

connected for steam distillation in the usual manner, the flask being supported on gauze and tripod and not on the water-bath. Before the admission of steam, the flask is heated by the burner flame and kept boiling until about 50 cc. of distillate is obtained. The distillate is returned to the flask, 100 cc. of water added and the mixture steam distilled until about 150 cc. of distillate is collected.

Lead oxide is added to the distillate in slight excess and the liquid filtered. The filtered liquid is evaporated to small bulk and allowed to crystallize. The yield is 65 g. of lead formate, equivalent to 20 g. of formic acid. If it is assumed that one mole of oxalic acid gives one mole of cellulose mono formate and that the cellulose mono formate is completely converted to formic acid, it follows that one mole of oxalic acid in this procedure should yield, theoretically, a maximum of one mole of formic acid. On this basis 126 g. of crystallized oxalic acid will give 46 g. of formic acid.

$$126 : 46 :: 80 : X$$

$$X = 27.2$$

The theoretical yield of formic acid is therefore 27.2 g. If desired, the formic acid is recovered by dissolving the lead formate, precipitating the lead with hydrogen sulfide and distilling off the formic acid.

UNIVERSITY, ALABAMA

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

## THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. II. THE PREPARATION AND PROPERTIES OF GOLD-CARBON COMPOUNDS OF THE TYPE $R_2AuX$ AND $RAuX_2$ <sup>1</sup>

BY M. S. KHARASCH AND H. S. ISBELL<sup>2</sup>

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### Introduction

In 1902 Pope and Gibson<sup>3</sup> published a paper on the preparation of diethyl auric bromide and ethyl auric dibromide. Diethyl auric bromide was prepared by the action of ethylmagnesium bromide upon an ethereal solution of auric bromide. Ethyl auric dibromide was prepared by subjecting diethyl auric bromide, dissolved in chloroform, to the action of bromine.

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

<sup>2</sup> This work, as well as the other papers on organo-gold compounds in this series, was submitted by H. S. Isbell in 1926 to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>3</sup> Pope and Gibson, *J. Chem. Soc.*, 91, 2061 (1902). This early work was recently repeated and confirmed by Gibson and Simonsen (*ibid.*, 2531 (1930)), who prepared, in addition, diethyl gold iodide and diethyl gold acetylacetone.

These ethyl gold compounds are the only ones whose preparation is described in the literature. This fact appears remarkable if one examines the numerous compounds of arsenic, antimony, mercury, lead, tin and the organo-metallic derivatives of other metals which have since been described. The lack of organo-gold compounds is certainly not due to unfamiliarity of the organic chemist with the element, for gold salts have found considerable application in the identification of many organic substances, particularly amines.

In 1926 Feldt reviewed the subject of organic gold compounds. This investigator, whose research in the field of gold chemotherapy covered a period of fifteen years, had evidently overlooked the paper of Pope and Gibson and wrote as follows in the "Klinische Wochenschrift," summarizing his experience in the synthetic preparation of gold carbon compounds. "Organische Goldverbindungen waren nicht bekannt. Gold besitzt 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."<sup>4</sup> ("Organic compounds of gold are unknown. Gold has no affinity for carbon. Complex organic compounds of gold in which the gold is directly attached to carbon are incapable of existence, or at least cannot be isolated. This has been shown by prolonged experimentation.")

**The Significance of the Properties of Auric Salts in the Synthesis of Organic Gold Compounds.**—The failure to synthesize organic compounds may have been due to a lack of consideration of the following salient facts regarding auric salts: first, the tendency of auric salts to form compounds of the aurate type (*i. e.*,  $\text{HAuX}_4$ ); second, the insolubility of auric salts in most organic solvents; third, the interaction of auric salts with solvents that are commonly employed in the Grignard syntheses.

The tendency of auric salts in solution toward compound formation has been known for a long time. Thus it is postulated that if a water solution of gold chloride is acidified with hydrochloric acid, the solution contains hydrochloroauric acid,  $\text{HAuCl}_4$ . Again, when auric chloride is added to a water solution of sodium chloride, the sodium chloroaurate is supposed to be formed. Furthermore, a water solution of sodium chloroaurate contains fewer auric ions than a water solution of auric chloride which presumably exists in the form  $\text{H}^+(\text{AuCl}_3\text{OH})^-$ . Whether this difference is merely a common ion effect or the formation of a more stable chloroaurate complex is impossible to determine from the available data, but it can be brought out in a very striking manner by the following experiment. If a water solution of auric chloride is treated with sulfanilic acid, an instant precipitation of gold results. On the other hand, if to

<sup>4</sup> Feldt, *Klinische Wochenschrift*, Feb. 19, 1926.

another sample of the same solution of gold chloride one or two moles of sodium chloride are added, followed by sulfanilic acid, it takes fifteen or more minutes (depending upon the concentration of the solution) before any precipitation of gold becomes noticeable. This experiment indicates that the concentration of auric ion, or the active oxidizing ion, has been suppressed. The change in the intensity of color of a water solution of auric chloride upon addition of sodium chloride is also quite significant.

