THE CHEMISTRY OF GOLD CARBON COMPOUNDS.

By

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I am also greatly indebted to the personnel of the Hygienic Laboratory, U. S. P. H. S., Washington D. C. through whose financial assistance this work was made possible.

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The Chemistry of Gold Carbon Compounds.

The object of this investigation has been to produce some new organic gold carbon compounds for the study of their therapeutic action, especially in regard to their action on spirochetes and tubercle bacilli. Only the chemical phases of this problem are discussed here, the pharmacology of the gold compounds prepared in the course of this investigation will be reported by Professor Carl Voegtlin of the Hygienic Laboratory, U. S. P. H. S., Washington, D. C. As a chemotherapeutic agent gold has been used from time to time. The earliest reference is found in the Bible. Thus Stahl in his Observations Chymico-Physico Medicae states[1] - "Moses burnt up the golden calf with alkalie and sulphur, and gave the solution of liver of sulphur containing gold to the Israelites to drink". Recently, the gold treatment of tuberculosis was summarized by Greenbaum[2] as follows: "In conclusion, I may say, that despite all our efforts, we have thus far no specific gold compound, which would be in tuberculosis, what arsphenamine is in syphilis. But I believe that in the not far distant future a powerful gold compound will be elaborated, which will act specifically against tuberculosis. The gradual development from gold cyanide to diethylamincanthariden gold cyanide, to Krysolgan (gold sodium salt of amino thiophenol carbonic acid), to Sanocrysin (gold sodium thiosulphate) and to Triphal (sodium salt of aurothiobenzimidazolcarbonic acid), seem

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(1) Roscoe and Schorlemmer, Treatise on Chemistry (1913), Vol. II, page 519.

(2) F. R. Greenbaum, D.Sc. The Catalyst, 11, 10. March 1926.

to point that we are very close to a solution. Perhaps the day is not very far, when we will have not only a specific against tuberculosis but a prophylactic as well against this 'white plague'".

Although the outlook for the future is promising, even from this review, we realize that the field has not been covered. Only inorganic salts, their nitrogen complexes and auro-sulfur compounds have been investigated. The sulfur compounds of gold which have been somewhat effective in the treatment of tuberculosis and syphilis are similar to Moses's solution of the golden calf.

In an extensive investigation I have prepared a number of new types of gold compounds whose therapeutic action is being investigated. This dissertation deals with the preparation and properties of these compounds. Due to the diverse nature of the work it is necessary to divide this report in several portions. These are:

1. Gold Carbon Compounds of the Type R_2AuX.
2. "Auration" - The Direct Introduction of Gold into Organic Compounds.
3. Aurous Chloride Carbonyl.
4. Mercapto-acids and their gold mercaptides.
5. Seleno-salicylic acid and its gold salts.
6. Dimethylglyoxime auric chloride.
7. Auric Imide Compounds.

Gold Carbon Compounds.

While thousands of organic metallic derivatives of arsenic, antimony, mercury, lead, tin and many other organic metallic com-

pounds have been described, not a single copper or silver organic compound has been isolated and in only one case has a true gold organic compound been described. Surely this lack of organic compounds is not due to the organic chemist's unfamiliarity with the element, for gold has found considerable use in the identification of many compounds either as salts or as coordination compounds. Rather it is due to the inherent properties of the metal. Thus as recently as 1926, A. Feldt[3] writes as follows in the Klinische Wochenschrift, summarizing his experiences in that field over a period of fifteen years: "Organische Goldverbindungen waren nicht bekannt. Gold bestzt keine Verwandtschaft zum Kohlenstoff. Komplexe organische Goldverbindungen, in denen das Gold unmittelbar am C sitzt, sind nicht existenzfähig, zum mindesten nicht isolierbar. Monatelange dahingehende Versuche schlugen daher fehl".

The reason for the non-existence of gold carbon compounds is undoubtedly traceable to the position of the metal in the electromotive series. Gold is the lowest member of the common metals, a close neighbor of chlorine in the series, one should expect the ion to be a powerful oxidizing agent, i. e. to exhibit a strong attraction for electrons. This is the first stumbling block in the preparation of gold carbon compounds for when this tendency for electrons is satisfied gold does not remain in the form of a compound but is precipitated as the metal.

The next difficulty is one which is not forced to our attention but undoubtedly has hampered progress to a great extent, namely the tendency to auric chloride to react with most organic solvents.

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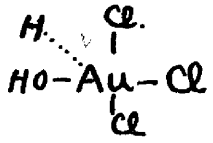
(3) A. Feldt. Klinische Wochenschrift, Feb. 19, 1926.

The properties of anhydrous auric chloride are entirely different from hydrous auric chloride or from the commercial "Chloride of gold" which is chlorauric acid. Gold chloride in the presence of salts has different properties than in pure water solution. Thus, we have observed that a water solution of auric chloride reacts immediately with sulphanilic acid to give a black precipitate of metallic gold. But if to the water solution we add a little sodium chloride, it takes a considerable time (15 or more minutes depending upon concentrations) for the precipitation of gold. This is probably due to the suppression of the auric ion (Au^{+++}). Further evidence of this is the fact that the color of the solution on addition of salt becomes less yellow. It is logical that if auric chloride reacts with sodium chloride to give sodium chlorаurate that auric chloride would react with water to give a similar product



In order to intelligently work with this product, it is necessary to know the structure of the reacting material. If auric chloride is combined in an unknown fashion with its solvent it is not surprising that it does not react as anticipated with the Grignard or other reagents. This lack of knowledge of the fundamentals of the chemistry of gold, coupled with its ease of reduction have been largely responsible for the lack of progress in the production of organic gold compounds.

Gold Compounds of the Type R_2AuX.

In 1902 Pope and Gibson[4] prepared the first organic gold

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(4) Pope and Gibson, Jour. of the Chem. Soc. 91, 2061(1902).

compound, diethylauric bromide. This was prepared by the action of the Grignard reagent on auric bromide in ether solution. By treating this compound with the calculated quantity of bromine ethylauric dibromide was prepared, also an ammonium compound to which they gave the following formula $(C_2H_5)_2AuBrNH_2$. No other organic gold compounds have been reported.

In the extensive work on the gold carbon compounds which I have carried out, I have been led to an interpretation of the action of auric halides on the Grignard reagent, and have formulated a theory which accounts for the low yields of some of the gold carbon compounds, the apparent non-existence of others, and the stability of gold carbon compounds toward heat.

This interpretation and predictions may be formulated as follows:

1. Compounds of the type R_2AuCl where R is more electronegative than methyl should be incapable of existence at room or very slightly elevated temperatures.

2. Relative electropositive radicals which lie below the methyl group will form stable compounds of the type R_2AuX.

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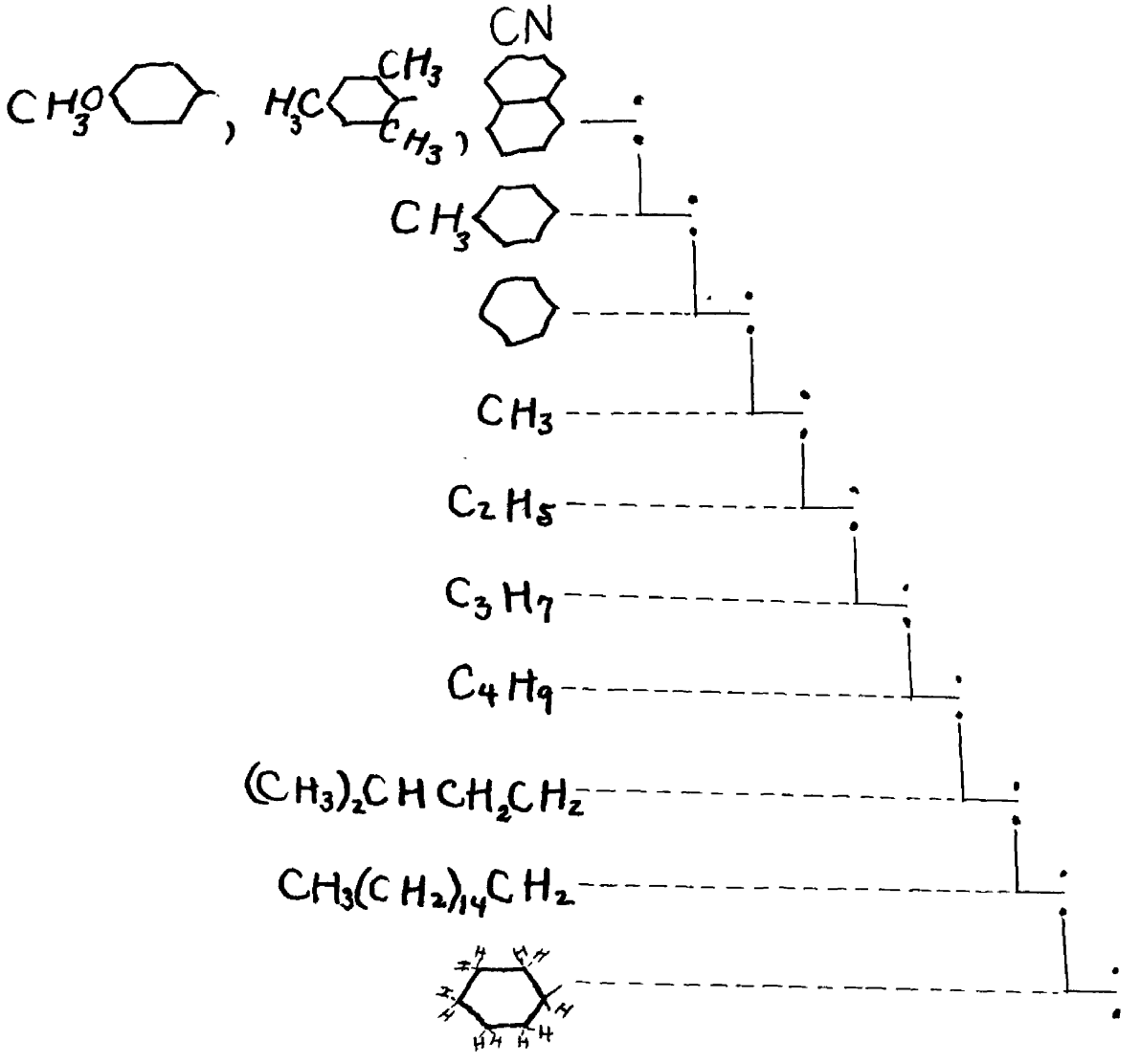
Table of Electronegativity of Organic Radicals.



In this Table we indicated the decreasing tendency to hold electrons, or the decreasing electronegativity of the radicals.

* Private comm. M. S. Kharasch

Since we have a means of determining the electronegativity of radicals in similar combination, if we locate the limit of electronegativity for a stable gold compound we can predict that all radicals less negative should form stable compounds. The limit of electronegativity will depend somewhat upon the conditions under which the compound must exist. Thus we may say radicals more negative than the phenyl will not be stable. But if we lower the temperature and remove all acid and other substances which might decompose these products then it might be possible to prepare compounds with still more negative groups.

By the procedure used in preparing compounds of the type R_2AuX through the Grignard reagent the limit of negativity is close to the ethyl radical. All radicals below the ethyl radical which we have tried have given stable compounds.

Method of Stabilizing Gold Carbon Compounds.

We will now consider the stability of compounds of the type R_2AuX as X varies. Previously the only compound of this type which had been prepared was diethylauric bromide. It was found feasible to synthesize the chlorides and bromides directly by starting with the organo magnesium halide and treating with the corresponding gold halide. In this manner either chlorides or bromides could be made. When gold chloride is treated with an organo magnesium bromide the organic gold bromide is obtained, the bromide is also obtained when gold bromide is treated with the organo magnesium chloride. The corresponding cyanides may be prepared by shaking an ether or benzene solution with silver cyanides for sometime, the alkyl gold cyanide and silver chloride are formed.

An examination of the accompanying table reveals that the order of melting points is chlorides, bromides and cyanides. Since

many of the halides are oily liquids a decided advantage lies in the higher melting points of the cyanides as it is thus possible to convert these products into crystalline compounds, which are easily purified.

The decomposition points increase from chlorides to cyanides. This also is an advantage in the purification of the cyanides.

Stability of Compounds of the Type R_2AuX

Radicals	Chloride		Bromide		Cyanide	
	Melts	Decomposes	Melts	Decomposes	Melts	Decomposes
Diethyl	48°	48°	58°	58°	D.	132°
Di-n-propyl	Liquid	107°	Liquid	95°	84°	128°
Di-iso-propyl	D.	95°	D.	100°	88°	121°
Dibutyl	-	-	Liquid	65°	D.	125°
Di-isoamyl	-	-	-	-	70°	135°
Dicyclohexyl			148°	140°	152°	155°
Dibenzyl	D	70°	D.	77°	D.	122°

Not only is this an advantage in the preparation of these compounds but it makes an important difference in their keeping qualities. The cyanides may be kept for months in brown bottles without darkening while most of the chlorides may only be kept a few days without decomposition. The only halides which may be kept for sometime are those of the more positive radicals such as cyclohexyl. The results show that the molecule R_2AuX may be stabilized

by the replacement of the halogen in the original compounds by the cyanide radical.

Method of Preparing Gold Carbon Compounds of the Type R_2AuX by the Grignard Method and the Explanation of the Poor Yield Obtained.

