

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE NATIONAL INSTITUTE OF HEALTH OF THE UNITED STATES PUBLIC HEALTH SERVICE]

**THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. III.  
DIRECT INTRODUCTION OF GOLD INTO THE AROMATIC  
NUCLEUS  
(PRELIMINARY COMMUNICATION)<sup>1,2</sup>**

BY M. S. KHARASCH AND HORACE S. ISBELL

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### Introduction

In previous papers by Kharasch and Isbell<sup>3</sup> the applicability of the Grignard reagent in the preparation of gold carbon compounds is discussed. The authors point out that in their experience the use of the Grignard reagent is definitely limited to the preparation of gold compounds of the ethyl radical and radicals that lie below the ethyl radical in the Table of Electronegativity of Radicals.<sup>4</sup> This limitation of the Grignard reagent, as well as the inapplicability of other indirect methods, to the preparation of aromatic gold compounds forced us to investigate the direct action of anhydrous gold chloride on aromatic compounds.

Fortunately, the direct action, whenever possible, of anhydrous auric chloride upon aromatic substances leads to the introduction of the gold into the aromatic nucleus and the formation of a compound  $RAuX_2$ . Our preliminary results indicate that direct "auration" is as general a reaction as nitration, halogenation or mercuration, except that it is a much faster reaction and the products of the reaction are much less stable.

**Previous Work.**—The action of aqueous solutions of auric chloride upon organic substances has been studied exhaustively.<sup>5</sup> The results of these studies may be summarized as follows: first, the reduction of a water solution of gold chloride by organic substances is a function of the hydrogen-ion concentration and in general the reduction is more rapid in alkaline solution. Second, organic substances may be divided into three classes based upon their behavior toward a water solution of gold chloride: (1) a class of substances which neither reduce nor extract gold chloride from a water solution (the saturated hydrocarbons belong in this class); (2) organic substances which are oxidized by a water solution of gold chloride

<sup>1</sup> Published by permission of the Surgeon-General.

<sup>2</sup> This work is being continued by M. S. Kharasch and T. M. Beck.

<sup>3</sup> Kharasch and Isbell, *THIS JOURNAL*, **52**, 2919 (1930); *ibid.*, **53**, 2701 (1931).

<sup>4</sup> Kharasch and Marker, *ibid.*, **43**, 3131 (1926); Kharasch and Flenner (unpublished work).

<sup>5</sup> Lenher, *ibid.*, **24**, 357, 918 (1902); **35**, 550 (1913). See also Mellor. "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, 1923, Vol. III, pages 600–603, for numerous references.

with the consequent precipitation of metallic gold; (3) a class of substances which extract the gold chloride from a water solution.

**Behavior of Anhydrous Gold Chloride toward Organic Reagents.**—Our studies of the behavior of anhydrous gold chloride toward organic substances make it quite evident that the solvents belonging in Class 3, cited above, in reality do not extract gold chloride from water but a hydrated complex. Furthermore, our experience indicates that aromatic substances, as well as oxygen-containing aliphatic compounds, either react with anhydrous gold chloride to give, at least as intermediates, gold carbon compounds or combine with that reagent to form complexes. Saturated hydrocarbons and alkyl halides in the aliphatic series, and nitrobenzene in the aromatic series, appear to be the only compounds unaffected by anhydrous gold chloride. Nitrobenzene, incidentally, in spite of the appreciable solubility of anhydrous gold chloride in it, is thus far the only aromatic compound which we have found not to interact or form very stable complexes with that reagent.

The above conclusions are based upon the following considerations: (1) the behavior of anhydrous auric chloride toward benzene and other substances; (2) the behavior toward benzene and other aromatic substances of hydrated auric chloride or anhydrous auric chloride previously treated with small quantities of ether, alcohol, glacial acetic acid, etc.

**The Reaction of Anhydrous Auric Chloride and Benzene.**—When dry benzene is added slowly to anhydrous auric chloride, a vigorous reaction ensues—hydrogen chloride is evolved and 1,2,4,5-tetrachlorobenzene and aurous chloride may be isolated from the mixture. On the other hand, if finely divided anhydrous auric chloride is added to a large quantity of dry benzene (thiophene free), an immediate evolution of hydrogen chloride takes place and the solution acquires a red color which in a few minutes turns brown. If allowed to stand for a few moments longer, a bright yellow precipitate is formed. The precipitate thus formed is aurous chloride and the solution contains phenyl chloride.<sup>6</sup> The yield is 97.7% of the calculated amount.

