186. *The Organic Compounds of Gold. Part III. Monoethyldibromogold (Monoethylgold Dibromide).*

By Abraham Burawoy and Charles S. Gibson.

A more costly but much more convenient method than that already indicated (J., 1931, 2407) is described for the preparation of diethylmonobromogold * from ethylmagnesium bromide and pyridinotrichlorogold or pyridinotribromogold; the use of pyridinotrichlorogold is to be preferred on account of the ease with which it is prepared.

The constitution (I) of diethylmonobromogold previously suggested has been confirmed. Its molecular weight in freezing bromoform is the same as that in benzene. Its non-salt-like character is again emphasised and the pure compound is a comparatively stable substance, although it darkens very slowly on exposure to light and decomposes at or immediately above its melting point. When treated with aqueous ethylenediamine, followed by an

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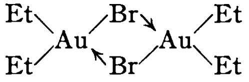
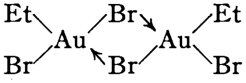
* In previous papers of this series, the compound has been named " diethylgold bromide." Since, like the compound described in the present paper, it is not a salt, the name " diethylmonobromogold " is preferable.

excess of silver nitrate and moderately concentrated nitric acid, it is unaffected; the nitric acid merely liberates the compound unchanged from its co-ordination compound with ethylenediamine, the result being that bromine ions are not present in the final solution, the silver nitrate is unaffected, and the insoluble diethylmonobromogold is recovered quantitatively by extraction with ligroin.


(I.)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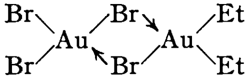
(III.)

The product of the reaction between one molecular proportion of diethylmonobromogold and rather less than two molecular proportions of bromine in chloroform solution was described by Pope and Gibson (J., 1907, **91**, 2064) as monoethylauric dibromide, $(C_2H_5)Br_2Au$; it is now named "monoethyldibromogold." Using precisely the same method, Kharasch and Isbell (*J. Amer. Chem. Soc.*, 1931, **53**, 2712) repeated the preparation of the compound, but did not record any analytical figures and, unfortunately, gave incorrect descriptions of its properties and reactions (see p. 862).

The compound is more conveniently prepared from the reactants in carbon tetrachloride solution, in which it is less soluble than in chloroform and from which it crystallises readily. It is only necessary to wash the product with a little pure carbon tetrachloride, in which diethylmonobromogold is very soluble, to obtain it chemically pure. Gold and bromine determinations confirm the above empirical formula, and the molecular weight of the compound in freezing bromoform shows that its composition is $[Au(C_2H_5)Br_2]_2$. Since the compound is formed by the replacement of two ethyl groups in diethylmonobromogold by bromine atoms, its constitution is either (II) or (III), of which (II) implies the possibility of *cis*- and *trans*-isomerism.

Monoethyldibromogold is less stable than would appear from Pope and Gibson's description. It remains unchanged for about three days in clean glass-stoppered vessels, or in open vessels if dust is excluded, either in darkness or in light; decomposition then begins, and more rapidly if the temperature is a few degrees above the normal. Under ordinary conditions, the change in appearance is hardly appreciable, but microanalysis indicates a high gold and a low bromine content. All the experiments, therefore, had to be carried out on freshly prepared specimens, and this is implied throughout the paper.

The decomposition was investigated quantitatively at the ordinary temperature and at 80—85° : ethyl bromide only was given off, and pure aurous bromide remained unless the decomposition temperature was so high that it decomposed. Typical experiments, described on p. 863, show that the decomposition is quantitatively represented by the equation

$$[Au(C_2H_5)Br_2]_2 = 2AuBr + 2C_2H_5Br$$

(Incidentally, this affords a satisfactory method for preparing pure aurous bromide.) The decomposition of monoethyldibromogold can be explained by constitution (III), but more easily by constitution (II).