Naturally it is to be expected that anhydrous gold chloride would also combine readily with many organic substances. The proof of the validity of this statement will be taken up in other papers.<sup>5</sup> For the present, suffice it to say that except for nitrobenzene and aliphatic hydrocarbons, most substances either react or form double compounds with anhydrous auric chloride or bromide. In the case of ether this combination can be illustrated by the following experiment. It was found by us that anhydrous auric chloride, under well controlled conditions, reacts with anhydrous benzene to form phenyl auric dichloride.<sup>5</sup> However, if we suspend the anhydrous auric chloride in anhydrous ether, or some other oxygen-containing substance, or add any of these substances to anhydrous benzene, no phenyl auric dichloride is formed.

With the above facts in mind it is not at all surprising to find that auric chloride does not react smoothly with a Grignard reagent, and that the yields of the gold carbon-compounds are very small.

**Criteria Regarding Types of Gold-Carbon Compounds That May Be Prepared by the Grignard Reagent.**—The facts cited above are of fundamental importance in interpreting the low yields of gold-carbon compounds by the Grignard reagent. However, in addition to the limiting factors mentioned previously, there are still others of equally vital importance. Our experience regarding these additional limitations of the use of the Grignard reagent in the preparation of organo-gold compounds may be summarized as follows.

(1) Gold-carbon compounds in which the gold is directly attached to three carbon radicals, *i. e.*,  $\text{AuR}_3$ , cannot be prepared by the Grignard reagent; at least our numerous efforts, under a variety of conditions, with a variety of radicals have been totally unsuccessful. Other indirect methods were also of no avail. We have prepared numerous compounds of the type  $\text{R}_2\text{Au}(\text{CN})$ , but do not consider them, in the absence of definite proof, as compounds in which the three valences of the gold are attached directly to the carbon atoms.

(2) There appears to be a definite limitation to the use of the Grignard reagent in that it is impossible (at least we were unable to accomplish the synthesis) to prepare by that method gold-carbon compounds of the

<sup>5</sup> Kharasch and Isbell, unpublished work: IV, Direct Auration: III, Gold-Nitrogen Compounds.

type  $R_2AuX$ , if the radical  $R$  is a strongly electronegative radical. This limitation is forced upon us by our laboratory experiences: first, our inability, after many trials and under a variety of experimental conditions, to prepare by the use of the Grignard reagent any gold-carbon compounds of the phenyl radical and those radicals which are above the phenyl radical in the table of electronegativity of radicals<sup>6</sup> (the tolyl, naphthyl, *p*-methoxyphenyl, etc.); second, the successful isolation of the gold-carbon compounds of the ethyl radical and radicals below the ethyl radical in the above-mentioned table.<sup>7</sup> Thus, the gold-carbon compounds of the type  $R_2AuX$  of the following radicals were readily prepared: ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, isoamyl, cyclohexyl, benzyl and phenylethyl.

**That the electronegativity of the radical as a whole is of prime importance in determining whether a stable gold-carbon compound will be formed becomes apparent from the fact that such radicals as benzyl and phenylethyl, although they contain phenyl nuclei, yielded extremely stable gold-carbon compounds. The explanation is that both of these radicals are extremely weak electronegative radicals compared with the phenyl radical and are to be found at the bottom of the table of electronegativity of radicals. The gold compounds of the benzyl and phenylethyl radicals were sufficiently stable to enable us to sulfonate the benzene ring with the aid of fuming sulfuric acid. The table of radicals thus served as an excellent guide in the preparation of gold-carbon compounds, for it enabled us to pick out successfully the range of radicals which yielded stable gold-carbon compounds.**

#### **General Properties and Stabilization of Gold-Carbon Compounds.—**

It has been found feasible to synthesize the compounds of the type  $R_2AuCl$  and  $R_2AuBr$  by starting with the organomagnesium halide and treating that with the corresponding gold halide. It is to be noted that irrespective of whether one starts with gold chloride and an organomagnesium bromide or gold bromide and an organomagnesium chloride, the bromides of the gold-carbon compounds were formed in each case.