However, if the reaction given above is stopped at the point where the brown precipitate is formed, a different result is obtained. This may be accomplished by the addition of ether, a few cc. of acetic acid, alcohol, ethyl acetate or other reagents containing oxygen. If an equal volume of ether is added a yellow solution results, without the formation of any aurous chloride. Upon evaporation of the ether-benzene mixture yellow crystals are obtained. These may be separated from the adhering gold chloride by

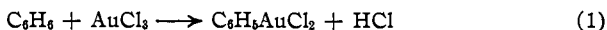
<sup>6</sup> In this connection the statement of Lenher, *THIS JOURNAL*, 35, 552 (1913), is quite pertinent: "It has not been possible to produce aurous type of compounds (inorganic) by the use of an organic reducing agent." Under anhydrous conditions the formation of aurous chloride is quite the usual occurrence.

thorough washing with water and crystallization from alcohol. Beautiful, long, narrow crystals, which are almost colorless, are thus obtained. The analysis and behavior of the compound indicate that it is phenyl auric dichloride. The yield is 0.41 g. from 2 g. of auric chloride.

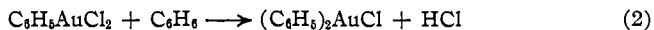
*Anal.* Subs. (dried over  $P_2O_5$ ), 0.0597: Au, 0.0342. Calcd. for  $Au(C_6H_5)_2Cl_2$ : Au, 57.14. Found: Au, 57.17.

The compound is difficultly soluble in water, readily soluble in salt solution, very soluble in alcohol, difficultly soluble in ether, insoluble in benzene and petroleum ether. It decomposes at 73–75° or upon long standing.

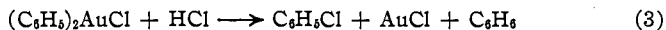
The first step of the reaction may therefore be postulated as follows



It is quite likely that the molecule of phenyl auric dichloride reacts then with another molecule of benzene to give diphenyl auric chloride and hydrogen chloride.



The compound diphenyl auric chloride is evidently an exceedingly unstable substance and in the presence of hydrogen chloride the following decomposition takes place



Our assumption of the instability of diphenyl auric chloride is based upon our attempts to prepare this substance directly from auric chloride and the Grignard reagent, and some rather extensive experiments to prepare the compound from phenyl auric dichloride and phenyl magnesium bromide. In all of the above experiments we were unable to isolate the compound diphenyl auric chloride.

The evidence adduced points to the conclusion that the addition of ether to the mixture of anhydrous auric chloride and benzene, at a point where the brown color is formed, effectively blocks the interaction of the phenyl auric dichloride with benzene by forming a stable complex between the ether and the phenyl auric dichloride.

Additional evidence regarding the combination of ether with anhydrous auric chloride lies in the fact that when we add ether to the benzene solution prior to the addition of gold chloride, no phenyl auric dichloride is formed. Furthermore, neither chloroauric acid nor hydrated gold chloride gives any gold organic compound when treated with benzene, as in the formation of phenyl auric dichloride. That this inhibiting effect of the ether is not due to a dilution effect is shown in a most striking manner by the fact that one drop of benzene in 10 cc. of petroleum ether reacts vigorously with dry auric chloride, while pure benzene will not react with anhydrous auric chloride which is simply moistened with ether.

**Effect of Substituents upon Reactivity of Aromatic Substances and Anhydrous Auric Chloride.**—Thus far the following gold–carbon com-

pounds have been prepared by direct auration: phenyl auric dichloride, tolyl auric dichloride, diphenyl auric dichloride, methylsalicylate auric dichloride and *o*-nitroanisole auric dichloride. The latter substance has not been analyzed as yet. Only a preliminary study has been made of the action of gold chloride and of different types of radicals, their rates of reaction and the stability of the products. The time interval before the addition of the ether depends upon the particular compound into which gold is being introduced. If a reaction takes place with a high speed, obviously it is extremely difficult to stop that reaction at one of the intermediate stages.

Very negative radicals react very vigorously with auric chloride. Thus in a qualitative way we might arrange the aromatic hydrocarbons in the following order according to the vigor of their reaction with auric chloride: naphthalene, diphenyl, toluene and benzene. This arrangement of the substances is the same as that found for the electronegativity of the radicals.<sup>4</sup> The instability of these organo-auric dichlorides is also in perfect accord with the hypothesis developed in the preceding section, that slightly electronegative radicals should form more stable compounds toward hydrolytic agents than the compounds of the more electronegative radicals.