Monoethyldibromogold is slightly soluble in carbon tetrachloride and more soluble in chloroform and tetrachloroethane, forming purple solutions. The immediate production of this colour when a colourless solution of diethylmonobromogold containing gold tribromide in suspension is stirred is evidence of the formation of monoethyldibromogold under these conditions. The amount of the compound formed at once is, however, small on account of the low solubility of gold tribromide. The solubility in bromoform is adequate for molecular-weight determinations at the freezing point; the solution is deep red. The solutions of the compound in the above solvents are stable at the ordinary temperature for some time, but ultimately deposit a yellowish precipitate (aurous bromide $\longrightarrow$ gold).

In ether, alcohol, acetone, and ligroin (b. p. 60—80°) monoethyldibromogold rapidly decomposes, aurous bromide and/or gold being precipitated, and from the solutions diethylmonobromogold (m. p. 58—60°, decomp.) is recovered. The decomposition in ligroin (b. p. below 40°) is slower but similar. Generally, monoethyldibromogold is decomposed by solvents which are comparatively readily brominated or oxidised; in all these cases diethylmonobromogold is recovered and the bromination or oxidation of the solvent is due to the action upon it of the gold tribromide.

Monoethyldibromogold does not dissolve in benzene as described by Kharasch and Isbell (*loc. cit.*); the benzene is at first coloured red, this colour rapidly disappears, and a brownish precipitate of aurous bromide and/or gold is formed. The solution contains diethylmonobromogold and brominated benzene: this behaviour is exactly similar to that of the compound towards ligroin, ether, etc. Similarly, monoethyldibromogold does not dissolve in olive oil: the latter remains colourless, but an insoluble residue similar to that obtained with benzene remains. There is no evidence of the direct addition of the gold complex at the double bond as suggested by Kharasch and Isbell, but only of ordinary bromination by gold tribromide accompanied by reduction of the latter.

When monoethyldibromogold is treated with an aqueous solution of potassium bromide, a solution of potassium bromoaurate is obtained and diethylmonobromogold is produced as a colourless crystalline precipitate. Its behaviour towards an aqueous solution of sodium chloride is exactly similar and not as described by Kharasch and Isbell, who stated that the compound dissolved completely and also assumed that complexes of the chloroaurate type are produced. Monoethyldibromogold is very slowly attacked by water; on long standing, the latter becomes red and a brownish precipitate (aurous bromide and diethylmonobromogold) remains, the obvious changes taking place (compare Kharasch and Isbell, *loc. cit.*). Apart from the simultaneous production of a colourless precipitate of diethylmonobromogold, the behaviour of the compound towards water is exactly similar to that of gold tribromide, which is slow but definite. It is considered important to avoid such substances as ligroin, water, and alcohol, as used by Kharasch and Isbell in the isolation of monoethyldibromogold, for the reasons stated above.

Co-ordination compounds of the type $[(C_2H_5)BrAuQ]Br$, where Q represents a diamine, have not been obtained. When monoethyldibromogold is treated rapidly with aqueous ethylenediamine, bisethylenediaminogold tribromide, $[Au\,en_2]Br_3$ (Gibson and Colles, J., 1931, 2410), and ethylenediaminodiethylgold bromide, $[AuEt_2en]Br$ (Gibson and Simonsen, J., 1930, 2531), are obtained.

Although no derivative of monoethyldibromogold has been obtained, sufficient evidence now exists that it is a chemical individual. Constitution (III), indicating a compound formed from and easily split up into gold tribromide and diethylmonobromogold, is in keeping with its behaviour towards easily brominated or oxidisable organic solvents, towards water and aqueous solutions of sodium chloride and potassium bromide, and towards ethylenediamine. The fact that the colour of the compound is not very different from that of gold tribromide is additional, if only slight, evidence in favour of constitution (III), which indicates the presence of a gold atom attached to four bromine atoms, to three by ordinary co-valencies and to one by a co-ordinate link; in the molecule of gold tribromide there are two such gold atoms.* Although the major portion of the evidence now available is in favour of constitution (III), constitution (II) is not impossible and it is probable that the configuration of the compound cannot be determined by purely chemical methods. The dipole moment of the compound compared with that of diethylmonobromogold might elucidate the structure, but monoethyldibromogold has too small a solubility in a suitable solvent (carbon tetrachloride) to permit of its determination.