The gold-carbon compounds  $R_2AuCl$  or  $R_2AuBr$  have characteristic odors, suggestive of pine needles or of bromocamphor. The odors are decidedly nauseating. The gold-carbon compounds are soluble in pyridine, benzene and chloroform, less readily soluble in ether and petroleum ether, difficultly soluble or insoluble in acetone and alcohol and practically insoluble in water. Most of them are somewhat soluble in olive oil. They are all light sensitive and are readily decomposed by heat.

<sup>6</sup> Kharasch and Marker, *THIS JOURNAL*, **48**, 3130 (1926); Kharasch and Flenner (unpublished work); Kharasch and Legault (unpublished work); Kharasch and Pines (unpublished work).

<sup>7</sup> The gap between the phenyl and ethyl radicals still remains to be filled.

The diethyl gold chloride and bromide are well-defined crystalline solids, but as the length of the chain is increased the melting point first decreases to a minimum, while subsequent lengthening of the chain increases the melting points again. In addition to the difficulties involved in the isolation of many of the gold-carbon compounds because of their low melting points, their instability in general was a quite troublesome feature. Thus, most of the compounds  $R_2AuCl$  could be kept without decomposition for but a few days—the only compounds which may be kept for some time without appreciable decomposition are those of extremely weakly electronegative radicals, such as the benzyl and cyclohexyl radicals.

**Organo-Gold Cyanides.**—We were extremely fortunate in that both of the above difficulties, *i. e.*, low melting point and instability, were overcome by the replacement of the halogen by the (CN) radical.<sup>8</sup> This was accomplished by shaking an ether or benzene solution of the compound  $R_2AuCl(Br)$  with silver cyanide. An examination of the table reveals the fact that the cyanides have the highest melting points, followed by bromides, and that the chlorides have the lowest melting points. The advantages that accrue from the fact that the decomposition points of the cyanides are so much higher than the chlorides are quite obvious.

TABLE I  
STABILITY OF COMPOUNDS OF THE TYPE  $R_2AuX$

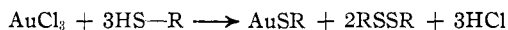
Compound	Chloride		Bromide		Cyanide	
	Melts, °C.	Dec., °C.	Melts, °C.	Dec., °C.	Melts, °C.	Dec., °C.
Diethyl	48	48	58	58	92	92-160
Di- <i>n</i> -propyl	Liq.	107	Liq.	95	Slight dec.	Shows dec.
		Gas 120			84	128-147
Di-isopropyl	Dec.	95	Dec.	100-130	88-90	121-133
		Gas 120				
Di- <i>n</i> -butyl	.....		Liq.	65	Dec.	125-130
Di-isobutyl	.....		Liq.	.....	112-113	160
Di-isoamyl	.....		Liq.	.....	70	135-140
Dicyclohexyl		180-190	Dec. 148	Dec. 140-148	152, s.d.	155
Dibenzyl	Dec.	70-110	Dec.	77	Dec.	122
				Detonates 85		
Diphenylethyl	.....		112-115	105-115	.....	.....

Furthermore, the cyanides of most of the compounds can be kept in brown bottles without darkening. The compounds  $R_2Au(CN)$  when freshly prepared are soluble in benzene. Many of these compounds, particularly the compounds from the benzyl radical, upon standing for a period of time become insoluble in benzene, although the empirical formula of the compound remains the same.

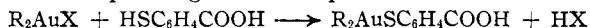
<sup>8</sup> The halogen can evidently be replaced by any negative radical. Thus, shaking the organo-gold bromides with silver sulfate gave the corresponding organo-gold sulfates.

The above-mentioned behavior of the organo-gold halides toward silver cyanide is of considerable interest if one bears in mind that auric chloride reacts with silver salts to give compounds of the chloraurate type. The tendency toward formation of chloraurate complexes is entirely absent under anhydrous conditions in the organic gold compounds of the type  $R_2AuX$ . However, they still form complexes with various nitrogenous substances such as pyridine, hexamethylenetetramine, etc.

**Organo-Gold Sulfur Compounds.**—Very striking also is the behavior of gold-carbon compounds of the type  $R_2AuX$  toward thio compounds. Thus it is well known that when an auric salt is treated with a mercaptan, the auric ion is reduced to the aurous state and the mercaptan salt of the aurous compound is formed.



However, when gold is firmly attached to two organic radicals, it is possible to prepare the corresponding sulfur compounds



The mercaptides of these compounds while readily soluble and stable in alcohol are easily hydrolyzed in water containing less than 33% of alcohol.

**Behavior of Organo-Gold Compounds toward Reducing Agents.**—Gold-carbon compounds of the type  $R_2AuX$  are much more stable toward reducing agents than auric salts. Thus, while stannous chloride, sodium hydrosulfide and hydroquinone instantly reduce auric chloride, the organic gold compounds react with these reagents much more slowly. Of interest is the observation that while mercury diphenyl and diethyl when treated with dibenzyl auric bromide precipitate metallic gold, mercury dibenzyl is without any effect on that substance.

