3% yield was obtained along with benzaldehyde from benzyl chloride. All solids were identified by the mixed melting point method. A vigorous reaction, causing distillation, set in soon after distillation of the solvent from diphenylmethane and selenium dioxide; the reaction mixture remaining in the flask was nearly pure benzophenone. Other data are given in the table.

Toluene derivative	Reaction temp., °C.	Time, hours	Product	M. p., °C.	Yield, %
p-Nitrobenzyl bromide	140–150°	2	*p*-Nitrobenzaldehyde	105–106	56
Benzyl chloride	Refluxed without solvent	3	Benzaldehyde	(B. p. 173–180)	49
Diphenylmethane			Benzophenone	47–48.5 (b. p. 294–298°)	47
Triphenylmethane	Refluxed without solvent	0.2	Triphenylcarbinol	160–162	15

Reaction of Hypobromite with Benzylpyridinium Halides.—Two grams of *p*-nitrobenzylpyridinium chloride in 20 cc. of water was treated with hypobromite (100 cc. of water, 10 g. of sodium hydroxide and 3 cc. of bromine). At once the reaction mixture was washed with ether, and the aqueous layer acidified. Bromine was removed with sodium bisulfite, and dissolved ether by boiling. The precipitate thus obtained melted at 237–238.5° (mixed m. p. with *p*-nitrobenzoic acid was not depressed), and amounted to 1.1 g. (82%).

The other hypobromite reactions were carried out in a similar fashion.

Summary

The action of selenium dioxide on several toluenes and of alkali and hypobromite on certain benzylpyridinium halides has been studied. It was found that oxidation with selenium dioxide proceeds with greater difficulty than in the case of acetophenone; and that alkaline hypobromite converts *p*-nitrobenzylpyridinium halides into *p*-nitrobenzoic acid in good yield.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Chemistry of Organic Gold Compounds. V. Auration of Aromatic Nitriles

BY M. S. KHARASCH AND THOMAS M. BECK[1,2]

Introduction

Kharasch and Isbell, in their investigation of organic gold compounds,[3] discovered that certain derivatives of auric chloride of the type $RAuCl_2$ (R being an aromatic radical), which cannot be prepared by the usual Grignard reaction, may be prepared by the direct action of anhydrous auric chloride on the organic compound. For example, phenyl auric dichloride is readily obtained by the action of auric chloride on benzene. It was further pointed out that a definite relation exists between the stability of the various substituted phenyl auric dichlorides and the relative electronegativities of the R groups,[4] in that the more highly electronegative radicals give compounds too unstable to be isolated, and that the hydrides of the least electronegative radicals are too unreactive with auric chloride. In general, the preparation by this method of compounds of the type described was limited to benzene derivatives whose substituent radical lies between tolyl and nitrophenyl in electronegativity.

In an extension of this work, an investigation of the action of auric chloride on weakly electronegative radicals of the benzene series was undertaken. This paper deals with the direct auration of aromatic nitriles, the position taken by the gold, and the stability of the gold–carbon bond toward a variety of chemical reagents.

Previous Work on the Action of Auric Chloride on Nitriles.—Henke[5] investigated the reaction of auric chloride with aceto-, propio- and benzonitriles, reporting the formation of molecular complexes of the type $RCN \cdot AuCl_3$. However, he does not specify whether his auric chloride was anhydrous; furthermore, his analytical results do not justify the assigned formulas.

Lenher[6] states that methyl, ethyl, benzyl and phenyl cyanides each extract auric chloride from its aqueous solutions without reducing the gold. Obviously his gold chloride was hydrated, and consequently his observations have no bearing upon the work described in this investigation.

(1) This communication is an abstract of a dissertation submitted by Thomas M. Beck in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago, 1932.

(2) The authors wish to take this opportunity to express their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

(3) Kharasch and Isbell, THIS JOURNAL, **53**, 3053 (1931).

(4) Kharasch and Reinmuth, *J. Chem. Educ.*, **8**, 1713 (1931), Kharasch, Reinmuth and Mayo, *ibid.*, **11**, 88 (1934).

(5) Henke, *Ann.*, **106**, 280 (1858).

(6) Lenher, THIS JOURNAL, **35**, 549 (1913).

