ing. of II gave these fractions: (1), 86 mg. of neosamine C, dihydrochloride, $[\alpha]^{28}D$ +65° (c 1.0, water) [lit.[13] $[\alpha]^{23}D$ +69° (c 0.87, water)], R_f (BAW 221) 0.17 (lit.[12] 0.17); (2), an intermediate fraction, whose components were identified by papergrams and ion exchange,[11] and which was calculated from rotation to contain 145 mg. of neosamine C and 72 mg. of deoxystreptamine hydrochloride; (3), 160 mg. of optically inactive deoxystreptamine hydrochloride; (4), 430 mg. of recovered neamine, hydrochloride $[\alpha]^{28}D$ +82° (c 1.0, water) [lit.[2] $[\alpha]^{25}D$ +83° (c 1.0, water).

Conclusive evidence for the identity of the hydrolysis product and neosamine C was provided by the N-acetylation[14] of the former to N,N'-diacetylneosamine C, m.p. 209–221° (undepressed on mixture with an authentic sample[15] melting 210–214°), $[\alpha]^{28}D$ +38° (c, 0.6, water) [lit.[15] $[\alpha]^{25}D$ +37° (c 0.8, water), R_{NAG} (BAW 415) 1.35 (lit.[15] 1.32). Neosamine was earlier assigned D-glucose stereochemistry[16] from degradative and rotation evidence; the assignment has been confirmed recently by comparison of the diaminohexose with synthetic 2,6-diamino-2,6-dideoxy-D-glucose.[15]

Both N,N',N'',N'''-tetraacetylneamine (II) and N,N',N'',N'''-tetrabenzoylneamine (III) consume selectively two moles of periodate when treated at room temperature with 0.1 N periodate. Since a maximum of one mole of periodate may be consumed in vic-glycol cleavage of the deoxystreptamine moiety and a like amount in the neosamine C moiety in II and III, these results establish a 4-(rather than 5-)glycoside linkage on deoxystreptamine and a pyranose (rather than furanose) structure for neosamine C in neamine. Confirmation of the attachment of neosamine C at C-4 in deoxystreptamine (providing a vic glycol for cleavage) is provided by the observation that no deoxystreptamine may be detected after the two-molar periodate oxidation of II, with subsequent hydrolysis with refluxing 48% hydrobromic acid (cf. above).

From the rotation of methyl N,N'-diacetyl-α-neosaminide C,[15] $[M]D$ +32,800, and the value of A_G for methyl N-acetyl-D-glucosaminides,[17] +17,390, one may derive by Hudson's rules[18] the value B_{AcC} +15,400 for N,N'-diacetylneosaminides C, while the rotation of a 4-substituted N,N'-diacetyldeoxystreptamine is known from $[M]D$ +3,900 for 4-O-methyl-N,N'-diacetyldeoxystreptamine.[19] Combination of these values and the molecular rotation of N-tetraacetylneamine (II) into the equation $[M]_{AcNe} = [M]_{AcDe} + A_{AcC}$

(13) K. L. Rinehart, Jr., and P. W. K. Woo, J. Am. Chem. Soc., 83, 643 (1961).

(14) S. Roseman and J. Ludowieg, ibid., 76, 301 (1954).

(15) K. L. Rinehart, Jr., M. Hichens, K. Striegler, K. R. Rover, T. P. Culbertson, S. Tatsuoka, S. Horii, T. Yamaguchi, H. Hitomi and A. Miyake, ibid., 83, 2964 (1961).

(16) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, ibid., 80, 6461 (1958).

(17) P. W. Kent and M. W. Whitehouse, "Biochemistry of the Aminosugars," Butterworths Scientific Publications, London, 1955, p. 234.

(18) C. S. Hudson, J. Am. Chem. Soc., 31, 66 (1909); cf. W. Pigman, in "The Carbohydrates," Academic Press, Inc., New York, N. Y., 1957, p. 70.

(19) T. H. Haskell, J. C. French and Q. R. Bartz, J. Am. Chem. Soc. 81, 3482 (1959).

