B-strain may become important when groups much larger than methyl are attached to the central atom because both the angles of distortion and the angle force constant will increase.

## Summary

1. It is shown, by a semi-quantitative calculation, that the B-strain postulated by H. C. Brown is too small to account for the observed weakness of trimethylamine as an acid.
2. A comparison of ordinary steric forces (F-strain) in hydrocarbons of related structure shows that the steric strains in trimethylboron-alkyl amine compounds are probably of the same nature as those in the hydrocarbons.
3. The importance of the reference acid in establishing basic strengths is re-emphasized.
4. It is pointed out that B-strain will be base-strengthening rather than base-weakening when the angles are less than tetrahedral.

CORVALLIS, OREGON
BERKELEY, CALIFORNIA RECEIVED FEBRUARY 7, 1947

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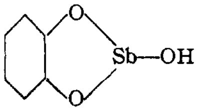
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

# Antimonylcatechol. I. Coördination of Simple Amines and Alcohols

BY L. M. WHEELER AND C. K. BANKS

The combination of inorganic, trivalent antimony with phenols and $\alpha$-hydroxyacids has long been known, but only a few derivatives with alcohols have been reported[1] and these compounds are unstable in the presence of water. Since antimonylcatechol[2] (I) appeared to be of interest in the treatment of filariasis,[3] efforts were made to solubilize this compound. It is insoluble in water, aqueous ammonia, alcohol, ether, chloroform and other solvents and dissolves only in strong sodium hydroxide and concentrated hydrochloric acid. However, it was noted that in the presence of both an alcohol and an amine, antimonylcatechol readily formed solutions from which crystalline products could be isolated. Both the alcohol and the amine were combined, in some fashion, with the antimonylcatechol in the isolated products. That such combinations were not fortuitous was readily demonstrated. The ratios of combination were always the same regardless of the reactants and experiments showed that no combination occurred in aqueous solution when only the alcohol or the amine was present.



I

The atomic ratio of antimony to nitrogen was always one within experimental limits. The products dissolved readily in water to give nearly neutral solutions which could be decomposed with strong acids to yield antimonylcatechol, the alcohol and the amine salt. When both the alcohol and amine were low-boiling, prolonged heating at 100° in a high vacuum resulted in the loss of these fragments, leaving antimonylcatechol. Preparations containing ammonia or other volatile amines would lose the nitrogenous constituent during prolonged shelf storage, resulting in decreased solubility and altered crystalline properties. If the amines were relatively non-volatile, the products were stable to heat and storage.

Solutions of these compounds in water appeared to undergo hydrolysis on standing and a hydrated form of antimonylcatechol was separated. An excess of any amine would stabilize the solutions indefinitely. Aqueous solutions appeared to have all the properties of salt solutions, particularly in that they were excellent conductors of electricity, showing about forty per cent. the conductance of equimolar sodium chloride solutions.

Determinations of carbon and hydrogen in the presence of antimony were extremely variable, but both antimony and nitrogen were readily determined. To further elucidate the structures, inductive postulations were necessary.

The alcohols used were methanol, propanol, glycols, glycerol, sorbitol, mannitol, dextrose, galactose and levulose. The amines studied consisted of ammonia, diethyl- and triethylamine. The properties of the resulting products are given in Table I.

The reaction product of antimonylcatechol and tartaric acid[4] was also investigated. When equimolar amounts of the two substances were heated in water containing a four-fold excess of sodium bicarbonate, a product similar in every respect to the alcohol–amine complexes was formed.

## Experimental

**Alcohol–Amine–Antimonylcatechol Complexes.**—Antimonylcatechol (0.2 mole) was suspended in 100 ml. of water in which had been dissolved 0.2 mole of the alcohol and 0.5 mole of amine in a 500-ml. round-bottomed flask equipped with stirrer and condenser. The temperature of the vigorously stirred solution was raised to 80–90° and was maintained at this temperature for fifteen minutes after complete solution occurred. The hot solutions were filtered rapidly and cooled. The products crystallized on cooling or on adding acetone to the cold solution. They were recrystallized from hot water, methanol or

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(1) Meerwein, *Ann.*, **476**, 113 (1929).

(2) Causse, *Bull. soc. chim.* [3] **8**, 245 (1892).

(3) Feinberg, U. S. Patent 2,330,962, Oct., 1943.

(4) U. S. Patent 1,688,964.

