CCCXXVIII.—*The Organic Compounds of Gold. Part II. Co-ordination Compounds.*

By Charles Stanley Gibson and William Morris Colles.

It is now shown that the material used for the preparation of gold alkyl derivatives, described as gold tribromide (Gibson and Simonsen, J., 1930, 2531) or auric bromide (Pope and Gibson, J., 1907, **91**, 2063; compare also Kharasch and Isbell,* *J. Amer. Chem. Soc.*,

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* In their previous paper (*J. Amer. Chem. Soc.*, 1930, **52**, 2918) Kharasch and Isbell did not give any intimation that they proposed to develop the work of Pope and Gibson (*loc. cit.*), and in their later paper (*ibid.*, 1931, **53**, 2701), which was presented for publication some five months after that of Gibson and Simonsen (J., 1930, 2531) had appeared, they have applied the reaction between the Grignard reagent and gold halides on the same lines and used precisely the

1931, **53**, 2701), was actually hydrated bromoauric acid probably of the formula $HAuBr_4,3H_2O$ (Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324). Contrary to the statements in the literature (*e.g.*, Mellor, "Treatise on Inorganic and Theoretical Chemistry," III, 607), pure gold tribromide is almost insoluble in warm dry ether and also in dry ether containing anhydrous hydrogen bromide. Moreover, it does not react with alkylmagnesium halides. Gold tribromide is also very sparingly soluble in water, but readily soluble in aqueous solutions of hydrogen bromide and soluble chlorides and bromides. When water is added to a suspension of gold tribromide in anhydrous ether containing hydrogen bromide, heat is evolved and solution takes place, practically the whole of the gold compound being obtained in the ethereal layer. A more convenient method of obtaining from pure gold tribromide an ethereal solution of bromoauric acid for the preparation of the gold alkyl compounds is described on p. 2411.

The highest yield of diethylgold bromide so far obtained in the present work is 17·4%, calculated on the quantity of pure gold, the actual initial material, six molecular proportions of ethylmagnesium bromide being used. Theoretically, this quantity of the Grignard reagent would react with one molecular proportion of a compound having the composition $HAuBr_4,3H_2O$ to give half a molecular proportion of a compound of the formula $(AuR_2Br)_2$. The yield is 10·2% with three molecular proportions of the Grignard reagent, 14·1% with five, and, as stated by Pope and Gibson, diminishes if more than six molecular proportions are employed. Even under the best conditions unchanged inorganic gold compound and metallic gold are always isolated.

It has been found convenient to isolate the ethylenediamine compound in the first instance, especially in the cases of those dialkylgold bromides which are not solid at the ordinary temperature. These salts when pure can be kept almost indefinitely and the dialkylgold bromide can be recovered easily from them by treatment with hydrobromic acid. By this method we have prepared di-*n*-propylgold bromide and the corresponding di-*n*-butyl compound from *ethylenediaminedi-*n*-propylgold bromide* (I; $R = C_3H_7$) and *ethylenediaminedi-*n*-butylgold bromide* (I; $R = C_4H_9$) respectively. The two former compounds, the physical properties of which are being examined in detail, have been described by Kharasch and Isbell (*loc. cit.*); of these, di-*n*-propylgold bromide was obtained

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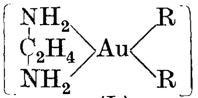
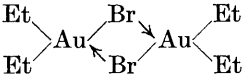
same methods as the original authors (P. and G.). In the circumstances, the form of the present paper has had to be modified, but I wish to emphasise that the present series of investigations is being continued by myself and co-workers on the lines originally planned.—C. S. GIBSON.

by them in small yield and, from the analytical data given, it may not have been pure. Up to the present, we have been able to prepare di*cyclo*hexylgold bromide (of which Kharasch and Isbell obtained 0·081 g. from 2 g. of auric chloride) neither from pure gold tribromide nor from bromoauric acid prepared as originally described.[*]


(I.)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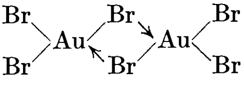
(III.)

It has been shown that the constitution of diethylgold bromide should be represented as (II) (Gibson and Simonsen, *loc. cit.*) and it would appear desirable to write it as always having the double formula. Presumably, the other dialkylgold halides are constituted similarly.[†] Actually, it appears that in all the so-called " tervalent " gold compounds the metal has a co-ordination number of 4 and it is suggested that this method of regarding them is more in keeping with modern ideas and tends to remove the anomaly of the presence of a tervalent metal in Group I of the Periodic Classification (compare Sidgwick, " Electronic Theory of Valency," 1927, p. 262). There is little evidence for the existence of the tervalent gold ion, Au^{+++}, and it is suggested that the formula of gold tribromide will be found to be $(AuBr_3)_n$, where n is at least 2. In this case its constitution will be represented as (III). The molecular weight of gold tribromide, which does not appear to have been determined, is under investigation in these laboratories.

