504. *Hydrazine. Part IV.* The Bromostannates and Bromostannites of Hydrazine, Dimethyl Ketazine, and Pentan-3-one Hydrazone.*

By W. Pugh.

(*With Notes on the Optical Properties of the Crystals.* By H. C. G. Vincent.)

Dihydrazinium hexabromostannate, hydrazinium tribromostannite, and dihydrazinium tetrabromostannite have been prepared. These salts, or mixtures of tin bromides and hydrazine hydrobromide, yield on treatment with acetone and diethyl ketone the bromostannates and bromostannites of dimethyl ketazine and pentan-3-one hydrazone respectively.

DIHYDRAZINIUM CHLOROSTANNATE has been described recently (Part I, *J.*, 1952, 4138) and shown to form compounds with aliphatic ketones. These compounds were at first reported as ketone addition compounds, but were subsequently (Part II, *J.*, 1953, 354) shown to be chlorostannates of dimethyl ketazine and of certain hydrazones acting as bases. No salts of such bases had hitherto been described.

Similar bromostannates and bromostannites have now been prepared from mixtures of the tin bromides and hydrazine hydrobromide, in aqueous solution (hydrazine salts), and in acetone–water and diethyl ketone–water mixtures respectively (ketazinium and hydrazonium salts). Mixtures of the simple salts also dissolved in ethyl methyl and di-*n*-propyl ketones, forming viscous solutions, but these could not be induced to crystallise, even after several months at −10°. It was noted that the chlorostannates (Part II, *loc. cit.*) also separated with increasing difficulty from these same ketones.

Like the corresponding chlorostannates, these ketazinium and hydrazonium salts hydrolyse completely in acid solution, forming hydrazinium ions and free ketone. It was thus possible to estimate the hydrazine formed by Andrews's method. The figures quoted for nitrogen in the Experimental section were obtained in this way. In one case, also, the acetone was distilled and estimated by Messinger's method (Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39; Cassar, *Ind. Eng. Chem.*, 1927, **19**, 1061).

EXPERIMENTAL

Dihydrazinium Hexabromostannate.—Tin foil (3 g.) was added in small pieces to an excess of well-cooled bromine and, after the addition of hydrobromic acid (48%; 6 c.c.) and water (4 c.c.), the excess of bromine was removed by boiling. Hydrazine hydrate (28%; 8 c.c.) was then added and the clear yellow solution was crystallised over sodium hydroxide. Successive crops, dried on filter-papers and *in vacuo*, had identical composition and were free from contamination with hydrazine hydrobromide (compare the preparation of the chlorostannate, Part II, *loc. cit.*) [Found: N_2H_4, 9·6; Br, 72·0; Sn, 17·9. $(N_2H_5)_2SnBr_6$ requires N_2H_4, 9·6; Br, 72·2; Sn, 17·9%]. The same *salt* was obtained, after long storage, from the mother-liquors of the crystallisation of the ketazinium bromostannate described below.

The crystals are orthorhombic, being yellow rectangular plates (colourless in microscope

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* Part III, *J.*, 1953, 1934.

mounts) without pronounced cleavage. The optic axial plane is parallel to the surface of the plates, with $Bx^{\alpha}(\gamma)$ parallel to the elongation, the plates giving an optic normal figure. They are optically positive, with small $2V$ of about 20°. Dispersion is fairly strong, red > violet. Elongation is positive. Refractive index of (*a*) is considerably above 1·84 and beyond the range of suitable immersion liquids. Double refraction is also extreme.

The salt deliquesces in damp weather only, and it decomposes on heating, with partial sublimation. It is insoluble in ether, benzene, chloroform, carbon tetrachloride, and light petroleum, but very soluble in water. Concentrated aqueous solutions remain clear when kept, but dilution causes precipitation of gelatinous tin hydroxide. The salt reacts with and dissolves in the simple aliphatic ketones, forming ketazinum and hydrazonium bromostannates.

