these bands are most intense in fresh solutions; changes that occur in solution (see below) result in loss of these absorptions, (2) identical bands are produced when tropenium fluoroborate is treated with tetramethylammonium bromide or iodide in methylene chloride,[12] (3) a plot of ν in cm.$^{-1}$ against the ionization potential of the halide ions[15] gives a straight line, (4) the separation of the two bands of the tropenium iodide complex is in agreement with that expected[16] for the different electron affinities of the $P_{3/2}$ and $P_{1/2}$ states of iodine atom as observed in other[16,17] charge-transfer complexes of halide ion, (5) X-ray data[18] on solid tropenium iodide gives evidence for a weak charge-transfer bond between the iodide ion and the tropenium ion, which might be expected to persist in ion-pairs.

Solutions of the halides in methylene chloride are not stable unless rigorously protected from the atmosphere; decomposition begins with slight exposure. We find that this is due to preliminary hydrolysis of tropenium halide to tropenyl alcohol and hydrogen halide, followed by (1) hydride abstraction from tropenyl alcohol by tropenium to give cycloheptatriene and tropone (*i.e.*, hydroxytropenium),[19] and/or (2) oxidation of hydrogen halide to halogen[20] (as trihalide ion) followed by attack of halogen on tropenyl alcohol to cause an oxidative rearrangement to benzaldehyde.[21] Results of decomposition studies in dilute methylene chloride solution:[22] ((sample): (a) % recovered tropenium ion, (b) % tropone, (c) % cycloheptatriene, (d) % benzaldehyde, (e) % total recovered C_7 species, (f) % total recovered C_7 species if tropone assumed equal to cycloheptatriene) (tropenium chloride with one drop water): (a) 29.8, (b) 23.8, (c) 33.9, (d) 0, (e) 87.5, (f) 97.6; (tropenium bromide with one drop water): (a) 38.3, (b) 19.4, (c) 29.5, (d) 2.19, (e) 89.4, (f) 99.5; (tropenium bromide one week in glass stoppered flask): (a) 33.4, (b) 11.6, (c) 12.2, (d) 7.18, (e) 63.4, (f) 65.0; (tropenium iodide one week in glass stoppered flask: (a) 40.4, (b) 6.90, (c) not measured, (d) 33.9, (e) 81.4, (f) 88.2 (tropenium fluoroborate 48 hours with trace water): (a) 58, (b) 13, (c) 15, (d) 0, (e) 86, (f) 88. These results indicate that with the chloride and fluoroborate reaction (1) occurs, that reaction (2) predominates with the iodide, and that both are operative with the bromide.

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value of 150 mhos in acetonitrile at this concentration found by Dauben and Gadecki.[11]

[11] F. A. Gadecki, Ph. D. Thesis, University of Washington, 1957.

[12] Conversion in this process does not exceed 10%; if halide does replace fluoroborate in ion-pairs to any great extent the entity formed differs from that dissolved away from a halide crystal, perhaps by inclusion of solvent. Winstein[3] reports that addition of tetrabutylammonium bromide to tropenium fluoroborate in ethylene dichloride gives tribromide ion. We find that tetramethylammonium bromide alone in methylene chloride gives tribromide ion on standing; however, tribromide ion is not responsible for the 402 mμ band of tropenium bromide. Solutions of tropenium tribromide[13] in methylene chloride show no bands in the visible.

[13] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2026 (1956), first reported the preparation of tropenium tribromide but did not recognize it as a tribromide salt. Its characterization is reported by Dauben and Harmon.[2c,14]

[14] H. J. Dauben, Jr., and K. M. Harmon, Abstracts, Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., Oct. 25, 1958.

[15] L. Helmholz and J. E. Mayer, *J. Chem. Phys.*, **2**, 245 (1934).

[16] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

[17] R. Platzmann and J. Franck, *Z. Physik*, **138**, 411 (1954).