Action of Anhydrous Auric Chloride on Nitriles.—The results described in this paper indicate that anhydrous auric chloride reacts with various nitriles, forming two types of compounds: first, addition compounds of the type postulated by Henke; and, second, aromatic ring substitution compounds.

The aliphatic nitriles form, almost exclusively, addition compounds with anhydrous auric chloride. The general method of preparation consists of treating auric chloride with a slight excess of the nitrile. The formation and structure of such compounds are readily understood if one bears in mind that trivalent gold shows a strong tendency to complete its electronic octet by combining with some atom or ion having an unshared electron doublet. This is shown by the ease with which auric chloride combines with water to form a hydrate,[7] or with a chloride ion or four succinimide ions[8] to form complex negative ions. In the case of the aliphatic nitriles, the auric chloride may complete its octet with the extra doublet of the nitrogen.

Aromatic nitriles differ from those of the aliphatic series in that their reaction with anhydrous auric chloride results in direct auration. Moreover, some of the reactions of the resulting aromatic derivatives of gold chloride point to the existence of a shared electron pair between the nitrogen and gold atoms, of the type encountered in the case of the aliphatic nitrile complexes. This shared electron pair is indicated by increased stability toward various reagents, and by the absence of certain properties characteristic of a tri-substituted gold atom.

Preparation of the Aromatic Nitrile–Gold Compounds.—The aromatic nitrile–gold compounds are prepared by adding auric chloride to either the pure nitrile or its solution in nitrobenzene. This mixture is allowed to stand for a certain time, varying from a few minutes for phenylacetonitrile to several hours for some of the substituted benzonitriles, and the compounds then obtained by diluting the mixture with ether. Auric dichloride derivatives were prepared in this way from benzonitrile, ortho and para tolunitriles, alpha and beta naphthonitriles, meta and para nitrobenzonitriles, para bromobenzonitriles, phenylacetonitrile and para nitrophenylacetonitrile.

These gold compounds are bright yellow, crystalline solids, melting with some decomposition usually well above 100°. On the basis of gold and chlorine analyses, they have an empirical formula corresponding to $RAuCl_2$, where RH is the original nitrile. Although differing markedly in many properties from previously described aromatic auric dichlorides,[3] nevertheless their empirical formulas, together with the fact that they are converted by dilute hydrochloric acid into the original nitrile and chloro-auric acid, indicate beyond reasonable doubt that the gold dichloride radical is attached directly to the ring, at least in the cases of the substituted benzonitrile derivatives. While this evidence does not preclude the possibility that the gold might be attached in some fashion to the side chain in the case of the phenylacetonitrile–gold compound, yet the fact that this compound bears such a striking resemblance in its properties to the auric dichloride derivative of benzonitrile is a rather clear indication of a similarity in structure.

Position of the Gold Dichloride Group.—The position of the gold atom on the ring has not been proved definitely in all of the compounds. It appears that, except in the cases of acids or substances containing a labile hydrogen atom, the nitrile auric dichlorides are quite unaffected by reagents which might ordinarily be expected to replace the gold. The halogens are exceptions, but even with them it is necessary to use heat and pressure to bring about a reaction.

In three cases where the position of the gold in the aromatic ring has been ascertained, it was found that the auric dichloride group follows the usual rules for substitution in the benzene ring; that is, it assumes a position meta to the nitrile group. Furthermore, none of the reactions of the other compounds, where the position of the gold dichloride group has not been definitely determined, indicates an exception to this rule.

Structure of the Gold–Nitrile Compounds.—It is submitted on the basis of a careful study of the chemical properties of all the gold–nitrile compounds, in comparison with the gold aryl hydrocarbon molecules, that an electron pair is shared between the nitrogen and the gold atoms. Briefly, the bases for this suggestion are as follows.

1. The stability and the unique properties of the aromatic nitrile–gold are characteristic of the

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(7) Hittorf and Salkowski, *Z. physik. Chem.*, **28**, 546 (1899).

(8) Kharasch and Isbell, This Journal, **53**, 3059 (1931).

cyanide group. They are not due to the low electronegativity induced by the cyanide group, since nitrotolyl auric dichloride, which contains a radical of equally low electronegativity, shows none of these properties. Furthermore, these anomalous properties are also shown by cyanomethyl phenyl auric dichloride, in which the radical has a definitely higher electronegativity.

