

son of the properties of the products thus supplies additional evidence that the method effects a sharp separation of the amyloses.

β -Amylose has an $[\alpha]_D$ value at 20° of 189° which varies with the temperature according to the formula $[\alpha]_D^t = 191.9 - 0.13t$. It is practically free from phosphorus, gives a blue color with iodine which according to Tanret's method of analysis is free from violet, is precipitated by alcohol and by iodine, and retrogrades. The speed of retrogradation is increased by previous heating of the solution. β -Amylose represents $16 \pm 1\%$ of the original starch.

α -Amylose has a $[\alpha]_D^t$ value at 20° of 195.5° which varies with temperature according to the formula $[\alpha]_D^t = 220.1 - 1.23t$. It contains 0.076% of phosphorus, gives a red-violet color with iodine which according to Tanret's method of analysis is free from blue, it is not precipitated by alcohol in absence of electrolyte, or by iodine; it does not retrograde. It represents $84 \pm 1\%$ of the original starch.

The specific optical rotation of potato starch is expressed by the formula $[\alpha]_D^t = 214.2 - 1.00t$. Heating starch dispersions at 130° or above causes a decrease in the $[\alpha]_D$ value.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE HYGIENIC LABORATORY, UNITED STATES PUBLIC HEALTH SERVICE]¹

THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. I. AUROUS CHLORIDE CARBONYL AND A METHOD OF LINKING CARBON TO CARBON

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In the course of our systematic investigation of organic gold carbon compounds, we became interested in the theoretical aspects of the type of organic radicals which might form stable compounds with monovalent gold. In view of the fact that at that time our only method of preparing gold carbon compounds was by the Grignard reagent, we were naturally led to a search for some monovalent gold compounds which might be soluble in organic solvents. The literature revealed none. A method of attacking this problem was suggested by the fact that the carbonyl of platinous chloride dissolves in organic solvents. Accordingly, we decided to investigate the action of carbon monoxide with gold salts.

Previous Work.—The action of carbon monoxide on a water suspension of aurous chloride leads to the formation of a colloidal gold solution.³

¹ Published by permission of the Surgeon General.

² This work was done in 1925 and submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the doctorate degree in 1926.

³ Donau, *Monatsh.*, **26**, 525 (1905); *ibid.*, **27**, 71 (1906).

Under anhydrous conditions this reaction was studied by Diemer,⁴ who records that aurous chloride is decomposed into metallic gold and phosgene when heated in a stream of carbon monoxide. However, it was thought advisable to repeat his experiments at low temperatures.

When dry auric chloride was placed in a U-tube, immersed in a bath heated to 100° and dry carbon monoxide passed through the tube, a volatile gold carbon compound was formed which distilled to some extent into the receiver. Upon passing carbon monoxide over dry auric chloride one observes that the auric chloride is converted into yellow aurous chloride, which then reacts with more carbon monoxide to give the gold carbonyl compound. The same gold carbon monoxide product is formed whether one starts with aurous or auric chloride. When auric bromide was used only a small amount of crystals was formed, while with aurous iodide no combination took place.

The compound aurous chloride carbonyl was prepared by us in March, 1925. Later in the same year the preparation of the same compound was reported by Manchot and Gall.⁵ The observations of these investigators regarding the optimum temperature for the dry method of preparing this compound, and the fact that either aurous or auric chloride gave the same product, are in accord with our experience. Fortunately, however, our investigation covers phases in the preparation and study of the properties of this interesting compound not touched upon by these investigators, so that no overlapping of effort has occurred. We naturally consider the priority of publication of Manchot and Gall as entitling them to the credit of having discovered this compound.

Methods of Preparation of Aurous Chloride Carbonyl

A. Action of Carbon Monoxide upon Dry Aurous or Auric Chloride.—

A series of experiments was performed in order to ascertain the optimum condition for the preparation of aurous chloride carbonyl. The results are summarized in Table I.

As may be seen from Table I, the yields of aurous chloride carbonyl were best when a rapid stream of carbon monoxide was used and the temperature maintained around 110°. The aurous chloride carbonyl then sublimes in the form of laminar crystals. The low yields at all times are due to the decomposition of the aurous chloride carbonyl into metallic gold, carbon monoxide and phosgene.



