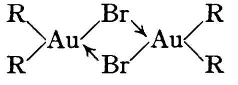
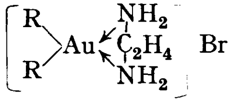
72. *The Organic Compounds of Gold. Part VI. Heterocyclic Compounds.*

By Abraham Burawoy and Charles S. Gibson.

The early work on the action of magnesium on αε-dibromopentane in ether (Grignard and Vignon, *Compt. rend.*, 1907, **144**, 358; von Braun and Sobecki, *Ber.*, 1911, **44**, 1918) showed that the resulting solution contained, besides dimagnesium pentamethylene dibromide, magnesium compounds of decamethylene dibromide and higher homologues of the type Br·$[CH_2]_{5x}$·Br. In spite of the complexity of such a product, von Braun and Sobecki were able to prepare normal products from the interaction of dimagnesium pentamethylene dibromide and certain typical organic compounds; Hilpert and Grüttner (*Ber.*, 1914, **47**, 177, 186) indicated that according as the interaction of magnesium and αε-dibromopentane in ether proceeded rapidly or slowly, the yield of the normal product was 50% or 90%. Heterocyclic compounds of the type $C_5H_{10}{>}XR$, where X = P, Sb, or Bi and R = an alkyl or an aryl group, were prepared by Grüttner and Wiernik (*Ber.*, 1915, **48**, 1473) and, where X = As, by Zappi (*Bull. Soc. chim.*, 1916, **19**, 151) by the action in ethereal solution of the product of the reaction of magnesium and αε-dibromopentane and compounds of the type $RXCl_2$. Under somewhat analogous conditions, using diethyl-lead dichloride and dimethyltin dichloride, Grüttner and Krause (*Ber.*, 1916, **49**, 2666) obtained diethyl*cyclo*pentamethyleneplumbine and Grüttner, Krause, and Wiernik (*Ber.*, 1917, **50**, 1549) obtained dimethyl- and diethyl-*cyclo*pentamethylenestannines, $C_5H_{10}{>}XR_2$. Bygdèn (*Ber.*, 1915, **48**, 1236) prepared *cyclo*pentamethylenesilicon dichloride, $C_5H_{10}{>}SiCl_2$, using silicon tetrachloride. All these compounds have definite boiling points and were separated by fractional distillation, and the isolation of derivatives containing ring systems larger than that produced by dimagnesium pentamethylene dibromide either was not attempted or was unsuccessful.

Since organo-gold compounds of type (I) cannot be distilled even under highly reduced

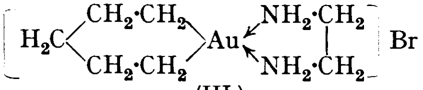
(I.) 

 (II.)

pressure and are not sufficiently stable, when solid at the ordinary temperature, to allow of prolonged recrystallisation, any organo-gold compounds formed by the mixture produced by the action of magnesium on αε-dibromopentane in ethereal solution have to be isolated in the form of their co-ordination compounds (those with ethylenediamine being the most easily accessible), which, corresponding to compounds of type (I), are of type (II).

In the first experiments (1931—32), carried out by one of the authors (C. S. G.) and Mr. W. M. Colles, the reaction between magnesium and αε-dibromopentane was performed rapidly and this mixture was allowed to react with hydrobromoauric acid in ethereal solution under conditions similar to those obtaining in the earlier investigations (J., 1930, 2531; 1931, 2407). The only organo-gold compound isolated was a colourless crystalline salt, becoming slightly coloured on exposure to light, and having the molecular formula $C_{12}H_{28}N_2BrAu$. Since Grüttner and collaborators obtained only *cyclo*pentamethylene derivatives, this compound was believed to be a *cyclo*pentamethylene derivative and was described as ethylenediamino*spiro*bis(pentamethylene)gold bromide. The colourless oily product, which cannot be purified, obtained from this by treatment in aqueous solution with hydrobromic acid was described as *spiro*bis(pentamethylene)gold bromide (Gibson, *Nature*, 1933, **131**, 130). The erroneous conclusions as to the constitutions of these two compounds are now corrected in the light of further experimental work.

In the second series of experiments, commenced in 1934, with pyridinotrichlorogold (J., 1931, 2407; 1934, 860) and the mixture obtained by the slow reaction between $\alpha\varepsilon$-dibromopentane and magnesium, not only was the salt $C_{12}H_{28}N_2BrAu$ again isolated in the largest amount, but also a colourless salt, $C_7H_{18}N_2BrAu$, was obtained in less quantity. The latter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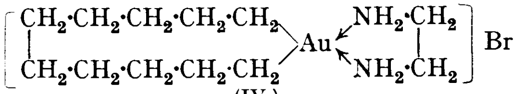
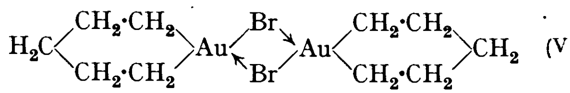

(IV.)

is obviously *ethylenediamino*cyclo*pentamethylenegold bromide* (III) and the compound $C_{12}H_{28}N_2BrAu$ must be *ethylenediamino*cyclo*decamethylenegold bromide* (IV), the composition being analogous to that of the *cyclo*pentamethylene compound. These two organo-gold compounds, like all such compounds containing tervalent gold, obey the rules that the gold atom has an octet of electrons and an effective atomic number of 84.

