691. *Hydrazine. Part VI.* Salts of Dimethyl Ketazine and Certain Hydrazones. The Halogeno-antimonites and -bismuthites.*

By W. Pugh.

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

Chloro-, bromo-, and iodo-antimonites and -bismuthites of dimethyl ketazine, butanone hydrazone, pentan-3-one hydrazone, and heptan-4-one hydrazone have been prepared by crystallisation of mixtures of the halides of antimony and bismuth and hydrazine from ketone-water mixtures, sometimes in strongly acid solutions. The optical properties of the crystals have been examined and preliminary evidence is presented to show that solutions of these salts in acetone are good conductors of electricity.

Part I * of this series described certain chlorostannates, isolated from ketone–water mixtures, which were reported as hydrazinium salts containing ketone of crystallisation. It then seemed unlikely that hydrazine salts and ketones might condense together under the strongly acid conditions prevailing, because the formation of ketazines and hydrazones is held to take place most generally in neutral or alkaline solution. [The work of Gilbert

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* Parts I—V, *J.*, 1952, 4138; 1953, 354, 1934, 2491, 2493.

(*J. Amer. Chem. Soc.*, 1929, **51**, 3394), discussed below, shows that dimethyl ketazine is completely hydrolysed in strongly acid solution.] Moreover, ketones had been estimated in these compounds by the 2 : 4-dinitrophenylhydrazone method, which we have now abandoned because its results are about 25% low. In Part II * the authors re-formulated these compounds, tentatively, as salts of dimethyl ketazine and of certain hydrazones, basing their views partly on the remarkable tenacity with which ketone is retained in them when they are heated *in vacuo* to near the melting point, and partly on a revised estimation of ketone by Messinger's method (Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39), the revised value being confirmed by combustion analysis for carbon and hydrogen. Thus, $(N_2H_5)_2SnCl_6,3C_3H_6O$ became $[Me_2C\!:\!N\cdot NH\!:\!CMe_2]_2SnCl_6$. Salts of these bases had never before been described, but a similar series of bromostannates and bromostannites has since been reported (Part IV *), and the present paper adduces further evidence to characterise them as salts and describes a number of similar salts containing complex anions of antimony and bismuth.

The view that these new compounds are salts is based on the following properties: they are highly crystalline, hard, dense, and salt-like; in colour, and in behaviour towards water, acids, and alkalis, they resemble the corresponding ammonium and potassium salts, the chloro-compounds being colourless, the bromo-compounds yellow, and the iodo-compounds scarlet; they are hydrolysed in water, insoluble basic salts of the heavy metals being precipitated, but, with the exception of the iodo-salts, they dissolve readily in dilute acids, the solutions containing hydrazine salts and free ketone [it is true that they have low melting points (<200°), and decompose when heated above their melting points, but these properties are shared also by the simple hydrazine salts]; they are insoluble in light petroleum, benzene, carbon tetrachloride, chloroform, alcohol, and ether, but are very soluble in ketones. These properties, which are common to the whole class, will not be repeated under the individual salts described later in the Experimental section.

However, the most convincing evidence of their salt character is the fact that acetone solutions of these substances are excellent conductors of electricity. Accurate measurements of conductivities are now in progress and the following approximate values of the molecular conductivity, μ, at dilutions v litres per mole, of (i) dimethyl ketazinium tetrachlorobismuthite, (ii) dimethyl ketazinium tetrachloroantimonite, (iii) bis(dimethyl ketazinium) hexabromostannate, and (iv) tris(dimethyl ketazinium) octadecaiodopenta-antimonite are given to show the order of the conductivities. The measurements were made in acetone solution (undried) at 17°. A value for potassium iodide as a reference electrolyte was obtained at the same time. It being borne in mind that these large ions may have low mobilities, the conductivities indicate that the salts are ionised in acetone solution to approximately the same degree as potassium iodide, and they also indicate the probability that salts (i) and (ii) are binary electrolytes, while salts (iii) and (iv) are, respectively, ternary and quaternary electrolytes.

