157. *The Organic Compounds of Gold. Part VII. Methyl and Ethyl Compounds.*

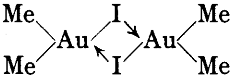
By Frederick H. Brain and Charles S. Gibson.

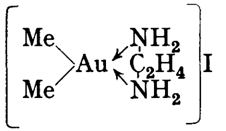
Dimethylmonoiodogold and certain derivatives, the simplest compounds in this series so far described, have been prepared. Their melting and decomposition points are, in general, the highest in the series of methyl, ethyl, *n*-propyl and *n*-butyl compounds.

Certain new derivatives of diethylmonobromogold have also been investigated chiefly with a view to preparing a stable compound containing 5-covalent auric gold. Such a stable compound has not been obtained.

The first organic gold compounds to be described (Pope and Gibson, J., 1907, **91**, 2061) were diethylmonobromogold and certain of its derivatives; but the earliest experiments (June, 1907) were attempts to prepare a methyl compound. Actually, in these experiments, from the action of methylmagnesium iodide on ethereal solutions of hydrochloroauric and hydrobromoauric acids, a benzene solution of a gold compound containing iodine and carbon was obtained and, on one occasion, the compound was isolated in the crystalline but not pure condition. Since diethylmonobromogold, prepared later, was more easily isolated, the possibility of isolating a methyl compound was deferred. In order to facilitate the *X*-ray crystallographic study of organic gold compounds it has become all the more desirable to reinvestigate the preparation of methyl derivatives and, chiefly as a result of our much greater knowledge of organic gold compounds, accumulated during the last few years, this has been rendered comparatively easy.

When an ethereal solution of methylmagnesium iodide is allowed to react with pyridinotrichlorogold suspended in dry pyridine, and the product worked up in a manner based on that finally adopted for the preparation of diethylmonobromogold (Burawoy and Gibson, J., 1934, 860), *dimethylmonoiodogold* (I) having the empirical formula $(CH_3)_2AuI$ is obtained. The compound crystallises in colourless, doubly refracting needles which have a higher melting-decomposition point than the diethyl analogue (Gibson and Simonsen, J., 1930, 2536) : di-*n*-propyl- and di-*n*-butyl-monobromogold are liquids at the ordinary temperature. The crystals are much harder and more easily manipulated than those of diethylmonobromogold, the only compound of this type so far submitted to *X*-ray crystallographic examination (Burawoy, Gibson, Hampson, and Powell, J., 1937, 1690). The compound is soluble but not stable in benzene at the ordinary temperature and this explains the failure to isolate it in the pure state in the experiments of thirty years ago. Nevertheless, it is possible to determine the molecular weight in freezing benzene and this is twice that corresponding to the empirical formula, indicating the correctness of the constitutional formula assigned to the compound.


(I.)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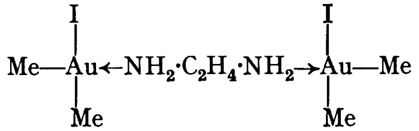
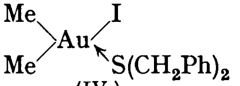
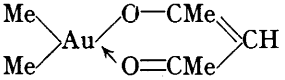

$$Me{-}\overset{\displaystyle I}{\underset{\displaystyle Me}{Au}}{\leftarrow}NH_2{\cdot}C_2H_4{\cdot}NH_2{\rightarrow}\overset{\displaystyle I}{\underset{\displaystyle Me}{Au}}{-}Me$$
(III.)


(IV.)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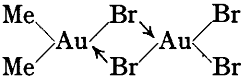

(VI.)

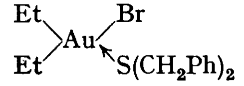
Dimethylmonoiodogold has been further identified by conversion into the colourless stable salt, *ethylenediaminodimethylgold iodide* (II), which is utilised in the isolation of the parent substance. When an aqueous solution of this salt is acidified with hydrochloric acid, the parent substance is immediately precipitated and this is soluble in ligroin. If hydriodic acid is used, the colourless stable non-electrolyte, *monoethylenediaminotetramethyldi-iododigold* (III), practically insoluble in ligroin, is obtained. The corresponding compound from diethylmonobromogold cannot be prepared in this way and, indeed, all attempts to isolate it have failed (see below). On the other hand, monoethylenediamino-tetra-*n*-propyldibromodigold is easily obtained and its decomposition has been studied in some detail (Burawoy and Gibson, J., 1935, 219). Apart from the fact that the compound (III) has no melting point, its behaviour when suspended in warm benzene or when its solutions in other solvents are heated appears to be similar to that of the above tetra-*n*-propyl compound.