TABLE I

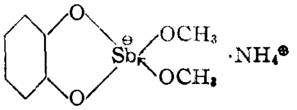
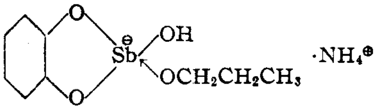
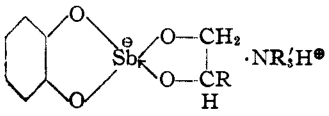
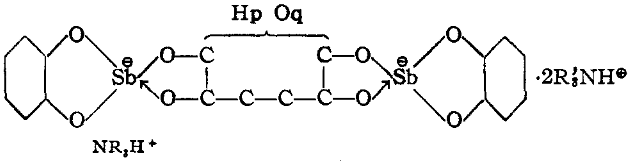
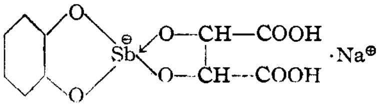
ANTIMONYLCATECHOL COÖRDINATE COMPOUNDS

| Alcohol | Amine | Recrystallization solvent | M. p., °C. | Assay,[a] % Antimony[b] | Assay,[a] % Nitrogen[c] | Atomic ratio Sb/N |
|---|---|---|---|---|---|---|
| Methanol | $NH_3$ | Methanol | 273 | 33.63 | 3.81 | 1.02 |
| Propanol | $NH_3$ | Water | 274 | 35.14 | 4.05 | 1.00 |
| Ethylene glycol | $NH_3$ | Water | 275 | 35.07 | 4.05 | 1.00 |
| Propylene glycol | $NH_3$ | Water | 269 | 34.17 | 3.92 | 1.00 |
| Glycerol | $NH_3$ | Water | 238 | 32.40 | 3.96 | 0.94 |
| Mannitol | $NH_3$ | Water | 272 | 34.75 | 4.02 | 1.00 |
| Glycerol | $(C_2H_5)_2NH$ | Water | 86–90 | 25.94 | 3.01 | 0.99 |
| Sorbitol | $(C_2H_5)_2NH$ | Water | 170 | 28.44 | 3.29 | 1.00 |
| Mannitol | $(C_2H_5)_2NH$ | Water–acetone | 114 | 28.44 | | |
| Dextrose | $(C_2H_5)_2NH$ | Water–acetone | 106 | 28.31 | | |
| Galactose | $(C_2H_5)_2NH$ | Water | 106 | 28.72 | 3.04 | 1.09 |
| Levulose | $(C_2H_5)_2NH$ | Water | 106 | 28.93 | 3.23 | 1.03 |
| Mannitol | $(C_2H_5)_3N$ | Water | 90 | 28.92 | 3.09 | 1.08 |
| Dextrose | $(C_2H_5)_3N$ | Water | 90 | 28.98 | 3.28 | 1.02 |

[a] Analytical results are due to A. W. Spang, Margaret McCarthy Ledyard and Elizabeth Selvig. [b] Modification of the arsenic method of Cislak and Hamilton, THIS JOURNAL, 52, 638 (1930). [c] Micro-Kjeldahl method.

TABLE II

STRUCTURAL COMPARISONS

| Postulated structure | | | | | Molecular weight | | | Composition, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | From assays | | Antimony | | Nitrogen | |
| | | | | $n H_2O$ | Formula | Sb | N | Calcd. | Found | Calcd. | Found |
|  | | | | 3 | 364 | 362 | 368 | 33.45 | 33.63 | 3.85 | 3.81 |
|  | | | | 1 | 342 | 347 | 346 | 35.60 | 35.14 | 4.00 | 4.05 |
|  | | | | | | | | | | | |
| R | | From | $NR_3'H^+$ | | | | | | | | |
| —H | | Ethylene Glycol | $NH_4^+$ | 2 | 344 | 347 | 346 | 35.40 | 35.07 | 4.07 | 4.05 |
| $—CH_3$ | | Propylene Glycol | $NH_4^+$ | 2 | 358 | 356 | 357 | 34.01 | 34.17 | 3.91 | 3.92 |
| $—CH_2OH$ | | Glycerol | $NH_4^+$ | 2 | 374 | 376 | 354 | 32.56 | 32.40 | 3.75 | 3.96 |
| $—CH_2OH$ | | Glycerol | $N(C_2H_5)_2H_2^+$ | 4 | 466 | 470 | 465 | 26.18 | 25.94 | 3.01 | 3.01 |
|  | | | | | | | | | | | |
| p | q | From | $NR_3H^+$ | | | | | | | | |
| 10 | 2 | Sorbitol | $N(C_2H_5)_2H_2^+$ | 4 | 858 | 856 | 852 | 28.34 | 28.44 | 4.26 | 3.29 |
| 10 | 2 | Mannitol | $N(C_2H_5)_2H_2^+$ | 4 | 858 | 856 | | 28.34 | 28.44 | | |
| 10 | 2 | Mannitol | $NH_4^+$ | 2 | 710 | 701 | 697 | 34.30 | 34.75 | 3.94 | 4.02 |
| 10 | 2 | Mannitol | $N(C_2H_5)_3H^+$ | 0 | 842 | 842 | 907 | 28.92 | 28.92 | 3.33 | 3.09 |
| 8 | 2 | Dextrose | $N(C_2H_5)_2H_2^+$ | 4 | 856 | 860 | | 28.44 | 28.31 | | |
| 8 | 2 | Galactose | $N(C_2H_5)_2H_2^+$ | 4 | 856 | 848 | 922 | 28.44 | 28.72 | 3.27 | 3.04 |
| 8 | 2 | Levulose | $N(C_2H_5)_2H_2^+$ | 4 | 856 | 842 | 922 | 28.44 | 28.93 | 3.27 | 3.04 |
| 8 | 2 | Dextrose | $N(C_2H_5)_3H^+$ | 0 | 840 | 840 | 854 | 28.98 | 28.98 | 3.33 | 3.28 |
|  | | | | 0 | 401 | 402 | | 30.36 | 29.92 | | |

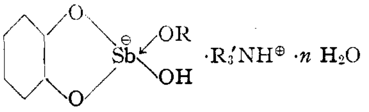
acetone–water mixtures. The properties of the compounds are listed in Table I.