v (l.)	20	40	100	500	2500
μ, KI	86	—	—	—	—
μ, $C_6H_{13}N_2BiCl_4$, (i)	28	34	43	67	86
μ, $C_6H_{13}N_2SbCl_4$, (ii)	54	—	—	—	—
μ, $(C_6H_{13}N_2)_2SnBr_6$, (iii)	—	70	—	—	—
μ, $(C_6H_{13}N_2)_3Sb_5I_{18}$, (iv)	143	—	—	—	—

The stability of dimethyl ketazine in water has been investigated by Gilbert (*loc. cit.*) who states that it is soluble in water, yielding an alkaline solution, and that if the hydroxyl ions are removed by acids more are produced. In strong mineral acids, it is completely hydrolysed to hydrazinium ions and acetone. Hydrolysis is, however, reversible, involving acetone hydrazonium ion as well as hydrazinium ion, and the measurements show that, even at low acidities, hydrolysis of dimethyl ketazine is extensive, being 30—70% at pH 5 and 40—90% at pH 4·6, the actual proportion depending on the concentration of ketazine. While hydrolysis is promoted by acids, it is repressed by addition of acetone, but, according to a footnote (*loc. cit.*, p. 3402), Gilbert reaches the conclusion that, in presence of acetone, dimethyl ketazine does not function as a base. The hydrolysis and formation of dimethyl ketazine, according to Gilbert, involve reaction between acetone, hydrazinium ions, and hydrogen ions :

$$Me_2C{:}N{\cdot}N{:}CMe_2 + H^+ + H_2O \rightleftharpoons [Me_2C{:}N{\cdot}NH_3]^+ + Me_2CO$$

and

$$[Me_2C{:}N{\cdot}NH_3]^+ + H_2O \rightleftharpoons [N_2H_5]^+ + Me_2CO$$

On the other hand, Conant and Bartlett (*J. Amer. Chem. Soc.*, 1932, **54**, 2881) suggest that the formation of semicarbazones and related substances proceeds by reaction between neutral molecules of semicarbazide and ketones. This reaction was shown to be catalysed, not only by hydrogen ions, but also by acid molecules in the Brönsted sense. They showed, too, that these semicarbazones, like the ketazines, are progressively hydrolysed at increasing acidities.

Since all these observations were made in very dilute solutions, the conclusions to be drawn from them are not necessarily valid for the concentrated solutions used for the preparation of the ketazinium and hydrazonium salts described in this series. It is particularly to be noted that some of these salts separate from strongly acid solutions—*e.g.*, it needs a very high concentration of hydrobromic acid to keep antimony bromide in solution, even in the presence of hydrazine bromide—while some others are best prepared from strongly acid solution by treatment with less ketone than is theoretically needed—*e.g.*, the bromo- and the iodo-salts. These two facts show that dimethyl ketazinium ions and ketone hydrazonium ions must exist in considerable concentration in strongly acid solution, without the need of excess of ketone to repress hydrolysis; they also make it difficult to sustain Conant and Bartlett's view that condensation occurs between neutral molecules and ketone molecules; neutral molecules of hydrazine are not to be expected in such acid solutions.

It may then be that condensation, under these conditions, proceeds between hydrazinium ions and ketone molecules, as suggested by Gilbert, the process being subject to general acid catalysis, as suggested by Conant and Bartlett. It may be significant in this connection that attempts to make complex fluoro-salts of ketazines and hydrazones have failed (Part III, *loc. cit.*), possibly because the fluoro-acids are relatively inactive catalytically. This cannot, however, be the whole explanation, because attempts to make the chloro- and bromo-aluminates of these bases have also failed (Part V, *loc. cit.*). An important factor, no doubt, is favourable ionic sizes for building up of the crystal pattern.