Bis(dimethyl Ketazinium) Hexabromostannate.—A solution of stannic bromide and hydrazine monohydrobromide in aqueous hydrobromic acid, prepared from tin (3 g.) as described above, was treated with twice its volume of acetone. Much heat was liberated and the clear yellow solution slowly deposited yellow rhombs which, after being recrystallised from acetone–water (4 : 1) and dried *in vacuo*, had m. p. 138—139° [Found: C, 17·4; H, 3·2; N, 6·8; Br, 58·0; Sn, 14·5. $(C_6H_{13}N_2)_2SnBr_6$ requires C, 17·5; H, 3·2; N, 6·8; Br, 58·2; Sn, 14·5%]. The same *salt* was obtained by adding acetone to the mother-liquors from the crystallisation of dihydrazinium hexabromostannate.

The crystals are orthorhombic or monoclinic, with ill-defined platy habit. There is no cleavage or twinning apparent and the optic axial plane is probably parallel with the plates. Optically positive. $2V^{\gamma} = 60°$. Dispersion is weak or absent. Refractive indices (D): α = 1·623, β = 1·654, γ = 1·758. Double refraction is extreme, $\gamma - \alpha$ = 0·135.

The salt resembles the preceding one in solubility and deliquescence. Its aqueous solution readily decomposes, losing acetone and slowly depositing dihydrazinium hexabromostannate. Acetone may be completely distilled out, and estimated in the distillate, 4 moles being recovered per mole of salt.

Bis(pentan-3-one Hydrazonium) Hexabromostannate.—The mother-liquors from the crystallisation of dihydrazinium hexabromostannate were treated with diethyl ketone until, after shaking, the mixture separated into two layers. Much heat was generated and when the mixture was cooled the lower layer yielded large yellow needles of the *hexabromostannate*, m. p. 162—163° (decomp.) [Found: C, 15·0; H, 3·3; N, 7·0; Br, 59·8; Sn, 14·8. $(C_5H_{13}N_2)_2SnBr_6$ requires C, 15·0; H, 3·3; N, 7·0; Br, 59·9; Sn, 14·9%].

The crystals are monoclinic, being deep yellow, needle-like prisms (colourless by transmitted light in microscopic mounts) greatly elongated parallel to *c*, with perfect longitudinal fibrous cleavage. Twinning is absent. The optic axial plane is perpendicular to (010) and to the elongation direction. $\widehat{\beta c} = 14°$. Optically negative. $2V^{\alpha}(\mathrm{D}) = 73°$. Dispersion is slight, red > violet. Elongation negative or positive. Refractive indices (D): α = 1·652, β = 1·701, γ = 1·729. Birefringence high, $\gamma - \alpha$ = 0·077.

The salt is insoluble in common organic solvents and it is much more susceptible than the dimethyl ketazinium salt to the hydrolytic action of moisture. It smells strongly of diethyl ketone in moist air.

Hydrazinium Tribromostannite.—Anhydrous stannous bromide (2·8 g., 1 mol.) and hydrazine monohydrobromide (1·14 g., 1 mol.) were dissolved in warm water (2 c.c.), yielding a pale yellow solution which gave a thick magma of crystals at 0°. Nearly all the solid redissolved, however, on attempted filtration. Better control of crystallisation was secured by dissolving the same quantities in 50% aqueous alcohol (5 c.c.); subsequent cooling then yielded pearly, white, micaceous plates which were filtered off and washed under suction, successively with 70% alcohol and absolute alcohol, and dried *in vacuo* (Found: N_2H_4, 8·3; Br, 61·1; Sn, 30·2. $N_2H_5SnBr_3$ requires N_2H_4, 8·2; Br, 61·3; Sn, 30·4%). The *salt* is very deliquescent when moist and oxidises rapidly in air, becoming yellow. Once properly dried, however, it is not unduly deliquescent, nor does it oxidise so readily. It swells considerably at about 150° and decomposes with vigorous gas evolution at 180°.