+ B_{AcC}, where $[M]_{AcNe}$ +43,300 is the molecular rotation of II, $[M]_{AcDe}$ is the rotational contribution of the 4-substituted-N,N'-diacetyldeoxystreptamine moiety, and A_{AcC} and B_{AcC} have the usual meanings[18] for a glycoside of N,N'-diacetylneosamine, C, yields A_{AcC} = +24,000 or +31,800 (depending on the sign of $[M]_{AcDe}$).[20] In either case the high positive value agrees well with that expected for an α-linked glycoside (as shown in I).[18,20] This conclusion may also be reached, though less quantitatively, from the high molecular rotation of neamine hydrochloride ($[M]D$ +38,800)[2] relative to the corresponding value for neosamine C hydrochloride ($[M]D$ +16,800).[16] Except for the assignment of absolute stereochemistry to the substituted deoxystreptamine (i.e., 4- vs. 6-substitution), the present data establish the structure for neamine.

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A STUDY OF THE REACTIONS OF VARIOUS TIN(II) COMPOUNDS WITH CALCIUM HYDROXYLAPATITE

Sir:

We wish to report the results of a series of investigations carried out in aqueous media involving the reaction between calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, and these tin(II) salts: SnF_2, $SnCl_2 \cdot 2H_2O$, $SnSO_4$, $SnClF$, and Sn_2ClF_3. The reactions led in each case, except for that involving $SnCl_2 \cdot 2H_2O$, to the formation of a basic tin(II) phosphate having a molar Sn/PO_4 ratio of 2.0, to which we have assigned the empirical formula $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$ (calculated: Sn, 66.2; PO_4, 26.5. Found: Sn, 65.8; PO_4, 26.5). The reaction involving $SnCl_2 \cdot 2H_2O$, however, resulted in the formation of $Sn_3(PO_4)_2$.

Experimental.—Calcium hydroxylapatite for use in these studies was prepared according to the method of Hayek and Stadlmann.[1] Stannous fluoride was obtained by treating SnO with HF.[2] The mixed chlorofluorides were prepared according to procedures previously outlined in this laboratory.[3,4] Commercial preparations of both $SnCl_2 \cdot 2H_2O$ and $SnSO_4$ were employed.

(1) E. Hayek and W. Stadlmann, Angew. Chem., 67, 327 (1955).

(2) W. H. Nebergall, J. C. Muhler and H. G. Day, J. Am. Chem. Soc., 74, 1604 (1952).

(3) W. H. Nebergall, G. Baseggio and J. C. Muhler, ibid., 76, 5353 (1954).

(4) W. H. Nebergall, U. S. Patent 2,882,204.

The reactions were studied in molar proportions such that there existed initially a 1:1 ratio of Ca to Sn atoms. The amounts of reactants and the volume of water used in each case were adjusted such that the initial concentration of tin(II) was in the range 0.03–0.05 M for each reaction studied. A solid phase persisted throughout the duration of each reaction. Initially this solid was simply calcium hydroxylapatite, then a mixture of partially reacted materials, and finally the completed reaction products. The reactions were carried out at reflux temperature in an inert atmosphere of nitrogen gas from which all traces of oxygen had been removed by bubbling the gas through a train of wash bottles containing amalgamated zinc and solutions of vanadium(II) ions.[5] This precaution also was employed during filtration of the reaction mixtures in order to prevent any air oxidation of the tin(II) ion.

All products were dried either *in vacuo* over P_4O_{10} or by use of a conventional drying pistol. Identifications were made by means of X-ray diffraction powder patterns when possible, along with chemical analyses. A modification of the Martin–Doty method[6] was used for the colorimetric determination of phosphate; tin(II) was determined by an accurate procedure which we devised in this laboratory and which soon will be published elsewhere.

Results and Discussion.—A summary of the reactions studied is given in Table I.