The complex antimony and bismuth salts, described below, were made from cold or warm aqueous-acid solutions of the component metal salts and hydrazine salts, by treatment with acetone, ethyl methyl ketone, diethyl ketone, or di-*n*-propyl ketone. With one exception, acetone alone yielded ketazinium salts, its homologues yielding hydrazonium salts under similar conditions. The exception is di-*n*-propyl ketone, which yielded its ketazinium heptaiododiantimonite. Crystallisation of this salt proved difficult and the mixture was kept on a boiling-water bath for a few hours to remove excess of ketone. The higher temperature probably accounted for further condensation. The bromo- and iodo-salts produced from the higher ketones crystallised easily, provided the quantity of ketone added was less than was theoretically needed to condense with the hydrazine present; but the slightest excess of ketone caused dissolution of the precipitated salt with separation of a viscous liquid which could not be induced to crystallise; it dried to a gummy mass. The iodo-salts are least soluble and separate most easily. It has not been possible to crystallise any hydrazonium chloro-salts of antimony, or bismuth, for treatment in these cases with ethyl methyl, or diethyl, ketone resulted in the immediate separation of a second phase and neither phase could be induced to crystallise.

EXPERIMENTAL

Analytical Methods.—Hydrazine and antimony were determined by iodate titration (Andrews's method), the latter after having been separated as sulphide; bismuth was determined as oxide, after repeated evaporation with nitric acid and ignition below the m. p.; halogens were determined by Volhard's method. The iodo-compounds required special treatment because they are incompletely decomposed in hot acid solution, even with silver nitrate. Iodo-antimonites were dissolved in sodium hydroxide solution (halogen-free) saturated with hydrogen sulphide, and antimony sulphide was precipitated by acidification with sulphuric acid, a double precipitation being necessary to separate traces of adsorbed iodide; iodide was then determined in the combined filtrates. All ordinary methods of dissolution failed for the iodo-bismuthites and these were dissolved in a small volume of acetone, to which was then added, rapidly, a warm dilute solution of sodium hydroxide. After being boiled, the mixture was filtered and the bismuth hydroxide was dissolved in warm dilute nitric acid; the resulting solution usually carried a trace of adsorbed iodide and was treated separately from the filtrate by Volhard's method.

Carbon and hydrogen determinations were made in the conventional combustion train, but the results, while being of the correct order, are not as good as those for the inorganic constituents. Silbert and Kirner's modification of the combustion tube filling (*Ind. Eng. Chem. Anal.*, 1936, **8**, 353), designed to overcome interference caused by the presence of arsenic, antimony, and other elements, was tried in two instances, but the results were no better. Wherever possible, therefore, direct determinations of acetone and ethyl methyl ketone have been made, by Messinger's method, after distilling off the ketone from dilute acid solution (from dilute alkali, followed by an acid wash to fix hydrazine, in the iodo-antimonites).

Dimethyl Ketazinium Tetrachloroantimonite.—Antimony trichloride (4·56 g.; 1 mol.) and hydrazine monohydrochloride (1·37 g.) or dihydrochloride (2·1 g.; 1 mol.) were dissolved in 3N-hydrochloric acid (5 c.c.), and acetone (5 c.c.) was added. The mixture became hot, and on cooling yielded a mass of needles. Sufficient acetone was then added to redissolve the crystals and the solution was allowed to evaporate slowly in a partly covered vessel, yielding colourless needles of *dimethyl ketazinium tetrachloroantimonite*, m. p. 109—110° (Found : C, 19·1; H, 3·6; N_2H_4, 8·4; Cl, 37·6; Sb, 32·4; C_3H_6O, 30·3. $C_6H_{13}N_2SbCl_4$ requires C, 19·1; H, 3·5; N_2H_4, 8·5; Cl, 37·7; Sb, 32·3; C_3H_6O, 30·1%). A similar, but less pure, product was obtained by boiling a solution of antimony trichloride, in chloroform–acetone (2 : 1), with a suspension of hydrazine monohydrochloride, and washing the solid product with a similar chloroform–acetone mixture.