In addition to these two compounds, analytical evidence was obtained of the existence of gold compounds having a higher carbon content, and therefore presumably containing larger heterocyclic rings, together with a mixture of hydrocarbons, from which *n*-triacontane was isolated.

Apart from the isolation of these two derivatives of heterocyclic gold compounds, this work emphasises the complex nature of the mixture resulting from the interaction of magnesium with $\alpha\varepsilon$-dibromopentane in ethereal solution under various conditions.

On acidification with hydrobromic acid of an aqueous solution of ethylenediamino*cyclo*decamethylenegold bromide (IV), a colourless oil separates. This is soluble in ligroin, but the residue remaining after evaporation decomposes too quickly to allow of its identification. When ethylenediamino*cyclo*pentamethylenegold bromide (III) is submitted to the same process, a colourless crystalline product of empirical formula $C_5H_{10}BrAu$ is obtained. This also is unstable and undergoes extensive decomposition in a closed apparatus in three days. The compound is insoluble in water and sparingly soluble in alcohol and *cyclo*hexane. It is readily soluble in chloroform, bromoform, carbon tetrachloride, ether, and benzene, but undergoes rapid decomposition in the solutions. Its molecular weight in bromoform was 434·3 after five minutes (calc. for $C_5H_{10}BrAu$, 347·2), 393 after 10 minutes, and 369 after 15 minutes. In view of the known constitution of dialkylmonobromogold compounds (J., 1930, 2531) and the above molecular-weight determinations it is reasonable


(V.)

to conclude that the above substance is *bis*(cyclo*pentamethylenemonobromogold*) (V). From this it follows that the compound obtained from (IV) by the action of hydrobromic acid would, if isolated, be bis(*cyclo*decamethylenemonobromogold).

EXPERIMENTAL.

*First Series of Experiments.—Ethylenediamino*cyclo*decamethylenegold bromide* (IV). The filtered ethereal solution obtained by allowing pure $\alpha\varepsilon$-dibromopentane (Johnson, J., 1933, 1531) (53 g.; 3 mols.) to react as completely as possible with magnesium (11 g.) in ether (150 c.c.) during 1½ hours—the conditions for the rapid reaction—was added to an ethereal solution (250 c.c.) of hydrobromoauric acid (Gibson and Colles, J., 1931, 2407), prepared from gold tribromide

(33 g.), the reaction conditions described by Gibson and Simonsen (J., 1930, 2531) being maintained. After 3 hours, the mixture was treated and stirred with ice-water (50 c.c.) and then with acetic acid (10 c.c.) and water (40 c.c.). The liquids were filtered rapidly from precipitated gold and the separated ethereal solution was washed rapidly with water until free from water-soluble gold compound and then treated with ethylenediamine until, after thorough mixing, no further colourless precipitate was formed. The mixture was extracted many times with small quantities of water until all the precipitate had dissolved. (The washed ethereal solution contained hydrocarbons, from which *n*-triacontane, m. p. 66°, was isolated.) The combined aqueous solutions after acidification with hydrobromic acid (cloudy precipitate) were rapidly extracted with ether, the ethereal solution again treated with ethylenediamine, and the water-soluble product extracted as before. This procedure is necessary to separate hydrocarbon by-products as completely as possible; the various operations and especially the extractions with ether must be carried out rapidly, otherwise a considerable amount of decomposition of the "parent" gold compound takes place. The aqueous solution was evaporated under reduced pressure at the ordinary temperature, and the almost colourless, crystalline salt (0·08 g.) separated. The combined product from four such experiments was recrystallised three times from warm water (80°), *ethylenediamino*cyclo*decamethylenegold bromide* being obtained in small colourless needles, which darkened a little on standing and decomposed slowly at 150° and rapidly at 180° (Found: C, 30·5, 30·5; H, 6·0, 5·85; N, 5·7, 6·0; Br, 17·7, 17·5; Au, 40·4, 40·1. $C_{12}H_{28}N_2BrAu$ requires C, 30·2; H, 5·9; N, 5·9; Br, 16·7; Au, 41·3%). The compound (IV) is readily soluble in ethyl alcohol and in warm water; it is sparingly soluble in cold water. In spite of its being a salt, it is difficult, especially when only small quantities are available, to eliminate traces of hydrocarbon by-products.

