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.	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

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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).

been shown to be very sensitive to stereochemical differences of similar carbohydrates.[13] The earlier assignment[1] of stereochemistry to neosamine C is thus confirmed.

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(13) *Cf.* J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 395–399.

(14) Undergraduate Research Participant, supported by a grant (NSF G-8521) from the National Science Foundation.

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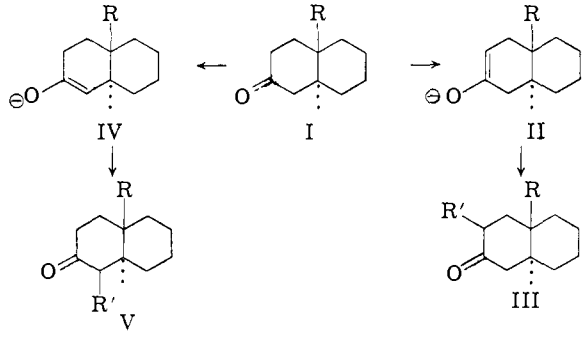
THE α-ALKYLATION OF ENOLATES FROM THE LITHIUM-AMMONIA REDUCTION OF α,β-UNSATURATED KETONES

Sir:

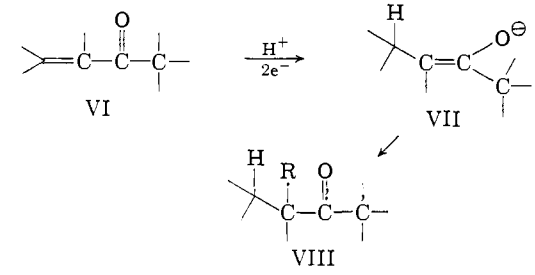
The alkylation of carbonyl compounds is an important synthetic reaction which is attended by a number of problems some of which we have attempted to deal with previously with the introduction of the enamine alkylation reaction.[1]



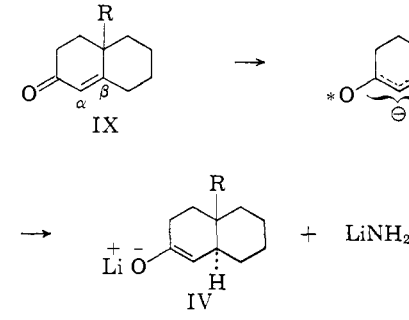
An important problem with which this communication is concerned is that of introducing a group on *either side* of the carbonyl of an unsymmetrical ketone. The *trans*-2-decalone system (I) will serve to illustrate this problem: Direct alkylation of I with electrophilic reagents in the presence of base leads to structures of type III,[2] *via* the anion II which happens to be the more stable one in this particular system.

We have now shown that it is possible to generate the less stable anion (IV) and to make use of it to introduce groups on the other side of the carbonyl (leading to V).

The principle of this new synthetic process is illustrated by the general equation VI → VII → VIII.



We will first consider the generation of the anion (*e.g.*, IV) from an α,β-unsaturated ketone (*e.g.*, IX). Addition of an electron from lithium and liquid ammonia to IX produces an intermediate X with carbanion character at the β-carbon atom.[3] This intermediate was postulated to remove a proton from ammonia with the formation, for reasons which we have discussed previously,[4] of a



trans decalone derivative as its enolate IV which is precisely that which we are trying to generate. That a proton is transferred to X by ammonia was established as follows: decomposition with D_2O (after replacing the ammonia by benzene) of the product from the addition of lithium to a liquid ammonia solution of IX, R = H, gave a saturated ketone (I, R = H) which contained deuterium as shown by its infrared spectrum, but all of the deuterium could be removed by warming with dilute aqueous base: the product after such treatment showed no excess deuterium over the natural abundance. No deuterium therefore was introduced on the β-carbon, where it would have remained, and the proton on that carbon must have come from the ammonia rather than from subsequent acidification.

Two experiments serve to show that the resulting enolate ion is indeed IV: addition of methyl iodide to the reduction mixture from IX, R = H, instead of decomposition by acid, with the usual work-up, gave in 55% yield *trans* 1-methyl-2-decalone (V, R = H, R′ = CH_3) characterized by the formation in good yield of its 2,4-dinitrophenylhydrazone, m.p. 180–182° (reported[5] m.p. 179–180°), mixed melting point determination with an authentic sample confirmed the identity of the substance.

Replacement of the ammonia, following the lithium reduction of IX, R = CH_3, by ether, and addition to a mixture of Dry Ice and ether, produced a β-keto acid salt which gave, after acidifica-

(1) G. Stork, R. Terrell and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954); G. Stork, Abst. of the 16th National Organic Symposium, June 1959, pp. 44–52.

(2) *Cf.* Y. Mazur and F. Sondheimer, *J. Am. Chem. Soc.*, **80**, 5220 (1958).

(3) G. Stork and J. Tsuji, *ibid.*, **83**, 2783 (1961).

(4) G. Stork and S. D. Darling, *ibid.*, **82**, 1512 (1960).

(5) D. K. Banerjee, S. Chatterjee and S. P. Bhattacharya, *ibid.*, **77**, 408 (1955).