The crystals, probably monoclinic, are colourless, acicular, (010) plates elongated parallel to crystallographic axis *c*. The optic axial plane is perpendicular to (010). $Bx^a\widehat{(\gamma)c}$, 3° (approx.). Bx^o is perpendicular to (010). Elongation positive. Optically positive. $2V\gamma(D) = 70°$. Axial dispersion strong, red > violet, and horizontal dispersion apparent. n_D : $\alpha = 1·642$, $\beta = 1·670$, $\gamma = 1·750$. Birefringence very high, $(\gamma - \alpha) = 0·118$.

Dimethyl Ketazinium Tetrabromoantimonite.—Clear solutions containing antimony bromide and hydrazine bromide can be obtained only with a large excess of hydrobromic acid. Antimony trioxide (3 g.) was boiled with concentrated hydrobromic acid (10 c.c.), and the turbid mixture was treated with hydrazine hydrate (50%; 2 g.) and acetone (40 c.c.). The opalescent yellow solution, on slow evaporation in air, deposited a flocculent precipitate, which was filtered off, and the resulting clear yellow solution yielded yellow needles of *dimethyl ketazinium tetrabromoantimonite*, m. p. 112—114° (Found : C, 12·5; H, 2·2; N_2H_4, 5·7; Br, 57·9; Sb, 22·2. $C_6H_{13}N_2SbBr_4$ requires C, 13·0; H, 2·4; N_2H_4, 5·8; Br, 57·8; Sb, 22·0%). A peculiarity, unique to this salt, is that it seems to undergo slow decomposition; the antimony and bromide content remain practically unchanged, but the hydrazine titre diminishes, and more and more ammonia is found in the product.

The crystals are monoclinic, well-formed, yellow pinacoids, modified by prism and dome faces, elongated parallel to *c*; or they are slender needles with the same elongation. They are colourless in mounts and show a good (010) cleavage. The optic axial plane is perpendicular to (010). $Bx^a(\gamma)$ is inclined 10° to *c* in the symmetry plane. Optically positive. $2V(D) = 49\frac{1}{2}°$. Axial dispersion moderate, red > violet; horizontal dispersion apparent. n_D : $\alpha = 1·741$, $\beta = 1·761$, $\gamma = 1·86$ (calc.). Birefringence high, $(\gamma - \alpha) = 0·12$.

Butanone Hydrazonium Tetrabromoantimonite.—Antimony trioxide (2 g.) and hydrazine hydrate (50%; 2 g.) were warmed together with concentrated hydrobromic acid, a large excess of acid being necessary to get complete solution. The warm solution was then treated, drop by drop with good mixing, with ethyl methyl ketone (0·8 c.c.), a yellow precipitate being formed at once. This redissolved on warming to yield a clear yellow solution, which gave yellow crystals of *butanone hydrazonium tetrabromoantimonite* (4 g.), m. p. 123—125° (Found: C, 8·6; H, 2·4; N_2H_4, 6·1; Br, 60·4; Sb, 23·0; C_4H_8O, 13·8. $C_4H_{11}N_2SbBr_4$ requires C, 9·1; H, 2·1; N_2H_4, 6·1; Br, 60·5; Sb, 23·0; C_4H_8O, 13·6%). The quantity of ketone added (0·8 c.c.) was approx. 80% of that required to condense all the hydrazine present. An excess of ketone caused separation of a yellowish, heavy, oily layer which contained the whole of the hydrazonium salt and did not crystallise.

The crystals are monoclinic, with modified pinacoidal habit, somewhat elongated parallel to *c*. Cleavage absent, and colourless in mounts. The optic axial plane is parallel to (010), and $Bx^a(\alpha)$ is inclined at about 40° to *c*. Negative. $2V(\alpha) = 75°$ (approx.). Axial dispersion perceptible, red > violet. n_D : $\beta = 1{\cdot}84$ (approx.). Birefringence moderate.