The rapidity with which the compound is removed from the high temperature environment influences the yield. It is quite likely that higher pressures of carbon monoxide would favorably influence the yield.

⁴ Diemer, *THIS JOURNAL*, **35**, 550 (1913).

⁵ Manchot and Gall, *Ber.*, **58B**, 2175 (1925).

TABLE I
FACTORS INFLUENCING THE YIELD OF AUROUS CHLORIDE CARBONYL FROM AURIC CHLORIDE

Temp., °C.	Gas used	Yield of aurous chloride carbonyl	Remarks
100	CO	Poor	A small amount of phosgene was formed
50	CO	Poor	Extracted aurous chloride carbonyl with benzene
100	CO	Very poor	Applied suction to distil product
120	CO	Fair	Used a rapid stream of carbon monoxide gas
110	CO	20%	A rapid stream of carbon monoxide was passed over the auric chloride. This was by far the best yield ever obtained by this method.
100	CO	Fair	A rapid stream of carbon monoxide was passed over the auric chloride
100	HCl + CO	Poor
100	CO + Cl ₂	Very poor	Much phosgene formed

Of interest is the experiment in which a mixture of carbon monoxide and chlorine was passed through the tube containing the auric chloride. The object of the chlorine was to regenerate the gold formed in the decomposition of the aurous chloride carbonyl. However, we found this procedure to be a fairly good one for making phosgene, but it gave an extremely poor yield of aurous chloride carbonyl. This latter observation is in disagreement with that of Manchot and Gall,⁵ who recommended the simultaneous passage of chlorine and carbon monoxide over gold chloride in the production of the carbonyl compound. No yields, however, are recorded by these investigators and no mention is made of the formation of phosgene.

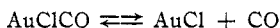
B. Action of Carbon Monoxide upon Aurous Chloride or Auric Chloride in the Presence of an Inert Solvent.—Since large amounts of aurous chloride carbonyl were needed for our work and the methods described above gave only small yields, another method of preparation of this compound was attempted and found to give quantitative yields. The method of procedure is as follows.

Dry carbon monoxide is passed through a benzene suspension of aurous chloride at *room temperature*. The aurous chloride gradually dissolves. If the amount of benzene is not too large it may be noted that the yellow crystals of aurous chloride are gradually converted into the colorless crystals of aurous chloride carbonyl. The method is quantitative provided all moisture is excluded, and the aurous chloride is free from metallic gold.

The preparation of aurous chloride free from metallic gold is a rather difficult procedure since the aurous chloride is ordinarily prepared by heating auric chloride. It was desired to see, therefore, whether we could not prepare the aurous chloride carbonyl by passing carbon monoxide through a solution of auric chloride. In this case, of course, the use of benzene or any solvent which is acted upon by dry auric chloride is excluded. We found that the chlorinated hydrocarbons were admirably adapted for our

purpose. Thus, by passing carbon monoxide through a solution or suspension of auric chloride in tetrachloro-ethylene at 100–140°, the auric chloride was reduced to aurous chloride, with the formation of phosgene, and the aurous chloride then combined with the carbon monoxide to give the corresponding carbonyl. In view of the fact that the solution of the aurous chloride carbonyl loses carbon monoxide very readily when heated, this affords an excellent method for preparing pure aurous chloride.

Molecular Weight and Stability of Aurous Chloride Carbonyl.—The compound aurous chloride carbonyl was shown to be monomolecular. Its molecular weight in benzene solution, as determined by the freezing point method, is 223 as compared with the calculated value of 260. This difference may be due to the presence of some phosgene in the benzene solution, or to the fact that the product AuClCO is dissociated to some extent.



Pertinent to this is the observation that the solid AuClCO loses carbon monoxide in vacuo, leaving behind a residue of aurous chloride.

Reactions of Aurous Chloride Carbonyl with Various Reagents.—A series of qualitative and quantitative reactions of a benzene solution of aurous chloride carbonyl with various reagents is given in Table II.

