87. *Gold Imides.*

By AMIN M. TYABJI and (the late) CHARLES S. GIBSON.

Auric imides of the type $M^I[AuX(imido)_3]$ (X = halogen) from succinimide, and of the type $M^I[AuX_2(imido)_2]$ from *o*-benzoicsulphonimide (saccharin) and phthalimide have been prepared, and their reactions, especially towards hydrolytic agents, studied.

THE present communication reports observations on complex salts formed by reaction between alkali gold halides and cyclic imides containing a five-atom ring, and the products of their hydrolysis. The complexes obtained are similar in type to the succinimido-gold complexes described by Pope (B.P. 338 506/1929; U.S.P. 1 809 384/1931), but no compound of the type $M^I[Au(imido)_4]$ as claimed by Kharasch and Ishbell (*J. Amer. Chem. Soc.*, 1931, **53**, 3059), where imido = $C_6H_4(CO)(SO_2)N-$ or $C_6H_4(CO)_2N-$, was isolated. From both Pope's observations and our own, it would appear that the central gold atom is unable to accommodate four such bulky groups within its orbit.

Baeyer and Co. (D.R.-P. 347 139, 348 070) describe a saccharino- and a sulphonamido-saccharino-compound of gold. A formula has only been given for the latter product, and it should be modified to, *e.g.*, $\{[NH_2\cdot SO_2\cdot C_6H_3(CO)(SO_2)N]_3 \equiv Au \leftarrow OH_2\}$, if it can be shown to be unimolecular, in order to conform to the well-established structural formula for quadricovalent auric compounds of the type $B \rightarrow AuX_3$ where $B = R_3N$, R_2S, R_2O, R_3P, RCN, or similar electron donor (cf. Obituary Notice, Gibson, *J.*, 1951, 625; Mann and Purdie, *J.*, 1940, 1235; Henke, *Annalen*, 1858, **106**, 280).

On mixing of an aqueous solution of an alkali auric halide with succinimide, saccharin, or phthalimide, together with an equivalent of alkali, or alternatively, with the alkali salt of the imide, crystalline complexes were obtained, and the composition of these remained constant whatever proportions of the reactants were chosen. However, only the most convenient preparatory methods have been recorded below.

Potassium bromoaurate and potassium succinimide afforded the new compound, potassium trisuccinimidobromoaurate (I), which is similar to Pope's compound (II; R = alkyl or H), but differs from it in being a salt. It was quite stable in aqueous solution, and was unaffected by recrystallisation from boiling water, from which it was obtained in colourless crystals, though the solutions were yellow. With saccharin and phthalimide in place of succinimide, the new compounds, potassium bis-*o*-benzoicsulphonimidodibromoaurate (III) and potassium diphthalimidodibromoaurate (IV), were obtained. It will be seen that these compounds correspond to Pope's $\{[(CH_2{\cdot}CO)_2N]_2AuX_2\}M^I$ ($X =$ halogen).

$$\underset{\text{(I)}}{\{[(CH_2{\cdot}CO)_2N]_3AuBr\}K} \qquad \underset{\text{(II)}}{\{[(CH_2{\cdot}CO)_2N]_3Au \leftarrow NH_2R\}}$$

$$\underset{\text{(III)}}{\{[C_6H_4(CO)(SO_2)N]_2AuBr_2\}K} \qquad \underset{\text{(IV)}}{\{[C_6H_4(CO)_2N]_2AuBr_2\}K}$$

Although (III) is sufficiently stable to allow of its isolation from hot aqueous solutions in the form of red crystals, yet it cannot be recrystallised, for it is decomposed by hot water (by a sort of " disproportionation ") to the original bromoaurate and the insoluble white compound, monoaquotris-*o*-benzoicsulphonimidogold (V) :

$$3\{[C_6H_4(CO)(SO_2)N]_2AuBr_2\}K + 2H_2O = 2\{[C_6H_4(CO)(SO_2)N]_3Au \leftarrow OH_2\} \quad \text{(V)}$$
$$+ 2KBr + KAuBr_4$$

The hydrolysis is incomplete, as the supernatant liquid becomes acid in reaction, and the gold content of (V) is low. Calcium bis-*o*-benzoicsulphonimidodichloroaurate formed a yellow microcrystalline powder, which decomposed in a similar manner when heated with water. The decomposition product was not investigated. The corresponding sodium salt, on the other hand, resisted hydrolysis by boiling water. The solutions exhibited the interesting property of forming stable yellow gels on cooling. These gels were re-formed when the yellow powder was dissolved in hot water and the solution then allowed to cool.