Pentan-3-one Hydrazonium Tetrabromoantimonite.—This *salt* was made in the same way as the butanone hydrazonium salt described above, with similar quantities of reagents and diethyl ketone. It forms pale yellow crystals, m. p. 90—92°, which yield a yellow melt (Found: C, 10·8; H, 2·4; N_2H_4, 5·9; Br, 58·9; Sb, 22·4. $C_5H_{13}N_2SbBr_4$ requires C, 11·0; H, 2·4; N_2H_4, 5·9; Br, 58·9; Sb, 22·5%).

The crystals are monoclinic pinacoids, often with oblique termination and flattened parallel to (010), and elongated parallel to *c*. Cleavage is absent, and the colour in mounts is very pale yellow. The optic axial plane is parallel to (010) and $Bx^a(\alpha)$ is inclined at about 43° to *c*. Optically negative. $2V(\alpha) = 50—55°$. Axial dispersion marked, red < violet. n_D: $\alpha = 1{\cdot}79$, $\beta = 1{\cdot}83$ (approx.), γ (not determined). Birefringence moderate.

Tris(dimethyl Ketazinium) Octadecaiodopenta-antimonite.—Antimony trioxide (1·5 g., 1 mol.) was dissolved in the minimum quantity of hydriodic acid (*d* 1·5; 10 c.c.), and the solution, after having been filtered from a small black residue, was diluted with an equal volume of water and treated with hydrazine hydrate (50%; 2 g., 2 mols.) previously neutralised with hydriodic acid. The clear, dark orange solution was then treated with acetone; a yellow powder was precipitated; good crystals were obtained by adding warm acetone, cooling, and recrystallising from acetone–water (2 : 1). The ruby-red crystals of *tris(dimethyl ketazinium) octadecaiodopenta-antimonite*, dried *in vacuo*, had m. p. 153—154° [Found: C, 7·1; H, 1·3; N_2H_4, 3·0; I, 70·5; Sb, 18·8; C_3H_6O, 11·0. $(C_6H_{13}N_2)_3Sb_5I_{18}$ requires C, 6·7; H, 1·2; N_2H_4, 3·0; I, 70·6; Sb, 18·8; C_3H_6O, 10·8%]. The composition of this salt is so unusual that particular efforts were made to establish its identity. Several preparations were made, varying the proportions of antimony to hydrazine from 0·5 to 2·0, and the conditions of crystallisation; in some cases, too, fractional crystallisation was used. In every case, the product had the above composition. (All the iodoantimonites described herein are decomposed with difficulty by acids; the best solvent for their analysis is sodium hydroxide containing hydrogen sulphide. They are also sparingly soluble in chloroform, alcohol, and ether, but insoluble in benzene, light petroleum, and carbon tetrachloride.)

The crystals are biaxial, poorly shaped grains with no pronounced cleavage but some tendency to elongation, reddish orange in mounts. Optically negative. $2V(\alpha)$ very large. Axial dispersion distinct, red < violet. Elongation negative. Pleochroism distinct, with maximum absorption (deep orange yellow) for vibrations perpendicular to the elongation, and pale orange yellow for vibrations parallel to the elongation. n_D of α is much above 1·84. Birefringence, very high. System uncertain.

Butanone Hydrazonium Tetraiodoantimonite.—A warm, clear orange solution of antimony oxide and hydrazine iodide in hydriodic acid, prepared as described for the above ketazinium salt, was treated, drop by drop, with ethyl methyl ketone (1 c.c.), yielding an orange precipitate. (An excess of ketone caused separation of a dark red oil which could not be crystallised.) The mixture was cooled well, and the crystals of *butanone hydrazonium tetraiodoantimonite* were recrystallised from hot dilute hydriodic acid (in which they are sparingly soluble), yielding dark orange prisms, m. p. 153—154° (Found: N_2H_4, 4·4; I, 71·1; Sb, 17·2; C_4H_8O, 9.9. $C_4H_{11}N_2SbI_4$ requires N_2H_4, 4·4; I, 71·0; Sb, 17·0; C_4H_8O, 10·0%).

