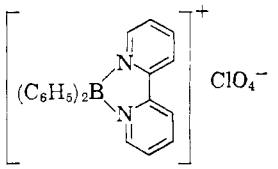
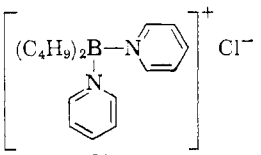
4.65; Cl, 10.23; N, 8.08. Found: C, 55.70; H, 4.86; Cl, 10.70; N, 7.79. Contrary to results obtained with simpler types of amine borane complexes, the amine moiety of III cannot be titrated with perchloric acid in non-aqueous solvents.

While there is almost certainly no true boronium ion intermediate involved in the reaction leading to II, Davidson and French[3] have provided evidence for the existence of boronium ions under other conditions. From conductance and spectrophotometric studies they conclude that diphenylboronium ions are produced by the action of silver perchlorate (or aluminum chloride) on diphenylchloroborane in polar solvent. Subsequently, these workers found that the addition of α,α'-bipyridine to such a solution leads to the formation of a stable perchlorate salt to which they assigned the structure IV.[4] We wish to suggest that the 2:1 complex which pyridine is reported[5] to form with dibutylchloroborane may reasonably be a chloride salt having the structure V.



IV



V

From the findings presented above and from other reports,[6] it is evident that bisamine complexes of boronium ions are formed under a variety of conditions, and it seems justifiable to conclude that such ions represent a very stable type of structure.

Preliminary investigation indicates that iodine also reacts with pyridine borane and pyridine to form a complex salt analogous to II.

(3) J. M. Davidson and C. M. French, *J. Chem. Soc.*, 114 (1958).
(4) J. M. Davidson and C. M. French, *Chem. and Ind.*, 750 (1959).
(5) I. W. Gerrard, M. F. Lappert and R. Shafferman, *J. Chem. Soc.*, 3828 (1957).
(6) (a) R. W. Parry and co-workers, *J. Am. Chem. Soc.*, **80**, 4 (1958), *et seq.*; (b) H. C. Kelly and J. O. Edwards, *ibid.*, **82**, 4842 (1960); (c) J. Goubeau and H. Schneider, *Chem. Ber.*, **94**, 816 (1961).

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INTRODUCTION OF A NEW HETERO ATOM INTO A SUGAR RING[1]

Sir:

We wish to report the first preparation of a sugar structure with an atom other than oxygen in the sugar ring. Specifically we have prepared an analog of methyl α-D-xylopyranoside wherein sulfur replaces the normal ring oxygen. The compound is thus methyl α-D-xylothiapyranoside or methyl 5-deoxy-5-mercapto-α-D-xylopyranoside. The preparation is part of our program to substitute sulfur and nitrogen for the ring oxygen in a number of sugars and sugar derivatives. The compounds are of both chemical and biochemical interest as sugar analogs and as antimetabolites of possible value in medical chemistry. The following methods of synthesis and structure determination of methyl α-D-xylothiapyranoside were used.

1,2-*O*-Isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-xylofuranose[2] was treated with the sodium salt of benzyl mercaptan in ethanol to form 1,2-*O*-isopropylidene-5-deoxy-5-thiobenzyl-α-D-xylofuranose, m.p. 103°, $[\alpha]^{25}D$ −64.2° (*c* 1.24, methanol). *Anal.* Calcd. for $C_{15}H_{20}O_4S$: C, 60.81; H, 6.76; S, 10.81. Found: C, 60.78; H, 6.74; S, 11.03.

Removal of the benzyl group with sodium in liquid ammonia[3] gave 1,2-*O*-isopropylidene-5-deoxy-5-mercapto-α-D-xylofuranose, m.p. 85°, $[\alpha]^{25}D$ −40.4° (*c* 1.22, methanol). *Anal.* Calcd. for $C_8H_{14}O_4S$: C, 46.62; H, 6.79; S, 15.53. Found: C, 46.68; H, 6.98; S, 15.61. Titration with iodine in acid solution[4] indicated that 98% of the thiol groups were free.

When 1,2-*O*-isopropylidene-5-deoxy-5-mercapto-α-D-xylofuranose was refluxed for 1 hour in 1% methanolic hydrogen chloride the thiol activity disappeared. The isopropylidene group was hydrolyzed and the methyl glycoside of 5-deoxy-5-mercapto-D-xylose was formed. Hydrochloric acid was removed by adsorption on Dowex-1(OH). Concentration of the effluent gave a sirup which crystallized. The product was recrystallized from ethyl acetate and then from ethanol, m.p. 113°, $[\alpha]^{25}D$ +332° (*c* 1.14, water). *Anal.* Calcd. for $C_6H_{12}O_4S$: C, 40.00; H, 6.66; S, 17.77; OCH_3, 17.22; mol. wt., 180. Found: C, 39.92; H, 6.49; S, 17.54; OCH_3, 16.42; Rast molecular weight, 189. The compound showed no thiol activity when tested with acidic iodine solution. When the methyl glycoside was heated at 80° in *N* sulfuric acid for 0.75 hr. the specific rotation decreased to +197°, confirming that the glycoside had the alpha configuration.

Methyl α-D-xylothiapyranoside consumed large amounts of periodate probably because of oxidation of the ring sulfur. However, one mole of formic acid was produced per mole of glycoside as would be expected if the sugar ring were six membered. The formic acid was identified by steam distillation and reduction with magnesium to formaldehyde which yielded the characteristic dimedon adduct, m.p. 189°.[5]

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(1) Journal Paper No. 1852 of the Purdue University Agricultural Experiment Station, Lafayette, Indiana.
(2) P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **102**, 317 (1933).
(3) N. C. Jamieson and P. K. Brown, *Can. J. Chem.*, **39**, 1765 (1961).
(4) R. M. Evans and L. N. Owen, *J. Chem. Soc.*, 244 (1949).
(5) R. E. Reeves, *J. Am. Chem. Soc.*, **63**, 1476 (1941).