The influence of different substituents in the benzene nucleus on the rate of reactions with anhydrous gold chloride is quite marked. Strongly electronegative groups, *i. e.*,  $\text{NH}_2$ ,  $-\text{N}(\text{CH}_3)_2$ ,  $\text{OH}$ , increase the speed of reaction and decrease the stability of the products. Weakly electronegative groups have the opposite effect. Thus the reaction between phenol and auric chloride is almost instantaneous, while the reaction with nitrobenzene is extremely slow, at ordinary temperature. Combinations of the two types of effects, for example, methyl salicylate and *o*-nitroanisole react to give fairly stable products. Between the substances which react extremely rapidly with auric chloride and lead to very unstable substances and those that react slowly are a large number of compounds which in the future will form the foundation for a chemistry of organic gold compounds.<sup>7</sup>

**Gold Chloride as a Halogen Carrier.**—If benzene is added dropwise to anhydrous gold chloride, a vigorous reaction takes place and 1,2,4,5-tetrachlorobenzene may be isolated from the residue. On the other hand, if a large quantity of benzene is added at one time, phenyl chloride is formed. We have shown previously that an intermediate compound, phenyl auric dichloride, is formed. This compound, similar to other

<sup>7</sup> Not only do the aromatic compounds undergo direct auration but aliphatic compounds containing active hydrogen atoms undergo a similar reaction. Thus, malonic acid reacts with anhydrous auric chloride with the liberation of hydrogen chloride and the formation of a gold organic compound. The latter resembles in properties phenyl auric dichloride. These reactions are being investigated.

organo-metallic compounds, reacts with chlorine gas to give auric chloride and phenyl chloride. In the presence of chlorine gas auric chloride can thus function as a halogen carrier. In actual experiments benzene was rapidly chlorinated when auric chloride was used as a catalyst. The chlorine was practically completely absorbed and one or more chlorine atoms easily introduced into benzene. Phenylauric dichloride reacted equally well as a catalyst.

This definite mechanism of the catalytic effect of auric chloride is of interest particularly when one bears in mind similar catalytic activity on the part of other metal catalysts where no such intermediates have been isolated, *i. e.*, iron and aluminum. It is hard to see, however, in view of the difference in position of these metals in the electromotive series, how the isolation of the intermediate gold organic substances helps the theory of intermediate compound formation as applied to the other catalysts.

The gold halides may also be employed as condensing agents in the Friedel and Craft syntheses in place of the aluminum halides.

**Properties of Aryl Gold Dichlorides.**—Upon heating, the aryl gold dichlorides decompose at their melting points. They are instantly acted upon by strong reducing agents, such as stannous chloride or hydroquinone, and metallic gold is formed. This behavior of the aryl gold dichlorides is similar to that of the alkyl gold dichlorides and strikingly different from that of the dialkyl gold chlorides, which are very stable to reducing agents.

With thiosalicylic acid the aryl gold dichlorides react like auric chloride, namely, the auro-thiosalicylic acid is formed. The aryl gold dichlorides are also insoluble in water but quite soluble in sodium chloride solution, probably forming the chloroaurate complexes  $\text{Na}^+(\text{RAuCl}_3)^-$ .

In the case of phenyl gold dichloride the complex with sodium chloride, while stable toward heat in 0.4 *M* concentration, is rapidly decomposed in alkaline solution with the separation of metallic gold.

The analyses of the aryl gold dichloride offered some difficulty. Since they had to be washed with water to extract the unchanged gold chloride, they most likely combined with that reagent to form the complex  $\text{H}^+(\text{RAuCl}_2\text{OH}^-)$ , an assumption suggested by the ready solubility of the aryl gold dichlorides in sodium chloride. In view of the fact also that the substances were rather unstable, they had to be analyzed rapidly. The phenyl gold dichloride, which is the most stable of the aryl gold dichlorides we had prepared thus far, could be dried *in vacuo* to constant weight over phosphorus pentoxide. In the case of the other compounds, we had to work much more rapidly and thereby dry the materials less thoroughly. The analyses therefore indicate that while all solvents of crystallization had been completely removed from them, they all still contained a molecule of water of hydration. With better facilities, however, than we had available at the time, the water of hydration undoubtedly could be removed readily.

### Experimental Part

**The Reaction between Phenyl Auric Dichloride and Phenylmagnesium Chloride.**—To 1.726 g. of phenylauric chloride dissolved in 200 cc. of anhydrous ether at  $-10^{\circ}$ , the Grignard reagent from 1.044 g. (1.25 equivalents) of phenyl bromide was added drop by drop. During the addition of the reagent a small amount of gold precipitated. When the reaction seemed to be complete, 200 cc. of petroleum ether was added. The excess of Grignard reagent was then decomposed and the ether extract washed repeatedly with water and finally dried with sodium sulfate. The ether extract contained considerable gold. Upon evaporation of the ether, gold was precipitated. The product of the reaction was unstable and we were unable to isolate a gold-carbon compound.

**The Preparation of Tolyly Auric Dichloride.**—Tolyly auric dichloride is obtained by the action of auric chloride on toluene. Finely divided auric chloride is mixed with a small amount of toluene, whereupon hydrogen chloride is evolved, a brown precipitate separates, and the solution acquires a deep red color. After a few minutes ether is added, as in the case of benzene. Upon evaporation of the solvent the residue is washed with petroleum ether and then water. It is then crystallized from ether.

