UNIVERSITY OF CINCINNATI

May 13 1949

I hereby recommend that the thesis prepared under my supervision by Klingenberg, Joseph John

entitled The Zirconium-Specific Reaction of Glycolic Acid Derivatives

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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Form 668—G.S. and Ed.—500—3-42

THE ZIRCONIUM-SPECIFIC REACTION
OF
GLYCOLIC ACID DERIVATIVES.

A dissertation submitted to the

Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1949

by

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M.S. University of Cincinnati. 1947

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ACKNOWLEDGMENTS

The author is indebted to Dr. Ralph E. Oesper for his suggestion of this problem and for his guidance during its investigation and to the Titanium Alloy Manufacturing Division of the National Lead Co. for furnishing the zirconium samples used in this work.

Appreciation is also expressed for the grant of a Laws Fellowship which greatly assisted in the pursuance of this work.

THE ZIRCONIUM-SPECIFIC REACTION OF GLYCOLIC ACID DERIVATIVES.

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CHAPTER I

A STATEMENT OF THE PROBLEM

Although a number of methods for the gravimetric determination of zirconium are available they, in general, are difficult, tedious, and time consuming (174). Both inorganic and organic reagents are utilized. Ammonium acid phosphate and selenic acid are representative of the inorganic group, while the organic reagents include cupferron, benzenearsonic acid, 8-hydroxyquinoline, p-hydroxyphenylarsonic acid, and propylarsonic acid.

The phosphate procedure displays the best degree of selectivity and sensitivity but gives a zirconium phosphate precipitate which is variable in composition, slimy, and difficult to wash. It also is likely to hydrolyze during washing with consequent loss of some of its phosphorus content. In such cases the ignition necessarily yields a deficit of zirconium pyrophosphate. Furthermore, the presence of thorium requires two phosphate precipitations and cerium must be kept in the trivalent state. The basic selenite method is subject to interference by thorium, iron, and titanium.

The organic group of zirconium reagents lack selectivity. This defect is evidenced by the following table which presents the interfering elements for the various organic reagents (174):

Benzene arsonic acid -Si, W, Fe, Ti
Cupferron -Ce, Co, Fe, silica, Ti, Th, U, rare earths and most of the members of the hydrogen sulfide group
8-Hydroxyquinoline -Al, Cr, Co, Cu, Fe, Ni, alkalies, hydrochloric, nitric, phosphoric, and sulfuric acids
p-Hydroxyphenylarsonic acid -Ce, phosphates, Th, Sn, Ti
Propylarsonic acid -Sb, Bi, Sn

Recently Kumins (174) made the remarkable discovery that mandelic acid produces a white precipitate with zirconium salts in acid solution even in the presence of the complex-forming sulfate group. The precipitation can be carried out simply and rapidly; the product is readily separated by filtration and then can easily be dried and ignited. Further tests showed that the reaction is quantitative and selective in the presence of titanium, aluminum, iron, vanadium, chromium, tin, bismuth, antimony, cerium, calcium, thorium, copper, cadmium, and barium. Application of the method to a zirconium ore produced results which agree with the cupferron method within two parts per thousand.

Mandelic acid can be considered as the phenyl derivative of glycolic acid ($HOOC-CH_2OH$). In view of the many useful analytical characteristics of the precipitate produced by mandelic acid and zirconium a further study of the action of zirconium salts with substituted mandelic acids and other glycolic acid derivatives seems desirable. These derivatives would be expected to retain the same selective action on zirconium as mandelic acid but, by utilization of the "weighting effect", to produce precipitation reactions of greater sensitivity and perhaps products of better analytical characteristics.

CHAPTER II

THE ANALYTICAL CHEMISTRY OF ZIRCONIUM

A. GENERAL CHEMISTRY (325).

Zirconium is quadrivalent in all its compounds. In solution it exists mainly as the zirconyl ion (ZrO^{++}). Hydrogen sulfide does not precipitate zirconium from acid solutions. However zirconyl hydroxide, $ZrO(OH)_2$, begins to precipitate at a pH of approximately three. Consequently zirconium appears in the ammonia group of the ordinary qualitative analysis scheme.