[18] A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izvest. Akad. Nauk, S. S. S. R., Otdel Khim. Nauk*, **1**, 32 (1960).

[19] Such hydride transfer has been reported by T. Ikemi, T. Nozoe and H. Sugiyama, *Chemistry and Industry*, 932 (1960).

[20] The production of halogen by homolysis of tropenium halide cannot be excluded, but seems unlikely in light of the stability of the halides in the absence of moisture.

[21] The rearrangement of tropenium derivatives to benzaldehyde by halogen was first reported by Dewar and Pettit[13] and has been investigated in detail by Dauben and Harmon.[2c,14]

[22] Decomposed solutions were analyzed by differential extraction followed by quantitative ultraviolet spectral analysis. Yields are based on the total original sample.

[22] (a) National Science Foundation Scholar, 1961; (b) National Science Foundation Scholar, 1960; (c) American Chemical Society—Petroleum Research Fund Scholar, 1961.

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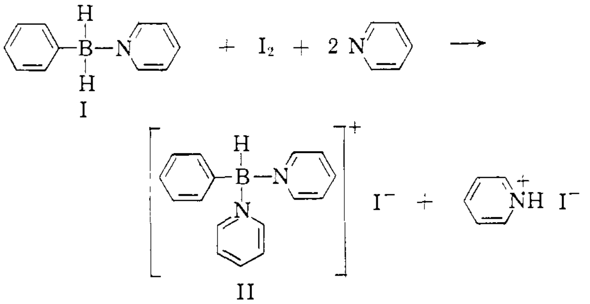
RECEIVED OCTOBER 16, 1961

BISAMINE COMPLEXES OF BORONIUM IONS. THE REACTION OF IODINE WITH PYRIDINE PHENYLBORANE

Sir:

Hawthorne has reported that iodine reacts with pyridine phenylborane (I) in an aqueous medium to produce benzeneboronic acid.[1] We wish to report that in chloroform solution in the presence of excess pyridine I reacts with iodine to form, in addition to pyridinium iodide, a boron-containing iodide salt for which structure II is proposed.



The cation of II formally may be considered to be the bispyridine complex of the phenylboronium ion.[2]

Compound II, a white crystalline solid when freshly recrystallized from chloroform–pentane (m.p. (dec.) 199–202°), turns yellow rapidly in air. *Anal.* Calcd. for $C_{16}H_{16}BIN_2$: C, 51.36; H, 4.28; I, 33.9; N, 7.49. Found: C, 51.55; H, 4.26; I, 35.4; N, 7.29. Infrared spectrum (in $CHCl_3$): 4.12 μ (B–H stretching); BH_2 bending mode absorption found in I at 8.63 μ is absent in II.

Iodine fails to react with II (except for the formation of triiodide ion) indicating that the hydrogen bonded to boron is not hydridic.

In a chloroform slurry, II undergoes rapid metathesis with silver perchlorate to afford the corresponding perchlorate (III). The fine white needles (recrystallized from acetone–chloroform, m.p. (dec.) 182–184°) appear to be stable in air. *Anal.* Calcd. for $C_{16}H_{16}BClN_2O_4$: C, 55.45; H,

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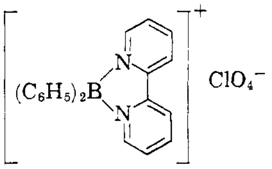
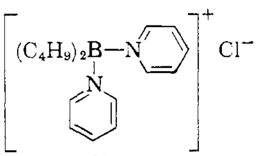
[1] M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 4291 (1958).

[2] The nomenclature of inorganic complex ions appears to offer the only unambiguous name for II, namely, phenylhydridobis-(pyridine)boron(III) iodide.

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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RECEIVED NOVEMBER 6, 1961

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°, $[\alpha]^{25}\text{D}$ −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°, $[\alpha]^{25}\text{D}$ −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°, $[\alpha]^{25}\text{D}$ +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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RECEIVED DECEMBER 2, 1961

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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).