japan)*, in press.

[8] K. L. Rinehart, Jr., A. D. Argoudelis, W. A. Goss, A. Sohler, and C. P. Schaffner, *J. Am. Chem. Soc.*, **82**, 3938 (1960).

[9] S. Roseman and J. Ludowieg, *ibid.*, **76**, 301 (1954).

[10] R. C. G. Moggridge and A. Neuberger, *J. Chem. Soc.*, 745 (1938).

[11] K. L. Rinehart, Jr., and P. W. K. Woo, *J. Am. Chem. Soc.*, **83**, 643 (1961).

[12] A preparation of 2,6-diamino-2,6-dideoxy-D-glucose by another route was reported recently [H. Weidmann and H. K. Zimmermann, *Angew. Chem.*, **72**, 750 (1960)]. We have N-acetylated a sample of the latter diaminohexose preparation (generously provided by Drs. Weidmann and Zimmermann) and have found it, too, to be identical with the acetylated derivatives of the natural compound (*cf.* table).