

CCCXXXIV.—*The Organic Compounds of Gold.*  
*Part I. Diethylgold Bromide and Some Derivatives.*

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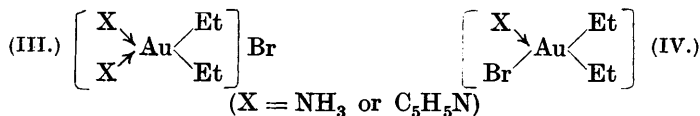
DIETHYLGOLD bromide,  $\text{Au}(\text{C}_2\text{H}_5)_2\text{Br}$ , first described by Pope and Gibson (J., 1907, **91**, 2061), has now been completely analysed and the previous work confirmed. The molecular weight determined by the cryoscopic method in benzene shows, however, that the compound has twice the above formula and its constitution may be conveniently written concisely (I) on Sidgwick's method. In the



unassociated form, the gold atom would have an incomplete octet, which is complete in the associated form.

Diethylgold bromide is not a salt and is insoluble in water. It is, however, slowly acted upon by water, the presence of ionised bromine then becoming manifest. From the work now described, which proves definitely that gold in these organic compounds has normally a co-ordination number of 4, it may be assumed that in the presence of water diethylgold bromide tends to form an *aquo*-salt (II), which is soluble in water and gives the usual reaction for the bromine ion.

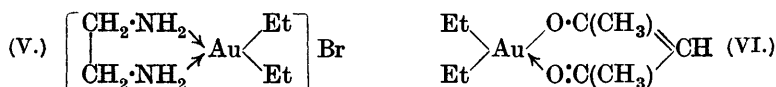
The composition of amminodiethylgold bromide,  $(\text{C}_2\text{H}_5)_2\text{AuBr}\cdot\text{NH}_3$  (*loc. cit.*, p. 2065), has been confirmed and a corresponding *pyridino*-diethylgold bromide,  $(\text{C}_2\text{H}_5)_2\text{AuBr}\cdot\text{C}_5\text{H}_5\text{N}$ , isolated. These two colourless, highly crystalline compounds are very similar in properties. They are both sensitive to light, soluble in organic solvents and almost insoluble in water. They are, however, soluble in dilute aqueous solutions of ammonia and pyridine respectively and these solutions contain ionised bromine. It appears, therefore, that when aqueous solutions of ammonia and pyridine dissolve diethylgold bromide, soluble unstable salts having the constitution (III) are formed. These substances then suffer loss of base



during isolation with the formation of compounds (IV) which are no longer soluble in water but can be recrystallised from suitable organic solvents.

The correctness of these views regarding the constitution of the

isolable ammonia and pyridine derivatives is emphasised by the preparation of the typical salt, *ethylenediaminodiethylgold bromide*, which is soluble in water and crystallises from ethyl alcohol in colourless plates, gradually decomposing above 182°. Its aqueous solution yields an immediate precipitate with silver nitrate and its constitution must be represented as (V). Although it darkens slowly on exposure to light, its stability is greater than that of the



analogous diammino- and dipyridino-compounds; this is explained by both basic groups being directly attached to the C<sub>2</sub>H<sub>4</sub> group and one cannot be liberated on isolation of the compound.

Through the kindness of Dr. R. C. Menzies, who supplied the thallos acetylacetonate, it has been possible to prepare *diethylgold acetylacetonate* by the simple mixing of the former compound and an equivalent quantity of diethylgold bromide in alcoholic solution. The gold content, physical properties, and reactions of the compound indicate that it should be represented constitutionally as (VI). As in the corresponding dimethylthallium and diethylthallium acetylacetonates, the presence of the two ethyl groups in this monochelate compound gives to the gold a stable covalency of 4 (compare Menzies, Sidgwick, Cutcliffe, and Fox, J., 1928, 1288). This colourless compound is apparently insoluble in water but freely soluble in all organic solvents. Its low melting point (9—10°) is in marked contrast to that of trimethylplatinum acetylacetonate (Menzies, J., 1928, 565) and those of the dimethylthallium and diethylthallium compounds.

Diethylgold acetylacetonate in alcoholic solution decomposes when exposed to light, giving beautiful gold mirrors showing the characteristic colours of thin gold films by transmitted light; the mirrors are fairly adherent and are obtained in varying thicknesses according to the concentration of the solution and the duration of exposure. When once the photo-decomposition has started, it appears to continue when the light source is removed. The decomposition proceeds more rapidly in the light of a mercury vapour lamp than in daylight. Brilliant gold mirrors are also produced by gentle heating of the compound, but these are less adherent than those formed by photo-decomposition.

Diethylgold acetylacetonate is decomposed by bromine in chloroform solution, diethylgold bromide being produced. When alcoholic solutions of sodium iodide and diethylgold acetylacetonate are mixed, *diethylgold iodide* is obtained. This compound is analogous to the

bromide in all its properties, having a low melting point (67—68°), being volatile, and freely soluble in liquid hydrocarbons. Its constitution is obviously similar. *Ethylenediaminodiethylgold iodide* is readily prepared by mixing a slight excess of ethylenediamine with a solution of the iodide in ligroin. Like the corresponding bromide, this beautifully crystalline, colourless salt darkens slowly on exposure to light, but the two substances are the most stable of the organic gold compounds described in the present paper.