The crystals are orthorhombic plates and scales with pronounced basal cleavage. The optic axial plane and $Bx^{\alpha}(\gamma)$ are normal to the plane of the plates. Optically positive. $2V$ = 35—40° approx. Axial dispersion is strong, red < violet, giving anomalous blue interference tints for sections normal to Bx^{α}. The refractive index of α is considerably above 1·84 and is beyond the range of suitable immersion media. The birefringence is moderate.

Dihydrazinium Tetrabromostannite.—Anhydrous stannous bromide (2·8 g., 1 mol.) and hydrazine monohydrobromide (3·4 g., 3 mols.) were dissolved in warm water (3 c.c.), and the solution was mixed with alcohol (10 c.c.). On being cooled the lower layer crystallised, forming yellowish rectangular prisms which were washed with alcohol and dried *in vacuo* [Found: N_2H_4, 12·4; Br, 61·1; Sn, 22·8. $(N_2H_5)_2SnBr_4,H_2O$ requires N_2H_4, 12·2; Br, 61·3; Sn, 22·8%]. Crystallisation of mixtures containing smaller proportions of hydrazine bromide from more dilute alcoholic solutions yielded products which were obviously mixtures of the tribromo- and the tetrabromo-stannite, the final fractions, obtained from liquors containing the alcohol washings, tending towards pure tetrabromostannite.

The *salt* is deliquescent and is oxidised readily in moist air. It softens at 60° and melts at 81—83°. It suffers no loss in weight during several days over sulphuric acid *in vacuo*. It is decomposed by water, yielding gelatinous tin hydroxide; it is soluble in dilute acids, and in acetone, but insoluble in other common organic solvents. The crystals are orthorhombic, being usually stout prisms modified by pinacoid faces, but bladed and greatly elongated platy forms occur. They have no pronounced cleavage. The optic axial plane is parallel to the elongation and the α bisectrix is normal to the surface of the plates; elongation is positive. $2V(\alpha) = 85°$ (approx.). Optically negative; axial dispersion is weak, with red $<$ violet in the bisectrix containing α. The refractive indices are beyond the range of immersion media; birefringence is rather high.

Dimethyl Ketazinium Tribromostannite.—Molar proportions of stannous bromide (1·4 g.; freshly prepared and anhydrous) and hydrazine monohydrobromide (0·6 g.) were dissolved in a mixture (2 c.c.) of equal volumes of ethanol and acetone, and the solution was then shaken with an equal volume of ether. The mixture, on being kept at 0° for several hours, yielded colourless plates which, after being washed with cold alcohol–ether and finally with ether, and dried, *in vacuo*, had m. p. 52—54° (Found: N, 5·7; Br, 49·0; Sn, 24·1; C_3H_6O, 24·6. $C_6H_{13}N_2SnBr_3,H_2O$ requires N, 5·7; Br, 49·0; Sn, 24·3; C_3H_6O, 23·7%). The crystals lose water (4% by weight) on desiccation over sulphuric acid. The same *salt*, m. p. 53—54°, was obtained during an attempt to make bis(dimethyl ketazinium) tetrabromostannite from molar proportions (1 : 2) of the simple salts, and crystallising from warm acetone–water (4 : 1). [Bis-(dimethyl ketazinium) tetrabromostannite was not obtained in any circumstances in this work.]

The salt occurs as monoclinic or triclinic, ill-shaped plates, with poor cleavage parallel to the plates. One optic axis emerges nearly perpendicular to the plates. $2V(\text{D}) = 90°$ (approx.). The axial dispersion is moderate, red $>$ violet in the γ bisectrix, and horizontal dispersion is distinct. Refractive indices (D): $\alpha = 1·65$, $\beta = 1·72$, $\gamma = 1·79$. These values are approximate only, because the crystals are attacked slightly by immersion liquids.

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DEPARTMENTS OF CHEMISTRY AND GEOLOGY,
UNIVERSITY OF CAPE TOWN.

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