**Sulfonation of Organo-Gold Compounds.**—As previously indicated, the stability of organo-gold compounds toward various chemical agents increased as the electronegativity of the radical attached to the gold decreased. Notable among these properties of gold-carbon compounds of the weakly electronegative radicals is their stability toward acids. Thus, the dibenzyl and diphenylethyl auric salts were readily sulfonated under properly controlled conditions. The type of the inorganic radical X, attached to the molecule  $R_2AuX$ , made little difference in the ease of sulfonation, for the chlorides, bromides and cyanides as well as the sulfates were sulfonated by the use of fuming sulfuric acid (25% excess  $SO_3$ ). It was noticed, however, that in the case of the bromides some free bromine was formed, which caused the decomposition of some of the gold compound. The sulfonated organoauric salts were usually isolated first in the form of their calcium salts. The latter by double decomposition with sodium sulfate were converted into the sodium salts.

The calcium salts of the sulfonated gold compounds are fairly soluble

in water and very stable toward reducing agents. Hydroquinone, sodium formate or sodium stannite have no immediate effect, and it is only by prolonged boiling that gold can be detected in the compounds by the above reagents.

**Gold-Carbon Compounds of the Type  $\text{RAuBr}_2$ .**—A number of organo-gold dibromides were prepared by treatment of the compounds  $\text{R}_2\text{AuBr}$  with bromine in chloroform. The benzyl, phenylethyl and cyclohexyl gold dibromides were thus prepared. All of these substances as well as the ethyl compound described by Pope and Gibson<sup>3</sup> were obtained as ruby-red needles.

The organo-gold dibromides are in general much less stable than the di-organo-gold bromides. Thus, while the latter substances are quite stable toward reducing agents, the treatment of the organo-gold dibromides with stannous chloride or hydroquinone leads to the formation of metallic gold in a few minutes, while with sodium hydrosulfite an immediate separation of gold takes place.

Solutions of the organo-gold dibromides in organic solvents such as benzene, chloroform and carbon tetrachloride are intensely colored. Strikingly, however, in solvents which contain unsaturated groups, such as olive oil, oleic acid, methyl cyclohexene, etc., these ruby-red compounds yield colorless solutions. This change in color of the solution is suggestive not of a true solution of the compounds  $\text{RAuBr}_2$  but rather of an addition to the double bond, yielding substances of the type  $\text{R}_2\text{AuBr}$ .

### Experimental Part

**The Preparation of Organo-Gold Compounds of the Type  $\text{R}_2\text{AuX}$ .**—The general method employed for the preparation of organic gold compounds of the type  $\text{R}_2\text{AuX}$ , which gave the most satisfactory results, is given below in detail for the preparation of di-phenylethyl auric bromide. Modifications of this method whenever desirable are indicated under the respective compounds in the main table.

**The Preparation of Di-phenylethyl Auric Bromide.**—An ether solution of phenylethylmagnesium bromide was prepared from 42.8 g. of phenylethyl bromide, 6.6 g. of magnesium turnings and 500 cc. of anhydrous ether. Thirty grams of auric chloride was added to 500 cc. of anhydrous ether which previously had been cooled to  $-15^\circ$ . To this latter solution, vigorously stirred with a mechanical stirrer, a filtered solution of the phenylethylmagnesium bromide was added dropwise.

The addition of the Grignard reagent required about fifty minutes. Although the reaction appears to be almost instantaneous, a period of ten minutes was allowed before the addition of about 50 g. of finely crushed ice. The precipitated magnesium hydroxide was dissolved in 500 cc. of 2% acetic acid and after the addition of about 200 cc. of benzene the ether-benzene solution was separated and successively washed with portions of a 5% aqueous sodium bromide solution until all gold was removed from the ether-benzene layer. The use of a dilute sodium bromide solution instead of pure water facilitated the removal of auric bromide from the ether layer. Finally, the ether-benzene solution was washed with distilled water, separated and evaporated to a small volume at room temperature *in vacuo*. Di-phenylethyl auric bromide crystallized on evaporation. The filtrate was diluted with ten volumes of 95% ethyl alcohol, which