With the hope of obtaining a more convenient initial material than bromoauric acid for the preparation of organic gold compounds by means of the Grignard reaction, we investigated a number of co-ordination compounds of gold, which, not being salts, might be soluble in ether and behave suitably in the reaction. The compounds investigated can be readily prepared, *e.g.*, from pyridine, by the reaction :

$$M[AuX_4] + C_5H_5N = MX + [C_5H_5N{\cdot}AuX_4]$$
$$(M = \text{univalent metal, } X = Cl \text{ or } Br)$$

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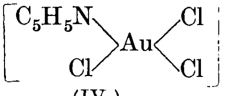
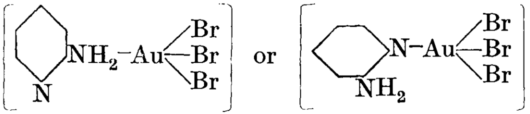
[*] Probably the most remarkable compound referred to by Kharasch and Isbell is diacetylgold bromide, which, however, was not analysed and no details of its preparation are given.

[†] The non-existence of gold alkyls or aryls of the type AuR_3 referred to by Kharasch and Isbell (*loc. cit.*, p. 2703) has been previously commented upon (Gibson, " Troisième Conseil de Chimie Solvay ; Rapports et Discussions," 1928, p. 422). The explanation of their non-existence would appear to be that in such compounds the gold atom could not be 4-covalent as it can be in compounds of the types $(AuR_2X)_2$, $(AuRX_2)_2$, $(AuX_3)_n$, and the co-ordinated compounds described here and in the previous papers of this series.

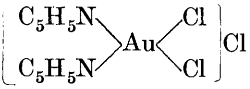
From sodium chloroaurate the compound [$C_5H_5N{\cdot}AuCl_3$] which was described by François (*Compt. rend.*, 1903, **136**, 1557) was obtained and this on recrystallisation from pyridine gave a salt, [$(C_5H_5N)_2AuCl_2$]Cl, also described by François. These two compounds should be written fully as (IV) and (V) respectively and they have been compared with the new analogous bromine derivatives, *pyridinotribromogold*, [$C_5H_5N{\cdot}AuBr_3$], and *dipyridinodibromogold bromide*, [$(C_5H_5N)_2AuBr_2$]Br. Pyridinotrichlorogold and pyridinotribromogold can be crystallised from alcohol, acetone, and chloroform. They are insoluble in water and can be used for estimating gold; they are only very sparingly soluble in ether. In spite of their sparing solubility they yield diethylgold bromide when their suspensions in ether (with or without pyridine) are treated with ethylmagnesium bromide, but the yield is less satisfactory than that obtained in the method already developed. *Quinolinotribromogold*, iso*quinolinotribromogold*, 2-*aminopyridinotribromogold* (VI), and *di-2-pyridylaminotribromogold* (VII) have also been prepared.



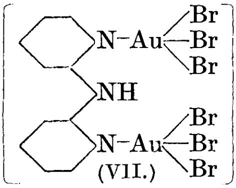
(IV.)



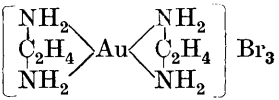
(VI.)



(V.)



(VII.)



(VIII.)

Pyridinotrichlorogold and pyridinotribromogold are exactly analogous to pyridinodiethylbromogold and amminodiethylbromogold recently described by Gibson and Simonsen (*loc. cit.*; compare Kharasch and Isbell, *loc. cit.*, who merely remark that dialkylgold bromides are soluble in pyridine). These new co-ordination compounds are extremely stable; they are but slowly attacked by aqua regia and only slowly reduced to metallic gold when suspended in sulphurous acid.

Ethylenediamine also forms a co-ordination compound with gold tribromide under the same conditions of reaction. This compound is best purified by solution in the minimum quantity of water and adding alcohol until crystallisation commences. It is stable when pure, but suffers reduction somewhat readily if impurities are present. It is a salt, *diethylenediaminogold tribromide*, and its constitution would appear to be best represented as in (VIII).

It is immediately decomposed by hydrobromic acid. In the present work the bromoauric acid liberated was identified by conversion into pyridine bromoaurate (Gutbier and Huber, *Z. anorg. Chem.*, 1914, **85**, 383), which was obtained in quantitative yield and analysed.