TABLE II

REACTIONS OF A BENZENE SOLUTION OF AUROUS CHLORIDE CARBONYL

- 1 Pyridine \longrightarrow $\text{AuCl}\cdot\text{pyridine} + \text{CO}$
- 2 Hexamethylenetetramine \longrightarrow $\text{AuCl}(\text{CH}_2)_6\text{N}_4 + \text{CO}$
- 3 Aniline \longrightarrow Unstable compound⁶ + Au (?)
- 4 Dimethylaniline \longrightarrow Au (?)
- 5 Methylamine \longrightarrow Au (?)
- 6 Ammonia \longrightarrow Au (?)
- 7 Urea \longrightarrow No apparent reaction
- 8 Succinimide \longrightarrow No apparent reaction
- 9 AgCN \longrightarrow No replacement of the chlorine in the aurous chloride carbonyl
- 10 PCl_3 \longrightarrow $\text{AuCl}\cdot\text{PCl}_3 + \text{CO}$
- 11 KI \longrightarrow $\text{AuI} + \text{CO} + \text{KCl}$
- 12 AuCl_3 \longrightarrow $\text{AuCl} + \text{COCl}_2$
- 13 H_2O \longrightarrow $2\text{Au} + \text{CO} + \text{CO}_2 + 2\text{HCl}$
- 14 CH_3OH \longrightarrow Au (?)
- 15 $\text{C}_2\text{H}_5\text{OH}$ \longrightarrow Au (?)
- 16 $\text{C}_3\text{H}_7\text{OH}$ \longrightarrow Au (?)
- 17 $\text{C}_6\text{H}_5\text{OH}$ \longrightarrow Au (?)
- 18 CH_3COOH \longrightarrow No apparent reaction
- 19 $(\text{C}_2\text{H}_5)_2\text{Hg}$ \longrightarrow $\text{Au} + \text{C}_2\text{H}_5\text{HgCl} + (?)$
- 20 $(\text{C}_6\text{H}_5)_2\text{Hg}$ \longrightarrow $\text{Au} + \text{C}_6\text{H}_5\text{HgCl} + (?)$
- 21 I_2 \longrightarrow $\text{AuI} + (?)$
- 22 Br_2 \longrightarrow $\text{AuCl}\cdot\text{Br}_2 + \text{CO}$

⁶ In the presence of a small amount of benzene a white gelatinous precipitate is formed which gradually turns purple, liberating metallic gold.

A number of interesting facts may be noted from examination of Table II. It appears that most compounds containing a basic nitrogen, when treated with aurous chloride carbonyl, yield carbon monoxide and a double compound of aurous chloride and the base. On the other hand, substances containing amide or imide groups are not acted upon by aurous chloride carbonyl. Thus, there is no reaction with succinimide or urea.

In the class of oxygen compounds, alcohols decompose aurous chloride carbonyl into metallic gold while with acids, *i. e.*, glacial acetic acid, there is no apparent reaction. This property is quite likely related to the difference in ease of oxidation of the different types of molecules.

The interaction of aurous chloride carbonyl with mercury diethyl or mercury diphenyl leads to the formation of metallic gold, the corresponding alkyl or aryl mercuric halide and undoubtedly the *bis*-hydrocarbons. These latter products were not sought for in these reactions, but their existence is indicated by the behavior of the Grignard reagent with aurous chloride carbonyl.

Reaction of Aurous Chloride Carbonyl with the Grignard Reagent and a Method of Linking Carbon to Carbon.—The investigation of the action of the Grignard reagent on aurous chloride carbonyl had a two-fold purpose. In the first place, it was thought possible to prepare aurous carbon compounds by this method. Secondly, it was undertaken as a part of a broader investigation under way by one of us regarding the mode of attachment of carbon monoxide in carbonyl compounds.

In all of the cases investigated the action of aurous chloride carbonyl with the Grignard reagent of various types of organic radicals led to similar results, *i. e.*, the liberation of carbon monoxide, precipitation of metallic gold and formation of the *bis*-hydrocarbon. No condensation products of carbon monoxide and the Grignard reagent were formed. A huge excess of the Grignard reagent was used (5 moles) and a careful but unsuccessful search made for the possible products of condensation of carbon monoxide with the Grignard reagent. Aurous chloride carbonyl thus acts in a strikingly different manner from nickel carbonyl, for Blanchard and Gilliland⁷ have demonstrated that the latter compound when treated with phenylmagnesium bromide gives triphenylmethane, triphenylvinyl alcohol, pentaphenylethane, tetraphenylethylene and a non-crystallizable oil comprising more than half of the entire product.