In the preparation of this type of compounds the Grignard method was used.(6) This is the method generally used for the preparation of organo metallic compounds from the metallic chlorides. With most metals this method gives good yields. In the case of mercury, lead, tin and many other metals yields of 90% or higher are recorded. With gold, however, the yields were extremely low and as already pointed out in the case of radicals such as the phenyl and those that lie about it, no gold carbon compounds were formed.

Conditions were varied in order to improve these yields. Pope and Gibson report that the yields were not affected whether they worked at -10° or at the temperature of liquid air. My experience was very similar. In a large number of determinations, I obtained the highest yields when the temperature was kept down to at least -10°. I also found that when six moles of Grignard reagent were used no gold carbon compound could be isolated.

Considerable gold appeared to be deposited on the decomposition of the Grignard complex. Different reagents were added prior to the addition of ice for the purpose of destroying the complex in such a manner that the compounds would not be reduced. The addition of absolute alcohol prior to the addition of ice appeared to give slightly better results. Perhaps, this slight difference is due to the slower action of the alcohol thus preventing local overheating.

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(6) See also Pope and Gibson, Jour. of the Chem. Soc. 91, 2061(1902).

Auric chloride and auric bromide with alkyl magnesium bromides gave yields of the same order but auric chloride with alkyl magnesium chlorides gave slightly better yields of the chlorides than were obtained for the bromides of the same radicals.

The low yields obtained are therefore not accountable by the procedure employed, but may be due to the fact that the solvent probably reacts with the gold chloride. In auric chloride we have a compound which has a strong tendency to form so-called coordination compounds with organic bases. It is then possible that gold chloride will form such compounds also with ether. The products may be ionized in an entirely different manner from auric chloride and consequently will not react in the normal fashion with the Grignard reagent. The attempt to carry out the reaction between the Grignard reagent and auric chloride in petroleum ether an inert solvent in which both are insoluble was not satisfactory, the reaction taking place at the surface of the particles forming an adherent layer of gummy material which prevented further reaction.

Another possible interpretation of the extremely low yields by the use of the Grignard reagent lies in the fact that the gold chloride actually reacts with ether. This conclusion or suspicion is based upon the following considerations: Anhydrous auric chloride reacts vigorously with benzene but if we wet the auric chloride with anhydrous ether it does not react. Or, if we add anhydrous auric chloride to a mixture of benzene and a small amount of ether a reaction does not take place. But a small amount of benzene dissolved in petroleum ether reacts readily with auric chloride. This clearly shows that auric reacts differently in the presence of ether in an inert solvent(7).

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(7) The reaction between auric chloride and aromatic compounds is treated in detail on page 22 of this dissertation.

General Properties of Gold Carbon Compounds of the Type R_2AuX.

The preparation of compounds of the type R_2AuX by the Grignard method has been discussed. The purification and final separation of the products largely depends upon their physical properties. Attempts have been made to prepare some of these compounds by the action of di-alkyl mercury compounds and auric halides. But due to the fact that the alkyl mercuric chloride formed and the resulting gold compounds have similar solubilities, a separation of the products has not been successful, although their characteristic odors were observed.

The gold carbon compounds have similar odors. The odor is quite characteristic, suggestive of pine needles or of brom-camphor. It is decidedly nauseating. They are light sensitive and are readily decomposed by heat. Some of them are liquids which may be purified by washing with alcohol. The ethyl compound crystallizes easily. As we increase the length of the chain, the melting point decreases to a minimum subsequently lengthening increases the melting point again.

The gold compounds of the type R_2AuX are soluble in pyridine, benzene, chloroform; less easily soluble in ether, petroletum ether; difficultly soluble or insoluble in acetone, alcohol; and insoluble in water. Most are somewhat soluble in olive oil. Olive oil solutions were used for toxicity tests (pharmacological work done by Dr. Voegtlin) on a number of these products. The cyanides when freshly prepared are soluble in benzene, although frequently after standing for a period of time they become insoluble. This was particularly noticed in the case of the benzyl compound. It may be explained either as a rearrangement of the cyanide group or by a growth of the crystals.

The conversion of the halides into cyanides by the use of silver cyanide shows the decidedly different behavior of the compounds R_2AuX from auric chloride. Auric chloride reacts with silver salts to give compounds of the nature of silver chloraurate. This tendency seems to have disappeared in the di-substituted organic gold compounds. Although these compounds do not readily form stable complexes of the chloraurate type they readily form complexes with pyridine, hexamethylenetetramine and other nitrogen compounds. These have been investigated qualitatively in an attempt to prepare a water soluble neutral complex.

As there is a decided difference from auric chloride in the tendency of these compounds to form complexes so also there is a difference in the ease of reduction.

This is shown qualitatively by the action of reducing agents such as hydroquinone, stannous chloride and sodium hydrosulfide on these compounds. Gold chloride reacts immediately with these reducing agents whereas the organic compounds are decomposed very slowly as shown in the experimental part. Not only is the reaction of these compounds different toward powerful reducing agents which carry gold chloride to metallic gold but the reactions toward milder reducing agents, which form aurous compounds from auric chloride, is different. Thus they form auric mercaptides. These will be treated in another portion of this dissertation.

Experimental Work.

The Preparation of Organo-Gold Compounds of the Type R_2AuX.

The method[8] employed for the preparation of organic gold compounds of the type R_2AuX which gave the most satisfactory yields was as follows:

Three to fifteen grams of finely pulverized anhydrous auric chloride or bromide are added with vigorous stirring to 150 to 400 c.c. of anhydrous ether held at -10° in a freezing mixture. Three molecular equivalents of a Grignard reagent previously prepared and cooled to -10° are then added with vigorous stirring. After a few minutes a few c.c. of absolute alcohol are added, followed in a few minutes by crushed ice. Subsequently, dilute acetic acid (1%) is added until all of the magnesium hydroxide has dissolved. The ether and aqueous layers are separated and the aqueous layer is washed with about 100 c.c. of petroleum ether. (Benzene is used for the benzyl compound.) The combined ether petroleum ether extracts are washed with water until the wash water does not give a test for gold. The solution is then filtered, and the solvent is evaporated in a current of air. Exposure of the compound to strong light must be avoided. The residue is frequently an oil, which, after washing with alcohol, sometimes crystallizes upon scratching the container with a glass rod. If the product is an oil it is washed four or five times with small quantities of alcohol and dried to constant weight in vacuo over phosphoric anhydride. Solids may be crystallized from petroleum ether, washed with alcohol and dried. The compounds are white crystalline solids or colorless oils. The yields of R_2AuX are usually from 0.05 to 0.1 gram for each gram of gold halide used.

All of the products obtained are difficultly soluble or in-

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(8) This method is essentially the same as the method of Pope and Gibson. Jour. Chem. Soc. 91, 2061(1902).

soluble in alcohol; most are slightly soluble in petroleum ether; and all are soluble in ether, benzene, chloroform, and pyridine. The odors are similar to one another and resemble slightly the odor of diethyl mercury, although more intense and aromatic.

Each of the dialkyl auric halides shown in the table formed alcohol soluble compounds with thiosalicylic acids, but every one was precipitated upon diluting the alcoholic solution with water.

Dialkyl Auric Halides.

Name	Structure	Analysis: Wt. of sample	Analysis: Wt. of Au	Analysis: Calc. % of Au	Analysis: Found% of Au	Melting point	Decomposition point	Yield	Remarks
Diethylauric chloride		0.1232	0.0831	67.80	67.45	48° V.S.D.	Begins 48°C.	2 g. $AuCl_3$ gave 0.3 g.	Odor fainter than that of diethyl auric bromide. Decomposes on standing in a few days.
Diethylauric bromide						58° V.S.D.	Begins 58°C.	Very small	
Di-n-propyl-auric chloride		Converted to cyanide. See same for analysis.				Light yellow oil	Begins 107 gas 120°	6 g. $AuCl_3$ gave 0.2 g.	
Di-n-propyl-auric bromide		0.0302	0.0156	54.42	51.7	Light yellow oil	Begins 95°	Yield small	Pine like nauseating odor
Di-isopropyl-auric chloride		Converted to cyanide. See same for analysis.				D.	Begins 95° gas 120°		Slightly soluble in alcohol. Crystalline solid, appears to liquefy at 75-80° with the separation of gold.

Abbreviations:

V. S. D. - very slight decomposition.
D. - decomposes without melting.

Dialkyl Auric Halides

Name	Structure	Analysis				Melting point	Decomposition point	Yield	Remarks
		Wt. of sample	Wt. of Au	Calc. % of Au	Found % of Au				
Di-isopropyl-auric bromide		Converted to cyanide. See same for analysis.				D.	100-130°		Crystalline solid. Decomposes into a liquid and metallic gold.
Dibutyl auric bromide		0.0793	0.0398	50.40	50.19	Liquid	65°	2 g. Au gave 0.3 g.	Difficultly soluble in alcohol. Pine like odor.
Di-isoamyl auric bromide		0.0866	0.0407	47.03	47.00	Liquid		2 g. Au gave 0.2 g.	
Dicetyl auric bromide		A compound with the characteristic odor of these compounds was obtained. It contained gold and had the correct properties for this compound.							

Dialkyl Auric Halides

Name	Structure	Analysis				Melting point	Decomposition point	Yield	Remarks
		Wt. of sample	Wt. of Au	Calc. % of Au	Found % of Au				
Dibenzyl-auric chloride		0.0659	0.0313	47.54	47.50	D.	70-86°C.	2 g. Au gave 0.3 g.	Difficultly soluble in ethe more soluble in benzene, an benzyl chloride.
Dibenzyl-auric bromide		0.0244 0.0518	0.0106 0.0216	42.94	43.44 41.70	D.	Begins 77°C. Detonates 85°C.	2 g. Au gave 0.476 g.	Difficultly soluble in organic solvents including et more soluble in benzene and benzyl chloride.
Dicyclohexyl-auric bromide		0.0789	0.0351	44.49	44.49	D. 148	140-148	2 g. Au gave 0.081 g.	113 g. dissolved in 13 c.c. of olive oil. Soluble in benzene, ether and chlorofo

Dialkylauric Cyanides.

Name	Structure	Analysis				Melting point	Decomposition point	Remarks
		Wt. of sample	Wt. of Au	Calc. % of Au	Found % of Au			
Diethylauric cyanide		See diethylauric chloride for analysis		69.61		D.	132°C. to 145°C.	Insoluble in olive oil. Crystalline solid.
Di-n-propylauric cyanide		0.0756	0.0481	63.75	63.63	84°C.	128°C. to 147°C.	Easily soluble in olive oil. 6 g. $AuCl_3$ gave a yield of 0.124 g
Di-isopropylauric cyanide		0.0912	0.0581	63.75	63.71	88-90°C.	121°C. to 133°C.	Easily soluble in olive oil, benzene, ether and chloroform. Very good keeping qualities.
Dibutylauric cyanide		See dibutyl auric bromide for analysis		58.46		D.	125°C. to 130°C.	Soluble to 0.7 M/100 in olive oil Yield 0.35 g. from 6 g. of gold. Crystalline solid, but difficult to crystallize.
Di-isoamylauric cyanide		See di-isoamyl auric bromide for analysis		53.97		70°	135°C. to 140°C.	Easily soluble in ether benzene and petroleum ether. It has a faint odor.

Dialkylauric Cyanides.

Name	Structure	Analysis: Wt. of sample	Analysis: Wt. of Au	Analysis: Calc. % of Au	Analysis: Found % of Au	Melting point	Decomposition point	Remarks
Dicetylauric cyanide	This compound was not obtained pure. It is very stable but has similar solubilities to the hydrocarbon $C_{32}H_{66}$.							
Dibenzylauric cyanide		0.0582	0.0280	48.65	48.11	D.	122°	After standing six weeks, still white and decomposition point had not changed. Soluble in dilute ammonium hydroxide on warming.
Dicyclohexylauric cyanide		0.0530	0.0268	50.64	50.57	152°C. S. D.	155°C.	Insoluble in alcohol, ethyl acetate and acetone, very difficultly soluble in ether, more soluble in benzene and chloroform.

Qualitative Tests on Dibenzylauric Bromide.

Benzene, ether or alcohol solutions are not reduced quickly in the cold by hydroquinone or sodium stannite, but after standing 12 to 18 hours or by boiling 2 to 3 minutes, gold is precipitated.

Dibenzylauric bromide in ether or benzene solution is quickly reduced to metallic gold by diphenyl mercury or diethyl mercury; dibenzyl mercury does not produce any reduction.

Dilute ammonium hydroxide dissolves on slight warming with dibenzyl auric bromide, probably forming a compound similar to diethylauric bromide amine,[8] $[(C_2H_5)_2AuNH_2Br]$.

Hexylmethylenetetramine in alcohol dissolves dibenzylauric bromide. A white precipitate is formed on dilution with water, dilute hydrochloric acid, or dilute sodium hydroxide.

Succinimide, diethylbarbituric acid, acetamide, urea, anthranilic acid, glycine or sulphanilic acid in water or alcoholic solutions do not exert any solvent action on dibenzylauric bromide.

The Reaction Between Phenyl Magnesium Bromide and Auric Chloride.

When an attempt to prepare diphenyl gold bromide is made the resulting petroleum ether solution contains gold which cannot be washed out by water, but on evaporation metallic gold separates. Although a number of attempts were made to prepare diphenylauric bromide we were not able to isolate it.

Diphenyl[9] in considerable quantity was separated from the ether solution which melted at 70°C. When mixed with pure diphenyl the melting point was not changed.

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(9) A small amount of diphenyl may be formed during the preparation of the Grignard reagent.

P-Tolyl magnesium bromide gave similar results to phenyl magnesium bromide. Di-β-tolyl was identified, m. p. 114°C.