The compound (IV) was so susceptible to hydrolysis that some decomposition was unavoidable during its preparation, but its solubility in acetone enabled easy separation from the product of hydrolysis, which could be obtained in quantity by using an excess of alkali in the preparation of (IV). The free acid gave correct analyses for diphthalimidodihydroxyauric acid (VI), soluble in hot water and in aqueous alcohol, differing in this

$$\{[C_6H_4(CO)_2N]_2Au(OH)_2\}H \quad \text{(VI)}$$

respect from (V), which appeared to be non-ionic. In view of the easy hydrolysis of phthalimide to phthalamic acid (Landsberg, *Annalen*, 1882, **215**, 197; Boon and Leigh, *J.*, 1951, 1500), this compound is possibly a derivative of phthalamic acid.

Thus a certain gradation becomes apparent both in the capacity of the cyclic imides to co-ordinate with gold halides on the one hand and in the relative stability of the bromogold imides on the other. The succinimide complex is the most stable, containing three imido-groups besides the halogen, whereas the other two imides studied afford complexes of the type $[(\text{imido})_2AuX_2]M^I$. The derivative from saccharin undergoes a curious type of hydrolysis to the aquo-complex $\{[C_6H_4(CO)(SO_2)N]_3Au \leftarrow OH_2\}$, whereas the phthalimido-analogue suffers simple replacement of the two halogen by hydroxyl groups.

EXPERIMENTAL

Potassium Trisuccinimidobromoaurate (I).—(*a*) Potassium bromoaurate (5 g.) in water (10 ml.) was mixed with a solution of succinimide (2·4 g., 3 mols.) in an equivalent quantity of N-potassium hydroxide. When the clear solution was cooled to 0°, yellowish crystals separated, which were washed at the pump and recrystallised from boiling water to afford a colourless crystalline powder of the *potassium* salt (I) (Found : C, 22·7; H, 2·3; N, 6·5; Br, 13·1; Au, 31·3. $C_{12}H_{12}O_6N_3BrKAu$ requires C, 23·6; H, 2·0; N, 6·9; Br, 13·1; Au, 32·3%).

(*b*) Potassium bromoaurate (2·5 g.) in water (10 ml.) was mixed with potassium succinimide (2·5 g., 3 mols.), and the mixture warmed and then cooled; the resulting crystals were recrystallised as above (Found : Br, 13·5; Au, 31·9%). The salt suffers no apparent change when heated to 250°. The aqueous solutions are yellow and, after warming, acid in reaction.

o-*Benzoicsulphonimide* (*Saccharin*) *Derivatives.*—*Potassium bis-*o*-benzoicsulphonimidodibromoaurate* (III). This preparation has to be carried out in dilute solution, as the product cannot be recrystallised. Potassium bromoaurate (2·9 g.) in water (30 ml.) was mixed with the potassium derivative of saccharin (2·2 g.) in water (30 ml.). When the hot solution was cooled to 0°, a red microcrystalline precipitate was formed. This was filtered off, washed with cold water, and dried (yield 44%). When heated, the product darkened and sintered above 220°. Four separate preparations were analysed (Found: Br, 21·0, 21·7, 22·0, 21·6; Au, 25·6, 25·8,. 25·5, 25·4. $C_{14}H_8O_6N_2Br_2S_2KAu$ requires Br, 21·0; Au, 25·9%).

Though sufficiently stable to be isolated from hot aqueous solutions of the components, the *potassium* salt underwent profound changes when its aqueous solutions were boiled for a time: the solutions became acid and dark from the presence of bromoaurate ions. The new colourless crystalline compound formed, too insoluble to be recrystallised, was impure *monoaquotris*-o-*benzoicsulphonimidogold* (Found: N, 5·6; S, 11·5; Au, 23·8. $C_{21}H_{14}O_{10}N_3S_3Au$ requires N, 5·5; S ,12·6; Au, 25·9%).