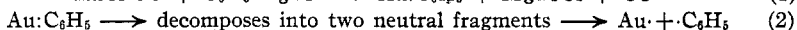
Aurous chloride carbonyl appears to act toward a Grignard reagent somewhat as does cupric chloride.⁸ Aurous chloride also acts similarly. However, much better yields of the *bis*-hydrocarbons were obtained by the use of a Grignard reagent on a benzene solution of aurous chloride carbonyl

⁷ Blanchard and Gilliland, *THIS JOURNAL*, **48**, 410 (1926).

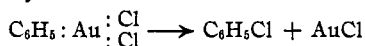
⁸ Job and Reich, *Compt. rend.*, **174**, 1358 (1922); Reich, *ibid.*, **177**, 322 (1923); Gilman and Parker, *THIS JOURNAL*, **46**, 2823 (1924).

than by the use of aurous chloride. The lower yield in the case of aurous chloride may be ascribed to the fact that aurous chloride is insoluble, that its reaction product with the Grignard reagent is sticky and insoluble. The aurous chloride is thus occluded and a large amount does not enter into reaction and may subsequently be recovered unchanged.

Mechanism of Action of Aurous Chloride Carbonyl and the Grignard Reagent.—The action of aurous chloride carbonyl or aurous chloride upon the Grignard reagent may be formulated as follows



Thus the tendency of monovalent gold to take one electron from the phenyl group leads quantitatively to the formation of gold and diphenyl. In contrast to this, trivalent gold tends to take two electrons from the phenyl group and consequently phenylauric dichloride decomposes not into diphenyl but into phenyl chloride⁹



Upon a theoretical basis it appeared interesting to study the stability of the molecule RAu . It may be seen that if the radical R gives up the electrons readily the compounds should be extremely unstable. On the other hand, if we choose for R a strongly electronegative radical, a more stable compound RAu should be obtained. The benzyl, phenyl, *o*- and *p*-tolyl and naphthyl radicals were chosen for the investigation. These radicals, as may be seen from the Table of Electronegativity of Radicals, form a series ranging from slightly electronegative to very decidedly electronegative radicals.¹⁰

The experiments fully justified our expectations. Thus, when benzyl- and phenylmagnesium bromides are treated with aurous chloride carbonyl, there is an instant precipitate of gold, while the *o*- and *p*-tolyl Grignard reagents precipitate gold slowly, leading to the formation of 2,2-dimethyldiphenyl and 4,4-dimethyldiphenyl, respectively. Furthermore, the Grignard reagent from the α -naphthyl radical forms a clear red solution when treated with aurous chloride carbonyl, which does not precipitate gold until heated.¹¹

⁹ Kharasch and Isbell, unpublished work.

¹⁰ Kharasch and Marker, *THIS JOURNAL*, **48**, 3130 (1926); Kharasch and Reinmuth, *J. Chem. Ed.*, **5**, 408 (1928).

¹¹ The investigation is being continued using radicals more strongly electronegative than the α -naphthyl radical, *i. e.*, radicals like *p*- and *o*-methoxyphenyl, methoxynaphthyl, etc. It is of interest to point out that theoretically silver, copper, mercury, and other metals should form a series of organo-metallic compounds the stability of which toward heat should increase with the increase in the electronegative character of the radicals attached to the metal. In the field of organo-mercuric compounds this prediction is well substantiated.

In the latter case, however, a reaction similar to those described above takes place, and α, α' -dinaphthyl is formed. The yields of the *bis*-hydrocarbons are quantitative upon the basis of aurous chloride carbonyl employed. The yields of the *bis*-hydrocarbons recorded in the experimental part are those of the pure products. Some losses were incurred during the crystallizations of the materials or in the preparation of solid derivatives from liquids formed in the reaction.