2. It is a known fact that the nitrogen of the nitrile group and the gold in trivalent gold compounds each possess an extra valence, and that these valences are complementary in nature and therefore probably capable of satisfying each other.

3. The formation of such a bond causes the trivalent gold to become less reactive, as is demonstrated by the fact that the reactivity of auric chloride is greatly lowered in propionitrile solution. Also, the formation of such a bond would saturate completely both the gold and the nitrogen, thereby preventing the formation of addition compounds or ions.

Furthermore, the definite, although slight, solubility of these compounds in salt solutions, as compared with their almost complete insolubility in water, suggests that in the presence of chloride ion the gold to nitrogen bond may be slightly dissociated, permitting a partial replacement of nitrogen by chloride ion, and resulting in an equilibrium between the cyanophenyl auric dichloride and the cyanophenyl trichloro-aurate ion in the solution. Such an equilibrium offers a mechanism to explain why the nitrile–gold chloride compounds, which are so stable against many reagents, are so readily decomposed by such substances as hydrochloric acid or pyridine, which are capable of sharing an electron pair with trivalent gold.

One might object to such a bond between gold and nitrogen on stereochemical grounds, since it involves the sharing of valence electrons between meta groups. A reasonable solution to this difficulty lies in the possibility of electron sharing between gold and nitrogen atoms of different molecules, leading to the formation of polymers. The validity of this suggestion unfortunately could not be demonstrated, due to experimental difficulties in determining the molecular weights.

Effect of the Electronegativity of the Radical.—The varying degrees of electronegativity of the substituted rings might be expected to produce certain definite variations in the properties of gold compounds. This has been found to be the case, and is illustrated by the fact that the velocity of formation and the reaction of the gold compound with bromine at room temperature and at 100° all place the compounds in the order of benzyl cyanide, para-nitrobenzyl cyanide, alpha-naphthonitrile, ortho- and para-tolunitrile, benzonitrile, para-bromobenzonitrile, meta- and para-nitrobenzonitrile, and 2,5-dichlorobenzonitrile. The first compounds in this list reacted rapidly with auric chloride and the resulting gold compounds underwent bromination (formation of polybromo compounds) accompanied by the evolution of hydrogen bromide. Those at the end of the list reacted slowly and gave gold compounds whose gold could not be replaced by bromine even at 100°.

Experimental Part

Reaction of Propionitrile with Auric Chloride.—By adding a small amount of anhydrous auric chloride[8] to a saturated solution of auric chloride in propionitrile and allowing the mixture to stand with occasional stirring for about an hour, the gold chloride is converted into the addition compound. This is an orange-yellow crystalline solid, soluble in alcohol, insoluble in ligroin, and slightly soluble, with slow decomposition, in toluene. It is converted to an orange oil by ether, and to a sticky gum by water. It melts at 85–89° with decomposition.

Anal. Calcd. for $C_3H_5NAuCl_3$: Au, 55.0; Cl, 29.7. Found: Au, 54.7; Cl, 29.3.

Preparation of the Nitrile Auric Dichlorides.—The general method for preparing these compounds consists of allowing anhydrous auric chloride to stand for several hours in contact with an excess of the nitrile, if the nitrile is liquid; or with a thin paste of the nitrile and nitrobenzene, if it is solid. At the end of this time the undissolved gold chloride is converted into a yellow solid, and the desired compound may then be obtained as a precipitate by diluting with dry ether. It is usually necessary to extract the crude material repeatedly with ether, until constant analyses are obtained. In certain cases it is possible to purify by dissolving in nitrobenzene and precipitating with ether.

A slight exception to this method should be noted in the cases of phenylacetonitrile and its derivatives, in that the auration of these compounds is complete in a few minutes instead of several hours.

In the following table are listed the melting points and analytical data of the nitrile auric dichlorides, together with the results from the bromine treatment, used to determine the position of the $AuCl_2$.