α Napthyl. On the addition of α napthyl magnesium bromide dropwise to auric bromide, a brown flocculent precipitate forms. On decomposition a large amount of metallic gold separates, and the resulting solution does not contain gold.

"Auration" - Direct Introduction of Gold into Organic Compounds.

The use of the Grignard reagent in the preparation of gold carbon compounds has been discussed in the preceding section of this dissertation. It has been pointed out in that section that this method is unsatisfactory for the preparation of gold carbon compounds for a number of reasons. In the first place the yields of the di-alkyl compounds obtained by this method are extremely small, and numerous modifications in the method of carrying out the Grignard reaction have not materially increased the yield of gold carbon compounds. Secondly, one is limited by this method to radicals, in so far as we know at the present time, to radicals which lie below the phenyl radical in the Table of Electronegativity of radicals,[10] i.e. radicals decidedly less electronegative than the phenyl radical. Thirdly, the method while apparently simple requires considerable technique and practice before consistent results are obtained.

These limitations make quite evident the necessity of another method of preparing gold carbon compounds. Various indirect methods have been tried without success, others are still being investigated. I have found that anhydrous auric chloride acts upon aromatic compounds leading to gold carbon compounds. We call this process of introducing gold into aromatic molecules "direct auration". My preliminary results indicate that direct auration is as general a reaction as nitration or mercuration, except that it is a much faster reaction and the final products much less stable. This characteristic feature of all aromatic auric compounds will be discussed later in the paper.

The action of aqueous solutions of auric chloride upon organic

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(10) This thesis page 7 .

compounds has been studied[11]. It is noted that some organic compounds immediately reduce aqueous solutions of auric chloride to metallic gold, while others extract the auric chloride from water solution. The mechanism of this reduction has not been studied or for the most part the products formed have not been investigated.

Other investigators record that gold chloride is either soluble in organic solvents or is reduced completely to metallic gold by them[12]. My own experience has been that when anhydrous auric chloride is added to benzene hydrogen chloride is evolved and if the reaction is allowed to continue aurous chloride and phenyl chloride or phenyl tetrachloride may be isolated from the reaction products. A study of this reaction has indicated that the first step in this reaction is the formation of phenylauric dichloride.

$$C_6H_6 + AuCl_3 \longrightarrow C_6H_5AuCl_2 + HCl$$
$$C_6H_5AuCl_2 \longrightarrow C_6H_5Cl + AuCl.$$

The isolation of phenylauric dichloride may be carried in the following manner. Finely divided anhydrous auric chloride is added to dry benzene (thiophene free). An evolution of hydrogen chloride colors the solution red which in a few minutes turns brown. At this point one adds an equal volume of anhydrous ether. The solution is filtered and upon evaporation of the solvent, beautiful long narrow crystals of phenylauric dichloride are obtained. These crystals are very similar in appearance to those of chlorauric acid ($HAuCl_4.3H_2O$) except that they are insoluble in water. The product may be crystallized from alcohol.

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(11) V. Lenher, Jour. Am. Chem. Soc. 24, 357; 35, 550; 24, 918. See Mellor, Comprehensive Treatise of Inorganic and Theoretical Chemistry - Vol. 3, page 600.

(12) V. Lenher, Jour. Am. Chem. Soc. 35, 552(1913) states: "It has not been possible to produce the aurous type of compounds by the use of

However, it we do not add ether at the point mentioned above but let the reaction continue, the brown solution and precipitate change in a few moments to bright yellow. This residue is aurous chloride.

It is likely that after the first chlorine atom on the molecule of auric chloride has reacted with a molecule of benzene the second may react in similar manner giving diphenyl auric chloride ($(C_6H_5)_2AuCl$). This compound according to the theory advanced (page 5 of previous section) for the decomposition of compounds of the type R_2AuX where R is negative should decompose giving aurous chloride and in the presence of HCl phenyl chloride and benzene. Our experience in attempts to prepare diphenylauric chloride $(C_6H_5)_2AuCl$ directly from auric chloride by means of Grignard reagent showed that it was a very unstable compound, and further work on the action of phenyl magnesium bromide on phenylauric dichloride further bears out this fact. The evidence points to the conclusion that the addition of ether to the reacting products at the point where the maximum quantity of phenyl auric dichloride is present prevents further reaction and consequently the conversion of the gold organic compound to aurous chloride.

Further evidence that ether prevents the reaction lies in the fact that if we add ether to the benzene prior to the addition of gold chloride no phenyl auric dichloride formed. Neither chlorauric acid nor hydrous gold chloride give any product when treated with benzene, as in the formation of phenyl auric dichloride. That this inhibiting action of ether is not due to a concentration effect is shown by the fact that one drop of benzene in ten cubic centimeters of petroleum ether reacts vigorously with dry auric chloride, while pure benzene will not react with auric chloride which is simply moistened with ether.

Ether tends to form the so-called oxonium compounds; gold chloride tends to form complexes. One should expect these to combine. The nature of this combination is not known but it probably results in a different ionization from that of the simple molecule $AuCl_3$.

Other substances besides ether will also serve to inhibit the further reaction of the gold compound and permit its separation. A few cubic centimeters of ethyl acetate or a couple drops of glacial acetic acid dissolved in a small amount of benzene served apparently as well as ether. On the addition of these agents a decided change occurs: the mixture turns from red to a light yellow. Anhydrous gold chloride is reddish brown while chlorauric acid is light yellow. This difference in color is closely analogous to the change observed upon the addition of ether.

Thus far the following gold carbon compounds have been prepared by this method: Phenylauric dichloride, tolylauric dichloride, diphenylauric dichloride, methylsalicylate-auric dichloride, and ortho-nitroanisolauric dichloride. Only a preliminary study has been made of different organic radicals, their rates of reaction and the stability of the products. The time interval before the addition of the ether in the method 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 products.

Very negative radicals react very vigorously with auric chloride. Thus in a qualitative way we might place in a series the aromatic hydrocarbons napthalene, diphenyl, toluene and benzene according to the vigor of their reaction with auric chloride. These are in the same order as the order of their electronegativity (see table

page 6, first section). The instability of the products is of the same order; which is in perfect accord with the theory developed in the preceding section, that slightly negative radicals should form stable compounds and more negative radicals less stable. Substituted aromatic hydrocarbons exhibit large differences in the speed of their reaction and the stability of their products.

The influence of different substituted groups is marked. Negative groups, i. e. OH, NH_2, Cl and bromine increase the speed of reaction and decrease the stability of the products. Positive groups have the opposite effect. Combinations of the two for example methyl salicylate and o-nitroanisol react to give fairly stable products. The reaction between phenol and auric chloride is almost instantaneous, while the reaction between nitrobenzene and probably other compounds which yield more positive radicals is slow. Between the extremely fast reactions and the very slow are a large number of reactions which in the future will form the foundation for a chemistry of organic gold compounds(13).

Gold Chloride as a Halogen Carrier and the Interpretation of the Action of Metallic Halogen Carriers.

If benzene is dropped on anhydrous gold chloride a vigorous reaction takes place and 1,2,4,5 tetrachlorbenzene may be isolated from the residue. Or if an excess of benzene is used phenyl chloride is obtained. We have shown previously that an intermediate compound, phenyl auric dichloride, is formed. This compound, similar to other organic compounds, probably reacts with chlorine gas to give auric

(13) Not only the aromatic compounds undergo direct auration but aliphatic compounds containing active hydrogen undergo a similar reaction. Thus malonic acid reacts with anhydrous $AuCl_3$ liberating hydrochloric acid and producing a gold organic compound, which resembles phenyl auric dichloride. These are being investigated.

chloride and phenyl chloride. Thus is seen the possibility of the use of auric chloride as a halogen carrier.

Chlorinations were made of benzene using auric chloride as a catalyst. The chlorine was practically completely absorbed and one or more chlorine atoms easily introduced into benzene. Phenyl-auric dichloride reacted equally well as a catalyst.

The mechanism of the action of iron, aluminium and other similar catalysts has been a question for sometime. This clear case of intermediate compound formation with gold chloride throws additional evidence in favor of the theories of intermediate compound formation. Since the gold intermediate compound can only be isolated when the reaction is inhibited at a definite stage it is possible that if we could stop the reaction of ferric chloride at a similar point it would be possible to isolate a similar compound. Likewise we might extend our reasoning to the action of aluminium chloride on benzene.

The reaction of gold halides with aromatic hydrocarbons resembles those of aluminium halides even to the Friedal Craft reaction.

I have prepared condensation products of aromatic radicals with different organic halides by means of the catalytic action of auric chloride or bromide. These condensations are being studied and will be subsequently reported.

These results furnish evidence in favor of the theory of intermediate compound formation for the mechanism of the action of some halogen carriers and of the Friedal Craft condensation reaction. It is possible that although gold is expensive it may be possible to effect chlorinations or condensations which do not take place as satisfactorily with cheaper catalysts.

Experimental Work.

The Reaction Between Auric Chloride and Benzene.

(A) Formation of Aurous Chloride.

Finely pulverized auric chloride is added to dry benzene. A vigorous evolution of hydrogen chloride gas takes place, and, a brown flocculent precipitate forms. If the reaction is allowed to proceed the brown precipitate gradually changes to light yellow. This yellow precipitate as indicated by the analysis is aurous chloride. Yield 97.7% of the calculated amount.

Anal. Subs. 0.1974: Au, 0.1688. Calc. for AuCl: Au, 84.75. Found: Au, 85.56.

(B) Preparation of Phenylauric Dichloride.

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 c.c. of acetic acid, alcohol, or other reagents. If an equal volume of ether is added a yellow solution results. Upon evaporation of the ether benzene mixture yellow crystals are obtained. After washing successively with petroleum ether and water followed by crystallization from dilute alcohol, pure phenylauric dichloride is obtained. The yield is 0.41 g. from 2 g. $AuCl_3$.

Anal. Subs. (dried over P_2O_5) 0.0597: Au, 0.0342. Calc. for $Au(C_6H_5)Cl_2$, 57.14. Found: Au, 57.17%.

The compound is light yellow to colorless. It forms long narrow crystals, 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.

Attempts to prepare phenylauric chloride by the addition of ether in various proportions to benzene, prior to the addition of auric chloride, showed that no reaction took place in the presence of ether.

Chlorauric acid $HAuCl_4 3H_2O$ did not react with benzene at room temperature. Neither the formation of hydrogen chloride nor a gold compound could be detected.

Phenylauric chloride when shaken with benzene for a short time darkened, evidently decomposing on the surface. On subsequent extraction with ether most of the phenyl auric chloride was recovered.

Shaking a benzene suspension of phenylauric chloride with silver cyanide, gave a precipitate of silver chloride. We were not able, however, to remove all the halogen by this treatment.

Reactions of Phenylauric Chloride.

Sodium chloride solution dissolves phenylauric chloride, probably forming a complex of the chloraurate type. This solution is stable upon boiling. It gives a slightly acid reaction. The addition of sodium carbonate or sodium hydroxide greatly decreases the stability. After the addition of sodium carbonate, metallic gold is precipitated on warming the solution.

Reactions of Aqueous M/25 Solution of Phenylauric Chloride

+ sodium bicarbonate ⟶ no observable change.

+ hydroquinone ⟶ immediately reduced to gold.

+ drop of stannous chloride ⟶ immediate purple color.

+ few c.c. of hydrochloric acid ⟶ on warming became slightly yellower.

+ ammonium hydroxide ⟶ white precipitate, which dissolved on addition of acetic acid and was not reprecipitated on a second addition of acetic acid.

+ glycine ⟶ no apparent reaction.

+ thiosalicylic acid ⟶ aurothiosalicylic acid.

+ alcoholic solution of iodine ⟶ yellow cloud of aurous iodide (?).

The Reaction Between Phenylauric Chloride and Phenyl Magnesium Chloride.

To 1.726 g. of phenylauric chloride dissolved in anhydrous ether at -10°, the Grignard reagent from 1.044 g. (1 ¼ equivalents) phenyl bromide was added drop by drop. A small amount of gold precipitated. An equal volume of petroleum ether was then added. The excess of Grignard reagent was then decomposed and the ether extract washed repeatedly with water. The ether solution contained considerable gold. Upon evaporation of the solvent gold was precipitated. The product of the reaction was unstable and consequently we were not able to isolate a gold compound.

Phenylauric Chloride and Benzyl Magnesium Chloride.

To 1.726 gram of phenylauric chloride dissolved in anhydrous ether, was added the Grignard reagent from 0.81 g. of benzyl chloride in the same manner as described previously.

The ether petroleum ether washings contained gold; evaporation gave a light yellow to colorless oil, was fairly stable but darkened in about an hour. Treatment with silver cyanide did not remove all the halogen. (Possibly some phenyl chloride was present). After

conversion to the cyanide, by shaking in benzene solution with silver cyanide and evaporation of the solvent, a small amount of a white solid was obtained by the addition of alcohol. (The product stood over night prior to the addition of alcohol). There was not enough product for analysis.

The Preparation of Tolylauric Chloride.

Tolylauric chloride is obtained by the action of auric chloride on toluene. Finely divided auric chloride is mixed with a small amount of toluene, whereupon a red solution and brown precipitate appear; simultaneously hydrogen chloride is evolved. After a few minutes ether is added, as in the case of the phenyl compound. On evaporation of the solvent and after washing the residue with petroleum ether and water respectively, followed by crystallization from ether, tolylauric chloride is obtained.