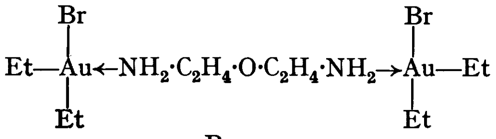
The preparation of *dibenzylsulphidodimethylmonoiodogold* (IV) is not attended by any reduction of the gold compound. By interaction of dimethylmonoiodogold with thallous acetylacetone *dimethylgoldacetylacetone* (V) is readily prepared. It has a much higher melting point than the diethyl analogue (Gibson and Simonsen, *loc. cit.*) and, although it is light-sensitive, its sensitivity is much less. Its solution in ethyl alcohol remains colourless in the dark and when exposed to light it becomes intensely blue by transmitted light and brown by reflected light. This change takes place more rapidly in the light of a mercury vapour lamp and a gold film is produced on the sides of the glass vessel, the solution retaining its blue colour after six days. When dimethylgoldacetylacetone is decomposed with hydrobromic acid, *dimethylmonobromogold*, analogous to (I), is obtained. This is a colourless crystalline compound having a higher melting-decomposition point than the corresponding diethyl compound and when it is treated with bromine it is converted into *monomethyldibromogold* (VI), which crystallises in deep red prisms. It decomposes in an analogous manner to the corresponding ethyl and *n*-propyl compounds and is presumably similar to them in constitution (Gibson and Burawoy, *loc. cit.*).

Although it has not been possible to prepare a co-ordination compound of diethyl sulphide and diethylmonobromogold (not less than 88% of the latter being recovered unchanged), the colourless crystalline *dibenzylsulphidodiethylmonobromogold* (VII), analogous to (IV), is easily obtained and not more than one molecular proportion of dibenzyl sulphide will combine with one Et_2AuBr unit. This indicates that there is no tendency of formation of a non-electrolyte containing 5-covalent auric gold or of a salt which would contain 4-covalent auric gold. Neither does dibenzylsulphidodiethylmonobromogold combine with quinoline, and when treated with ethylenediamine it is decomposed and ethylenediaminodiethylgold bromide is produced.

The anomaly of the apparent non-existence of a non-electrolyte in the diethyl series derived from ethylenediamine and analogous to compound (III) still remains. In investigating this, *mono-*(ββ′*-diaminodiethyl ether*)*tetraethyldibromodigold* (VIII) and *mono-*NN*-diethylethylenediaminotetraethyldibromodigold* (IX) have been obtained: their preparation makes the non-existence of the monoethylenediamino-compound all the more obscure.

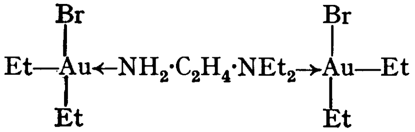
(VII.)





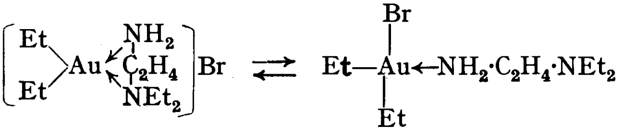
$$Et-\overset{Br}{\underset{Et}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot O\cdot C_2H_4\cdot NH_2\rightarrow\overset{Br}{\underset{Et}{Au}}-Et$$

(VIII.)

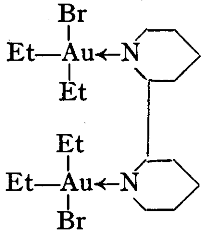


$$Et-\overset{Br}{\underset{Et}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot NEt_2\rightarrow\overset{Br}{\underset{Et}{Au}}-Et$$

(IX.)