Experimental Part

The Preparation of Aurous Chloride Carbonyl from Dry Auric Chloride.—Carbon monoxide gas, liberated by the action of concentrated sulfuric acid on formic acid, was dried by allowing it to bubble through concentrated sulfuric acid. It was then passed through a U-tube containing anhydrous auric chloride, immersed in a sulfuric acid-bath. The gases evolved were led through an empty U-tube and then through a wash bottle containing a benzene solution of aniline in order to absorb any phosgene formed as the result of the interaction of the auric chloride and carbon monoxide.

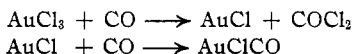
At about 45° the first appearance of a reaction was noted. At 50° some colorless crystals began to appear in the cooler portions of the U-tube. Upon gradually raising the temperature the rate of distillation of the crystals increased, reaching a maximum between 100 and 130°. The gold chloride slowly turned yellow and finally changed to brown, whereupon the residue was reduced to metallic gold. The yield of aurous chloride carbonyl by this method was extremely low.

Anal. Subs., 0.1222, 0.0294; Au, 0.0926, 0.0222. Calcd. for AuClCO: Au, 75.65. Found: Au, 75.78, 75.51.

When thus prepared aurous chloride carbonyl is obtained in clear, colorless, laminar crystals, which frequently give a mother-of-pearl appearance. It is soluble, without decomposition, in benzene, and in anhydrous ether, while in acetone there is slight decomposition, probably due to small amounts of water contained in the acetone. It reacts with water giving a gas and metallic gold, but it dissolves in glacial acetic acid without appreciable reduction or liberation of gas.

Formation of Phosgene by the Action of Carbon Monoxide upon Auric Chloride.—The gas from the reaction of auric chloride and carbon monoxide was, as previously stated, absorbed in a benzene solution of aniline.¹²

The product of the reaction of phosgene and aniline, *i. e.*, diphenylurea (m. p. 237°) was isolated from this mixture. For further confirmation the diphenylurea was converted into the bromine derivative, the properties of which agreed with those cited in the literature. Hence we may conclude that auric chloride and carbon monoxide react thus



A Preparation of Aurous Chloride Carbonyl in the Presence of an Inert Solvent.—Aurous chloride (1.869 g.) is suspended in dry benzene (50 cc.), kept at 20–30° and carbon monoxide is passed through the suspension until the yellow aurous chloride is converted into a colorless, crystalline product. Benzene is then added and the mixture very gently warmed to dissolve the crystals. Any residual solid is collected on a filter and from the filtrate most of the aurous chloride carbonyl may be precipitated by the addition of petroleum ether. The balance of the product may be obtained by evaporation of the solvent *in vacuo*. The yield is 1.990 g. or 95% of the calculated amount.

¹² This method for the determination of phosgene is described by André Kling and René Schmutz, *Compt. rend.*, **168**, 773 (1919).

Anal. Subs., 0.1345: Au, 0.1017. Calcd. for AuClCO : Au, 75.65. Found: Au, 75.61. *Mol. wt.* Subs., 0.0552: Benzene, 5.0; t , 0.365°. Calcd. for AuClCO : 260. Found: 223.

Pyridine Aurous Chloride.—Pyridine reacts in benzene solution with aurous chloride carbonyl with the evolution of a gas and the formation of a white, flocculent precipitate.

Anal. Subs., 0.1320: Au, 0.0846. Calcd. for $\text{C}_5\text{H}_5\text{NAuCl}$: Au, 63.24. Found: Au, 64.09.

The compound is insoluble in benzene, alcohol and water, somewhat soluble in acetone, giving white crystals on evaporation. It melts with decomposition at 92°.

Hexamethylenetetramine Aurous Chloride.¹³—The addition of a benzene solution of hexamethylenetetramine to a benzene solution of aurous chloride carbonyl results in the evolution of carbon monoxide and the separation of a white crystalline compound. The solid was collected on a filter, washed well with benzene and dried in vacuo.

Anal. Subs., 0.0656: Au, 0.0342. Calcd. for $\text{C}_6\text{H}_{12}\text{N}_4\text{AuCl}$: Au, 52.75. Found: Au, 52.14.