Anal. Subs. 0.0688: Au, 0.0364. Calc. for $C_7H_7AuCl_2$: Au, 54.87. Found: Au, 52.91.

The compound is yellow and crystalline. It is soluble in alcohol, ether, 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°C. gave light yellow crystals, whose properties were the same as those of tolylauric chloride.

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

The Preparation of Diphenylauric Chloride.

Diphenylauric dichloride, $C_{12}H_9AuCl_2$ was prepared from a petroleum ether solution of diphenyl and anhydrous auric chloride

by essentially the same method as was used for the preparation of phenylauric dichloride. Yield from 2 grams auric chloride: 0.127 gram.

Anal. Subs., 0.0430: Au, 0.0192. Calc. for $C_{12}H_9AuCl_2$: Au, 46.82. Found: Au, 44.95.

The compound is yellow and crystalline. It decomposes about 65°. It is soluble in alcohol and ether, insoluble in petroleum ether and water. 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 c.c. of petroleum ether. After the addition of four grams 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. Calc. for $C_8H_7O_3AuCl_2$: Au, 47.04. Found: 45.82.

The compound is light yellow and crystalline. It is more stable than the corresponding phenyl, tolyl or diphenyl compounds. It melts and decomposes at 107°. It is soluble in alcohol and ether; it is insoluble in petroleum ether, and water, but soluble in sodium chloride solution. An alcoholic solution decomposes with the precipitation of metallic gold and in one half minute on the addition of a saturated sodium bicarbonate solution.

o-Nitroanisolauric Chloride.

o-Nitroanisol when treated in cyclohexane solution with auric chloride reacted to give a crystalline compound. This was treated in the usual manner.

Anal. Subs., 0. : Au, 0. . Calc. for $C_7H_6O_3NAuCl_2$:

Au, . . Found Au, .

The compound was insoluble in petroleum ether, cyclohexane, and water; it is soluble in alcohol.

Qualitative Reactions Between Various Compounds and Auric Chloride.

The methyl ester of o-cresol reacted vigorously to give a brownish product insoluble in petroleum ether, and water. It was soluble in alcohol.

Naphthylene, bromnaphthylene, methyl ester of resorcinol, phenol, and aniline reacted very vigorously with auric chloride. Hydrogen chloride was evolved and the gold was reduced to the metal. We have not been able as yet to isolate any products from these compounds. Brombenzene appeared to give a product which has not been isolated. Dimethylaniline gave a red colored, flocculent precipitate, which was insoluble in ether.

Action of Benzene on Auric Chloride.

When benzene is dropped on anhydrous auric chloride a vigorous reaction takes place, and hydrogen chloride is evolved. 1,2,4,5, tetrachlorobenzene may be obtained on extraction of the residue with petroleum ether. The compound melted at 139-140°C. A nitro derivative was made by treating with fuming nitric acid and pouring the resulting solution on ice. Melting point 97°C. Mulliken[14] gives 137-141°C. as the melting point of 1,2,4,5, tetrachlorobenzene.

Phenylauric Chloride as a Halogen Carrier.

When 0.25 g. of phenylauric chloride was suspended in 50 c.c. of dry benzene and a stream of chlorine passed through absorption of the chlorine was almost complete.

(14) Mulliken - Identification of Pure Organic Compounds (1922), vol. 4, page 36 gives 137-141° for the melting point of this compound.

Distillation of the product:

Initial boiling point - 130°.

12 c.c. from 130° to 140°.

24 c.c. " 140° to 168°.

10 c.c. " 168° to 178°.

Residue in flask 4 c.c.

After three fractional distillations, 20 c.c. of chlorbenzene boiling between 132-135° were obtained. The balance of the product consisted of a mixture of ortho and para-dichlorbenzene from which three grams pure para-dichlorbenzene were separated by crystallization from alcohol. It melted at 53°, a mixed melting point determination with para-dichlorbenzene of known purity was 53°.

Condensation Reactions.

Condensation products were obtained by the action of auric chloride, or bromide on benzyl chloride, and on benzoyl chloride. These are of the same nature as produced by the Friedel Craft reaction. They will be reported at a later date.

Gold Chloride Carbonyl.

The reaction between carbon monoxide and aurous chloride was investigated not only with the idea of preparing compounds of possible therapeutic value but for the purpose of preparing an ether or benzene soluble aurous compound for synthetical use. For the preparation and purification of many compounds it is highly desirable to start with a substance which is soluble in anhydrous solvents. This is particularly true if the substance is to be employed in a Grignard reaction. It was thought likely that aurous chloride would form a carbonyl compound and that this would probably be soluble in organic solvents similar to most metallic carbonyl compounds.

The reaction between aurous chloride and carbon monoxide in water solution has been generally used for the preparation of colloidal gold solution[15]. But the reaction between auric chloride and carbon monoxide under anhydrous conditions had not been previously studied.

When dry auric chloride is placed in a U-tube and dry carbon monoxide is passed through a definite gold compound is formed. By varying the temperature it is possible to distill over a volatile gold compound, namely, aurous chloride carbonyl[16] (AuClCO). One may observe also on passing carbon monoxide over auric chloride that the reaction takes place in two steps. First, the conversion of red auric chloride into yellow aurous chloride. Second, the aurous

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(15) Donau. Monatsh. 26, 525(1905); ibid. 27, 71(1906).
(16) This compound was prepared in March 1925, subsequently (Nov. 1925) the preparation of the same compound was reported by Manchot and H. Gall, Ber. 58B, 2175(1925). Their observations, as to the optimum temperature, and that either aurous chloride or auric chloride gave the product, confirmed our observations.

chloride then reacts with more carbon monoxide to give the gold carbonyl compound. The same gold carbon monoxide product is produced from either aurous or auric chloride and carbon monoxide. Starting with auric bromide only a very small amount of crystals were obtained and with aurous iodide no product was produced. An examination of the gas after passing over auric chloride revealed the presence of large amounts of phosgene[17]. This was identified by absorbing in aniline and identifying the diphenyl urea thus formed.

Factors Influencing the Yield of Aurous Chloride Carbonyl.

A series of experiments were made in order to ascertain the conditions necessary to obtain the maximum yields of aurous chloride carbonyl by the distillation method. These experiments are summarized in the following table.

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(17) Diemer, Jour. Am. Chem. Soc. 35, 555. This author identified phosgene as a product of the reaction between aurous or auric chloride and carbon monoxide.
André Kling and Réne Schmutz, Compt. rend. 168, 773(1919). Detection and estimation of phosgene.

Factors Influencing the Yield of Aurous Chloride Carbonyl.

U-tube contained anhydrous	Temp. °C.	Passed through U-tube: Stream of	Passed through U-tube: Rate of flow	Remarks	Yield of gold carbinol
$AuCl_3$	100°	Cl+CO	Medium	Phosgene was formed in	Very poor
$AuCl_3$	100°	HCl+CO	"		Poor
$AuCl_3$	100°	CO	"	A small amount of phosgene was produced	Poor
$AuCl_3$	50°	CO	"	Extracted AuClCO with benzene	Poor
$AuCl_3$	100°	CO	"	Applied suction to distill product	Very poor
$AuCl_3$	120°	CO	Rapid		Fair
$AuCl_3$	110°	CO	"	Yield was about 20% theoretical	Best yield
$AuCl_3$	100°	CO	"		Fair

The first experiment in the preceding table was made with the object of ascertaining if it were possible to continuously regenerate the gold chloride from any gold that is reduced to the metal by passing chlorine gas through the U-tube simultaneously with carbon monoxide. I found this an excellent method for the synthesis of phosgene but it did not increase the yield of gold carbonyl[18].

The production of phosgene by the action of carbon monoxide on aurous chloride is of particular interest. This phosgene is de-

(18) Manchot and H. Gall, Ber. 58B-2175(1925), recommend the simultaneous passage of chlorine and carbon monoxide in the production of the carbonyl compound but do not give any yields or mention the production of phosgene. This work was done prior to their publication.

rived from the decomposition of the compound (AuClCO) at the temperature employed for its distillation. The reactions may be formulated as follows:

$$AuCl + CO \longrightarrow AuClCO.$$

$$2\,AuClCO \longrightarrow Au + CO + COCl_2.$$

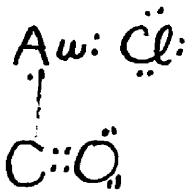
The amount of aurous chloride carbonyl at the end of the operation is an inverse function of the extent to which the decomposition reaction has proceeded. I obtained yields varying from one to twenty per cent, the balance of the product was decomposed leaving a residue of metallic gold. The rapidity with which the compound is removed from the high temperature environment influences the yield. I found that passing carbon monoxide through the tube at a high rate influenced favorably the yield. It is possible that the pressure of carbon monoxide is a factor and that higher pressures might give better yields.

Since the yields obtained by this method are extremely low, another method of preparation was devised by me which gave almost quantitative yields. The method of proceedure is as follows: dry carbon monoxide is passed through a benzene suspension of aurous chloride, at room temperature. The aurous chloride gradually dissolves, and if the amount of benzene is not too large, it may be noticed that the yellow crystals of aurous chloride are gradually converted into colorless crystals of aurous chloride carbonyl. The method is quantitative provided all moisture is excluded. Thus, in one run a yield of ninety-five per cent was obtained. Frequently, the benzene solution of the gold compound may be used without further treatment, but if the solid material is desired, it may be obtained easily by adding petroleum ether to a saturated benzene solution of the carbonyl compound.

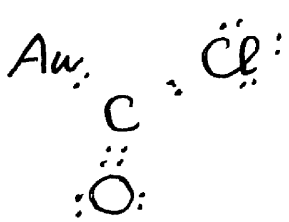
Aurous bromide carbonyl was prepared by the same method as outlined above. However, the iodide did not seem to react under these conditions.

A preliminary study has been made of some of the reactions of this compound in order to ascertain its structure. The compound AuClCO was shown to be monomolecular by the freezing point depression of the product in benzene[19]. It follows from the composition that only two sturctures are probable; namely:

I



II



It may be observed from these structures that the chlorine in (I) is essentially the same as that in aurous chloride; while that in (II) is essentially the same as the chlorine in acid chlorides. When an acid chloride is shaken for sometime with silver cyanide all of the chlorine is replaced, while the chlorine in aurous chloride is not removed by silver salts. When aurous chloride carbonyl is shaken with silver cyanide the chlorine is not replaced.

Second, on treatment of (I) with iodine one would expect the following reaction:

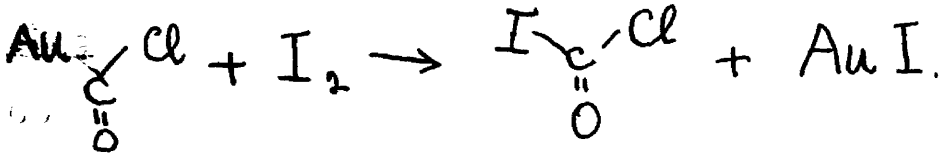
$$\underset{CO}{AuCl} + I_2 \xrightarrow{(A)} \underset{CO}{AuI} + ICl$$

---

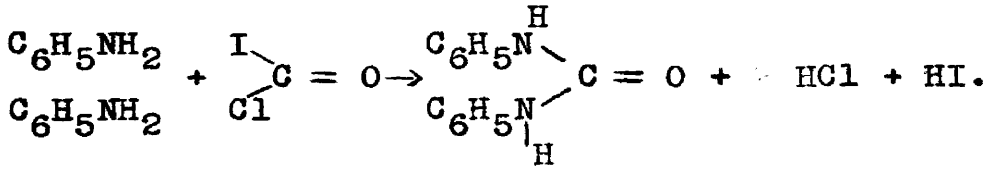
(19) The molecular weight of the product AuClCO as indicated by the freezing point depression is 223 as compared with 260 for AuClCO. This difference may be due to the presence of some phosgene in the benzene solution, or to the fact that the product AuClCO is dissociated into $\longrightarrow$AuCl.CO $\longrightarrow$AuCl + CO. Pertinent to this, is also the observation that if the solid AuClCO is put under a high vacuo it loses carbon monoxide, leaving behind a residue of aurous chloride

because aurous iodide is much less ionized than aurous chloride. If it happened that (A) was unstable it would decompose $\overset{AuI}{\underset{CO}{\cdot\cdot}} \rightarrow AuI + CO$. That $\overset{AuI}{\underset{CO}{\cdot\cdot}}$ is not formed by the action of carbon monoxide on aurous iodide is an experimental fact. Auric iodide $\overset{AuI}{II}$ decomposes into AuI and I_2 by analogy we should expect the compound to decompose according to the given reaction.

The treatment of II with iodine should result in the following reaction:



If we carried out the preceding reaction in the presence of aniline the following reaction should take place:



Experimentally the reaction went as expected for compound (I). A careful but unsuccessful search was made for diphenyl urea. The reaction with iodine thus points toward formula (I) as the correct one.

Reactions of Aurous Chloride Carbonyl in Benzene Solution.

$AuClCO$ + pyridine $\longrightarrow$ AuCl pyridine + CO.

$AuClCO$ + hexylmethylenetetramine $\longrightarrow AuCl(CH_2)_6N_4$ + CO.

$AuClCO$ + aniline $\longrightarrow$ unstable compound $\longrightarrow$ Au + (?).

$AuClCO$ + dimethylaniline $\longrightarrow$ Au + (?).

$AuClCO$ + methylamine $\longrightarrow$ Au + (?).

$AuClCO + NH_3 \longrightarrow$ Au + (?).

$AuClCO + (NH_2)_2CO \longrightarrow$ No apparent reaction.

