of the argument favors C_2O if one considers only the major products.

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TUNGSTEN TRIBROMIDE AND TUNGSTEN TETRABROMIDE

Sir:

The preparations of tungsten dibromide,[1,2,3] tungsten pentabromide,[1,4,5,6,7] and tungsten hexabromide[2,7] are well known. However, conspicuous for their absence among the known halides of tungsten are those of tungsten(III). Others[8] have attempted to prepare anhydrous tungsten trihalides but were unsuccessful. We wish to report the preparation of the first simple trihalide of tungsten, tungsten tribromide, and the preparation of tungsten tetrabromide.

Tungsten tribromide was prepared by the reaction between WBr_2 and excess liquid bromine in a sealed tube at 50° for two weeks. On removal of the excess bromine *in vacuo*, a black powder remained. An X-ray diffraction powder pattern of the resulting compound did not indicate the presence of any of the known tungsten bromides. Chemical analyses on several samples of the product indicated the formula WBr_3 (calcd. for WBr_3: W, 43.40; Br, 56.60. Found: W, 43.22 ± 0.07; Br, 56.30 ± 0.56). The preparation of other trihalides of tungsten by similar methods or by using WBr_3 as a starting material is being investigated.

From the available information on the tungsten halides Brewer, *et al.*,[8] estimated that the tungsten trihalides should not be thermally stable compounds. An examination of the effect of heat on WBr_3 confirmed this estimate. At about 80° *in vacuo* decomposition into WBr_2 and bromine became noticeable. The decomposition at this temperature was very slow, but accelerated with increasing temperature. At 300° the decomposition was rapid and complete; only at the latter temperature was a relatively small amount of a volatile higher bromide formed. X-Ray diffraction powder patterns of this volatile fraction showed that the major constituent was WBr_5.

In its inertness to water, concentrated hydrochloric acid, and air WBr_3 closely resembles $MoBr_3$. Attempts to prepare chloride or bromide complexes from WBr_3 and the aqueous hydrogen halides were unsuccessful because of the low solubility of the solid. This apparent low solubility in water and relative stability in air suggests that the solid WBr_3 exists in a polymerized form rather than a form of simple structure. The solid is slightly soluble in some polar organic solvents, *e.g.*, nitroethane, nitrobenzene and acetonitrile, producing wine-red solutions. Molecular weight determinations and identification of the species in these solutions are in progress.

An examination also is being made of the oxidation state of tungsten in WBr_3. The possibility of WBr_3 containing trivalent tungsten is of special interest since the only trivalent tungsten compounds known at the present time are confined to the anion complexes of tungsten(III), *e.g.*, $W_2Cl_9^{3-}$. The latter ion has been shown to have a dimeric structure[9,10] and is considered to be a derivative of the hypothetical dimer W_2Cl_6.

Although the tungsten tetrahalides WF_4, WCl_4, and WI_4 are known, the preparation of WBr_4 has not been reported. This compound was prepared by reducing WBr_5 with tungsten metal. The starting materials were placed in opposite ends of a Vycor tube along which a uniform temperature gradient was maintained: 630° at the tungsten end and 340° at the WBr_5 end. Upon cooling the tube after ten days a crystalline deposit was observed near the center of the tube. Analysis of this deposit indicated a compound having the formula WBr_4 (calcd. for WBr_4: W, 36.52; Br, 63.48. Found: W, 36.63; Br, 63.45). The X-ray diffraction powder pattern of this compound was similar to those[11] of $MoBr_4$, $NbBr_4$, and $TaBr_4$. The available data indicate the existence of an isomorphous series for these tetrabromides.

The magnetic susceptibilities and structural relationships of WBr_3 and WBr_4 with other tri- and tetrahalides of niobium, tantalum, and molybdenum are presently under consideration. In addition, a study is being made on the stability relations among the complete series of tungsten bromides, WBr_2 through WBr_6.

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(10) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(11) R. E. McCarley, P. J. H. Carnell, B. A. Torp and J. C. Boatman, to be published.