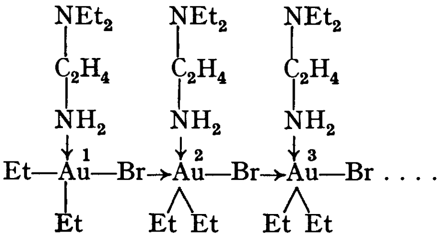


(X.) (XI.)



(XII.)

Compounds (VII) and (IX) are colourless non-electrolytes which decompose at their melting points with evolution of gas in a similar manner to monoethylenediaminotetra-*n*-propyldibromodigold. Compound (IX), in which a tertiary nitrogen atom in an aliphatic compound exhibits co-ordinating power, is closely related to NN*-diethylethylenediaminodiethylgold bromide* (X), a colourless crystalline salt the aqueous solution of which contains bromide ions; its molecular weight in water shows that normal dissociation has taken place. On the other hand, this compound is also soluble in such solvents as benzene and bromoform, in which it behaves as a non-electrolyte. To explain its solubility in non-polar solvents it is assumed that in these solvents it exists as a non-electrolyte to which constitution (XI), NN*-diethylethylenediaminodiethylmonobromogold*, is assigned in keeping with the known lesser co-ordinating power of the tertiary nitrogen atom. This change is reversible, since on recovery of the compound from its solutions in benzene, etc., it is again soluble in water. In addition, the molecular weights of this compound in freezing benzene and in freezing bromoform show that it is considerably associated in these solvents, the molecular weight increasing with increasing concentration. This association may be explained by the annexed formula, in which associated state the auric gold atoms 2, 3, etc. are 5-covalent and have an effective atomic number of 86 (the atomic number of radon) and the auric gold atom 1 would have its usual co-ordination number of four provided that ring formation is excluded. Although there is thus evidence as to the nature of the compound in aqueous solution and in solution in non-polar solvents, there is none concerning its constitution in the solid state. When compound (IX) interacts with pyridine, pyridinodiethylmonobromogold (Gibson and Simonsen, *loc. cit.*), which is insoluble in water, is obtained together with a second product, which is soluble in water and also in benzene and is presumably compound (X).



$$\begin{array}{ccccccc}
 & \mathrm{NEt_2} & & \mathrm{NEt_2} & & \mathrm{NEt_2} & \\
 & | & & | & & | & \\
 & \mathrm{C_2H_4} & & \mathrm{C_2H_4} & & \mathrm{C_2H_4} & \\
 & | & & | & & | & \\
 & \mathrm{NH_2} & & \mathrm{NH_2} & & \mathrm{NH_2} & \\
 & \downarrow 1 & & \downarrow 2 & & \downarrow 3 & \\
\mathrm{Et}— & \mathrm{Au} & —\mathrm{Br}\rightarrow & \mathrm{Au} & —\mathrm{Br}\rightarrow & \mathrm{Au} & —\mathrm{Br}\ \ldots\ldots \\
 & | & & \wedge & & \wedge & \\
 & \mathrm{Et} & & \mathrm{Et}\ \ \mathrm{Et} & & \mathrm{Et}\ \ \mathrm{Et} &
\end{array}$$

The possibility of obtaining a 5-covalent auric gold compound has also been explored by investigating the nature of the product formed by diethylmonobromogold with 2 : 2′-dipyridyl. If there should be a tendency for auric gold to become 5-covalent, a non-electrolyte might be formed in which one molecule of dipyridyl is co-ordinated to one Et_2AuBr unit. When the preparation is carried out with these quantities, dipyridyl remains in excess. The product isolated is *2 : 2′-dipyridyltetraethyldibromodigold* (XII), and there is no evidence of the formation of the salt which would have the same empirical formula and be 2 : 2′-dipyridyldiethylgold bromide. When compound (XII) is treated with ethylenediamine, ethylenediaminodiethylgold bromide is produced with elimination of 2 : 2′-dipyridyl.

This investigation has shown the small tendency—if any—of auric gold to become 5-covalent in this series of compounds.

EXPERIMENTAL.