TABLE II  
ORGANIC GOLD HALIDES

Di-substituted auric halide	Yield		M. p., <sup>a</sup> °C.	Dec. p., °C.	Gold analyses, %		Remarks
	AuCl <sub>3</sub> , g.	→ g.			Calcd.	Found	
Di-ethyl chloride	2	→ 0.3	48 V.s.d.	48	67.80	67.45	Dec., few days
Di-ethyl bromide	30	→ 2.2	58 V.s.d.	58	...	...	AuCl <sub>3</sub> , 45 g. → 5.5 g. of subst.
Di- <i>n</i> -propyl chloride	6	→ 0.2	Lt. yel. oil	107, gas 120	See cyanide		
Di- <i>n</i> -propyl bromide	Small		Lt. yel. oil	95	54.42	51.7	Pine needle odor
Di-isopropyl chloride			D.	95, gas 120	See cyanide		Sl. sol. EtOH; cryst. solid, liq. at 75–80° with gold sepn.
Di-isopropyl bromide			D.	100–130	See cyanide		Cryst. solid. Dec. to liquid and gold metal
Di- <i>n</i> -butyl bromide	2	→ 0.3	Liquid	65	50.40	50.19	Diff. sol. EtOH. Pine odor
Di-isobutyl bromide	2	→ ca. 0.2	Liquid		See cyanide		Colorless oil. Diff. sol. EtOH, easily sol. pet. ether
Di-isoamyl bromide	2	→ 0.2	Liquid		47.03	47.00	
Diacetyl bromide.	A compound with the characteristic odor of these compounds was obtained. It contained gold and had the correct properties						
Di-benzyl chloride	2	→ 0.3	D.	70–110	47.54	47.50	Diff. sol. Et <sub>2</sub> O. sol. Bz, BzCH <sub>2</sub> Cl
Di-benzyl bromide	2	→ 0.476	D.	77, det. 85	42.94	43.44	Diff. sol. org. solv. incl. ether; more sol. Bz, BzCH <sub>2</sub> Cl
						41.70	
Di-cyclohexyl bromide	2	→ 0.081	D. 148	140–148	44.49	44.49	Sol. Bz, Et <sub>2</sub> O, CHCl <sub>3</sub> ; olive oil, 0.113 g. in 13 cc.
Di-cyclohexyl chloride	60	→ 5.5		180–190	49.49	49.53	
Di-phenylethyl bromide	30	→ 3.77	112–115	105–115	40.47	40.49	
Di-phenylethyl sulfate			D.	105–108	43.30	43.21	

<sup>a</sup> V.s.d., very slight decomposition; D., decomposes without melting.



precipitated an additional quantity of di-phenylethyl auric bromide. The combined precipitates were crystallized from a chloroform–ligroin mixture.

Di-phenylethyl auric bromide is easily soluble in chloroform and benzene, less soluble in ether, ligroin, and almost insoluble in alcohol. It crystallizes from benzene or chloroform in long, branching needles. In a melting point tube it begins to darken at 105° and melts with decomposition at 112–115°.

TABLE III  
ORGANO–GOLD CYANIDES

Auric cyanide	M. p., °C.	Dec. p., °C.	Gold analyses, %	
			Calcd.	Found
1 Di-ethyl	92	Sl. dec. 92–160	See chloride	
2 Di- <i>n</i> -propyl	84	128–147	63.75	63.63
3 Di- <i>i</i> sopropyl	88–90	121–133	63.75	63.71
4 Di- <i>n</i> -butyl	Dec.	125–130	See bromide	
5 Di- <i>i</i> sobutyl	112–113	160	58.45	58.44
6 Di- <i>i</i> soamyl	70	135–140	See bromide	
7 Di-benzyl	Dec.	122	48.65	48.11 48.67 <sup>a</sup> 48.84 <sup>b</sup>
8 Di-cyclohexyl	152 sl. dec.	155	50.64	50.57

<sup>a</sup> Benzene-soluble product. <sup>b</sup> Benzene-insoluble product.

Remarks

- 1 Cryst. solid. Sol. pet. ether, Bz, olive oil, when new; insol. on standing
- 2 Easily sol. olive oil. AuCl<sub>3</sub>, 6 g. → 0.124 g.
- 3 Stable. Easily sol. olive oil, Bz, Et<sub>2</sub>O, CHCl<sub>3</sub>
- 4 Sol. to 0.7 M/100 in olive oil. Au, 6 g. → 0.35 g. Crystalline solid, but diff. to obtain in cryst. form
- 6 Easily sol. Et<sub>2</sub>O, Bz, pet. ether. Faint odor
- 7 Dec. pt. same after six weeks. Sol. warm NH<sub>4</sub>OH
- 8 Insol. EtOH, EtOAc, Me<sub>2</sub>CO; very diff. sol. Et<sub>2</sub>O; sol. Bz, CHCl<sub>3</sub>

**Preparation of Di-phenylethyl Auric Sulfate.**—A benzene solution of di-phenylethyl auric bromide was mixed with a large excess of silver sulfate and shaken until a test portion of the filtrate gave a negative test for halogen. The filtrate was evaporated *in vacuo*. A white crystalline residue remained which was dried to constant weight *in vacuo* at 40°.