EXPERIMENTAL.

The Material previously used for the Preparation of Gold Alkyl Compounds (Gibson and co-workers, *loc. cit.*).—The material used for analysis had been kept for several weeks in a vacuum desiccator over potassium hydroxide in the absence of light; it was " dry " and highly crystalline. A filtered solution of the material (about 1·2 g.) in water (50 c.c.) was divided into two portions, and sulphur dioxide passed through both until they were colourless. The precipitated gold was weighed, and the bromine determined in the filtrates by means of standard silver nitrate and potassium thiocyanate solutions [Found: Au (i) 0·1946 g., (ii) 0·1981 g.; Br (i) 0·3183 g., (ii) 0·3229 g. Atomic ratios Au : Br = (i) 1 : 4·04, (ii) 1 : 4·02]. This material is therefore bromoauric acid which, being soluble in ether, must contain water, probably of combination (see above).

New Method of preparing the Material.—Pure gold tribromide was prepared by a method based on that of Ephraim (*Ber.*, 1919, **52**, 241; compare, however, Meyer, *Compt. rend.*, 1909, **148**, 346). A solution of " fine " gold in aqua regia is evaporated to crystallisation on the water-bath, hydrochloric acid being added several times. The crystalline residue is dissolved in a moderate quantity of water, and the solution filtered from silver chloride after some hours. When sulphurous acid is slowly added to the mechanically stirred filtrate, the gold is deposited as a fine brown powder, which is washed by being mechanically stirred with hot water until the filtrate is free from chloride and then dried at 100°. A weighed quantity of this gold is placed in a wide-mouth glass stoppered flask (400 c.c.) together with some large glass beads to act as a mill. About twice the theoretical quantity of pure bromine is slowly added, the mixing being as thorough as possible. Although heat is evolved in this reaction, it is inadvisable to cool the flask unduly, for it is then difficult to get intimate contact between the reactants on account of the crystallisation of the gold tribromide; the contents of the flask should be almost fluid at room temperature. When the addition is complete the stopper is securely fastened, and the flask kept away from direct light for some 48 hours. The flask, with its stopper removed, is then placed over solid sodium hydroxide until free bromine is no longer present in the apparatus (48—60 hours). The gold tribromide is stable over sodium hydroxide at the ordinary pressure and is obtained in practically quantitative amount. *E.g.*, Au taken, 15·00, 7·75, 20·01 g.; $AuBr_3$ obtained, 33·19 (33·24), 17·12 (17·18), 43·60 (44·30) g. respectively. The quantities in parentheses are the calculated yields.

The solution of bromoauric acid now used for the preparation of gold alkyl compounds is made as follows: To the contents of the flask is added slowly the calculated quantity of concentrated hydrobromic acid (348·5 g. HBr/l.): all the gold tribromide should go into solution. (If the flask is cooled somewhat, crystalline bromoauric acid separates in quantity.) To this solution dry ether (50 c.c.) is added very slowly and with ice-cooling and again all should be in solution. The liquid is filtered through a fine sintered glass funnel with long sides into a separating funnel, the flask and filtering funnel being washed with successive and known quantities of dry ether (a total of not more than 100 c.c.) until the whole of the gold compound has been transferred. Fused calcium chloride is added in small quantities to the filtered solution, and the almost clear lower aqueous solution run off as long as it separates; the volume of this solution is always noted and is rather more than 80% of the volume of the hydrobromic acid used. Finally, more fused calcium chloride is added and the solution kept in the absence of light for some days. Three days before carrying out a preparation of gold alkyl compound, the contents of the separating funnel are transferred as completely as possible to another dry separating funnel containing fresh fused calcium chloride and immediately before being used this solution is filtered through another sintered glass funnel in a dry atmosphere into the reaction vessel. For about 15 g. of gold, the volume of the ethereal solution of bromoauric acid is about 250 c.c.

With this solution, the reaction is carried out as recently described (Gibson and Simonsen, *loc. cit.*); by using 6 mols. of ethylmagnesium bromide and starting with gold (15·01 g.), ethylenediaminodiethylgold bromide (Gibson and Simonsen, *loc. cit.*) (4·0 g.; 17·4%) is obtained. The ethylenediamine co-ordination compound is precipitated at once when ethylenediamine is mixed with the ligroin or ether–ligroin solution of the gold alkyl bromide. It can be recrystallised from water or aqueous alcohol. All the ethylenediamine compounds so far investigated can, after purification, be stored almost indefinitely.