This compound is insoluble in alcohol, benzene and ether. It reacts slowly with water, giving a colloidal solution of gold. It is not soluble in dilute acids or alkalis. It decomposes slowly over a range of temperature, the first sign of decomposition being at 150°.

Reaction of Aurous Chloride Carbonyl with Bromine.—Bromine (0.0376 g.) dissolved in chloroform was added to a molecular equivalent (0.0712 g.) of aurous chloride carbonyl. The whole was allowed to stand for twelve hours and then the chloroform was evaporated. Upon drying to constant weight in vacuo over sodium hydroxide, the residue gave the following analysis.

Anal. Subs., 0.1065: Au, 0.0539. Calcd. for AuClBr_2 : yield, 0.1072; Au, 50.24. Found: yield, 0.1065; Au, 50.61.

This experiment indicates that aurous chloride carbonyl reacts with one mole of bromine to give the auric halide. Therefore, none of the bromine is used in the oxidation of the carbonyl group. The analysis is of course no criterion that the compound is AuClBr_2 . It could also be a mixture of two moles of auric bromide and one of auric chloride.

Reaction of Aurous Chloride Carbonyl with Iodine.—Aurous chloride carbonyl was treated in benzene solution with slightly more than one equivalent of iodine. A yellow precipitate of aurous iodide formed.

Anal. Calcd. for AuI : Au, 60.84. Found: Au, 61.36.

The resulting benzene solution, when treated with a slight excess of aniline, did not give any solid derivative.

The Reaction of the Grignard Reagent with Aurous Chloride Carbonyl.—Aurous chloride carbonyl was added drop by drop to five molecular equivalents of the Grignard reagent at room temperature. Metallic gold precipitated with all the radicals tested except α -naphthyl. In the latter case warming the mixture on the water-bath for a half hour was necessary to bring the reaction to completion. After the addition of petroleum ether and decomposition of the excess Grignard reagent with ice, followed by water and dilute acid, the ethereal solution was washed free from all water-soluble substances. Upon evaporation of the ether, the residues were usually crystallized from alcohol or other solvents, until pure compounds were obtained. Although derivatives

¹³ An auric chloride hexamethylenetetramine, $\text{AuCl}_3 \cdot \text{C}_6\text{H}_{12}\text{N}_4$, is described by Moschatos and Tollens, *Ann.*, **272**, 277 (1893).

of the carbonyl group which could have been formed due to the interaction of the Grignard reagent and carbon monoxide were also looked for, only hydrocarbons were found. The final products of the reaction may be summarized in the equation



The reaction is probably quantitative, but there is loss in the purification of the products when small quantities of material are used. The yields recorded below are those of the pure products.

TABLE III
REACTION OF AUROUS CHLORIDE CARBONYL WITH GRIGNARD REAGENTS

Five moles of	One mole	Product	Yield, %	M. P., °C.	Remarks
Phenylmagnesium bromide	AuClCO	Diphenyl	106	70	Possibly some diphenyl formed in prepn. of Grignard
<i>o</i> -Tolylmagnesium bromide	AuClCO	Di- <i>o</i> -tolyl	61.3	Liq.	Deriv. diphenic acid, m. p. 226°
<i>p</i> -Tolylmagnesium bromide	AuClCO	Di- <i>p</i> -tolyl	91.5	118	
Benzylmagnesium chloride	AuClCO	Dibenzyl	70.0	52	
Naphthylmagnesium bromide	AuClCO	α, α' -Dinaphthyl	70.8	151	
Phenylmagnesium bromide	AuCl	Diphenyl	70.1	70	Some aurous chloride did not react

Summary

1. A quantitative method for the preparation of aurous chloride carbonyl is described.
2. The reactions of aurous chloride carbonyl with a variety of organic substances are described.
3. The mechanism of the action of aurous chloride carbonyl with a Grignard reagent is discussed. The intermediate formation of monovalent gold carbon compounds is postulated. The order of stability of these monovalent gold carbon compounds appears to agree with the relative order of the electronegativity of the radicals investigated.
4. A method of linking carbon to carbon is described. This method is preferable to the method in which cupric chloride is employed, for the new reagent, aurous chloride carbonyl, is soluble in organic solvents.
5. The preparation of a number of new compounds is described.

CHICAGO, ILLINOIS