(12) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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CHEMISTRY OF THE NEOMYCINS. XI.[1] N.M.R. ASSIGNMENT OF THE GLYCOSIDIC LINKAGES

Sir:

In the accompanying communication[1] the gross structures of neomycins B and C were completed. In the present report the stereochemistry of the ribose-neamine linkage is established by n.m.r. spectroscopy, thus completing the stereochemistry of neomycin C (except for the absolute stereochemistry of the substituted deoxystreptamine)[2]

(1) Paper X in this series: K. L. Rinehart, Jr., M. Hichens, A. D. Argoudelis, W. S. Chilton, H. E. Carter, M. Georgiadis, C. P. Schaffner and R. T. Sebillings, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

and allowing assignment of a suggested stereochemical formula[3] for neomycin B. The formulas of neomycins B and C (I and II, respectively) are given in the accompanying communication.

Assignment of an α- or β-linkage to ribose in neomycins B and C from rotational considerations is difficult, since strict application of Hudson's Rules of Isorotation[5] (as in neamine)[6] is impossible (the model compounds required, methyl α- and β-neobiosaminides containing ribofuranoside moieties, are unavailable) and application of the approximation employed earlier to show an α-linkage between neosamine C and ribose in neobiosamine C[7] gives a rather equivocal assignment, though it favors the β-ribofuranose.

However, the n.m.r. spectra of hexa-N-acetylneomycins B and C[8] allow the definitive assignment of a β-ribofuranoside linkage.[9] In both of these spectra the anomeric ribose proton appears as a singlet ($J \leq 1$ c.p.s.) at -0.50 p.p.m. relative to solvent HOD ($t = 31°$). This negligible coupling is only possible between *trans* protons at C-1 and C-2 (*i.e.*, with a β-configuration at C-1) of the D-ribofuranose ring, since the dihedral angles obtainable ($\leq 30°$) for the *cis* H-C(1)-C(2)-H configuration (*i.e.*, with an α-configuration at C-1) in a nonrigid 5-membered ring theoretically require $J \geq 6$ c.p.s.[10,11] and values actually reported for *cis* H-1, H-2 coupling are $J \geq 4$ c.p.s.[12] For *trans* H-1, H-2 coupling $J \leq 1.0$ c.p.s. has indeed been observed in some (though not in all) β-ribofuranosyl nucleosides.[13]

In addition to demonstrating the β-ribose linkage, n.m.r. spectra (in D_2O) also establish the α-linkage of neosamine B to ribose in neobiosamine B[14] and confirm the α-linkages previously assigned to neosamine C in neamine[6] and neobiosamine C.[7] In the neamine fragment the C-1 anomeric proton of neosamine C appears at -0.66 p.p.m. ($J_{12} = 3.1$ c.p.s., all chemical shifts measured relative to HOD solvent band at $t = 31°$) in N-tetraacetylneamine and at -0.79 p.p.m. ($J_{12} = 3.6$ c.p.s.) and -0.80 p.p.m. ($J_{12} = 3.5$ c.p.s.) in N-hexaacetylneomycins C and B, respectively.[15] In the latter compounds the C-1 anomeric protons of neosamines C and B from the neobiosamine fragments appear at -0.23 p.p.m. ($J_{12} = 2.7$ c.p.s.) and -0.30 p.p.m. ($J_{12} = 1.6$ c.p.s.) in N-hexaacetylneomycins C and B, respectively.[15] These small coupling constants agree well with $H_{1e}H_{2a}$, $H_{1e}H_{2e}$, or $H_{1a}H_{2e}$ configurations,[16] but exclude the $H_{1a}H_{2a}$ configuration required[16] for a β-linkage in light of the known stereochemistry at C-2 of neosamine C and B.[7,17] Thus, an α-configuration[14] ($H_{1e}H_{2a}$) may be assigned to both neosamines in all three disaccharides (neamine, neobiosamines B and C).[15]