Recovery of Gold Alkyl Compounds from their Co-ordination Compounds.—Amminodiethylbromogold (Gibson and co-workers, *loc. cit.*) was finely ground and suspended in water and after addition of hydrobromic acid the mixture was thoroughly stirred and then extracted with ligroin (b. p. 40—60°). Evaporation of the ligroin solution gave an almost quantitative yield of diethylgold bromide, m. p. 58°, identical with an authentic specimen. A solution in cold water of ethylenediaminodiethylgold bromide, when treated with hydrobromic acid, gave an immediate precipitate of diethylgold bromide, which, after being washed with water and dried, had m. p. 58°.

Ethylenediaminodi-n-*propylgold bromide* (I; $R = C_3H_7$) was prepared in the usual manner, 6 mols. of *n*-propylmagnesium bromide being used (yield, 2·2 g. from 15·0 g. Au). This on recrystallisation from water was obtained in colourless needles, turning violet at *ca.* 130° and decomposing extensively without melting at *ca.* 190° (Found: C, 23·3; H, 5·7; N, 6·3; Br, 18·95; Au, 46·3. $C_8H_{22}N_2BrAu$ requires C, 22·7; H, 5·2; N, 6·6; Br, 18·9; Au, 46·6%). When hydrobromic acid is added to an aqueous solution of the compound, di-*n*-propylgold bromide is obtained as an oil soluble in ligroin (b. p. 40—60°) (compare Kharasch and Isbell, *loc. cit.*). The physical properties of this substance and of di-*n*-butylgold bromide, obtained similarly from ethylenediamino-di-*n*-butylgold bromide (see below), are still under investigation.

Ethylenediaminodi-n-*butylgold bromide* (I; $R = C_4H_9$) was prepared as in the case of the di-*n*-propyl compound, from 6 mols. of *n*-butylmagnesium bromide, 4·5 g. of crude compound being obtained from 15·01 g. of gold. This crystallised from water or very dilute alcohol in colourless needles, gradually decomposing from *ca.* 190° (Found: N, 6·6; Br, 17·5; Au, 43·4. $C_{10}H_{26}N_2BrAu$ requires N, 6·2; Br, 17·7; Au, 43·7%). The compound was also obtained from bromoauric acid prepared as described in the previous papers.

All the co-ordination compounds described below were prepared by adding the base, either by itself or dissolved in alcohol, to a mechanically stirred, filtered solution of potassium bromoaurate made by dissolving pure gold tribromide in an aqueous solution of potassium bromide. The addition of the base was continued until the supernatant liquid was just colourless, as was the case with pyridine, quinoline, and *iso*quinoline, or until no further change in colour was noticed, as in the case of the other bases. The insoluble compound was mechanically stirred with successive quantities of water, dried, and purified in the manner described.

Pyridinotribromogold (as IV) as prepared is a deep red, crystalline powder, insoluble in water and very sparingly soluble in ether. When recrystallised from alcohol or acetone, it was obtained in bright red or scarlet needles, but some oxidation or bromination of the solvent was noticed. It is best recrystallised from chloroform (Found: C, 11·9; H, 1·4; N, 2·5; Br, 46·8; Au, 38·3. $C_5H_5NBr_3Au$ requires C, 11·6; H, 1·0; N, 2·7; Br, 46·5; Au, 38·2%). Pyridinotrichlorogold (bright yellow needles from chloroform), prepared in a similar way from sodium chloroaurate, has the properties described by François (*loc. cit.*). Both compounds decompose from about 150° without melting, pyridine being evolved in the first place. They are both somewhat soluble in pyridine (see below).

Pyridinotribromogold (48 g.) was suspended in dry ether (150 c.c.) and dry pyridine (20 c.c.), and the mixture mechanically stirred; the solution became deep red but only a small amount of the compound appeared to dissolve. A filtered ethereal solution of ethylmagnesium bromide (rather more than 3 mols.) was added under the usual conditions, followed by ice and an excess of hydrobromic acid to decompose unchanged initial material and any pyridinodiethylgold bromide that had been produced. The product was worked up in the usual way, and diethylgold bromide (2·3 g.) obtained, m. p. 57·58°. When pyridine was not added and only 2 mols. of ethylmagnesium bromide were used, the yield of diethylgold bromide was definite but much smaller. From pyridinotrichlorogold (24 g.) in ethereal suspension, without pyridine, 3 mols. of ethylmagnesium bromide being used, only 0·5 g. of diethylgold bromide was obtained. When pyridinotribromogold (36·8 g.) was added to a mechanically stirred and filtered solution of ethylmagnesium bromide (2 mols.), and the product worked up in the usual manner, the amount of diethylgold bromide (identified as ethylenediaminodiethylgold bromide) obtained was very small.