Second Series of Experiments.—The Grignard reagent was prepared by allowing magnesium to react slowly with the corresponding quantity of pure αε-dibromopentane, the ethereal solution being finally gently heated for 7 hours—the conditions of the slow reaction.

To a mechanically stirred suspension of pyridinotrichlorogold (40 g.) in dry pyridine (300 c.c.), a filtered solution prepared as described above from magnesium (10·2 g.), αε-dibromopentane (60 g.; 2½ mols.), and ether (100 c.c.) was added during 15 minutes, the whole being cooled in a freezing mixture. The mixture was stirred during a further 30 minutes and water (100 c.c.) at 0° was then added, followed by ligroin (b. p. 40—60°, 200 c.c.) and by hydrobromic acid (*d* 1·49, 450 c.c.), added at such a rate that the temperature did not rise above 30°. The mixture was stirred during another 30 minutes and then filtered from precipitated gold and unchanged pyridinotrichlorogold. The ligroin solution was separated, the aqueous solution extracted three times with fresh ligroin, and the combined ligroin solutions, after being washed with water, were shaken with ethylenediamine until no further colourless precipitate was produced. The precipitate was collected, washed by decantation with fresh ligroin, and finally separated from a small quantity of ligroin by evaporation at the ordinary temperature.

The product from four such preparations was dissolved in warm 20% aqueous alcohol and, after standing at the ordinary temperature, the solution (A) was decanted from an oily precipitate. This was dissolved in the minimum quantity of alcohol, and the filtered solution evaporated under reduced pressure over sulphuric acid. The residue (2 g.) was dissolved in alcohol and precipitated with ether. The colourless precipitate was recrystallised from warm aqueous alcohol, a mixture of ethylenediamine derivatives of organic gold compounds being obtained [Found: C, 39·9; H, 6·8; Au, 33·2. Calc. for $C_7H_{18}N_2BrAu$ (ethylenediamino*cyclo*pentamethylenegold bromide): C, 20·6; H, 4·4; Au, 48·4%. Calc. for $C_{12}H_{28}N_2BrAu$ (*cyclo*decamethylene compound): C, 30·2; H, 5·9; Au, 41·3%. Calc. for $C_{17}H_{38}N_2BrAu$ (*cyclo*pentadecamethylene compound): C, 37·3; H, 7·0; Au, 36·0%].

On evaporation, under reduced pressure, of filtrate (A) at about 60° and finally to small bulk at the ordinary temperature a crystalline material (10 g.) was obtained, which was recrystallised twice from warm alcohol, giving small colourless plates of pure *ethylenediamino*cyclo*pentamethylenegold bromide* (III), decomp. 150°, soluble in water and sparingly soluble in cold alcohol (Found: C, 21·0; H, 4·4; N, 7·35; Br, 20·1; Au, 48·4. $C_7H_{18}N_2BrAu$ requires C, 20·6; H, 4·4; N, 6·9; Br, 19·6; Au, 48·4%).

By the careful addition of water to the alcoholic filtrates obtained in the purification of compound (III), colourless precipitates were obtained. These were recrystallised several times from aqueous alcohol and finally from warm water (80°), the products being analysed at each stage [Found: (i) C, 32·9; H, 6·3; Au, 38·5; (ii) C, 32·6; H, 6·4; Au, 39·3; (iii) C, 31·6; H, 6·2; Au, 40·1; (iv) C, 31·6; H, 6·1; Au, 39·7; (v) C, 31·3; H, 6·0; Au, 39·8; (vi) C, 30·85; H, 6·1; Au, 40·25%]. They approximate in composition to ethylenediamino*cyclo*decamethylenegold bromide (IV); the analyses show the presence of traces of gold compounds of higher carbon content which are difficult to separate.

cyclo*Pentamethylenemonobromogold* (V).—To an aqueous solution of compound (III), a slight excess of hydrobromic acid was added; the colourless crystalline precipitate obtained was extracted with ligroin (b. p. up to 40°), in which it was sparingly soluble but moderately stable at low temperatures. The ligroin solution was washed with water, dried with anhydrous sodium sulphate, and concentrated at the ordinary temperature under reduced pressure, the product crystallising in long colourless needles, which decomposed explosively at 80° [Found: Br, 23·3; Au, 56·9. $(C_5H_{10}BrAu)_2$ requires Br, 23·0; Au, 56·8%]. The instability of the compound, its behaviour in various solvents, and attempts to determine its molecular weight have been described above.

The cost of this investigation has been met from grants from Imperial Chemical Industries Limited and from the Government Grants Committee of the Royal Society. One of the authors (A. B.) gratefully acknowledges a maintenance grant from the Academic Assistance Council.

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[*Received, January* 10*th*, 1936.]