*Sodium bis-*o-*benzoicsulphonimidodichloroaurate* was similarly prepared by mixing warm aqueous solutions of sodium chloroaurate (1 mol.) and the sodium derivative of saccharin (2 mols.). The salt occasionally separated as a canary-yellow powder, but usually as a gel. When heated, the *sodium* salt sintered at about 230° and was partly molten at 245° (Found: Cl, 10·5; Au, 29·1. $C_{14}H_8O_6N_2Cl_2S_2NaAu$ requires Cl, 10·8; Au, 30·1%). The corresponding *calcium* salt was similarly prepared from calcium chloroaurate (2 g.) in hot water (30 ml.) and the potassium salt of saccharin (2·2 g.) in hot water (30 ml.). The yellow microcrystalline compound sintered when heated to 225° and then decomposed slowly (Found: Cl, 10·9; Au, 29·1. $C_{28}H_{16}O_{12}N_4Cl_4S_4CaAu_2$ requires Cl, 10·9; Au, 30·2%). This substance was also decomposed by boiling in water, the insoluble product not being investigated.

Phthalimide Derivatives.—Potassium diphthalimidodibromoaurate (IV). When boiling solutions of potassium bromoaurate (1 mol.) and potassium phthalimide (2 mols.) or phthalimide and an equivalent of potassium hydroxide (2 mols.) were mixed and cooled, a yellow precipitate was formed, which was separated by means of acetone into two components: an insoluble, white, minor portion (see below) and a soluble major portion consisting of the yellow *potassium diphthalimidodibromoaurate* (Found: Br, 24·1; Au, 28·7. $C_{16}H_8O_4N_2Br_2KAu$ requires Br, 23·2; Au, 28·8%). The corresponding *acid* was prepared as follows: To a boiling solution of potassium bromoaurate (5 g.) was added potassium phthalimide (3·5 g., 2 mols.), the mixture cooled, the yellow precipitate filtered off, dried, dissolved in acetone, filtered from a small quantity of insoluble matter, and the salt precipitated by addition of ligroin. After one repetition of the acetone treatment, the substance was dissolved in boiling water, in which it is sparingly soluble, the solution filtered, and the clear filtrate treated with the calculated amount of hydrochloric acid and set aside to crystallise. The sample for analysis was further purified by one treatment with acetone (Found: N, 4·5; Br, 23·3, 23·2; Au, 30·5. $C_{16}H_9O_4N_2Br_2Au$ requires N, 4·3; Br, 24·6; Au, 30·3%). Both the acid and the potassium salt behave similarly on heating: they darken above 200° and yield a white sublimate of phthalimide.

Diphthalimidodihydroxyauric acid (VI). The white, insoluble compound (above) is the only product when double the amount of alkali is used in the preparation of (IV), the solution becoming decolorised when the reaction is complete. The compound was also prepared from (IV) by heating it with the calculated amount of potassium hydroxide solution in acetone and diluting it with water. The free *acid* was obtained on recrystallising the salt from hot water or aqueous alcohol containing sulphuric acid. Three different preparations were analysed (Found: C, 36·5, 36·6, 36·1; H, 2·7, 2·9, 2·6; N, 5·4, 5·0, 5·5; Au, 37·3, 37·7, 36·9. $C_{16}H_{11}O_6N_2Au$ requires C, 36·6; H, 2·1; N, 5·3; Au, 37·6%). The behaviour on heating is similar to that of the dibromo-compound.

Attempts to repeat Kharasch's Experiments.—Gold hydroxide (1·5 g., prepared according to Figurier; see Gmelin–Kraut's "Handbuch," V, 2, p. 262) and the sodium derivatives of saccharin (8 g.) were heated together with water for 5 days. No reaction had taken place, for the colourless residue obtained on evaporating the filtered solution did not contain any gold whatsoever. A similar result was obtained by heating together gold hydroxide (1·25 g.), phthalimide (3 g., 4 mols.) and 1 equiv. of sodium carbonate in water (100 ml.) for 24 hours on a water-bath.

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GUY'S HOSPITAL MEDICAL SCHOOL, UNIVERSITY OF LONDON, S.E.1.
SOMERSET COTTAGE, 61-D, BHULABHAI DESAI ROAD,
BOMBAY-26.

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