EXPERIMENTAL.

Modified Preparation of Diethylmonobromogold.—(i) *From pyridinotrichlorogold.* A solution of fine gold in aqua regia is freed from volatile acid by evaporation, diluted, treated with excess

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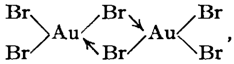
* The results (to be described later) of a detailed investigation of the gold bromides indicate that (1) gold tribromide has a molecular weight in boiling bromine indicating the formula $[AuBr_3]_2$ and therefore its constitution is probably  , and (2) the ammino-derivative of monoethyldibromogold referred to by Pope and Gibson was probably "a variety of fulminating gold" produced by the action of an aqueous solution of ammonia on the gold tribromide portion of monoethyldibromogold.

of calcium carbonate, and filtered. To the diluted stirred filtrate, pyridine is added until no further yellow precipitate is formed; this is washed with water by decantation and dried over phosphoric oxide in a vacuum. To a mechanically stirred suspension of the pyridinotrichlorogold (19 g.) in dry pyridine (200 c.c.), a filtered solution of ethylmagnesium bromide [prepared from magnesium (2·7 g.; 2·2 mols.), ethyl bromide (11·9 g.), and ether (45 c.c.)] is added drop by drop during 8—10 minutes, the mixture being cooled in a freezing mixture. Water at 0° (100 c.c.) is immediately added, followed by ligroin (b. p. 60—80°; 300 c.c.), and then hydrobromic acid (*d* 1·49; 300 c.c.) at such a rate that the temperature does not rise above 40°. The mixed liquids are filtered from precipitated gold and a little unchanged pyridinotrichlorogold. The ligroin solution is separated after shaking, washed with water, and treated with ethylenediamine until no further colourless precipitate is formed (usually three extractions); the precipitate is removed each time by extraction in water. The filtered aqueous solution of the ethylenediamine compound is made just acid with hydrobromic acid, and the colourless crystalline diethylmonobromogold filtered off, washed with water, and dried over phosphoric oxide; yield 3·3 g. (20%).

(ii) *From pyridinotribromogold.* This compound (40 g.), suspended in dry pyridine (200 c.c.), is treated with a filtered solution of ethylmagnesium bromide [prepared from magnesium (4·3 g.; 2·2 mols.), ethyl bromide (18·6 g.), and ether (50 c.c.)] in a similar manner, and the product isolated under the same conditions. As many as ten extractions with ligroin may be necessary; yield, 4·8 g. (18·5%).

The product obtained in (i) and (ii) was completely identified, m. p. 58—60° (decomp.). Its molecular weight in freezing bromoform (m. p. 7·6°; Δ 144) was 652, 679 (calc. for $[AuEt_2Br]_2$, 672) (compare Gibson and Simonsen, *loc. cit.*).

Monoethyldibromogold (compare Pope and Gibson, *loc. cit.*).—To a filtered solution of diethylmonobromogold (2·92 g.) in carbon tetrachloride (15 c.c.) a solution of bromine in carbon tetrachloride (1·56*N*, 11·0 c.c.; theo. for 1 mol., calculated from the empirical formula of the gold compound, 11·45 c.c.) is added, and the mixture kept in a glass-stoppered vessel for 48 hours; during most of this time the colour of the bromine persists and the compound rapidly crystallises. It is collected on sintered glass, washed with successive small quantities of carbon tetrachloride, dried on porous porcelain, and kept free from dust: yield, 2·1 g. The mother-liquor, allowed to evaporate spontaneously, yields a further small quantity.