Dimethylmonoiodogold (I).—Pyridinotrichlorogold (19 g.) was dissolved by heating in dry pyridine (150 c.c.), and the solution cooled in a freezing mixture. To the cold suspension of dipyridinodichlorogold chloride thus obtained, methylmagnesium iodide, prepared from magnesium (3·65 g.), methyl iodide (22 g.), and ether (100 c.c.), was slowly added; throughout these operations and for 10 minutes thereafter, vigorous mechanical stirring was maintained. Water (100 c.c.) was then slowly added, followed by ligroin (b. p. 60—80°, 150 c.c.) and concentrated hydrochloric acid (200 c.c.). After 10 minutes the liquids were filtered, the ligroin layer separated, and the clear aqueous solution extracted ten times with ligroin. The ligroin solution, after being washed thrice with water, was treated with ethylenediamine until no further precipitate (ethylenediaminodimethylgold iodide) was produced: this was thoroughly extracted with water. The filtered aqueous solution was then acidified with dilute hydrochloric acid, and the colourless flocculent precipitate separated, washed with water, and dried in a desiccator over phosphoric oxide (yield 4·3 g., 21%). The compound was purified by dissolving it in ligroin (b. p. 60—80°) and evaporating the filtered solution under reduced pressure at the ordinary temperature in a dry atmosphere.

So obtained, *dimethylmonoiodogold* crystallises in colourless needles which melt at 78·5° to a dark red liquid which detonates violently. It is insoluble in water and soluble in organic solvents, although somewhat sparingly so in ligroin (b. p. 40—60°) and ethyl alcohol. When its solution in ethyl alcohol is treated with alkali, gold is deposited as a brilliant coherent film (Gibson, B.P. 497,240). In solution in benzene and in bromoform the compound decomposes slowly at the ordinary temperature, but by rapid working it is possible to determine the molecular weight in freezing benzene (Found: Au, 55·7; I, 35·8; *M*, 667. $C_4H_{12}I_2Au_2$ requires Au, 55·6; I, 35·9%; *M*, 708).

Ethylenediaminodimethylgold Iodide (II).—The above compound (I) (0·8 g.) was dissolved in ligroin (b. p. 60—80°, 10 c.c.), and a solution of ethylenediamine in absolute alcohol added until no further precipitation took place. The compound was separated, washed with ligroin (yield 0·86 g., 92%), and purified by addition of warm ligroin to a solution in absolute ethyl alcohol until crystallisation commenced. It was obtained in colourless needles, m. p. 168° (decomp.) (Found: C, 12·4; H, 3·2; N, 6·9; I, 30·3; Au, 47·7. $C_4H_{14}N_2IAu$ requires C, 11·6; H, 3·4; N, 6·8; I, 30·7; Au, 47·6%).

Ethylenediaminodimethylgold iodide is readily soluble in water and hot alcohol, but is decomposed in the latter solvent on prolonged boiling.

Monoethylenediaminotetramethyldi-iododigold (III).—The mother-liquors from the purification of compound (II) were evaporated to dryness in a dry atmosphere under reduced pressure, the residue (0·4 g.) dissolved in water (10 c.c.), and the filtered solution acidified with dilute hydriodic acid. The colourless precipitate was washed with water and dissolved in warm acetone, and ligroin (b. p. 60—80°) added until crystallisation commenced (yield, 0·15 g.). The *compound* (III) was obtained in colourless needles which decomposed without melting (Found: C, 9·4; H, 2·6; N, 3·4; Au, 51·3. $C_6H_{20}N_2I_2Au_2$ requires C, 9·4; H, 2·6; N, 3·7; Au, 51·3%).

The compound is insoluble in water, but soluble in acetone and ethyl alcohol. Its conversion into a more sparingly soluble substance in benzene has been described and a similar change takes place, but more slowly, in warm alcohol and acetone.

Dibenzylsulphidodimethylmonoiodogold (IV).—Compound (I) (0·4 g.), dissolved in ligroin (b. p. 60—80°), was mixed with dibenzyl sulphide (0·24 g.) in the same solvent (total, 15 c.c.). The solution was evaporated to dryness in a dry atmosphere; the gummy residue quickly crystallised. This was extracted with warm ligroin and from the filtered solution the *compound* (IV) crystallised in compact prisms in almost theoretical amount. It had m. p. 77—78° (decomp.) (Found: C, 34·0; H, 3·6; I, 22·4; S, 6·3; Au, 34·4. $C_{16}H_{20}ISAu$ requires C, 33·8; H, 3·5; I, 22·4; S, 5·6; Au, 34·7%).