Dipyridinodibromogold bromide (as V) was prepared by recrystallising pyridinotribromogold from pyridine. The compound is a very sparingly soluble salt which decomposes without melting, giving off pyridine in the first instance. It is somewhat darker in colour (deep red needles) than the monopyridino-compound (Found : C, 19·9; H, 2·0; N, 3·8; Br, 40·7; Au, 33·2. $C_{10}H_{10}N_2Br_3Au$ requires C, 20·2; H, 1·7; N, 4·7; Br, 40·3; Au, 33·1%). The corresponding chloro-compound was prepared similarly and obtained in reddish-yellow needles. It does not melt on being heated, but at about 135° it loses pyridine and is converted into a bright yellow compound (probably pyridinotrichlorogold) and then suffers further decomposition. This dipyridinodichlorogold chloride, which was originally described by François (*loc. cit.*), is also a very sparingly soluble salt (Found : Au, 43·4. Calc. : Au, 42·7%).

Quinolinotribromogold was recrystallised from chloroform and obtained in deep red, lustrous prisms which decompose above 200° (Found : C, 19·5; H, 1·6; N, 2·4; Br, 42·2; Au, 34·75. $C_9H_7NBr_3Au$ requires C, 19·1; H, 1·25; N, 2·5; Br, 42·4; Au, 34·8%). Like the following compound, it is insoluble in water and is not a salt. It is almost insoluble in ether.

iso*Quinolinotribromogold*, when recrystallised from chloroform, is obtained in violet-red plates (brick-red as powder). In its general properties it is almost indistinguishable from the preceding compound (Found: C, 19·2; H, 1·6; N, 2·8; Br, 41·9; Au, 34·8%).

2-*Aminopyridinotribromogold* (VI) was obtained as a dull red precipitate and when recrystallised from chloroform formed almost black small prisms. It melts with profound decomposition at *ca.* 160° (Found: C, 11·95; H, 1·4; N, 5·6; Br, 43·6; Au, 37·1. $C_5H_6N_2Br_3Au$ requires C, 11·3; H, 1·4; N, 5·3; Br, 45·15; Au, 37·1%). As the compound is not a salt, its constitution must be one of the two suggested and since the compound is similar in colour and general properties to the above pyridino-, quinolino-, and *iso*quinolino-compounds, it seems probable that the gold atom is co-ordinated with the pyridine-nitrogen rather than with the nitrogen of the amino-group.

Di-2-pyridylaminotribromogold (VII), obtained in the first place as a brownish-red precipitate, is readily soluble in acetone and is best purified by precipitation with dry ether from its filtered solution in acetone. For analysis this operation was repeated and the substance obtained as a scarlet powder which decomposed on being heated (Found: N, 4·3; Br, 43·8; Au, 37·5, 37·45. $C_{10}H_9N_3Br_6Au_2$ requires N, 4·0; Br, 45·9; Au, 37·7%).

An attempt to prepare a co-ordination compound of gold tribromide and diphenylamine gave a dark green product, less soluble in acetone than the preceding compound and insoluble in ether. This material appears to consist largely of a compound containing two molecules of diphenylamine to one molecule of gold tribromide.

Diethylenediaminogold tribromide (VIII) was first obtained by the addition of ethylenediamine to the concentrated aqueous solutions of inorganic bromoaurates containing hydrobromic acid obtained in the attempted preparation of di*cyclo*hexylgold bromide. It is prepared by adding ethylenediamine to a concentrated aqueous solution of a bromoaurate, filtering off the yellow precipitate, dissolving this in the minimum quantity of cold water, and adding alcohol to the filtered solution. The purification should be repeated until the product is stable in air and obtained in bright yellow, small plates, readily soluble in water and insoluble in alcohol. It has no melting point. From its salt-like character and its composition, its constitution is believed to be that suggested (Found: N, 9·7; Br, 43·4; Au, 35·3. $C_4H_{16}N_4Br_3Au$ requires N, 10·1; Br, 43·0; Au, 35·4%). When its yellow aqueous solution was treated with hydrobromic acid, it became dark red owing to the formation of bromoauric acid. This was extracted with ether, leaving the aqueous solution practically colourless. When the ethereal solution was evaporated in a desiccator, dark red crystals were left. These were readily soluble in water and on addition of pyridine yielded a dark red, crystalline precipitate, very sparingly soluble in water. It was recrystallised from alcohol and proved identical with pyridine bromoaurate prepared by Gutbier and Huber (*loc. cit.*) (Found: N, 2·5; Br, 54·3; Au, 33·1. Calc.: N, 2·35; Br, 53·6; Au, 33·1%).

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