We have also investigated the n.m.r. spectra of N-pentaacetylparomomycin.[18] The spectrum in D_2O confirms the previously assigned[19] α-configuration of D-glucosamine in paromamine ($J_{12} = 3.5$ c.p.s., $\delta = -0.82$ p.p.m. relative to HOD, $t = 31°$): more importantly, it assigns conclusively an α-configuration[14] to neosamine B (= paromose[1]; $J_{12} = 1.8$ c.p.s., $\delta = -0.30$ p.p.m.) and a β-configuration to D-ribose ($J_{12} = ca.\ 1.0$ c.p.s., $\delta = -0.57$ p.p.m.). In light of the identity of the deoxystreptamine,[19] D-ribose[20] and neosamine B[1] fragments of the two antibiotics and the presently established like glycosidic linkages, the sole difference between the two antibiotics is the exchange of the 6-amino group of neosamine C in neomycin B for the 6-hydroxyl group of glucosamine in paromomycin. Further confirmation of the near stereoidentity of neomycin B and paromomycin is found in the methyl region of their derivatives' n.m.r. spectra determined in pyridine. In this solvent acetamido methyl groups are well separated[21] and give characteristic patterns, quite different for N-hexaacetylneomycins B and C, but identical for N-hexaacetylneomycin B and N-pentaacetylparomomycin except for the obvious lack of the signal for the N-acetyl group at C-6 of neosamine C in the latter spectrum. Thus, formula PI in the accompanying communication is suggested for paromomycin I.

(2) While deoxystreptamine itself is a *meso* form, substitution in the 1, 3, 4 or 6 position renders the molecule optically active.

(3) Neosamine B has been suggested[1,4] to possess L-idose stereochemistry and this is at present under investigation. Other structural points of neomycin B are identical with those of neomycin C.

(4) K. L. Rinehart, Jr., and A. D. Argoudelis, *inter alia*, (a) Abstracts of the 17th National Organic Symposium, Bloomington, Indiana, June 25–29, 1961, p. 96; and (b) Abstracts of the 1st Interscience Conference on Antimicrobial Agents and Chemotherapy, New York, Oct. 31–Nov. 2, 1961.

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(6) H. E. Carter, J. R. Dyer, P. D. Shaw, K. L. Rinehart, Jr., and M. Hichens, *J. Am. Chem. Soc.*, **83**, 3723 (1961).

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(12) R. J. Abraham and K. A. McLauchlan, *J. Mol. Phys.*, **5**, 192 (1962).

(13) C. D. Jardetzky, *J. Am. Chem. Soc.*, **84**, 62 (1962).

(14) For consistency this is referred to here as an α-configuration, though Hudson[5] defined an α-form in the L-sugar series as that which had the more negative rotation.

(15) In other derivatives the C-1 anomeric proton of neosamine C has these chemical shifts (relative to solvent HOD, $t = 33°$) and coupling constants (J_{12}): neamine base, -0.57 p.p.m. (3.0 c.p.s.); N-octamethylneamine hydrochloride, -1.67 p.p.m. (3.5 c.p.s.); neobiosaminol C hydrochloride, -0.80 p.p.m. (2.7 c.p.s.). For comparison, the C-1 anomeric proton of α-D-glucosamine hydrochloride appears at -0.78 p.p.m. ($J_{12} = 3.5$ c.p.s.), of β-D-glucosamine hydrochloride at -0.27 p.p.m. ($J_{12} = 8.5$ c.p.s.), of N-acetyl-α-D-glucosamine at -0.48 p.p.m. ($J_{12} = 2.6$ c.p.s.), and of N-acetyl-β-D-glucosamine at *ca.* $+0.05$ p.p.m. (largely obscured by water).

(16) R. U. Lemieux, R. K. Kullnig and R. Y. Moir, *J. Am. Chem. Soc.*, **80**, 2237 (1958); *cf.* also J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 397.

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

(18) T. H. Haskell, J. C. French and Q. R. Bartz, *ibid.*, **81**, 3482 (1959). The present sample was prepared by acetylation of commercial paromomycin.

(19) T. H. Haskell, J. C. French and Q. R. Bartz, *ibid.*, **81**, 3480 (1959).

(20) T. H. Haskell, J. C. French and Q. R. Bartz, *ibid.*, **81**, 3481 (1959).

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(22) National Science Foundation Predoctoral Fellow.

Further work is in progress on the stereochemistry of the deoxystreptamine and neosamine B fragments.

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THE PREPARATION OF A NEW BORON HYDRIDE $B_{18}H_{22}$

Sir:

We wish to report the synthesis of a new boron hydride which probably contains more boron atoms per molecule than any boron hydride yet isolated in quantity. At the present time we prefer the formulation $B_{18}H_{22}$ for this hydride although the difficulty in obtaining precise hydrogen analyses in a molecule of this size makes the hydrogen content questionable. A complete structural analysis is currently underway in the laboratory of Prof. William N. Lipscomb.