$AuClCO$ + succinimide $\longrightarrow$ No apparent reaction.

$AuClCO$ + AgCN $\longrightarrow$ No replacement of the chlorine atom.

$AuClCO + PCl_3 \longrightarrow AuCl.PCl_3 + CO$.

$AuClCO$ + KI $\longrightarrow$ AuI + CO + KCl.

$AuClCO + AuCl_3 \longrightarrow AuCl + COCl_2$.

$2AuClCO + H_2O \longrightarrow 2Au + CO + CO_2 + 2HCl$.

$AuClCO + CH_3OH \longrightarrow$ Au + (?).

$AuClCO + C_2H_5OH \longrightarrow$ Au + (?).

$AuClCO + C_3H_7OH \longrightarrow$ Au + (?).

$AuClCO + C_6H_5OH \longrightarrow$ Au + (?).

$AuClCO + CH_3COOH \longrightarrow$ No apparent reaction.

$AuClCO + (C_2H_5)_2Hg \longrightarrow Au + C_2H_5HgCl$ + (?).

$AuClCO + (C_6H_5)_2Hg \longrightarrow Au + C_6H_5HgCl$ + (?).

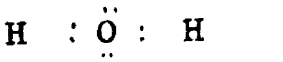
Decomposition Reactions of Aurous Chloride Carbonyl with Various Reagents.

In the preceding page I indicated the reactions of a number of reagents with aurous chloride carbonyl. The theory of these reactions may be understood from the following considerations. The bond between the gold and carbonyl group consists in a sharing of a "lone pair" of electrons with the carbonyl group, a pair of electrons which presumably belonged at one time to the gold atom. These are held in an outer shell which accounts for the instability of the union. This type of chemical combination commonly occurs in coordination compounds. As shown in the table of the reactions of aurous chloride carbonyl, the outstanding characteristic of this product is the ease with which it decomposes into carbon monoxide and aurous chloride. The reactions of this compound are therefore essentially those of aurous chloride and carbon monoxide.

Acetic acid does not precipitate gold from this compound while water, alcohol and phenol do. In parallel fashion the acidic nitrogen compounds urea, acid amides and succinimide apparently do not react with it; while pyridine and hexamethylenetetramine form stable compounds; aniline forms a definite but unstable compound; while the more basic ammonia and methyl amine lead to the precipitation of gold.

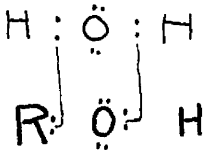
An explanation may be based upon the "Kharasch theory of partial poalrity" which is based upon the following considerations.

Let us assume that the arrangement of the electrons in the water molecule is as follows:



Now, if a hydrogen is replaced by a group R which is decidedly electro-

negative then there is a tendency for all the outer electrons of the oxygen atom to be displaced in the direction of the radical R and at the same time be pulled slightly in, i. e.,



While the reverse is true if R is less strongly electronegative.

According to this theory the position of the electrons about an atomic nucleus depends upon the radicals with which it is combined. Therefore, the attraction of the nucleus under consideration for electrons in neighboring atoms is conditional by the substituent groups, also the attraction of neighboring atoms for the electrons in the system under consideration is influenced by the substituent groups.

If we assume, that the reactions of aurous chloride carbonyl with nitrogen bases depend upon the tendency of the reacting substances to share lone electron pairs with the gold, since in general there are two "lone" pairs, one belonging originally to the gold and the other belonging to the nitrogen, we must consider not only the attraction of the nitrogen atom for the lone electron pair on the gold atom but also the attraction of the gold atom for the lone pair belonging to the nitrogen atom. Probably the latter attraction is the larger. Thus, substances which have a slightly greater tendency for sharing electrons than the carbonyl group might replace that group as exemplified in the case of the reaction of bases, such as aniline, pyridine and hexylmethylenetetramine. Other compounds, however, might have sufficient attraction to draw out the electrons to such an extent that they would require very little more activation in order to undergo oxidation-reduction reactions. The following

two factors are of importance in considering oxidation-reduction reactions: First, the energy necessary to remove the electrons from the atom A which is being oxidized; secondly, the energy liberated when these electrons drop into the inner shells of an atom B which is reduced(20). The function of the water or ammonia in this decomposition of the gold carbonyl is to draw out the electrons, i. e. activate them. Upon this basis we may classify the reactions previously mentioned into three groups:

First, no reaction of the gold carbonyl compound with the reagent due to the fact that the tendency of the reagent to share electrons with gold is too feeble to cause any reaction.

Second, double decomposition of the gold carbonyl with the reagent due to the fact that a stronger union is formed, i. e. energy is liberated by an interchange of the radicals.

Third, the attractive forces are so great that the molecule is activated to such an extent that oxidation reduction takes place.

Reactions of Aurous Chloride Carbonyl with the Grignard Reagent.

The action of the Grignard reagent on aurous chloride carbonyl was investigated for two reasons. First, it was thought possible to prepare by this method an aurous carbon compound, and second to obtain information as to the structure of aurous chloride carbonyl.

Structure (I) (page 39) would probably react as aurous chloride and carbon monoxide, while structure (II) (page 39) should react first as an acid chloride. In the first case carbon monoxide would for the most escape without reacting, while in the case of the acid chloride it would surely react and give with phenyl magnesium bromide benzaldehyde, benzophenone, triphenylcarbinol or condensation products

(20) Kharasch and Sher, Jour. Phys. Chem. 29, 626(1925).

of these. I was not able to isolate or obtain any evidence for any compound mentioned above. The only compound which I was able to isolate under the conditions described below was the bis-hydrocarbon.

Five molecular equivalents of Grignard reagent were used in each case in order, if it were possible, to saturate the carbonyl group with organic radicals(21). I was not able to effect this; however, carbon monoxide escaped and the reaction took place as between aurous chloride and the Grignard reagent.

Better yields were obtained of diphenyl from aurous chloride carbonyl in benzene solution on treatment with phenyl magnesium bromide than from aurous chloride, although either aurous chloride, carbonyl or aurous chloride probably react quantitatively give diphenyl. Aurous chloride is insoluble and the products forms with the Grignard reagent are sticky and insoluble, consequently they occlude aurous chloride with the result that a large amount of aurous chloride does not react.

This reaction probably takes place through the medium of an intermediate unstable compound as follows:

$$AuCl + C_6H_5MgBr \longrightarrow \overset{\text{Unstable}}{Au{:}C_6H_5} + MgBrCl$$

$$AuC_6H_5 \longrightarrow \overset{\circ}{A}u + C_6H_5\cdot$$

$$2C_6H_5\cdot \longrightarrow C_6H_5 : C_6H_5$$

This tendency of aurous gold to take just a single electron from the phenyl group leads to the formation of diphenyl quantitatively. In contrast to this auric gold tends to take two electrons from the carbon atom and consequently $C_6H_5AuCl_2$ decomposes not into diphenyl

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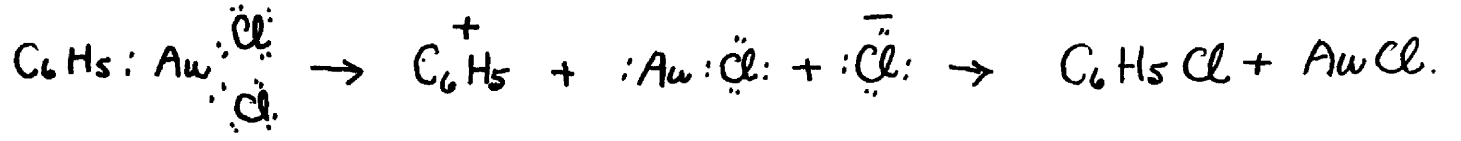
(21) The action of the Grignard reaction on $Ni(CO)_4$ was studied by A. A. Blanchard and W. L. Gilliland, Jour. Am. Chem. Soc. 48, 872(1926).

but into phenylchloride. The reaction is:



If we could obtain a radical so negative that it would not give up this electron to the aurous gold we should have a stable aurous gold compound. The benzyl, phenyl, ortho and paratolyl and naphthyl groups were chosen for the investigation of their action on aurous chloride carbonyl because they form a series of radicals from very slightly electronegative to very definitely electronegative. The precipitation of gold by the action of the benzyl and phenyl magnesium chlorides is almost instantaneous leading to dibenzyl and diphenyl, while the ortho and paratolyl precipitate gold slowly also leading to 2,2'dimethyldiphenyl, and 4,4'dimethyl-diphenyl, while the α naphthyl Grignard forms a clear red solution that does not precipitate any gold until heated or decomposed by water. This is clearly a case of the formation of an aurous gold carbon compound(22). However, when the α naphthyl mixture is heated a reaction similar to those reactions described above takes place and α,α'dinaphthyl is formed.

The evidence for the most probable structure of aurous chloride carbonyl shows that the aurous chloride group is still a unit and that carbon monoxide is held rather loosely. The investigation shows that this carbonyl compound may be used in place of aurous chloride in synthetic work, and affords a most excellent quantitative direct method for the preparation of bis-compounds.

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(22) Work is being continued on the formation of aurous carbon compounds from negative groups.

Experimental Work.

The Preparation of Aurous Chloride Carbonyl from 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; and 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 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 was extremely low.

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

Aurous chloride carbonyl when distilled is obtained in clear, colorless, laminar crystals, which frequently give a mother of pearl appearance. It is easily soluble without decomposition in benzene, and in anhydrous ether, while in acetone there is slight decomposition, probably due to a small amount 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(23). The product of the reaction of phosgene and aniline, i. e. diphenyl urea, was isolated from this mixture. The melting point of the diphenyl urea obtained was 237°. To further confirm the presence of this compound the bromine derivative was prepared according to the method outlined by Mulliken(24). The properties of the compound thus obtained agree with those cited by Mulliken. The formation of diphenyl urea under the conditions described proves that phosgene is a product of the reaction and that the reactions probably proceed as follows:

$$AuCl_3 + CO \longrightarrow AuCl + COCl_2$$

$$AuCl + CO \longrightarrow AuClCO.$$

A Quantitative Method for the Preparation of Aurous Chloride Carbonyl.

Aurous chloride (1.869 g.) is suspended in dry benzene (50 c.c.), kept at 20-30°, although it would undoubtedly work at other temperatures, higher or lower, and carbon monoxide is passed through the suspension until the yellow aurous chloride is converted into a colorless, crystalline product. Sufficient benzene is added, then very gently warmed to dissolve the crystals. Any solid is collected on a filter and from the filtrate most of the aurous chloride carbonyl compound may be precipitated by the addition of petroleum ether. The balance may be obtained by evaporation of the solvent in vacuo.

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(23) This method for the determination of phosgene is described by André Kling and René Schmutz, Compt. rend. 168, 773(1919).
(24) Mulliken - "Identification of Pure Organic Compounds". (Book). Vol. II, page 217.

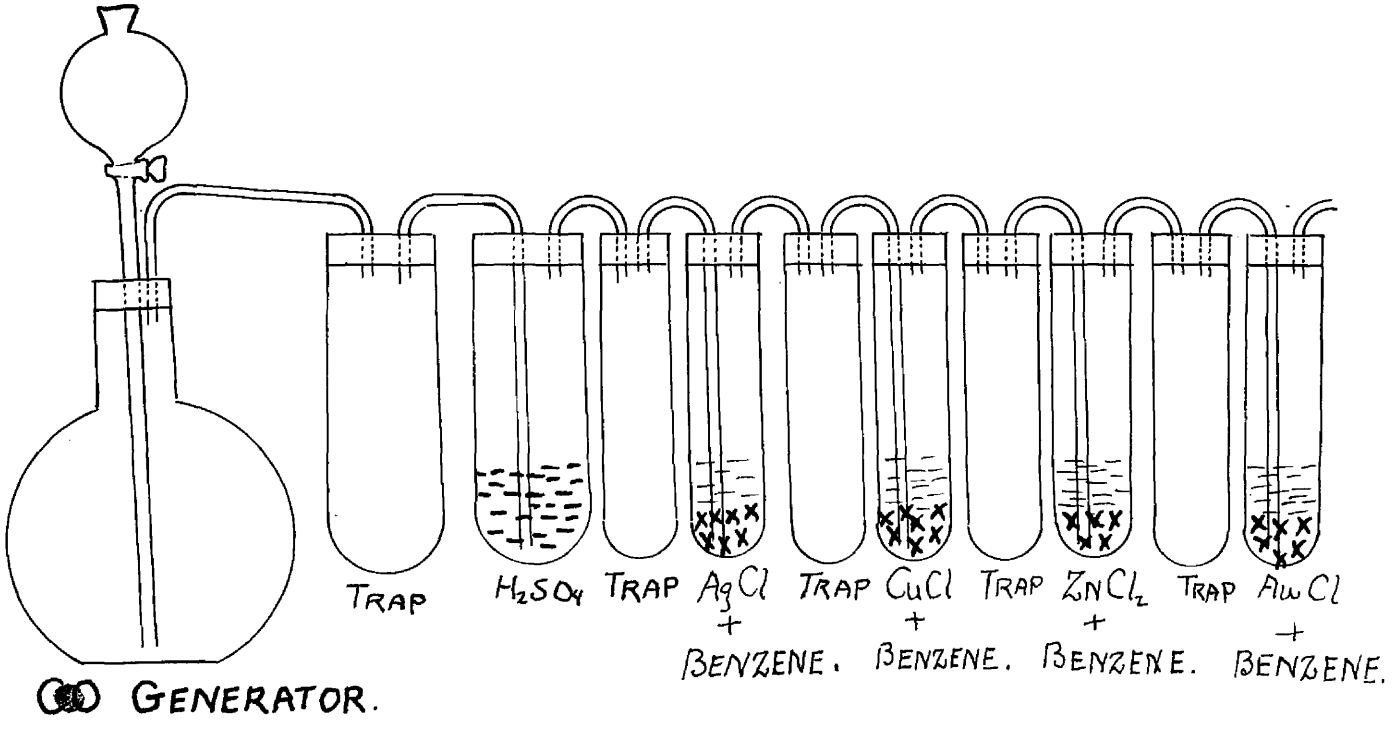
The yield is 1.990 g. or 95% of the calculated amount.