Dimethylgoldacetylacetone (V).—Compound (I) (1 g.), dissolved in ligroin (b. p. 60—80°), was mixed with a filtered solution of thallous acetylacetone (0·97 g., slightly more than 1 mol.) in absolute alcohol (25 c.c.), and the thallous iodide separated. The filtrate was evaporated to dryness at the ordinary temperature under reduced pressure. A solution of the residue in ligroin was filtered from a small quantity of thallous compound and evaporated in a dry atmosphere under reduced pressure. The *compound* (V) was obtained in long colourless needles (0·8 g., 87%), m. p. 84° (Found: C, 25·0; H, 4·0; Au, 60·4. $C_7H_{13}O_2Au$ requires C, 25·8; H, 4·0; Au, 60·4%).

Dimethylgoldacetylacetone has a characteristic odour and a not inconsiderable vapour pressure at the ordinary temperature. The behaviour of its solutions in ethyl alcohol when exposed to light has already been described.

Dimethylmonobromogold (as I).—A solution of the above compound (V) (0·6 g.) in alcohol (2 c.c.) was made strongly acid with hydrobromic acid and then diluted with water and extracted with ligroin (b. p. 40—60°). The ligroin solution was washed with water, dried (calcium chloride), filtered, and evaporated in a dry atmosphere under reduced pressure at the ordinary temperature. The *compound* crystallised in long colourless needles, m. p. 68—69° (decomp.), the pure substance being obtained in 66% yield (Found: Br, 25·8; Au, 63·2. $C_4H_{12}Br_2Au_2$ requires Br, 26·1; Au, 64·2%).

Monomethyldibromogold (VI).—A solution of dimethylmonobromogold (0·2 g.) in carbon tetrachloride (10 c.c.) was mixed with a solution of bromine in the same solvent (1·64 c.c. of 1·05N) and kept for 72 hours. The colour gradually deepened and deep red, prismatic crystals separated. The solution was evaporated completely to dryness at the ordinary temperature, and the residue washed carefully with successive small quantities of carbon tetrachloride (Found: Au, 53·3. $C_2H_6Br_4Au_2$ requires Au, 53·0%).

The *substance* dissolves very readily in chloroform to a deep red solution and its other properties have already been described.

Dibenzylsulphidodiethylmonobromogold (VII).—When concentrated solutions in ligroin (b. p. 40—60°) of diethylmonobromogold (1 g.) and dibenzyl sulphide (0·64 g.) were mixed, the *compound* (VII) was immediately precipitated (1·3 g., 80%). It was recrystallised from methyl alcohol and obtained in colourless needles, m. p. 91° (Found: C, 39·4; H, 4·7; S, 5·3; Au, 35·7. $C_{18}H_{24}BrSAu$ requires C, 39·3; H, 4·4; S, 5·8; Au, 35·9%).

No compound other than (VII) could be prepared from the above reactants and the compound was recovered unchanged when it was treated with an equimolecular quantity of quinoline in methyl-alcoholic solution. When a solution of the compound (0·4 g.) in chloroform was treated with a solution of ethylenediamine in absolute alcohol, the colourless precipitate obtained (0·25 g.) was ethylenediaminodiethylgold bromide (Found: Au, 49·1. Calc.: Au, 49·9%).

Mono-(ββ′*-diaminodiethyl ether*)*tetraethyldibromodigold* (VIII).—A colourless oil, which gradually solidified, was precipitated when a solution of diethylmonobromogold (1 g.) in ligroin (b. p. 60—80°, 15 c.c.) was mixed with ββ′-diaminodiethyl ether (0·16 g.) in absolute alcohol (0·5 c.c.). The solid (0·95 g.) after separation and washing with ligroin was dissolved in a small quantity of warm chloroform and to the filtered solution ligroin was added until a faint turbidity was produced; crystallisation then took place in the ice-chest. The *substance* was obtained in colourless needles, m. p. 87° with evolution of gas (Found : Br, 20·5; Au, 50·1. $C_{12}H_{32}ON_2Br_2Au_2$ requires Br, 20·7; Au, 50·9%). The compound was insoluble in water and in aqueous solutions of ββ′-diaminodiethyl ether. On warming with the latter, decomposition took place with the production of gold.