B. PREPARATION OF ZIRCONIUM SAMPLES FOR ANALYSIS (150).

The problem of getting zirconium into solution preparatory to its quantitative determination is a complex one. The methods employed vary according to the chemical state of the zirconium in the sample. Zirconium-containing alloys, in which the metal is in the free state, usually require treatment with a mixture of sulfuric, hydrofluoric, and nitric acids to effect solution. Excess hydrofluoric and nitric acids must be removed by evaporation of the solution to heavy fumes of sulfur trioxide. Zirconium-containing rocks and ores or minerals, such as zircon or baddeleyite, usually require fusion methods.[1] If the

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[1] There is an excellent discussion of fusion methods in Hillebrand and Lundell, Applied Inorganic Analysis, John Wiley and Sons, Inc., New York 1929., pages 698-713.

zirconium content is small the procedure ordinarily employed for silicate rocks is usually satisfactory. Sodium carbonate is the most common flux used in these operations and has been found acceptable when zirconium is present. Zirconium ores and minerals are difficult to decompose. The fusion with sodium carbonate is usually tedious and often incomplete. Other fluxes which have been recommended are potassium pyrosulfate, sodium pyrosulfate, sodium peroxide, potassium acid fluoride, ammonium fluoride and borax. Lundell and Knowles (187), working at the Bureau of Standards, found the borax procedure to be entirely satisfactory. The ground ore is added to a cooled borax melt in a platinum crucible. The mix, after covering, is thoroughly fused with a Meker burner and stirred occasionally with a platinum rod. When the melt is clear it is allowed to cool, placed in a beaker, treated with 1:5 hydrochloric acid, and digested, preferably overnight, on a steam bath. If a residue remains, it is refused usually with potassium acid sulfate and the dissolved melt combined with the original. Boric acid does not interfere in the cupferron or phosphate procedures. If, in other cases, interference does exist, boron is readily removed as methyl borate. It must always be remembered that phosphate will precipitate zirconium and the presence of phosphorus compounds considerably complicates the fusion procedure. The solution must always be kept sufficiently acid to prevent the hydrolysis of zirconium salts to one of its insoluble basic hydroxides.

C. SEPARATIONS (150).

The most suitable procedure for the separation of zirconium from other elements consists in precipitation of the phosphate in the presence of a solution containing 10 percent of sulfuric or hydrochloric acid by volume. Only hafnium, columbium, tantalum, and titanium show interference under these conditions although cerium should be kept in the trivalent state and thorium requires a double precipitation. Interference from titanium can be eliminated by adding hydrogen peroxide to the solution. Columbium and tantalum are most satisfactorily removed during the fusion process. Phosphorus, of course, interferes and it too is best removed by use of a sodium carbonate or sodium peroxide fusion process.

Cupferron can be used to advantage for a separation of zirconium from aluminum, chromium, or uranium (325), while hydrogen fluoride or oxalic acid affords a separation from the rare earths. Tannin has been found useful in separating zirconium from titanium (272).

D. DETERMINATIONS (150, 272, 325).

There are four generally accepted methods of determining zirconium; these are respectively the phosphate, basic selenite, cupferron, and arsonic acid. These will be reviewed in some detail while brief consideration will be given to various other procedures that have been proposed but which have not as yet come into general use. Details of analysis will not be included as these are readily available in the standard texts on analytical chemistry.

1. Phosphate Method.

The precipitation of zirconium as phosphate is quantitative in solutions containing up to 10 percent of sulfuric acid by volume. This phosphate precipitate is of uncertain composition and must be ignited to zirconium pyrophosphate for final weighing. The reaction is almost ideal for analytical purposes but unfortunately the precipitate tends to hydrolyze and loses some of its phosphorus content during washing. There will not be then sufficient phosphorus to give the equivalent yield of zirconium pyrophosphate on ignition and the results will be low. In such cases the ignited residue must be fused with sodium carbonate, the phosphorus removed by aqueous extraction, the residue fused with potassium pyrosulfate, dissolved in sulfuric acid, and precipitated twice with ammonium hydroxide. The disadvantages of such a tedious procedure are obvious.