*Anal.* Subs., 0.0766: Au, 0.0331. Calcd. for C<sub>22</sub>H<sub>36</sub>Au<sub>2</sub>SO<sub>4</sub>: Au, 43.30. Found: Au, 43.21.

Di-phenylethyl auric sulfate is easily soluble in chloroform, less soluble in benzene, ether and low boiling ligroin and very slightly soluble in ethyl alcohol. It is insoluble in water. In a melting point tube it begins to darken at about 105° and decomposes violently at about 108°.

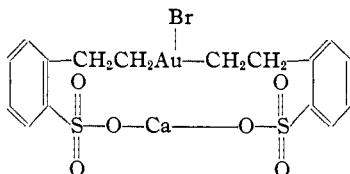
**Sulfonation of Di-phenylethyl Auric Bromide.**—To 1.25 g. of di-phenylethyl auric bromide dissolved in 10 cc. of chloroform and cooled to –15°, 6.25 cc. of cold fuming sulfuric acid (25% excess SO<sub>3</sub>) was slowly added while the mixture was kept in an ice-salt bath at –15°. After the solutions were thoroughly mixed the temperature was allowed to rise by removing the flask from the ice-bath. The temperature was allowed to rise to about 10°. That the reaction had proceeded to completion was ascertained by the facts that evaporation of a few drops of the chloroform layer did not give a residue of unchanged di-phenylethyl auric bromide and that the acid layer when poured into water gave a clear solution. The mixture was then cooled again to about –10° and slowly poured with stirring into a mixture of 50 g. of crushed ice containing 1.25 g. of

calcium bromide. The resulting solution was kept cold and, as soon as possible, neutralized with 25 g. of calcium carbonate. The solid that separated was collected on a small Büchner funnel and washed with a small amount of water. The residue showed only a faint test for gold while the filtrate gave a very strong test.

The filtrate was then mixed with about five volumes of absolute alcohol. A precipitate of calcium sulfate formed which was collected on a filter. The filtrate was then evaporated *in vacuo* at 20° to a volume of about 10 cc. It was then diluted again with three volumes of absolute alcohol and the small amount of calcium sulfate which formed was collected on a filter. The resulting filtrate was practically free from calcium sulfate and upon the addition of 500 cc. of absolute alcohol a very fine white precipitate separated. After standing overnight in the ice box the precipitate was collected on a filter, washed with alcohol and dried *in vacuo*. The weight of the dry material was 0.84 g.

The compound was further purified by dissolving it in the smallest possible quantity of water and precipitating it by the addition of absolute alcohol. The resulting precipitate was very fine and the solution filtered slowly. It was dried *in vacuo* over phosphorus pentoxide to constant weight.

*Anal.* Subs., 0.2064: Au, 0.0596; subs., 0.1088: 2.9 cc. of 1.098 *N*/20 KSCN; 0.1511: 4.0 cc. of 1.116 *N*/10 KMnO<sub>4</sub>. Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>6</sub>S<sub>2</sub>CaAuBr: Au, 28.77; Br, 11.66; Ca, 5.85. Found: Au, 28.88; Br, 11.69; Ca, 5.92. This corresponds to the formula<sup>9</sup>



The calcium salt when heated turns dark and begins to decompose at about 130°. It is insoluble in alcohol and organic solvents. It is fairly soluble in water. Strikingly, it is much more soluble in solutions of calcium chloride, bromide or sodium bromide than in pure water, thus recalling to mind the characteristics noted for ammonium succinimide aurate.

A water solution of the calcium salt is not reduced by hydroquinone, stannous chloride or sodium formate, thus indicating an extremely low ionization of the gold from the carbon atoms.

The following points are of importance in the sulfonation of the gold compounds.

(1) There was some decomposition of the organo-gold bromide by the fuming sulfuric acid, which resulted in the formation of some free bromine. This bromine decomposed some of the organic gold-carbon compound and led to the formation of some auric bromide. Thus, it would appear that the use of the organo-gold chlorides might be more advantageous than the use of bromides.

(2) Calcium bromide was added to the ice prior to pouring in the sulfonated mixture because it was found that the addition of calcium bromide or chloride at this point prevented the formation of much metallic gold.

(3) The success of the sulfonation depends to a large extent upon the technique. The following additional points are of importance. The period during which the fuming sulfuric acid is allowed to react must be regulated. A few drops of solution may be

<sup>9</sup> It is understood, of course, that a molecular weight determination is essential before one could state with certainty that the simple formula given for the calcium salt of the sulfonated di-phenylethyl auric bromide is correct or whether a number of the sulfonated molecules are linked together through the calcium atom.

tested in water or the chloroform layer may be sampled and its residue on evaporation noted.