**Sodium Antimonyltartratecatechol.**—Tartaric acid (16 g.) and sodium bicarbonate (32 g.) were dissolved in 180 ml. of water and heated to 80°. Antimonylcatechol (27.6 g.) was added slowly. After the reaction was completed, the solution was filtered hot and cooled. The product crystallized on standing and was recrystallized from water.

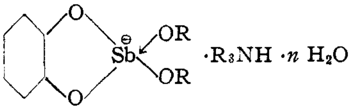
*Anal.* Found: Sb, 29.91, 29.92.

### Discussion of Structure

The structure of antimonyl compounds has not been investigated extensively. Doak[5] has shown that arylstibonic acids and their salts conform to a coördinate ion structure which may be represented as $RSb(OH)_5^- \cdot M^+$ in which antimony exhibits a coördination number of six. Similarly, it was suggested in previous work that some benzenearsonous acids are best represented as $RAs(OH)_3^- \cdot H^+$ where arsenic has a coördination number of four.[6] Triethoxystibine in ethanol forms the ion $(C_2H_5O)_4Sb^-$ which has strong acid properties[1] and the antimony-bis-catecholates have been postulated by Bodendorf[7] to have a coördinate ion structure. By analogy, these compounds might have structures II or III.

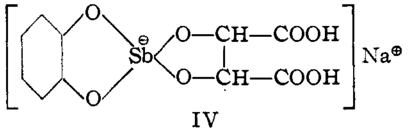


II



III

The strict one-to-one ratio of antimony to nitrogen, the water solubility, ionic type of conductance, all favor such a structural interpretation. Furthermore, the tartaric acid–antimonylcatechol complex (IV), can be explained by a similar postulation.



IV

A comparison of the experimental data with the postulated structures is given in Table II.

While these structures appear to satisfactorily explain the antimonylcatechols and related compounds, all postulations as to the structures of the antimony derivatives of tartaric, citric and malic acids are inadequate to explain the large number of variations obtained. While previous work has suggested that the compounds form complex ions, it is possible that reëxamination of the data in the light of the requirements for coördinate structures may elucidate the nature of the chemical linkages.

### Summary

1. Antimonylcatechol was found to react with alcohols and amines to form antimonylcatechol–alcohol–amine complexes having the properties of salts. Fourteen such compounds involving various alcohols and amines are reported.

2. The compounds are best explained as amine salts of an antimonylcatechol coördinate acid.

DETROIT, MICHIGAN RECEIVED AUGUST 18, 1947

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[5] G. O. Doak, THIS JOURNAL, **68**, 1991 (1946).

[6] C. K. Banks, *et al.*, *ibid.*, **69**, 5 (1947).

[7] K. Bodendorf, *Pharm. Press.* (Vienna), **38**, 8 (1933).

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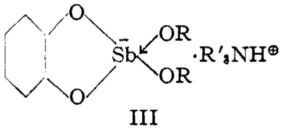
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

# Antimonylcatechol. II. Coördinates with Aminoalcohols

BY L. M. WHEELER AND C. K. BANKS

In the previous paper of this series[1] it was shown that antimonylcatechol would react with alcohols in the presence of amines to form compounds which could be represented by formula III. It was considered of interest to determine if aminoalcohols would also form similar compounds, and under what specific conditions.



III

Antimonylcatechol was dissolved by aqueous solutions of amino-alcohols when the aminoalcohol was in molecular excess.[2] It was frequently difficult to isolate the products directly from such reaction mixtures. They were easily isolated, however, when antimonylcatechol and the aminoalcohol reacted in aqueous suspension in the presence of an excess of ammonia or diethylamine. The product appeared to be independent of the amine used to catalyze the reaction. When the ratios of reactants were varied, the isolated products were more complex and appeared to incorporate a portion of the catalytic amine.

The products resulting from equimolar reaction were stable as solids and dissolved in water to give solutions which hydrolyzed slowly on standing. An excess of any amine appeared to prevent this hydrolysis. Like the products derived from amines and alcohols, the compounds appeared to have the properties of salts. When two moles of antimonylcatechol reacted with one of a poly-

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[1] Wheeler and Banks, THIS JOURNAL, **70**, 1264 (1948).

[2] J. G. Feinberg, U. S. Patent 2,330,962, Oct., 1943.