The oxidation of the $B_{10}H_{10}^{-2}$ ion[1-5] with aqueous ferric chloride has been reported[6] to produce an ion, $B_{20}H_{18}^{-2}$ (m.p. triethylammonium salt, 173–174°, I). An ethanolic solution of I was passed through an acidic ion exchange resin and the resulting solution was concentrated to a yellow syrup at steam bath temperature in the air or under reduced pressure in a vacuum system. The addition of water to a diethyl ether solution of the concentrate results in rapid hydrolysis accompanied by the evolution of hydrogen. The hydride was obtained by evaporation of the solvent followed by recrystallization from cyclohexane and sublimation. Yields of up to 60% have been obtained. Preliminary work indicates that a least one other new hydride is also produced. The purified hydride is stable in the air and melts at 177–178.5° without decomposition. *Anal.* Calcd. for $B_{18}H_{22}$: B, 89.95; H, 10.15. Found. B, 89.11; H, 10.44. A more precise analysis for hydrogen was carried out by the thermal decomposition of a weighed sample to the elements at 900°[7] (mole H_2 calcd. for $B_{18}H_{22}$, 2.18×10^{-3}. Found. 2.21×10^{-3}). Ebullioscopic molecular weights averaged 212.7 (calcd., 216.8). Titration with aqueous hydroxide ion revealed that the presumed $B_{18}H_{22}$ was a strong monoprotic acid (equiv. wt. 219.5). Unit cell dimensions and an accurate density determination[8] fixes the molecular weight at 216 ± 1. This value confirms the B_{18} formulation. The derived anion is bright yellow in color and has been separated as the triethylammonium and tetramethylammonium salts.

The infrared spectrum of the hydride exhibits an intense terminal B–H stretching band at 2850 cm.$^{-1}$ and shows B–H–B bridge absorption at 1950 cm.$^{-1}$. Extremely complex skeletal absorptions are present at longer wave lengths, a fact which suggests low symmetry in the hydride. Solutions of the hydride in hydrocarbon solvents exhibit a purple fluorescence. Three ultraviolet absorptions are observed: $(\lambda_{max}^{m\mu})_1/\epsilon_{max})$ 332/6,560; 273.5/3,560 and 217/15,900. The anion derived from the hydride has two major absorption bands in the ultraviolet: 352/5,950 and 216/11,600.

The B^{11} nuclear magnetic resonance spectrum of the hydride is complex and has not been resolved. Further work is in progress.

Acknowledgment.—The authors are indebted to Prof. William N. Lipscomb for information regarding the $B_{20}H_{18}^{-2}$ ion received prior to publication and the X-ray molecular weight value reported herein. This investigation was supported by Army Ordnance Contract No. DA-01-021-ORD-11878 with the Rohm and Haas Company.

(8) Private communication of results obtained by P. G. Simpson, R. Lewin and W. N. Lipscomb.

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CHEMISTRY OF THE NEOMYCINS. X.[1] NEOMYCINS B AND C

Sir:

Structures of the fragments of neomycins B and C—the unitary deoxystreptamine,[1,2,3] neosamine C,[4,5] neosamine B (incomplete stereochemistry),[6] and D-ribose[7]; the binary neamine[1] and neobiosamine B[6,8]—have been established in earlier investigations, and the stereochemistry of neosamine

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(7) J. Graff and D. Rittenberg, *Anal. Chem.*, **24**, 878 (1952).

(1) Paper IX: H. E. Carter, J. R. Dyer, P. D. Shaw, K. L. Rinehart, Jr., and M. Hichens, *J. Am. Chem. Soc.*, **83**, 3723 (1961).

(2) A. Kuehl, M. N. Bishop and K. Folkers, *ibid.*, **73**, 881 (1951).

(3) Professor R. U. Lemieux (personal communication) recently has confirmed by n.m.r. studies the all-*trans* stereochemistry[1] of deoxystreptamine.

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

(7) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, *ibid.*, **79** 4568 (1957).

(8) Earlier[4] the linkage between neosamine C and D-ribose was assigned to the C-2 carbon atom of ribose, from the 2-mole periodate uptake of methyl N,N,-dibenzoylneobiosaminide C. As is demonstrated in the present communication, the C-2 assignment was in error, for reasons not yet clear; it will be discussed in the full paper.