The concentration of the solutions in vacuo is usually attended with some decomposition unless a low temperature is maintained.

The precipitated calcium salt of the gold compound is very fine and may be best separated by the use of a centrifuge.

**Sulfonation of Di-phenylethyl Auric Sulfate.**—One gram of di-phenylethyl auric sulfate was gradually stirred into 4 cc. of fuming sulfuric acid (25% excess  $\text{SO}_3$ ) kept at  $-15^\circ$ . After thorough mixing, the temperature was allowed to rise to about  $15^\circ$ , when the di-phenylethyl auric sulfate seemed to be completely in solution. The mixture was then cooled to  $-10^\circ$  and poured on 50 g. of finely crushed ice. A nearly clear solution resulted. The acid was neutralized by adding calcium carbonate. The calcium sulfate and excess calcium carbonate was collected on a filter and the filtrate poured into 15 volumes of absolute alcohol. A flocculent precipitate resulted which consisted of the calcium salt of the sulfonated organic gold compound and a small amount of calcium sulfate. The precipitate was collected upon a filter. As the filtrate contained only a trace of gold, it was discarded. The precipitate was extracted with a few cc. of water. The gold compound went into solution leaving an insoluble residue of calcium sulfate. The water solution of the calcium salt of the sulfonated di-phenylethyl auric sulfate was poured into ten volumes of absolute alcohol. A very fine white precipitate resulted which was collected on a filter.

The compound corresponded in properties to that obtained by the sulfonation of the di-phenylethyl auric bromide. Thus it did not give the usual gold test with stannous chloride or hydroquinone but after decomposition by either heat or bromine a strong test for gold was obtained. Qualitative tests for calcium and sulfate ion were also obtained. The compound was water soluble.

Dibenzyl auric chloride and dibenzyl auric cyanide were also sulfonated in a manner similar to the di-phenylethyl auric bromide. The reaction proceeded smoothly and a solution was obtained which was not reduced by hydroquinone and exhibited similar properties to the corresponding di-phenylethyl gold compounds.

### Organo-Gold Sulfides

**The Preparation of Dicyclohexyl Auric Thiosalicylate.**—A quantity of dicyclohexyl auric chloride (1.9935 g.) was dissolved in 20 cc. of benzene, mixed with 0.7520 g. of thiosalicylic acid dissolved in 30 cc. of ethyl alcohol and the calculated equivalent of an alcoholic solution of potassium hydroxide ( $N/2$ ) necessary to react with the hydrochloric acid formed was added. The mixture was evaporated to dryness and the residue was washed free from chlorides with cold water followed by several washings with cold alcohol. The product was easily and completely soluble in one equivalent of sodium hydroxide dissolved in 50% alcohol, from which it was precipitated by the addition of acid. The product thus obtained was dried to constant weight over phosphorus pentoxide.

*Anal.* Subs.: 0.1170: Au, 0.0446. Calcd. for  $(\text{C}_6\text{H}_{11})_2\text{AuSC}_6\text{H}_4\text{COOH}$ : Au, 38.18. Found: Au, 38.12.

The compound decomposed at  $173$ – $180^\circ$ . It is quite stable when kept in brown bottles, as indicated by the fact that even after several months the salt of the compound was still completely soluble in dilute alcohol.

**The Preparation of Phenylethyl Auric Dibromide.**—A chloroform solution of di-phenylethyl auric bromide was mixed with a chloroform solution of bromine which contained approximately two equivalents of bromine. Upon spontaneous evaporation of the solvent ruby-red needles which formed in fan-like clusters were obtained. These

were washed first with a small quantity of chloroform, then ether, and dried *in vacuo* at 40° to constant weight over phosphorus pentoxide.

*Anal.* Subs., 0.0542: Au, 0.0231. Calcd. for  $C_8H_9AuBr_2$ : Au, 42.67. Found: Au, 42.62.

The compound is difficultly soluble in chloroform, almost insoluble in ether, benzene, petroleum ether and water. Phenylethyl auric dibromide decomposes at 150–160°.

**Preparation of Ethyl Auric Dibromide.**—This compound was prepared by the method used by Pope and Gibson. Three grams of di-ethyl auric bromide was dissolved in 25 cc. of chloroform and 1.5 g. of bromine dissolved in 30 cc. of chloroform was added. The mixture was allowed to stand overnight in an open beaker. All of the chloroform had evaporated and a reddish black residue remained. This was extracted successively with 15 cc. of cold chloroform and with five portions of petroleum ether. A quantity of unchanged diethyl auric bromide was thus recovered. The residue was washed with water and finally crystallized from chloroform; 0.95 g. of ethyl auric dibromide was thus obtained. The compound forms red needles difficultly soluble in chloroform and easily soluble in alcohol.