Anal. Subs., 0.1345: Au, 0.1017. Calc. for AuClCO: Au, 75.65. Found Au, 75.61.

Molecular Weight Determination of Aurous Chloride Carbonyl.

A benzene solution of aurous chloride carbonyl containing 0.0552 gram of gold in 5 c.c. was prepared. This corresponds to 16.614 grams of AuClCO in 1000 grams of benzene. This quantity of the compound depressed the freezing point of benzene 0.365°(25). This corresponds to a molecular weight of 223 as against the theoretical value 260.

The Reaction of Carbon Monoxide with Metal Halides in Benzene Suspension.



The apparatus shown in the above sketch was set up. In each

(25) This freezing point determination was kindly made by A. L. Flenner, to whom I hereby wish to express my thanks.

tube were placed 2 grams of the metal halide and 10 c.c. of dry benzene. After passing a rapid stream of dry carbon monoxide through for two hours, neither the aurous iodide, nor the silver, cuprous, mercurous, and zinc chlorides, had changed in appearance. After filtration of the supernatant benzene, it gave negative tests for both halogen and the metal. The residues were extracted with acetone. These extracts did not give a test for chlorides or metal. The aurous chloride was converted practically quantitatively into aurous chloride carbonyl, giving positive tests for chloride, and for gold.

The experiments were repeated using different solvents and varying the temperature from 20° to 100°C. Ether, acetone, ethyl acetate and toluene were tried as solvents. Only aurous chloride gave a compound under these conditions.

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. Calc. for C_5H_5NAuCl: 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°.

Hexylmethylenetetramine Aurous Chloride[26].

A benzene solution of hexylmethylenetetramine when added to a benzene solution of aurous chloride carbonyl evolves carbon monoxide,

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(26) A similar auric compound $AuCl_3C_6H_{12}N_4$ was prepared by H. Moschatos and B. Tollens, Ann. 272, 277(1893).

and a white crystalline compound separates. The solid was collected on a filter, washed well with benzene, and dried in vacuo.

Anal. Subs., 0.0656: Au, 0.0342. Calc. for $C_6H_{12}N_4AuCl$: 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 dilute acids or alkalies. 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. After standing 12 hours, on evaporation of the chloroform and subsequent drying to constant weight in vacuo over sodium hydroxide, the residue gave the following analysis:

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

This experiment shows quantitatively 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.

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. Au, 61.36. Calc. for AuI: Au, 60.84.

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 reaction at room temperature. Metallic gold precipitated with all radicals except α naphthyl. In the latter case warming 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. While only hydrocarbons were found, derivatives of the carbonyl group, such as triphenylcarbinol, benzophenone and benzaldehyde, were also looked for.

The final products of the reaction may be summarized in the following equation:

$$2C_6H_5MgBr + AuClCO \longrightarrow (C_6H_5)_2 + 2Au + CO.$$

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 are those of the pure products.

Aurous Chloride Carbonyl + Grignard Reagents.

5 moles of:	+ 1 mole	Product	Yield	Melting point	
Phenylmagnesium bromide	AuClCO	Diphenyl	106%	70°C.	Possibly some diphenyl formed in preparation of Grignard.
O-tolylmagnesium bromide	AuClCO	Di-o-tolyl	61.3%	Liquid	Derivative diphenic acid melting 226°C.
P-tolylmagnesium bromide	AuClCO	Di-p-tolyl	91.5%	118°C.	
Benzylmagnesium chloride	AuClCO	Dibenzyl	70.0%	52°C.	
α Naphthylmagnesium bromide	AuClCO	Di-α-naphthyl	70.8%	151°C.	
Phenylmagnesium bromide	AuCl	Diphenyl	70.1%	70°C.	Some aurous chloride did not react.

Mercapto Acids and Their Gold Mercaptides.

I have prepared organic gold compounds[27] of the type R_2AuX. These are insoluble in water. Hence it is desirable to prepare soluble derivatives from them. A method for the preparation of soluble metallic organic compounds was previously devised by M. Kharasch[28]. This method depends upon the fact that heavy metals form slightly ionized mercaptides. By the use of mercaptans which contain soluble groups, soluble salts of organo mercuri compounds have been prepared.

Inorganic auric salts are reduced by mercaptans[29], forming only aurous mercaptides. I found that when gold is tightly bound to two radicals, as in organic gold compounds of the type R_2AuX, it will react according to the following equation:

$$R_2AuCl + HSC_6H_4COOH \longrightarrow R_2AuSC_6H_4COOH + HCl.$$

However, I have not found this method successful for the preparation of water soluble organic gold compounds because the resulting compound is hydrolyzed in water solution. The addition of 33% or more of alcohol prevents this hydrolysis, but for therapeutic use this alcohol is very objectionable. Therefore, our problem is to obtain a mercaptide which will not be hydrolyzed[30].

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(27) This thesis page 13.
(28) Unpublished work.
(29) Voegtlin and Johnson obtained only aurous salts from mercapto acids and auric chloride. Our results have confirmed this.
(30) A preliminary investigation of the corresponding selenium compounds has shown that they are easily hydrolyzed. I have prepared seleno-salicylic acid and found that its sodium salt will carry organo-mercuri compounds into solution,(probably other similar selenium or tellurium compounds will serve the same purpose); also that it carries dibenzylauric chloride into dilute alcoholic solution presumably forming the sodium salt of dibenzylauric seleno-salicylic acid. This is the first auric organic selenide to be prepared. Aurous seleno-salicylic acid was prepared by the action of aurous chloride on seleno-salicylic acid. This is the first aurous organic selenide to be prepared. This work is being continued.

The Hydrolysis of Auric Mercaptides.

I prepared a series of mercapto acids to determine whether by changing the nature of the mercaptans we could eliminate hydrolysis. If we consider, that hydrolysis takes place according to the following equation

$$R_2AuSR' + H_2O \rightleftharpoons R_2\overset{+}{A}u + \overset{-}{SR'} + \overset{+}{H} + \overset{-}{OH} \rightleftharpoons R_2AuOH + HSR'$$

the amount of hydrolysis in neutral water solution will be conditioned by the relative ionization of R_2AuSR' compared with R_2AuOH and HSR'. Since we cannot change the radical R_2Au and consequently R_2AuOH we must vary the radical SR' in such a manner as to decrease if possible the ionization of R_2AuSR' and increase the ionization of HSR'. Non-polar molecules are not generally ionized, i. e. "the less polar the tighter the bond"(31). Since the group SR' is the negative radical in both cases a decrease in negativity will decrease the ionization of both RAuSR' and HSR'. The radical R_2Au is probably much more negative than H; consequently theoretically it would be possible to reduce the negativity of SR' to such a point that the compound R_2AuSR would be non-polar and therefore not ionized; while the compound HSR' would be slightly polar and ionized to some extent. Practically these conditions may never be realized because our ability to influence the negativity of a group by changing the organic radicals is very limited. With the corresponding oxygen compounds it is possible to produce this variation by changing the organic radical. Thus there is a marked difference in the acidic properties of the hydrogen on the hydroxyl group in alcohols, phenols, and naphthols. In like manner the ionization of the hydrogen from RSH should be

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(31) Lewis Valence and the Structure of Atoms and Molecules, page 84.

subject to change. Hence when we replace this hydrogen with gold the ionization of the gold should also be subject to change.

My plan was to make mercaptans at both ends of the series, that is, from positive radicals and from very negative. I prepared α mercapto-toluic acid especially to represent a positive radical and para-mercaptophenylacetic acid to represent the other extreme. In all, I prepared nine mercapto acids and tested their solvent action on organic auric halides.

It was qualitatively ascertained that all of these mercapto acids formed with organic gold halides of the type R_2AuX the corresponding mercaptides; and that all of these were hydrolyzed in water solution. Due to the fact that organic gold compounds are very difficult to prepare in appreciable quantities a quantitative study of their stability was not attempted(32). However, a study of the reduction of the corresponding aurous mercaptides was made.

The Stability of Aurous Mercaptides Towards Reduction.

I do not claim that the stability of aurous mercaptides towards reduction parallels the stability of auric mercaptides towards hydrolysis.

Most of the aurous salts were isolated in the free state; but since a few are difficult to separate in small quantities, because they are very soluble, these tests were run on equivalent quantities in solution. The strength of the mercapto acids was determined by titration with iodine. The reaction is according to the following equation:

$$RSH + I_2 \longrightarrow RSSR + 2HI.$$

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(32) A preliminary study was made on the stability of some corresponding organic mercury mercaptides.

The concentration of gold used in these tests was of the same order as that used in the therapeutic tests, namely 0.01 normal.

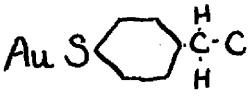
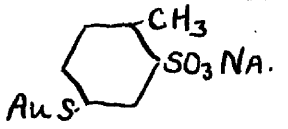
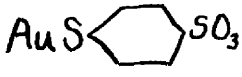
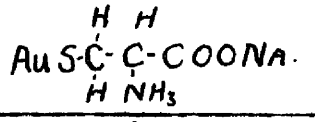
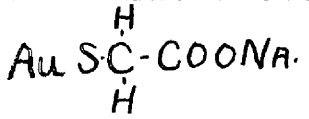
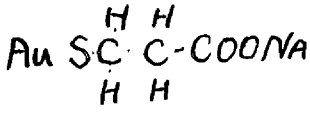
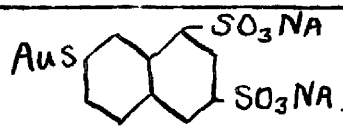
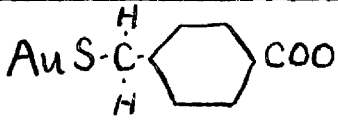
Reduction of Aurous Sulfur Compounds.

1 c.c. of $NaHCO_3$ soln.

plus 1 c.c. of M/25 mercapto acid.

" 1 c.c. of M/25 $NaAuI_2$ soln.

" 1 c.c. of 5% sodium hydrosulfide.

Order	Name	Structure formula	Time in minutes for first color	
			Trial 1	Trial 2
1	Sodium salt of p-auromercaptidephenylacetic acid.		53	75
2	Sodium salt of 4-auromercaptidetoluene 2 sulfonic acid		14.5	12.5
3	Sodium salt of p-auromercaptidebenzene sulfonic acid		15	12
4	Sodium salt of aurocysteine		6.5	6.25
5	Sodium salt of auromercaptideglycollic acid		4.5	6.5
6	Sodium salt of β -auromercaptidepropionic acid		2.5	3.25
7	Sodium salt of aurothiosalicylic acid		1.5	2.5
8	Auromercaptide of "G salt"		2.5	0.75
9	Sodium salt of αauromercaptidetoluic acid		1	0.5

The negativity of the complex radicals which we were forced to use is not known. We are justified, however, in assuming from the similarity in structure that certain radicals are slightly negative; others very negative. As mentioned before α-mercapto-toluic acid was prepared especially to represent the very slightly negative class. The gold salt of α-mercaptotoluic acid is least stable; while the gold salt of p-mercaptophenylacetic acid which was prepared to represent the other extreme is the most stable towards reduction. The only compound which appears out of place is the salt derived from mercapto G. acid. It is possible that this result is in error or that our speculation that the G. acid radical is very negative is wrong. The results show that when R is very negative the compound AuSR' is more stable towards reduction than when R' is less negative.

The Preparation of Mercapto-acids.

The preparation of mercapto-acids is accompanied by many difficulties. One must keep in mind that they are very easily oxidized by air to the disulfide, thus all filtrations and operations where they are exposed to air must be carried out with great dispatch. It is usually well to reduce the disulfide which has been formed just prior to the last purification step.

Several different means have been used for the reduction of the disulfide to the mercaptans. The reaction is as follows:

$$RS-SR + H_2 \longrightarrow 2RSH$$

The most satisfactory method of reduction is usually by zinc dust and sodium carbon carbonate. The introduction of zinc is occasionally objectionable and maybe avoided by the use of sodium hydroxide and glucose[33]. In this case organic material is left behind, which is

(33) Classz, Ber. 45, 2427(1912).

not desirable.

Aliphatic Mercapto Compounds.

For aliphatic compounds it is customary to start with the halide of the organic acid and replace the halogen, either directly with a sulfide or with a group which will break easily into a sulfide group.

These are illustrated by the methods we used for preparing thioglycollic acid and α mercaptopropionic acid[34]

α Mercapto-para-toluic Acid.