Mono-NN-*diethylethylenediaminotetraethyldibromodigold* (IX).—Diethylmonobromogold (1 g.) in ligroin (b. p. 60—80°, 15 c.c.) was mixed with *NN*-diethylethylenediamine (0·18 g.) in absolute alcohol (1 c.c.). The *compound* (IX) separated immediately as a colourless oil which rapidly crystallised. It was recrystallised from benzene–ligroin and obtained in colourless needles, m. p. 83·5° with evolution of gas (Found : C, 21·7; H, 4·8; N, 3·2; Br, 20·5; Au, 50·1. $C_{14}H_{36}N_2Br_2Au_2$ requires C, 21·4; H, 4·6; N, 3·6; Br, 20·4; Au, 49·9%).

When the compound was suspended in water (10 c.c.), in which it was insoluble, and pyridine (0·14 g., 1 mol.) added, an oil separated which crystallised in the ice-chest. The colourless substance, recrystallised from aqueous methyl alcohol (0·2 g.), had m. p. 64° and was pyridinodiethylmonobromogold (Gibson and Simonsen, *loc. cit.*, give m. p. 59—60°) (Found : Br, 19·2; Au, 47·7. Calc. : Br, 19·3; Au, 47·6%). The aqueous solution, when evaporated to dryness at the ordinary temperature, gave a residue which contained gold. It was not obtained crystalline, but, since it was readily soluble in water and also in benzene, it may have been *NN*-diethylethylenediaminodiethylgold bromide (see below).

NN-*Diethylethylenediaminodiethylgold Bromide* (X).—*NN*-Diethylethylenediamine (0·35 g.) in absolute ethyl alcohol was added to a solution of diethylmonobromogold (1·0 g.) in ligroin (b. p. 60—80°, 15 c.c.) and the colourless oil which separated was extracted with water, in which it was easily soluble. The aqueous solution was evaporated to dryness over concentrated sulphuric acid in a desiccator, the residue dissolved in benzene, and ligroin added until a slight turbidity appeared; the *compound* (X) slowly crystallised in the ice-chest and after separation (1·0 g.) was dried in a desiccator. It had m. p. *ca.* 26° and was hygroscopic (Found : C, 27·0; H, 6·0; N, 6·5; Br, 18·0; Au, 43·6. $C_{10}H_{26}N_2BrAu$ requires C, 26·6; H, 5·8; N, 6·2; Br, 17·7; Au, 43·7%). It dissolved readily in water, bromide ions being present in the solution; it also dissolved readily in benzene and in bromoform (Found : *M*, in water 215, in benzene 2000, 2186, in bromoform 1003. $C_{10}H_{26}N_2BrAu$ requires *M*, 451).

2 : 2′-*Dipyridyltetraethyldibromodigold* (XII).—When ligroin (b. p. 60—80°) solutions of diethylmonobromogold (0·7 g.) and 2 : 2′-dipyridyl (0·33 g., 1 mol.) were mixed, a somewhat gummy precipitate (0·78 g.) was produced. This was separated, washed with ligroin, recrystallised from ethyl alcohol, and obtained in colourless needles, m. p. 169° (decomp.) (Found: C, 26·3; H, 3·4; N, 3·8; Au, 47·4. $C_{18}H_{28}N_2Br_2Au_2$ requires C, 26·1; H, 3·4; N, 3·4; Au, 47·7%). The ligroin solution remaining after separation of the *compound* (XII) was evaporated to dryness; the residue (0·08 g.), after recrystallisation from ligroin (b. p. 40—60°), had m. p. 71°, not depressed by authentic 2 : 2′-dipyridyl. The compound (XII) (0·2 g.) was suspended in water (2 c.c.), ethylenediamine added, and the mixture gently warmed until solution was effected. Evaporation of this solution to dryness at the ordinary temperature and addition of chloroform to a solution of the residue in methyl alcohol gave colourless needles of ethylenediaminodiethylgold bromide (Found: C, 18·1; H, 4·6; Au, 49·2. Calc. : C, 18·2; H, 4·6; Au, 49·9%) formed by elimination of 2 : 2′-dipyridyl.

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