TABLE I

PRODUCTS OBTAINED BY AQUEOUS TREATMENT OF
$Ca_{10}(PO_4)_6(OH)_2$ WITH TIN(II) SALTS

Tin(II) salt used	Reaction time, hr.	Final pH of soln.	Insoluble products
SnF_2	48	3.00	$Ca_{10}(PO_4)_6(OH)_2$, $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
SnF_2	72	2.85	$Ca_{10}(PO_4)_6(OH)_2$, $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
SnF_2	96	2.75	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
$SnSO_4$	48	2.40	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$
$SnClF$	48	2.65	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
Sn_2ClF_3	60	2.80	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
$SnCl_2 \cdot 2H_2O$	48	2.50	$Sn_3(PO_4)_2$

The pH of these solutions was affected both by the hydrolysis of the tin(II) ion as represented by the equation $Sn^{+2} + H_2O \rightarrow SnOH^+ + H^+$, and by the relative basicities of the individual anions. The 1:1 ratio of Sn:Ca was employed on the basis of the assumption that a simple cationic exchange would take place and lead to the formation of tin(II) hydroxylapatite, $Sn_{10}(PO_4)_6(OH)_2$. However, the absence of a tin(II) phosphate with molar Sn/PO_4 ratio of 1.67 among any of the products eliminated this possibility.

In order to identify the basic tin(II) phosphate, which was formed in all but one of the reactions studied, a sample of it had to be separated from the accompanying insoluble by-products present in each of the mixtures obtained. This was necessary because X-ray diffraction studies of

(5) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).
(6) J. B. Martin and D. M. Doty, *ibid.*, **21**, 965 (1949).

these various mixtures revealed that the pattern of the basic tin(II) phosphate did not agree with any published for known phosphate compounds of tin(II) and hence it could not be identified simply by comparison. All attempts at isolating this material from mixtures containing the very insoluble CaF_2 were unsuccessful. In strong acid solutions CaF_2 exhibits sufficient solubility to permit its removal, but such conditions also cause a change in the structure of the basic tin(II) salt. Attempted extractions of the calcium with chelating agents such as EDTA were also inefficient under the mildly acidic conditions required to prevent alteration of the structure of $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$. However, isolation of this compound was effected by treating the mixture containing $CaSO_4 \cdot 2H_2O$ with a buffer solution of pH 4; gypsum is readily soluble under these conditions even at room temperature and the basic tin(II) phosphate remains unchanged.

Later, in succeeding studies, $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$ also was obtained directly as a hydrolysis product of $SnHPO_4$. The complete results of our investigations regarding the hydrolysis of $SnHPO_4$ will be discussed in a later publication.

The assignment of the empirical formula $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$ to this basic salt was based on its composition as determined by chemical analyses. The same procedure was used for the identification of $Sn_3(PO_4)_2$ as the product obtained from the reaction between $Ca_{10}(PO_4)_6(OH)_2$ and $SnCl_2 \cdot 2H_2O$. The X-ray diffraction pattern of our tribasic tin(II) phosphate did not agree with that published for this compound in the ASTM X-ray card file.

Finally, we have found that SnF_2, $Sn_2P_2O_7$, and $Ca_{10}(PO_4)_6(OH)_2$ in the molar ratio of 10:1:1, respectively, react to form $Sn_3(PO_4)_2$ and CaF_2.

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**THE REDUCTION OF OLEFINS BY MEANS OF
AZODICARBOXYLIC ACID in situ**

Sir:

Certain considerations[1] led us to the belief that the readily available[2] salts of azodicarboxylic acid might be a source of H_2N_2 (diimide, diazene), which, although at present a poorly defined species,[3] should act *in situ* as a potent reducing agent. We have now found that the aforementioned salts do

(1) Chemical reductions of olefins by means of hydrazine (*e.g.*, F. Aylward and M. Sawistowska, *Chem. and Ind.*, 404 (1961), and previous papers) has been shown to be oxygen dependent (*ibid.*, 433 (1961) and by independent observation in this Laboratory). Also, in the acidification of potassium azodicarboxylate (J. Thiele, *Ann.*, **271**, 127 (1892)) nitrogen and hydrazine are formed in addition to carbon dioxide. For this decomposition Thiele suggested diimide as an intermediate which would disproportionate into nitrogen and hydrazine. In the hydrazine reductions it was considered possible that the reaction with olefins was preceded by air oxidation to diimide, the active reducing agent and the possible intermediate in the azodicarboxylic acid decomposition.

(2) Prepared by hydrolysis of azodicarboxamide (Thiele, ref. 1), commercially available from Aldrich Chemical Company, Milwaukee, Wisconsin.

(3) (a) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 6; (b) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958); (c) D. A. Dows, G. C. Pimentel and E. Whittle, *ibid.*, **23**, 1606 (1955).