This acid was prepared by the potassium ethylxanthogenate method[34]. Para-toluic acid was brominated in bromoform solution[35]. The α bromotoluic acid obtained melted at 225°C. Five grams α bromotoluic acid was mixed with 20 c.c. of water and 2.5 equivalents of potassium ethylxanthogenate. The mixture stood 18 hours in a warm place; on acidifying, a white crystalline precipitate resulted (m. p. 237°C.). The precipitate was collected on a filter washed well with water. It was then dissolved in 20 c.c. of absolute alcohol and 10 c.c. of 25% ammonium hydroxide added. After standing 24 hours in a warm place the alcohol and ammonia were vaporized. The ethylxanthogenamide was extracted with ether and from the aqueous layer the free acid was obtained by the addition of hydrochloric acid. After filtration it was dissolved in three equivalents of sodium carbonate solution. An excess of zinc dust was added and after gently boiling at a volume of about 150 c.c. for eight hours the solution was filtered. The filtrate acid was acidified with

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(34) Bielman, Ann. 339-352(1905); ibid. 348, 125(1906).
(35) Yu, S. Zal'kínd, J. Russ. Phys. Chem. Soc. 46, 508. Chem. Abs. 8, 3187.

hydrochloric acid. A white precipitate of ∝mercapto P-toluic acid resulted, m. p. 155°.

This compound carried diethylmercuric chloride and similar salts into solution. This reaction is characteristic of mercapto acids.

Aromatic Mercapto Compounds.

There are two general methods for the preparation of aromatic thiophenols. The first class makes use of the diazonium compounds condensing them with hydrogen sulfide, sodium polysulfide or a compound of the nature of potassium ethylxanthogenate. The second type introduces thiosulfuric acid directly, a reaction analogous to sulfonation or nitration. On reduction this organic thiosulfate gives a thiophenol. The latter method is applicable only for a relatively few compounds. The former method maybe applied to any amine which undergoes the diazonium reaction.

Para-thiophenolacetic Acid.

P-thiophenolacetic acid was prepared by the following method. A cold solution of 3.36 grams sulfur, 26 grams crystallized sodium sulfide, 26 c.c. of water and 13 grams sodium hydroxide is added in small portions to the diazonium salt of p-aminophenylacetic acid, which is prepared from 14 grams p-aminophenylacetic acid, 50 c.c. of water, 24 c.c. of concentrated hydrochloric acid and 30 grams of ice, plus 6.9 grams of sodium nitrite dissolved in a little water. After heating on the water bath one half hour, the solution was acidified with dilute hydrochloric acid. The disulfide precipitated as a thick brown oil which crystallized on scratching the walls of the flask and cooling. The resulting precipitate was separated and

washed several times with water. It melted from 130-145°. It was practically insoluble in water, but readily soluble in sodium bicarbonate solution and alcohol.

It was reduced by gently boiling for 12 hours with a mixture of 6 grams zinc dust, 13 grams sodium carbonate, and 250 c.c. of water.

The mixture was filtered and the filtrate cooled and acidified with dilute hydrochloric acid. Para-thiophenolacetic acid separated from the solution as a brown sticky mass. It was dissolved in sodium bicarbonate and precipitated by the addition of acid. M. p. 76-80°. It forms a compound with diethyl mercuric chloride which is soluble in dilute sodium bicarbonate solution.

An aurous salt is prepared by treating an alcoholic solution of p-thiophenolacetic acid with the theoretical quantity of aurous chloride. After mixing 5 to 10 minutes the insoluble residue is separated by filtration and washed with alcohol. This precipitated gold salt is purified by dissolving in sodium bicarbonate solution and precipitating by the addition of dilute hydrochloric acid.

Anal. Calc. for $C_8H_7O_2S$ Au: Au, 54.12. Found: Au, 50.94.

The substance is evidently aurous thiophenolacetic acid but rather impure. It probably contains some of the free acid. The compound precipitates on the addition of acid to a solution of its sodium salt. It is soluble in sodium bicarbonate solution. In sodium bicarbonate solution sodium hydrosulfide or hydroquinone do not readily reduce it. It darkens, without melting, at 145-150°.

Thiosalicylic Acid and Its Gold Mercaptide.

Thiosalicylic[36] acid was prepared from anthranilic acid by condensing the diazonium salt with sodium polysulfide followed by

(36) The preparation of thiosalicylic acid by this method is covered

reduction.

Auric chloride reacts with thiosalicylic acid to give the aurous salt(37). When an alcoholic solution of auric chloride is added to an alcoholic solution of thiosalicylic acid a yellow precipitate results. After drying in vacuo over phosphoric anhydride the following analysis is obtained.

Anal. Subs., 0.0990: Au, 0.0554. Calc. for $C_7H_5O_2SAu$: Au, 56.29. Found 55.96.

This compound was easily soluble in sodium bicarbonate. It decomposed to a black residue at 20-212°C.

Phenyl auric chloride also reacts in alcoholic solution with thiosalicylic acid to give the aurous salt.

Anal. Subs., 0.0814: Au 0.0450. Calc. for $C_7H_5O_2SAu$: Au, 56.29. Found 55.28.

Aurous Para-thiocresol.

Aurous p-thiocresol was prepared by the following method: One gram auric chloride when treated in alcoholic solution with 1.2 grams of thiocresol gave a dark brown precipitate, which changed very quickly to a light yellow. After drying in vacuo over phosphoric anhydride 12 hours, the following analysis was obtained.

Anal. Subs., 0.1129: Au, 0.0671. Calc. for C_7H_7SAu: Au, 61.56. Found: Au, 59.43.

It is evident that an impure aurous salt was obtained. The gold content of $CH_3C_6H_4SAuCl_2$ is 50.07%; the result corresponds to the aurous salt.

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(37) This compound is described in Brit. patent 157,226 (1921), also covered in U. S. patent 1,207,284 - A. Feldt and P. Fritzsche.

Thiophenolic Sulfonic Acids.

Equivalent quantities of the amino sulfonic acid and sodium hydroxide are dissolved in the smallest possible volume of water. Then three equivalents of concentrated hydrochloric acid are added and sufficient ice to keep the temperature at 5° throughout the reaction. An equivalent of sodium nitrite is added and after shaking a few minutes the mixture is neutralized by adding in portions a saturated solution of sodium bicarbonate. An equivalent of sodium ethylxanthogenate is added; whereupon a yellow precipitate results. When approximately 0.25 gram of electrolytic copper powder is added, a vigorous effervescence of nitrogen takes place. The mixture is slowly heated to boiling. After filtration two equivalents of sodium hydroxide are added and boiling is continued four hours. Two equivalents of sodium carbonate are added and an excess of zinc dust. After boiling gently on the hot plate eight or ten hours reduction is usually complete(38).

The resulting solutions carry ethyl mercuric chloride and similar compounds into solution. In contrast to the corresponding carboxylic acids precipitation does not take place on the addition of acid. Due to this solubility in alkaline or acid solution the free mercapto sulfonic acids are very difficult to separate. A separation may be made by means of their heavy metal salts. Some of these are difficultly soluble; the metal may be removed with hydrogen sulfide. This method is not satisfactory because the metal salts are usually gelatinous and filter slowly; also the removal of the metal with hydrogen sulfide usually results in a colloidal precipitate of the metallic sulfide.

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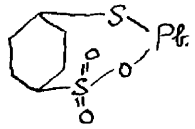
(38) β thionaphthol sulfonic acid was previously prepared by a method similar to the preceding. J. Pr. [2] 41, 223.

Para-thiophenol Sulfonic Acid.

P-thiophenol sulfonic acid is prepared from sulphanilic acid by the diazonium reaction as previously given.

The lead salt is prepared by adding lead acetate to a slightly acid solution of the above acid. A yellow precipitate results, which after drying in vacuo gives the following analysis:

Anal. Subs., 0.4332: $PbSO_4$, 0.3396. Calc. for $C_6H_4S_2O_3Pb$: Pb, 52.40. Found: Pb, 53.57. Subs., 0.3350: $BaSO_4$, 0.3650. Calc. for $C_6H_4S_2O_3Pb$: S 16.19. Found: S, 16.19.

The analysis shows that the compound is 

The free acid may be obtained by removing the lead with hydrogen sulfide. The mercury salt is relatively insoluble and may be used for the purification of the acid. When a suspension of this salt was treated with hydrogen sulfide, the mercury was precipitated in the form of the red mercuric sulfide.

The aurous salt mixed with sodium chloride was obtained by the action of aurous chloride on sodium P-thiophenolsulfonic acid. The product was precipitated by the addition of alcohol.

4-Mercaptotoluene-2-Sulfonic Acid.

4-Mercaptotoluene-2-sulfonic acid was prepared by the diazonium reaction from 4-aminotoluene-2-sulfonic acid. Its lead and mercury salts are easily soluble in water. It forms soluble compounds with organic mercury compounds and an aurous mercaptide. The free acid was not separated.

2-Mercaptonaphthalene 6,8-Disulfonic Acid.

2-Mercaptonaphthalene 6,8-disulfonic acid (Mercapto G acid) was prepared by the diazonium reaction. Its mercury salt is difficultly soluble and maybe used for its purification. This acid forms soluble organic mercuri compounds and an aurous salt.

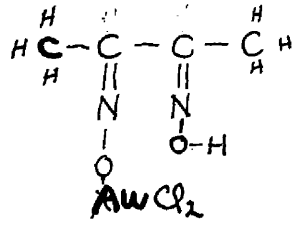
A Gold Salt of Dimethylglyoxime.

Our object here was to prepare and study the properties of gold derivatives of dimethylglyoxime. The preparation of gold salts of dimethylglyoxime had not been previously reported.

Metallic derivatives of dimethylglyoxime have received considerable attention by analytical chemists for the determination of metals. A method for the determination of gold based upon a previous observation of Wunder and Thüringer[39] was devised by J. Belluci and A. Chiucini[40]. On boiling gold solutions with dimethylglyoxime they observed that the gold was reduced quantitatively to the metal. They did not report an intermediate compound.

However, I found that by treating an alcoholic solution of dimethylglyoxime with a water solution of auric chloride dimethylglyoxime auric chloride $CH_3C(:NOH)C(:NOAuCl_2)CH_3$ is obtained. By modifying the conditions, i. e. the proportion of dimethylglyoxime, and the addition of alkalie, one may replace the two remaining chlorine atoms of the compound and produce other salts[41].

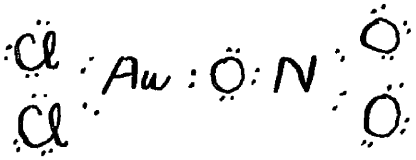
Dimethylglyoxime auric dichloride is of particular interest in relation to the structure of oxime salts. The auric salts of oxygen acids are hydrolyzed in water solution; thus auric nitrate, sulphate and acetate exist only in the absence of water or in the presence of concentrated acid. According to the generally accepted structure the compound should be a salt of an oxygen acid and we would expect hydrolysis to take place on addition of water. However, this does not take place. One may ask therefore why this abnormal stability if the gold is



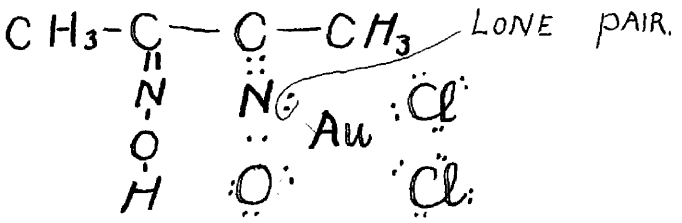
(39) M. Wunder and V. T. Thüringer. Zat. anal. Chem. 52, 660(1913).
(40) J. Belluci and A. Chiucini. Gazz. chim. ital. 49, II, 187(1919).
(41) The work on these is not complete.

attached to oxygen. Is it due to the marked difference in the polarity of the acid, or is the gold combined with nitrogen.

Gold has a decided tendency to form complexes of the chloraurate type, probably due to its strong attraction for electrons. If we compare the electronic structures of nitric acid[42] and of oximes, we will see that with nitric acid there are not any "lone electron pairs" on the nitrogen, while there is a "lone electron pair" in the case of the oximes. Coordination[43] or secondary valence compounds, arise from the attraction of large nuclei such as gold for these "lone electron pairs".



We should expect that with the oxime the gold atom would form a secondary valence bond with the nitrogen through this lone pair, thus giving rise to the stable chlorauric acid type of compound. We then have the



gold satisfied with electron pairs held in common with both the oxygen and nitrogen atoms. This makes the compound more stable. The idea may be extended to explain why heavy metal cyanides may react as though the metal were attached to the nitrogen while salts of metals with a smaller nuclear charge react in a different manner. The heavy electronegative metals form these secondary bonds which may become even stronger than the original primary bond.

This compound is not very stable in alkaline solution, probably due to the reducing nature of the dimethylglyoxime radical. It re-

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(42) Lewis, Valence and the Structure of Atoms and Molecules, p. 101.
(43) Lewis, ibid. p. 114.

acts with hydroquinone and other reducing agents precipitating gold. For the reason that the gold is only slightly less ionized than in inorganic compounds. The investigation was not carried further.

Experimental.

A water solution of auric chloride, when treated with 1 molecular equivalent of dimethylglyoxime dissolved in dilute alcohol gave a yellow brown precipitate. This upon drying *in vacuo* over phosphoric anhydride gave the following analysis.

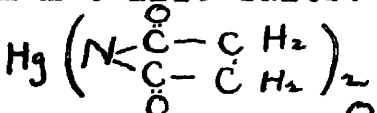
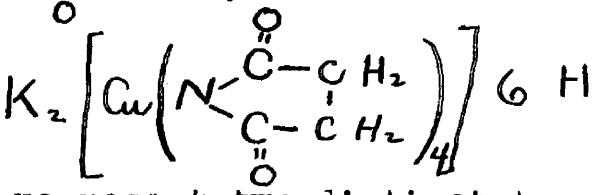
Anal. Subs., 0.1326: Au, 0.0682. Found: Au, 51.43. Calc. for $C_4H_7O_2N_2AuCl_2$: 51.43.