The reaction between magnesium ethyl bromide and gold tribromide is more complicated than was formerly believed. Under the conditions described later, products other than diethylgold bromide have been isolated in not inconsiderable quantities. These by-products are soluble in water and are less soluble in ether than diethylgold bromide. They are also insoluble in ligroin, which was used for extracting the looked-for product in the earlier investigation, and therefore they previously escaped notice. A preliminary investigation of these by-products has been made, but the final consideration of their nature must be postponed until they have been compared with the analogous compounds which are formed when other magnesium alkyl bromides react with gold tribromide.

#### EXPERIMENTAL.

The gold tribromide is made by dissolving fine gold in aqua regia, evaporating the solution free from nitric acid, and adding an excess of concentrated hydrobromic acid to the resulting chloroauric acid dissolved in water. After the mixture has been warmed for some time at a temperature not exceeding 70°, the cooled solution is placed in a separating funnel, and crystalline magnesium sulphate added until the solution is saturated. Ether is then added and almost the whole of the gold tribromide is obtained in the ethereal layer. The ethereal extract is washed several times with a saturated solution of magnesium sulphate and left standing for some hours with anhydrous magnesium sulphate, which, however, does not remove all the water. The filtered solution is then evaporated to dryness, finally in a vacuum desiccator containing potassium hydroxide. The material obtained is highly crystalline. It should not be kept under reduced pressure in the presence of potassium hydroxide, because it slowly loses bromine under these conditions, aurous bromide, insoluble in ether, being formed (compare Campbell, *Chem. News*, 1907, 96, 17).

*Diethylgold Bromide.*—The method now adopted for obtaining this compound may be illustrated by describing a typical preparation.

Gold tribromide (30 g.), dissolved in dry ether (250 c.c.), is placed in a 3-necked flask provided with a stirrer and a condenser. The

ethereal solution of magnesium ethyl bromide prepared from magnesium (6 g.) and ethyl bromide (27 g.) is forced by a stream of nitrogen through a fine muslin filter into the gold tribromide solution. The rate of mixing is regulated to take about 1 hour, both solutions being cooled in freezing mixtures and efficient stirring maintained. Stirring is continued for  $\frac{1}{2}$  hour after mixing, the bath is then replaced by cold water, and the stirring continued for  $\frac{1}{2}$  hour. The solution becomes dark green during the mixing, a dark-coloured solid separates, and the solution is finally dark red. With a greater excess of the Grignard reagent, the solution becomes almost colourless and a much smaller yield of the desired product is obtained. If the cooling of the reactants is not adequate, a more violent reaction ensues with the same result.

The stirring being continued and the mixture cooled in ice, powdered ice is added in small quantities—there should be no violent reaction at this stage—and finally dilute hydrobromic acid. The mixture is poured into a separating funnel, and the flask thoroughly washed out with ether. The ethereal solution, separated from solid matter (gold), is then washed several times with water. The first aqueous solution, which is almost colourless, is rejected. The subsequent ones are strongly coloured, the red colour becoming less intense, as also does that of the ethereal solution, as washing proceeds. These aqueous washings contain the by-products referred to above. The ethereal solution, which should finally be only pale yellow, is rapidly dried with calcium chloride and evaporated to small bulk in a current of nitrogen under reduced pressure at as low a temperature as is convenient. The evaporation is completed in a desiccator over sulphuric acid. The crystalline residue, having the characteristic odour of diethylgold bromide, may be a mixture if the washing of the ethereal solution has not been carried far enough. The red substance present, being insoluble in ligroin (b. p. 40—60°), is easily removed, the filtered ligroin solution being again evaporated in a vacuum desiccator over sulphuric acid. If water-soluble by-product is still present, the crystalline residue should be washed with a little water and dried before the extraction with ligroin. The colourless diethylgold bromide (3 g.), obtained in long needles, is sufficiently pure for the preparation of derivatives. It has m. p. 54—55°, and this is raised to 58° (compare Pope and Gibson, *loc. cit.*) by washing with a little methyl alcohol, in which the bromide is sparingly soluble. If the solution of diethylgold bromide in ligroin is evaporated at about 40°, the compound is obtained in small prisms having the same melting point. The molecular weight,\*

\* We are greatly indebted to Mr. S. Holt, M.Sc., for carrying out this determination.

determined by the cryoscopic method in benzene, shows that the compound is  $(\text{AuEt}_2\text{Br})_2$ , its constitution being probably that indicated (I) (Found: C, 14.3; H, 3.9; Br, 22.7; Au, 58.4;  $M$ , 641, 653. Calc. for  $\text{AuEt}_2\text{Br}$ : C, 14.3; H, 3.0; Br, 23.8; Au, 58.8%;  $M$ , 335).