The phosphate method is capable of high accuracy but the slimy nature of the precipitate makes it difficult to wash and this disadvantage coupled with the error introduced by loss of phosphorus pentoxide makes the method unsuitable for routine analysis.

The reagent ordinarily used in the phosphate method is disodium hydrogen phosphate. Recently Willard and Hahn (326) suggested the use of trimethylphosphate or metaphosphoric acid as reagent. These compounds, through slow hydrolysis, furnish phosphate ion in such small concentration that the zirconium phosphate produced has more time to form a crystalline precipitate. The precipitate so obtained is more dense and readily washed.

2. Basic Selenite Method.

This procedure involves precipitation of the zirconium by means of selenious acid in hot dilute hydrochloric acid solution (containing about 5-7 percent hydrochloric acid by volume). The precipitate is filtered, washed, and ignited to the oxide for weighing. The method affords a separation from aluminum, many rare earths, and moderate amounts of iron and titanium (using hydrogen peroxide). Cerium must be kept in the trivalent state. Thorium, tin and phosphorus are known contaminants and it seems likely that columbium and tantalum would also interfere. The basic selenite which forms initially is soluble in acids permitting reprecipitation. On standing the basic selenite slowly changes to zirconium selenite. Ignition to the oxide is necessary however. This method has been applied to steel and ore samples with some success (277, 278, 279, 280, 282). Here again, however, the procedure falls just short of being completely satisfactory.

3. Cupferron Method.

The cupferron method involves precipitation of zirconium as the cupferronate $\left(Zr(O\cdot NO\cdot N\cdot C_6H_5)_4\right)$ in sulfuric acid solution followed by ignition to the oxide. The process is accurate and gives a complete separation of zirconium from aluminum, chromium, sexavalent uranium, boric acid, and phosphorus, if present in small amounts. Unfortunately many elements interfere; these include titanium, thorium, cerium, the hydrogen sulfide group, iron, vanadium, columbium, tantalum, tungsten, silica, and quadrivalent uranium. While silica, tungsten, and the hydrogen sulfide group are fairly readily removed, other interfering elements require special procedures which are not always simple. It is frequently more convenient to precipitate the interfering elements along with the zirconium and correct for these elements in the ignited zirconium dioxide precipitate by subsequent analysis. This process is employed for iron and titanium in zirconium alloy steels and zirconium ores and minerals. The lack of selectivity in the cupferron method considerably lessens its value for routine zirconium analyses.

4. Arsonic Acid Method.

Next to cupferron the most useful organic reagents for zirconium are the group of arsonic acids. Their zirconium-precipitating action was first observed with the organic compound, phenyl arsonic acid (240). Later work showed that phenyl arsonic acid and its derivatives (2, 46, 47, 57, 68, 167, 276), alkyl arsonic acids (7, 44, 45, 117), and arsonic acid itself (9, 10, 54, 58, 268) will precipitate zirconium. Of these, benzenearsonic acid, p-hydroxyphenylarsonic acid, and n-propylarsonic acid appear to be the best. A very desirable improvement in analytical properties was obtained by the introduction of an azo group into the molecule (97, 207). With these reagents zirconium forms a colored precipitate which now possesses increased sensitivity and can be adapted to colorimetric determinations. p-Dimethylaminoazophenylarsonic acid was found best suited for this purpose. Thus the arsonic acids afford an excellent illustration of the manner in which organic molecules can be altered without changing their fundamental reaction with a given ion. In general, however, the arsonic acids produce precipitates with all quadrivalent elements of Group IV and this seriously limits their general acceptability.

5. Other Methods.

The well known organic reagent 8-hydroxyquinoline (oxine) also produces a precipitate with zirconium (11, 113, 294). Some selectivity is obtained by carrying out the precipitation in an acetate buffered solution; but aluminum, cobalt, chromium, copper, iron, and nickel interfere, likewise alkalies and hydrochloric, nitric, phosphoric, and sulfuric acids.