The crystals are monoclinic, showing stout pinacoidal forms with minor prism faces and well developed dome and pyramid termination; elongated parallel to *c*. They show poor cleavage, and simple twinning is common. Brownish-yellow in mounts. The optic axial plane is parallel to (010). One bisectrix makes an angle of 40° with *c* in the symmetry plane. Optically negative. $2V(\alpha) = 80°$ (estimated). Axial dispersion moderate, red > violet. Slightly pleochroic in yellow and brownish-yellow. n_D of α much above 1·84 and birefringence high.

Pentan-3-one Hydrazonium Tetraiodoantimonite.—This *salt* was prepared as described above for the butanone hydrazonium salt, but with diethyl ketone. However, it is increasingly difficult to get pure products from the higher ketones, the precipitates being contaminated with antimony iodide. The best product was obtained by fractional precipitation, discarding the first fractions, and allowing the mixture to cool slowly while small quantities of ketone were added. The product, after recrystallisation from hot dilute hydriodic acid and a trace of hydrazine iodide, was a coarsely crystalline, dark orange powder, m. p. 150—151° (Found: N_2H_4, 4·4; I, 69·6; Sb, 16·9. $C_5H_{13}N_2SbI_4$ requires N_2H_4, 4·4; I, 69·5; Sb, 16·7%).

The crystals are monoclinic with a pinacoidal habit and elongation parallel to *c*. Simple twinning is common. They are brownish-yellow in mounts. The optic axial plane is parallel to (010) and a bisectrix makes an angle of 35—40° with *c* in the symmetry plane. Optically negative. $2V(\alpha) = 80°$ (estimated). Axial dispersion perceptible, with red < violet. Slightly pleochroic in yellow and brownish yellow. n_D of α much above 1·84 and birefringence high.

Di-n-*propyl Ketazinium Heptaiododiantimonite.*—A warm, clear, orange solution containing antimony and hydrazine iodides in mol. ratio 1 : 1, and made as described for the above iodoantimonites, was treated with small amounts of di-*n*-propyl ketone. A heavy, red layer separated immediately. The mixture was shaken vigorously for several minutes, the aqueous layer was poured off, and the thick plastic, gummy residue was washed with dilute hydriodic acid. As the *salt* did not crystallise in the course of several days, even *in vacuo*, it was dried at 100° to constant weight (Found: C, 12·9; H, 2·4; N_2H_4, 2·4; I, 65·8; Sb, 17·9. $C_{14}H_{29}N_2Sb_2I_7$ requires C, 12·4; H, 2·1; N_2H_4, 2·4; I, 65·5; Sb, 17·9%). Examination under the polarising microscope showed it to be a crystalline material gummed together by uncrystallised liquor. The crystals appeared to be a single compound but they were too small for optical study.

Dimethyl Ketazinium Tetrachlorobismuthite.—Bismuth oxychloride (10 g., 1 mol.) and hydrazine dihydrochloride (4 g., 1 mol.) were dissolved in 5N-hydrochloric acid (10 c.c.), and the solution was poured into acetone (15 c.c.). The mixture became warm and slowly deposited colourless needles of *dimethyl ketazinium tetrachlorobismuthite* which, after recrystallisation from acetone, had m. p. 139—141° (Found: C, 15·0; H, 2·8; N_2H_4, 6·9; Cl, 30·6; Bi, 45·1; C_3H_6O, 24·8. $C_6H_{13}N_2BiCl_4$ requires C, 15·5; H, 2·8; N_2H_4, 6·9; Cl, 30·6; Bi, 45·0; C_3H_6O, 25·0%). Its composition, and that of the bromo-salt described immediately below, was unchanged after 12 months.