*Anal.* Subs., 0.0688: Au, 0.0364. Calcd. for  $C_7H_7AuCl_2H_2O$ : Au, 52.30. Found: Au, 52.91.

The compound is yellow and crystalline. It is soluble in alcohol, ether and benzene, and insoluble in carbon tetrachloride and petroleum ether. It darkens very quickly on exposure to strong light.

The addition of toluene to a nitrobenzene solution of auric chloride at  $-15^{\circ}$  gave light yellow crystals whose properties were the same as those of tolyly auric dichloride.

An ethyl acetate solution of auric chloride did not react with toluene.

**The Preparation of Diphenyl Auric Chloride.**—Diphenyl auric dichloride,  $C_{12}H_9AuCl_2$ , was prepared from a petroleum ether solution of diphenyl and anhydrous auric chloride by essentially the same method that was used for the preparation of phenyl auric dichloride. The yield from two grams of auric chloride was 0.127 g. of diphenyl auric dichloride.

*Anal.* Subs., 0.0430: Au, 0.0192. Calcd. for  $C_{12}H_9AuCl_2H_2O$ : Au, 44.91. Found: Au, 44.95.

The compound is yellow and crystalline. It decomposes at about  $65^{\circ}$ . It is soluble in alcohol and ether, insoluble in petroleum ether and water. It is soluble in sodium chloride solution.

**The Preparation of Methyl Salicylate Auric Dichloride.**—Methyl salicylate auric dichloride was prepared by dissolving one gram of methyl salicylate in 50 cc. of petroleum ether. After the addition of 4 g. of auric chloride, the method for the preparation of gold compounds by direct "auration" as previously given was used.

*Anal.* Subs., 0.0993: Au, 0.0455. Calcd. for  $C_8H_7O_3AuCl_2H_2O$ : Au, 45.11. Found: Au, 45.82.

The compound is light yellow and crystalline. It is quite stable and melts and decomposes at  $107^{\circ}$ . It is soluble in alcohol and ether, insoluble in petroleum ether and water. It is soluble in sodium chloride solution. An alcoholic solution of the compound is decomposed very rapidly when treated with an alkali or sodium bicarbonate solution. Metallic gold separates in all cases.

***o*-Nitroanisole Auric Dichloride.**—*o*-Nitroanisole when treated in cyclohexane solution with auric chloride reacted to give a crystalline compound. This was worked up in the usual manner. The compound was insoluble in petroleum ether, cyclohexane and water; it dissolved readily in alcohol.

### Summary

1. It is pointed out that anhydrous auric chloride reacts rapidly, at ordinary temperatures, with aromatic compounds except nitrobenzene, with the liberation of hydrogen chloride and the formation of compounds  $\text{RAuCl}_2$ .

2. It is shown that anhydrous auric chloride reacts with most oxygen-containing substances, forming complexes.

3. Nitrobenzene is shown to be the only solvent, thus far discovered, which dissolves gold chloride without undergoing a reaction with that reagent.

4. The effect of substituents in the benzene ring on the speed of reaction of the compounds with gold chloride is discussed.

5. The behavior of aryl gold dichlorides toward reducing reagents is discussed.

6. It is shown that the aryl gold dichlorides, while insoluble in water, dissolve in sodium chloride solution probably forming complexes of the chloroaurate type.

7. The effect of gold chloride as a halogen carrier is discussed from the standpoint of the intermediate compounds that have been isolated, and the further reaction of those substances and chlorine.

8. The preparation and properties of the following aryl gold dichlorides are described: phenyl auric dichloride, tolyl auric dichloride, diphenyl auric dichloride, methyl salicylate auric dichloride and *o*-nitroanisole auric dichloride.

CHICAGO, ILLINOIS

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## THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. IV. GOLD IMIDE COMPOUNDS<sup>1</sup>

By M. S. KHARASCH AND HORACE S. ISBELL

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### Introduction

The elements of the first sub-group in the periodic system, *i. e.*, copper, silver and gold, form two distinct classes of imide salts. Thus, copper in alkaline solution gives the well-known "biuret"<sup>2</sup> reaction with biuret and reacts readily also with other compounds which contain an imide group. Specifically, with succinimide, a complex salt,<sup>3</sup>  $\text{K}_2\text{Cu}(\text{C}_2\text{H}_2\text{O}_2\text{N})_4$

<sup>1</sup> Published by permission of the Surgeon-General.

<sup>2</sup> Schiff, *Ber.*, 29, 298 (1896); *Ann.*, 352, 73 (1907); Rising and Johnson, *J. Biol. Chem.*, 80, 709 (1928); Rising, Hicks and Moerke, *ibid.*, 89, 1 (1930).

<sup>3</sup> Tschugaeff, *J. Russ. Phys.-Chem. Soc.*, 7, 1083 (1906); *Ber.*, 40, 1973 (1907).