The amino-derivative of diethylgold bromide was again prepared as previously (*loc. cit.*, p. 2065). It can be recrystallised from benzene or cyclohexane. The substance is colourless when isolated, but rapidly becomes deep violet, even in artificial light. Its analysis proved somewhat difficult, but there is no doubt that the compound has the composition  $\text{AuEt}_2\text{Br}\cdot\text{NH}_3$ , as previously stated (Found: N, 3.1, 3.3; Au, 56.0. Calc.: N, 4.0; Au, 56.0%). It is not sufficiently soluble in benzene or cyclohexane at the freezing point for its molecular weight to be determined.

*Pyridinodiethylgold Bromide*,  $[\text{Au}(\text{C}_2\text{H}_5)_2\text{Br}\cdot\text{C}_5\text{H}_5\text{N}]$ .—Diethylgold bromide (0.5 g.), suspended in methyl alcohol (1.5 c.c.), was mixed with pyridine (0.2 g.) in methyl alcohol (2 c.c.). The solution obtained gave on addition of water, colourless needles which, after being washed with water, were purified by the careful addition of water to their solution in methyl alcohol. The compound rapidly darkened on exposure to light. It melted with decomposition at 59–60° and explosive decomposition set in at about 79°. The determination of gold proved difficult on account of the explosiveness of the compound even when partial decomposition had been previously effected with concentrated sulphuric acid (Found: N, 3.8; Br, 19.5; Au, 47.2.  $\text{C}_9\text{H}_{15}\text{NBrAu}$  requires N, 3.4; Br, 19.3; Au, 47.6%).

*Ethylenediaminodiethylgold bromide* (V) separated at once when a slight excess of ethylenediamine was added to a solution of diethylgold bromide in ligroin. It crystallised from absolute alcohol in small colourless plates, which turned red at about 182° and gradually decomposed above this temperature (Found: N, 6.9; Br, 19.9; Au, 49.0.  $\text{C}_6\text{H}_{18}\text{N}_2\text{BrAu}$  requires N, 7.1; Br, 20.2; Au, 49.9%).

*Diethylgold Acetylacetonone* (VI).—Thallos acetylacetonone (1.52 g.), suspended in absolute ethyl alcohol, was treated with diethylgold bromide (1.63 g.), dissolved in sufficient of the same solvent, and the mixture was stirred for some time, finally at about 40°. Thallos bromide, which separated at once, was removed and the filtrate and washings were evaporated over sulphuric acid in a desiccator. The residue was dissolved in ligroin (b. p. 40–60°), and the filtered solution again evaporated. The strongly cooled residue crystallised in colourless plates, which were rapidly separated from adhering mother-liquor; m. p. 9–10° (thermometer in liquid). Owing to its extreme sensitivity to light, the substance was analysed at once (Found: Au, 55.3.  $\text{C}_9\text{H}_{17}\text{O}_2\text{Au}$  requires Au, 55.7%).

*Diethylgold acetylacetonate* quickly decolorised a solution of bromine in carbon tetrachloride. If the addition of the bromine solution was continued until the colour of the latter just persisted, and the resulting solution was evaporated, a volatile lachrymatory substance (? bromoacetylacetonate) was evolved and a colourless crystalline residue remained. After recrystallisation of the latter from ligroin (b. p. 40—60°) it was proved identical with diethylgold bromide by the method of mixed melting points.

*Diethylgold Iodide*.—A mixture of diethylgold acetylacetonate and a small excess of sodium iodide in absolute alcohol became slightly warm, and a colourless precipitate was formed on the addition of water. This was separated, dried, and extracted with ligroin (b. p. 40—60°), in which it was readily soluble. On evaporation of this solution, the iodide was obtained in long colourless needles closely resembling those of diethylgold bromide.

*Diethylgold iodide* has m. p. 67—68° and begins to decompose vigorously at 70—71°. It is somewhat less soluble than the bromide in organic solvents and is insoluble in water. It decomposes violently when heated in a crucible and even when preliminary decomposition has been effected with concentrated sulphuric acid. The best way in which to estimate the gold content is to decompose the substance with a carbon tetrachloride solution of bromine before heating (Found: Au, 51.3.  $C_4H_{10}IAu$  requires Au, 51.6%).

*Ethylenediaminediethylgold Iodide* (formula as V).—This compound was prepared from diethylgold iodide and ethylenediamine in an exactly similar manner to that used for the corresponding bromide. It was crystallised from aqueous alcohol and obtained in colourless plates, m. p. 162° (decomp.), soluble in water and very sparingly soluble in alcohol. Its aqueous solution yielded an immediate precipitate with silver nitrate. Like the corresponding bromide, it darkened slowly on exposure to light, but it is a relatively stable compound (Found: N, 6.2; I, 28.5; Au, 44.4.  $C_6H_{18}N_2IAu$  requires N, 6.3; I, 28.7; Au, 44.6%).

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