The crystals are monoclinic, with an elongated prismatic and bladed habit, colourless in mounts, and without any pronounced cleavage. The optic axial plane is perpendicular to (010) and $Bx^a(\gamma)$ is inclined about 15° to *c* in the symmetry plane. Optically positive, $2V(D) = 53°$. Axial dispersion is marked, with red > violet, and horizontal dispersion is distinct. Length positive. n_D: $\alpha = 1·668$, $\beta = 1·688$, $\gamma = 1·80$. Double refraction very high, $(\gamma - \alpha) = 0·13$.

Dimethyl Ketazinium Tetrabromobismuthite.—Concentrated solutions of bismuth tribromide and hydrazine hydrobromide, made respectively from bismuth carbonate and hydrazine hydrate and hydrobromic acid, were mixed in approximately equimolar proportions and treated with three volumes of acetone. The mixture became warm and clear and on slow evaporation in a partly covered vessel gave yellow needles, which, after recrystallisation from aqueous acetone, proved to be pure *dimethyl ketazinium tetrabromobismuthite*, m. p. 144—146° (Found: C, 11·1; H, 2·0; N_2H_4, 4·9; Br, 50·0; Bi, 32·5; C_3H_6O, 17·6. $C_6H_{13}N_2BiBr_4$ requires C, 11·2; H, 2·0; N_2H_4, 5·0; Br, 49·9; Bi, 32·6; C_3H_6O, 18·1%).

The crystals are probably monoclinic and show somewhat elongated simple pinacoidal forms with dome terminations. They are colourless in mounts and have no pronounced cleavage. Optically positive, $2V(D) = 31°$. Dispersion very strong, red < violet, giving rise to imperfect extinction and anomalous interference colours in parallel light, in sections perpendicular to the bisectrices. Elongation is positive. n_D of $\beta = 1·8$ (approx.), the crystals being somewhat attacked by immersion liquids. Double refraction rather high.

Butanone Hydrazonium Tetrabromobismuthite.—A hot solution, obtained by warming bismuth trioxide (2·3 g., 1 mol.) with concentrated hydrobromic acid (4 c.c.) and hydrazine hydrobromide (1·13 g., 1 mol.), was treated, drop by drop and with vigorous stirring, with ethyl methyl ketone (0·8 c.c.). The liquid was cooled, an emulsion separating which crystallised on vigorous shaking. Subsequent cooling to 0° for a few hours yielded a crop (3 g.) of yellow prisms, *butanone hydrazonium tetrabromobismuthite*, m. p. 149—152° (Found: N_2H_4, 5·3; Br, 52·2; Bi, 34·0. $C_4H_{11}N_2BiBr_4$ requires N_2H_4, 5·2; Br, 52·0; Bi, 34·0%). The salt yields an orange-coloured melt which decomposes above the m. p.

The crystals are monoclinic, minute grains, and occasionally pinacoidal laths elongated parallel to *c*; colourless in mounts and with no cleavage. The optic axial plane is perpendicular to (010). Negative. $2V = 50°$ (approx.). Axial dispersion perceptible, red > violet. $Bx^a(\alpha)$ makes an angle of 35—40° with *c*. Attacked by available liquids, and refractive indices not determined. Birefringence moderate.

Pentan-3-one Hydrazonium Tetrabromobismuthite.—This *salt* was made in the same way as the above butanone derivative, but with diethyl ketone. The crystals are yellow prisms,

m. p. 120—124° (decomp.) (Found: C, 9·0; H, 2·1; N_2H_4, 5·1; Br, 51·0; Bi, 33·0. $C_5H_{13}N_2BiBr_4$ requires C, 9·5; H, 2·1; N_2H_4, 5·1; Br, 51·0; Bi, 33·2%). For the preparation of this and the salt previously described the quantity of ketone added must be less than is required to condense with all the hydrazine present, otherwise uncrystallisable viscous solutions are formed.

The crystals are monoclinic, with pinacoidal habit and elongated parallel to *c*. Cleavage is absent, and the colour in mounts is very pale yellow. The optic axial plane is parallel to (010) and $Bx^a(\alpha)$ is inclined at about 25° to *c*. Optically negative. $2V(\alpha) = 50$—55°. Axial dispersion marked, red > violet. n_D of $\beta > 1{\cdot}84$. Birefringence moderate.