Properties of Cyanophenyl Auric Dichloride.—The compound is very soluble in nitrobenzene and propionitrile, quite insoluble in water, ligroin, carbon disulfide and carbon tetrachloride, and only slightly soluble in sodium chloride solution. It is decomposed rapidly by alcohol

TABLE I

R in $RAuCl_2$	M. p., (dec.), °C.	Gold, %		Chlorine, %		Result of bromine treatment
		Calcd.	Found	Calcd.	Found	
Cyanophenyl	168	53.3	53.2	19.2	18.9	No reaction at 25°. Bromination 100°[a]
3-Cyano-4-methylphenyl	147–148	51.4	51.6	18.5	18.6	2-Methyl-5-bromobenzonitrile at 25°[b]
3-Cyano-6-methylphenyl	170–171	51.4	50.7	18.5	18.8	4-Methyl-3-bromobenzonitrile at 25°
α-Cyanonaphthyl	161–162	46.9	46.5	16.9	16.6	Bromination at 25°
β-Cyanonaphthyl	127	46.9	46.6			
3-Cyano-6-bromophenyl	172	43.9	43.7			3,4-Dibromobenzonitrile at 100°
m-Nitrocyanophenyl	185–187	47.5	47.6	17.1	17.5	No reaction at 100°
Cyanomethylphenyl	127–128	51.4	51.5	18.5	18.5	Bromination at 25°
p-Cyanomethylnitrophenyl	140–142	46.0	45.4	16.5	16.5	

[a] By bromination is meant the formation of polybromo compounds accompanied by the evolution of hydrogen bromide. [b] The identity of these nitriles was established by hydrolysis to the corresponding acids.

and acetone, and slowly by ether, benzene and toluene, the decomposition products being benzonitrile and aurous chloride or gold. Presumably the gold is reduced to the aurous state by these reagents, preceding the rupture of the gold–carbon bond.

It reacts with aqueous acids or bases to give benzonitrile and inorganic auric compounds, with ammonia to give benzonitrile and "fulminating gold" (AuN_2H_3), and with pyridine to give benzonitrile and a varying mixture of pyridine–auric chloride compounds. With reducing agents it gives benzonitrile and aurous chloride or gold, or, if there is no labile hydrogen present, it does not react. Alkyl halides behave as reducing agents, reacting with widely varying velocities. The gold could not be replaced with mercury, using mercury salts, nor could the chlorine be replaced with other anions by means of silver salts. Attempts to measure the molecular weight by means of the freezing point lowering of nitrobenzene did not give consistent results; the values obtained ranged from 15 to 30% above that of the monomeric formula.

Thermal decomposition, carried out under various conditions, gave, in identifiable quantities, gold, hydrogen chloride, benzonitrile and 2,5-dichlorobenzonitrile. The gold atom could not be replaced by halogens at room temperature; and at temperatures sufficiently high to bring it about, the replacement was always accompanied by further halogenation of the benzene ring.

3-Nitro-4-methylphenyl Auric Dichloride.—Auric chloride was added with stirring to ortho-nitrotoluene. After a minute, an equal volume of ether was added to stop the reaction. The addition of five volumes of ligroin caused the precipitation of an oily paste, which was separated and washed with ligroin until free from nitrotoluene, and with water until free from auric chloride. After drying *in vacuo* over phosphorus pentoxide, the solid residue was extracted with ether. The ether solution on evaporation left the desired compound as a pale yellow amorphous solid, which darkened rapidly on standing.

Anal. Calcd. for $C_7H_6NO_2AuCl_2 \cdot H_2O$: Au, 46.7. Found: Au, 45.8.

The compound is insoluble in water or ligroin, and soluble in alcohol, ether, acetone and sodium chloride solution. On treatment with bromine it gives a white crystalline solid melting at 44–45°. 2-Nitro-4-bromotoluene melts at 46–47°.

Summary

1. Auration by means of anhydrous auric chloride has been applied to aromatic nitriles.

2. A series of compounds of the type $RAuCl_2$ has been prepared, and the properties of these compounds studied.

3. The position of the $AuCl_2$ radical has been determined in several cases.

4. The effect of electronegativity of radicals on the stability of the gold to carbon bond has been studied.

5. Evidence is given indicating, in addition to the gold to carbon bond, the sharing of an electron pair between the gold and nitrogen atoms.

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