A number of other organic reagents have been found to precipitate zirconium quantitatively. Since these offer no advantages over the foregoing they will only be listed:

alizarin	(318)
aniline	(133, 318)
benzene sulfinic acid	(318)
benzylaniline	(133, 318)
dimethylaniline	(133, 318)
lactic	(251)
murexide	(19, 318)
1-nitroso-2-naphthol	(124, 318)
2-nitroso-1-naphthol	(318)
oxalate	(20)
phenylhydrazine	(133, 318)
piperidine	(133, 318)
pyridine	(133, 318)
quinalizarin	(318)
quinoline	(318)
salicyclic acid	(318)
sodium flavianate	(92)
tannin	(263, 264, 265, 318)
tartaric acid	(318)
o-toluidine	(318)
xylidines	(318)

Further information on them is available in Welcher (318).

Many inorganic precipitating agents have also been investigated especially during the early development of the analytical chemistry of zirconium. Here again they are generally inferior to the methods previously described and are presented only for the sake of completeness. The ammonia method (272) is very satisfactory for pure zirconium compounds but since this situation is rarely realized it is of no real practical importance. These reagents are:

ammonia	(272)
basic acetate	(128)
basic chromate	(128)
basic sulfate	(135, 250)
basic sulfite	(18)
iodate	(304)
oxychloride	(205)
peroxide	(34, 115)
thiosulfate	(232, 292, 293)

In some cases these reagents can be used advantageously for separations.

There are no satisfactory volumetric determinations for zirconium. A few colorimetric methods are available, the best of them involving the use of paradimethylaminophenylbenzenearsonic acid (97).

E. THE MANDELIC ACID METHOD (174).

Kumins, while investigating the chemistry of the Group IV elements, discovered that mandelic acid produces a precipitate with zirconium. This action had not been described in the literature. Further work showed him that the zirconium is precipitated quantitatively in hydrochloric acid solution and in sulfuric acid solution containing not over five percent free acid. (Sulfate ion interferes with most zirconium determinations because of its complex-forming ability with zirconium.) The following procedure for the determination of zirconium was developed by Kumins:

> A sample containing from 0.050 to 0.3 gram of zirconium oxide in solution was diluted to approximately 20 ml. with concentrated hydrochloric acid. To this were added 50 ml. of 16% mandelic acid and the whole was made up to 100 ml. The temperature was raised slowly up to 86°C and held there for 20 minutes. The resulting precipitate was filtered, washed with a hot solution containing 2% hydrochloric acid and 5% mandelic acid (this wash solution was necessary because the precipitate was sufficiently soluble in pure water to cause low results), and ignited to the oxide.

In addition, the mandelic acid was found to possess a high degree of selectivity not found in other zirconium reagents.

Titanium, aluminum, iron, vanadium, chromium, tin, bismuth, antimony, cerium, calcium, thorium, copper, cadmium, and barium did not interfere. The new method was applied to a zirconium ore, zirkite. When the zirkite was fused with borax, dissolved in 1:5 hydrochloric acid and the zirconium precipitated by mandelic acid, the results agreed with the cupferron method within two parts per thousand.

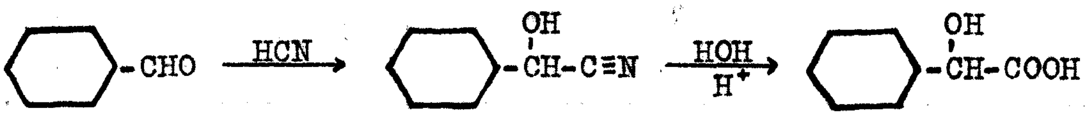
CHAPTER III

THE SYNTHESIS OF GLYCOLIC ACID DERIVATIVES.

Any of the various glycolic acids is potentially a good zirconium precipitant. Hence, a search of the literature was made to determine what glycolic acids are available and what successful methods for their synthesis have been reported. The search was confined to the aryl glycolic acids; and since the benzene series has been more completely investigated than other aromatic series, the bulk of the procedures are concerned with the production of mandelic acid and its derivatives.