Dimethyl Ketazinium Tetraiodobismuthite.—Bismuth iodide (5·9 g., 1 mol.) and hydrazinium iodide, prepared by adding a slight excess of hydriodic acid to hydrazine hydrate (50%; 1 g., 1 mol.), were warmed with acetone (20 c.c.), and the blood-red solution was filtered and evaporated slowly. The crude product was recrystallised from warm acetone–water (4 : 1), yielding ruby-red crystals of *dimethyl ketazinium tetraiodobismuthite*, m. p. 110° (decomp.). They were dried on paper and *in vacuo* (Found: N_2H_4, 3·9; I, 61·0; Bi, 25·4; C_3H_6O, 14·3. $C_6H_{13}N_2BiI_4$ requires C, 3·9; I, 61·3; Bi, 25·2; C_3H_6O, 14·0%). This salt, and all the other iodobismuthites described, are sparingly soluble in chloroform, alcohol, and ether, but insoluble in light petroleum, benzene, and carbon tetrachloride.

Monoclinic or triclinic, very minute, anhedrons, with no cleavage, and a deep red colour by transmitted light, even for the smallest grains, precluding precise optical determinations. Negative. $2V = 50°$ (approx.). Dispersion not perceptible. Strongly pleochroic in deep red and orange-red. n_D of α much above 1·84.

Butanone Hydrazonium Tetraiodobismuthite.—Half of the quantities of bismuth iodide and hydrazinium iodide used in the above preparation were digested on the water-bath with water (20 c.c.) until no more bismuth iodide would dissolve. The residue was filtered off and the filtrate was kept warm while ethyl methyl ketone (0·5 g.) was added. Slow addition of ketone, one drop per min., gave a well crystallised orange powder, *butanone hydrazonium tetraiodobismuthite*, which, after being dried *in vacuo*, had m. p. 162—164° (Found: N_2H_4, 4·0; I, 63·3; Bi, 26·0. $C_4H_{11}N_2BiI_4$ requires N_2H_4, 4·0; I, 63·3; Bi, 26·0%). Excess of ketone dissolves the salt, yielding a dark red liquid which is difficult to crystallise.

Crystals are monoclinic, minute, doubly-terminated prisms and pinacoids, somewhat elongated and with no cleavage, deep red in colour in mounts. The optic axial plane is probably parallel to (010), a bisectrix making an angle of 40—45° with the elongation, in the symmetry plane. Negative. $2V$ is large (70—80°) and dispersion is perceptible. Moderately pleochroic in dark red and light red. n_D for α, β, and γ much above 1·84. Birefringence rather high.

Pentan-3-one Hydrazonium Tetraiodobismuthite.—This *salt* was made in the same way as the butanone hydrazonium salt described above, but with diethyl ketone; it separates as ruby-red crystals, m. p. 169—170° (Found: C, 7·1; H, 1·6; N_2H_4, 4·0; I, 62·2; Bi, 25·8. $C_5H_{13}N_2BiI_4$ requires C, 7·3; H, 1·6; N_2H_4, 3·9; I, 62·3; Bi, 25·6%). This salt also dissolves in the slightest excess of ketone, giving uncrystallisable viscous liquids.

The crystals are monoclinic with well-marked pinacoidal habit, and (010) strongly developed, modified by dome and prism faces and elongated parallel to *c*. Cleavage is absent. The colour in mounts is deep red. The optic axial plane is parallel to 010), and Bx^a makes an angle of 40—45° with *c*. Negative. $2V$ (α) 70—80°. Dispersion perceptible. Red < violet. Rather strongly pleochroic in dark red and lighter red.

n_D for α, β, γ, much over 1·84. Birefringence rather high.

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DEPARTMENTS OF CHEMISTRY AND GEOLOGY,
UNIVERSITY OF CAPETOWN.

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