**Reactions of Ethyl Auric Dibromide: Behavior with Unsaturated Derivatives.**—Solutions of ethyl auric dibromide in all saturated organic solvents are intensely colored. However, solutions of this substance in unsaturated solvents are practically devoid of any color. Thus, the ethyl auric dibromide dissolves to a colorless solution in olive oil, methylcyclohexene, cyclohexene, etc. This phenomenon is probably due to the addition of ethyl auric dibromide to the double bond, giving rise to compounds of the type  $R_2AuBr$  which have very little color.

**Preparation of Benzyl Auric Dibromide.**—To 0.202 g. of di-benzyl auric bromide dissolved in 10 cc. of chloroform, 12 cc. of 0.0962 *N* bromine dissolved in carbon tetrachloride was added. After standing for two days the solvent was evaporated and the residue was washed with water and finally crystallized from chloroform.

*Anal.* Subs., 0.0745: Au, 0.0327. Calcd. for  $C_6H_5CH_2AuBr_2$ : Au, 44.01. Found: Au, 43.89.

The compound separates from chloroform in the form of dark needles. It is soluble in acetone and alcohol, imparting to these solvents a yellow color, while red solutions are obtained in chloroform and benzene. The compound is rather insoluble in carbon tetrachloride, petroleum ether and ether. Benzyl auric dibromide decomposes at about 140°. The change in appearance was slight and gradual over a considerable temperature range.

**The Preparation of Cyclohexyl Auric Dibromide.**—To 0.9 g. of di-cyclohexyl auric bromide dissolved in 20 cc. of chloroform, 48 cc. of 0.09 *N* bromine solution in chloroform was added. The mixture was allowed to stand overnight. The residue upon evaporation of the chloroform was washed with water and crystallized from chloroform.

*Anal.* Subs., 0.1025: Au, 0.0456. Calcd. for  $C_6H_{11}AuBr_2$ : Au, 44.81. Found: Au, 44.53.

The compound is obtained from chloroform in the form of dark red needles which decompose without melting at 150°. It is soluble in benzene, chloroform and carbon tetrachloride with a red coloration. However, yellow solutions are obtained in alcohol and ethyl acetate. Similar to the ethyl compound, cyclohexyl gold dibromide gives colorless solutions when dissolved in unsaturated solvents, like olive oil or methylcyclohexene.

### Summary

1. The limitations of the Grignard reagent in the preparation of gold-carbon compounds, of the type  $R_2AuX$ , are discussed.

2. It is pointed out that the table of electronegativity of radicals serves as an excellent guide in the preparation of gold compounds  $R_2AuX$ . Thus it has been found that gold compounds of the ethyl radical and all the radicals below the ethyl radical in that table can be readily prepared from the appropriate Grignard reagents and auric chloride. However, no stable gold-carbon compounds  $R_2AuX$  of the phenyl radical, or radicals more strongly electronegative than the phenyl radical, can be prepared by that method.

3. The stabilization of gold-carbon compounds  $R_2AuX$  through the preparation of the corresponding cyanides is described.

4. It is shown that although no inorganic sulfides of trivalent gold are known, when two of the valences of the gold are attached to organic radicals as in  $R_2AuX$ , it is possible to prepare compounds of the type  $R_2Au-S-R$ . It is further shown that these substances are hydrolyzed in water solution, a behavior characteristic of the amphoteric elements of the third group.

5. The stability toward acids of gold compounds  $R_2AuX$  of weakly electronegative radicals is discussed, and the sulfonation of di-phenyl-ethyl auric bromide and di-benzyl auric chloride is described.

6. The gold compounds  $R_2AuX$  have been found to be extremely stable toward powerful reducing agents.

7. The preparation of a number of gold compounds  $RAuX_2$  is described.

8. It is shown that compounds of the type  $RAuX_2$  are extremely unstable toward reducing agents.

9. The fact is emphasized that compounds  $RAuX_2$ , while insoluble in water, dissolve readily in sodium chloride solution. This fact is explained upon the assumption that complexes of the chloroaurate type are thus formed.

10. It is shown that gold compounds  $RAuX_2$  are intensely colored in chloroform solution, but that their colors disappear instantly when substances containing ethylene bonds are added to them. Direct addition of the gold complex to the double bond is postulated.

11. The preparation of a large number of organo-gold compounds is described and their behavior toward many reagents is given.