The compound was treated with sodium methoxide in excess of methyl alcohol, the mixture heated for 1 hour on the water-bath and acidified with nitric acid, and the bromine estimated by titration with silver nitrate and potassium thiocyanate {Found: Br, 41·5; Au, 51·1; *M*, in freezing bromoform, 781, 798. Calc. for $[(C_2H_5)Br_2Au]_2$: Br, 41·4; Au, 51·1%; *M*, 772. Found, by micro-methods, for a specimen which had been kept in diffused light in a glass-stoppered vessel for 1 week: Br, 37·5; Au, 55·8%}.

Decomposition of Monoethyldibromogold.—The following are typical experiments:

(i) The substance was heated at 80—85° for 1½ hours {Found: loss in weight, 28·4, 28·4. $[Au(C_2H_5)Br_2]_2$ requires for loss of 2EtBr, 28·2%}. The residue of yellowish-green crystals having an effloresced appearance was pure aurous bromide (Found: Au, 71·0. Calc.: Au, 71·1%).

(ii) Dry carbon dioxide was passed over the substance at the ordinary temperature, and the volatile product led into aqueous-alcoholic silver nitrate; the weight of the precipitate (silver bromide) was compared with the loss in weight of the substance. During 11 days, 0·5288 g. lost 0·1170 g. (22·1%); the silver bromide weighed 0·1995 g. (0·1170 g. of ethyl bromide should precipitate 0·2016 g. of silver bromide).

(iii) As in (ii), but the decomposition was continued for a longer period, and the bromine content of the residue was determined (by the sodium methoxide method described above) and compared with what it should be theoretically if the loss in weight was due to loss of ethyl bromide. After 15 days, 0·8442 g. lost 0·1757 g. (26·2%). The residue contained 33·9% of bromine; if the loss in weight were due to ethyl bromide, the residue should have contained 33·0% of bromine.

Action of Aqueous Ethylenediamine on Monoethyldibromogold.—A weighed quantity of monoethyldibromogold was treated rapidly with a slight excess of aqueous ethylenediamine, and the clear yellow solution, after slight warming, addition of a known excess of silver nitrate, and acidification with nitric acid, was titrated with potassium thiocyanate {Found: Br, 31·3, 31·3%, *i.e.*, three-quarters of the theoretical bromine content. $[Au(C_2H_5)Br_2]_2$ requires Br, 41·4%}. By extraction of the solid residue, left on filtration, with ligroin, diethylmonobromogold, m. p. 58—60° (decomp.), was obtained. For comparison, gold tribromide without any special purification was submitted to the same series of operations (Found : Br, 53·9. Calc. for $AuBr_3$: Br, 54·9%). This indicated that monoethyldibromogold, when treated with aqueous ethylenediamine, yields equimolecular quantities of bisethylenediaminogold tribromide and ethylenediaminodiethylgold bromide. When this mixture is acidified, the latter yields diethylmonobromogold and only the bromine in bisethylenediaminogold tribromide is ionised and estimated (compare p. 861).

In an attempt to prepare an ethylenediamine co-ordination compound, monoethyldibromogold (0·5 g.), suspended in carbon tetrachloride, was shaken with a slight excess of ethylenediamine in concentrated aqueous solution. The base was added gradually until the colour of the gold compound had disappeared. The yellow aqueous solution was separated from the carbon tetrachloride (which left no residue on evaporation), filtered, and treated with alcohol until no further yellow crystals of bisethylenediaminogold tribromide separated (Found : Au, 36·2. Calc. : Au, 35·4%) (compare Gibson and Colles, *loc. cit.*). The aqueous-alcoholic filtrate was evaporated free from alcohol and acidified with hydrobromic acid ; the colourless crystals which separated were identified, by comparison with an authentic specimen, as diethylmonobromogold, m. p. 58—60° (decomp.) : yield, 0·2 g. (92%).

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