It gave a strong qualitative test for chlorine. Dimethylglyoxime auric dichloride is soluble in acetone, being precipitated from this solution by the addition of ether. It is difficultly soluble in alcohol and water, on boiling the aqueous solution, metallic gold is precipitated. Addition of sodium hydroxide to a dilute alcohol-water solution of this compound results in a precipitation of gold.

Dimethylglyoxime auric dichloride dissolved in acetone, when treated with an alcoholic solution of potassium hydroxide, gives a light red flocculent precipitate; the addition of larger amounts of potassium hydroxide gives a yellow precipitate and finally a dark brown product is obtained. These salts are decomposed by water, thus making the purification of them very difficult.

Summary. Dimethylglyoxime auric dichloride has been prepared. It is not hydrolyzed in water solution like other auric salts of oxygen acids. In its action towards reducing agents it lies between the ionized gold salts and the very slightly ionized gold complexes.

Gold Nitrogen Compounds.

The purpose of this work was to prepare and study the properties of gold nitrogen derivatives, particularly those of the imide amide type. The formation of gold imide compounds is not reported in the literature. Imides such as succinimide, phtalimide, saccharine and barbital form metallic salts. Typical of these are mercury succinimide[44]  and complex copper compounds[45] of the type $K_2Cu(Suc)_4 6H_2O$. 

These compounds represent two distinct types[46] of imide metallic compounds. The first resemble inorganic metallic salts; the imide playing the rôle of the acid. They are ionized and give the reactions of inorganic salts. The other type is characterized by the production in solution of a relatively low concentration of metallic ion.

The tendency of gold to form complexes of the chloraurate type is strikingly shown by a class of gold imide compounds which we have prepared. These have structures similar to the complex copper imides. They may be represented by the general formula $HAu(imide)_4 3H_2O$. Barbital, succinimide, phtalimide, saccharine and probably other imides which, however, have not been investigated form compounds of this type.

These imide gold compounds are more stable towards heat or reducing agents than any previously prepared auric compounds. This marked stability is coupled with other physical properties which

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(44) Landsberg, Ann. 215, 209(1882).
(45) L. A. Tschugaeff, J. Russ. Phys. Chem. Soc. 7, 1083(1906). H. Ley and F. Werner, Ber. 40, 705(1907).
(46) A second class of mercury salts is claimed by E. Lyons. J. Am. Chem. Soc. 47, 830(1925).

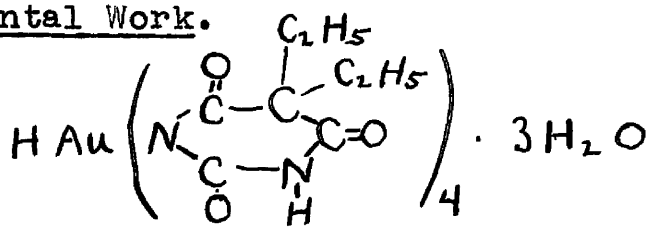
should make these compounds assume an important position in the arts. The gold imides are slightly soluble in 95% alcohol, more soluble in 50%, slightly soluble in water, insoluble in ether, benzene, carbon tetrachloride, petroleum ether, chloroform or acetone. While the free compounds are difficultly soluble in water, the alkalie salts or the sodium chloride addition compounds are very soluble. These soluble derivatives have a neutral to slightly alkaline reaction, are very slightly ionized, and very stable, thus making them suitable reagents for therapeutic use.

The very low concentrations of gold ions in solutions of these salts should make them excellent for electroplating baths. A decided advantage would lie in the non-poisonous character of the imide as compared to the poisonous potassium cyanide complex which is used at the present time. The cost of the imide would be greater than that of cyanide, but this might be offset by a greater "throwing power" or a smoother deposit.

Imides react with auric hydroxide very slowly to produce complex imides. It was found that this reaction could be greatly accelerated by the addition of salts. This is probably brought about by an increased concentration of the "aurate" ion in solution. A drop of hydrochloric acid, a small amount of auric chloride, or of sodium chloride, are particularly active in this respect, but other such as sodium acetate, or sodium hydroxide will serve the purpose equally well.

Experimental Work.

Auric Barbital



Barbital (di-ethylbarbituric acid) in water solution reacts with auric hydroxide very slowly to give a silky precipitate. A water solution of barbital on standing for two months with four grams of auric hydroxide, formed less than 0.5 gram of this silky precipitate. Even on warming on a steam bath the rate of formation was very slow. The addition, however, of a small amount of auric chloride or a drop of hydrochloric acid greatly accelerated the rate of formation; other chlorides had the same effect.

0.01 mole of auric hydroxide was mixed with 0.04 mole of barbital and 50 c.c. of water and a couple drops of concentrated hydrochloric acid were added. After digestion on the steam bath for 48 hours practically all the gold hydroxide had been changed to a white silky precipitate. Upon crystallization from 50% alcohol a pure compound resulted.

Anal. Subs., 0.1122, 0.1164, 0.1449, 0.0466, 0.0916: Au, 0.0232, 0.0236, 0.0294, 0.0096, 0.0188. Calc. for $HAu(Barb)_4.3H_2O$: Au, 20.41; N, 11.59. Found Au, 20.68, 20.27, 20.29, 20.60, 20.52; average 20.47; N, 11.74, 11.42; average 11.57.

The compound is white and crystalline. It is soluble in dilute alcohol, very difficultly soluble in water and 95% alcohol, insoluble in ether, benzene, and petroleum ether. It is not readily reduced by hydroquinone or sodium hydrosulfide. It decomposes at 200°, melting to a black liquid.

Sodium Salt of "Auric Barbital".

"Auric barbital" dissolves in sodium hydroxide solution forming a sodium salt which may be precipitated by the addition of alcohol. This salt is very soluble in water. It gives a slightly alkaline reaction and is very stable towards reduction. A water solution of this salt after careful acidification with hydrochloric acid gives a precipitate of "auric barbital".

Auric Succinimide.

A water suspension of auric hydroxide slowly dissolves in a solution of succinimide. The presence of chlorides or sodium acetate greatly accelerates the rate of reaction. Upon evaporation of the solution a solid is obtained. This may be crystallized from dilute alcohol yielding a white crystalline compound. For analysis the compound was dried over phosphorous pentoxide.

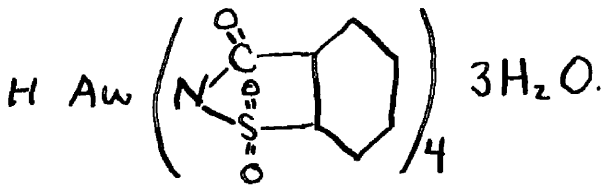
Anal. Subs., 0.2428, 0.0772, 0.2844, 0.0924: Au, 0.0750, 0.0242, 0.0872, 0.0286. Calc. for $HAu(Suc)_4.3H_2O$: Au, 30.53, N 8.67. Found: Au, 30.89, 31.09, 30.66, 30.92; Average 30.89.

The compound is soluble in dilute alcohol, difficultly soluble in water, insoluble in ether, benzene, carbon tetrachloride, petroleum ether, and acetone. It is soluble in sodium bicarbonate and sodium chloride solutions. It dissolves in concentrated sulfuric acid; and upon warming gold is precipitated. It is not readily reduced by hydroquinone, sodium hydrosulfide, and stannous chloride; it liberates iodine from hydrogen iodide very slowly; and does not oxidize dimethylaniline to a dyestuff like most auric salts. Upon heating it turns slightly purple at 235°C; it does not detonate in a melting point tube, but when a quantity is heated in a crucible it detonates with considerable force.

Sodium Salt of "Auric Succinimide".

0.04 mole of sodium carbonate is added to 0.01 mole of auric chloride; 0.04 mole of succinimide is then added. After digesting a short time a colorless solution results. After evaporation to a low volume, alcohol is added and a white precipitate is formed. Some sodium chloride precipitates. After several crystallizations a compound was obtained which gave the following analysis (dried over P_2O_5).

Anal. Calc. for ($NaAu(suc)_4.3H_2O$) Na Au $C_{16}H_{16}O_8N_4.3H_2O$: Au, 29.59; Na, 3.45. Found: Au, 28.50; Na, 4.52.

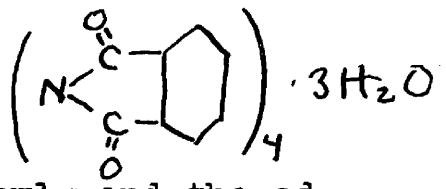
"Auric Saccharine" 

Auric hydroxide reacts, much more readily with saccharine than with any other compound which we tried, to form a complex imide. Due to the greater acidity of this group it is not necessary to add a chloride or other substance in order to accelerate the reaction.

0.01 mole of auric hydroxide is digested with 0.04 mole of saccharine in water solution. A yellow crystalline compound results. After crystallization from 50% alcohol and drying over phosphoric anhydride the following analysis is obtained.

Anal. Calc. for $HAu(H_4C_7O_3NS)_4.3H_2O$: Au, 20.41; N, 5.69. Found: Au, 20.14; N, 5.41.

The compound is soluble in dilute alcohol, almost insoluble in water, and 95% alcohol; insoluble in organic solvents, and slightly soluble in salt solutions. It decomposes gradually without melting, beginning at 135°C.

"Auric Phthalimide". 

The reaction with phthalimide proceeds slowly and the addition of salts is necessary. The separation of any unconverted phthalimide is difficult, due to its low solubility.

The sodium salt was prepared by the reaction between sodium carbonate, auric hydroxide and phthalimide. It was recrystallized several times from alcohol water mixtures.

Anal. Subs., 0.0938, Au, 0.0220, Na_2SO_4, 0.0094. Found Au, 23.45, Na, 3.24. Calc. $Na(Au\ H_4C_8O_2N)_4.3H_2O$; Au, 22.95, Na. 2.70.

The compound was difficultly soluble or insoluble in water, alcohol, acetone, ether, and slightly soluble in dilute alcohol. It was not reduced by hydroquinone or sodium hydrosulfide. It begins to decompose at 185°C., gradually becoming black as the temperature rises.

Summary.

1. A study of organic gold compounds has been made and the factors influencing their stability outlined. Positive organic radicals form stable auric compounds; under anhydrous conditions only very negative compounds form stable aurous compounds.

2. I prepared and studied the properties of the following new organic gold compounds of the type R_2AuX: Diethylauric chloride; di-n-propylauric chloride; di-n-propylauric bromide; di-isopropyl auric chloride; di-isopropylauric bromide; dibutylauric bromide; di-isoamyl auric bromide; dicetylauric bromide; dibenzylauric chloride; dibenzylauric bromide; and dicyclohexylauric bromide.

3. A method for the preparation of alkyl gold cyanides was devised and the following new compounds prepared: Diethylauric cyanide; di-n-propylauric cyanide; di-isopropylauric cyanide; dibutylauric cyanide; di-isoamylauric cyanide; dicetylauric cyanide; dibenzylauric cyanide; and dicyclohexylauric cyanide.

4. I discovered a new method, "direct auration", for the synthesis of organic gold compounds. This method opens up a broad field for future development, making possible the synthesis of many compounds. This was not possible prior to this work. By this method I have prepared the first aromatic organic gold compounds; also the first organic gold compounds which contain other than simple hydrocarbon radicals, i. e. carboxyl, hydroxyl, and nitrogroups. The following new compounds were prepared: Phenylauric dichloride, methylsalicylate auric dichloride, o-nitroanisolauric dichloride, biphenylauric dichloride, tolueneauric dichloride.

5. I found that auric chloride is an excellent halogen carrier, and that auric chloride or bromide acts as a condensation reagent in a manner similar to aluminium chloride. These facts are the result of "auration", and are therefore direct proof for the theory of intermediate compound formation as an explanation of the mechanism of the action of halogen carriers and of condensations of the nature of the Friedel Craft.

6. A new carbonyl compound (AuClCO) was prepared from aurous chloride, and a quantitative method for its synthesis developed. I studied its properties and showed that it was a molecular or secondary valence compound. Its benzene solution reacts like a solution of aurous chloride; reacting with many substances forming new coordination compounds, giving rise to a convenient method of preparing coordination compounds of the type AuClX. The following new coordination compounds were prepared: Aurous chloride pyridine, ($AuClNC_5H_5$); aurous chloride hexylmethylenetetramine, ($AuCl(CH_2)_6N_4$).

7. I found that either aurous chloride or aurous chloride carbonyl, when treated with an excess of the Grignard reagent, gives the bis-hydrocarbon. With very negative radicals a gold compound was formed which is decomposed by water.

8. The following new mercapto acids were prepared and their reactions with gold compounds investigated: P-thiophenolsulfonic acid, 4-mercapto-toluene 2-sulfonic acid, mercapto G. acid, αmercapto p-toluic acid, and Pmercaptophenylacetic acid.

9. The first auric mercaptides to be prepared were formed from the reaction between organic gold compounds of the type R_2AuX and mercapto acids.

10. The relative stability towards reduction of nine aurous mercaptides was studied.

11. The first gold organic selenide (auroselenosalicylic acid) was prepared; and the action of selenosalicylic acid on organic gold compounds studied.

12. The reaction between auric chloride and dimethylglyoxime was studied, and a new compound, dimethylglyoxime auric chloride, prepared.

13. A new class of gold compounds, complex auric imides, was discovered. A number were prepared and their properties studied. The compounds prepared are: "Gold succinimide"; "gold barbital"; "gold saccharine" and "gold phthalimide".