I. CYANHYDRIN SYNTHESIS.

Mandelic acid is made by the well known CYANHYDRIN SYNTHESIS (I) which involves the addition of hydrogen cyanide to benzaldehyde forming the nitrile of alpha-hydroxyphenylacetic acid. Hydrolysis of this compound produces the acid:



In actual practise the cyanhydrin is prepared by the action of acetic acid or ammonium chloride and sodium cyanide on the aldehyde or sodium cyanide on the bisulfite addition product of the aldehyde. These methods avoid the direct use of dangerous hydrogen cyanide. Hydrolysis may be carried out by means of hydrochloric acid or sodium hydroxide; the former is preferred. Mandelic acid is commercially available but

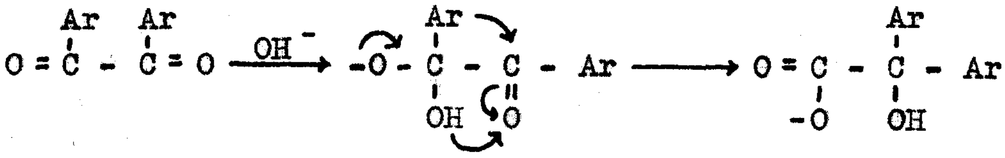
The method of synthesis can be extended to derivatives and homologues of mandelic acid and is important from that standpoint. The following compounds are reported by this method:

Glycolic acid,	1-naphthyl	(33, 37, 198)
	1-naphthyl-2-ethoxy	(253)
	1-phenylalkyl	(30)
Mandelic acid,		(21, 64, 111)
	o-amino	(123, 199)
	m-amino	(104, 106, 146, 228)
	p-amino	(106, 123, 144, 145)
	2-amino-5-bromo	(142)
	p-azoxy	(144)
	o-azo-beta-naphthol	(38, 199)
	m-azo-dimethylaniline	(228)
	m-azo-beta-naphthol	(228)
	m-azo-phenol	(38, 228)
	m-azo-resorcinol	(228)
	p-azo-dimethylaniline	(228)
	p-azo-beta-naphthol	(228)
	p-azo-resorcinol	(228)
	5-bromo-2-nitro	(142)
	p-carboxy	(275)
	o-chloro	(78, 158)
	m-chloro	(158)
	p-chloro	(158, 163, 288, 313)
	5-chloro-2-nitro	(142)
	6-chloro-2-nitro	(238)
	2,5-dichloro	(121)
	2,3-dimethoxy	(172)
	2,5-dimethoxy	(179)
	2,4-dimethyl	(283)
	2-ethoxy	(316)
	hexahydro	(329)
	p-hydroxy	(178)
	4-hydroxy-3-methoxy	(110, 269)
	2-hydroxy-3,5-dinitro	(118)
	p-methyl	(163, 283)
	methylenedioxy	(1)
	o-nitro	(1, 3, 140, 141, 143, 146, 247, 248)
	m-nitro	(3, 29, 106)
	o-nitroso	(141)
	2,4,6-trimethyl	(317)

This cyanhydrin method is limited only in that suitable aldehydes must be available.

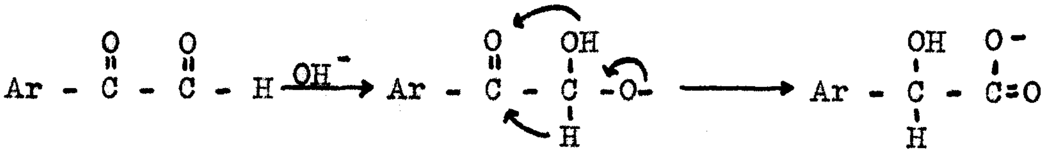
II. KETO-ALDEHYDE SYNTHESIS.

Another important source of glycolic acid derivatives resides in a benzilic acid-like rearrangement of diketone or keto-aldehydes of the type R-CO-CO-R (H) under the influence of alkali. Probably the mechanism of the benzilic acid rearrangement is (324):



$$O = \overset{\overset{\textstyle Ar}{|}}{C} - \overset{\overset{\textstyle Ar}{|}}{C} = O \xrightarrow{OH^-} {}^-O - \underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle Ar}{|}}{C}} - \underset{\underset{\textstyle O}{\|}}{C} - Ar \longrightarrow O = \underset{\underset{\textstyle -O}{|}}{C} - \underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle Ar}{|}}{C}} - Ar$$

Recent work (81) has shown that keto-aldehydes of this type do not rearrange in this manner but rather in accordance with a Cannizzaro type rearrangement:

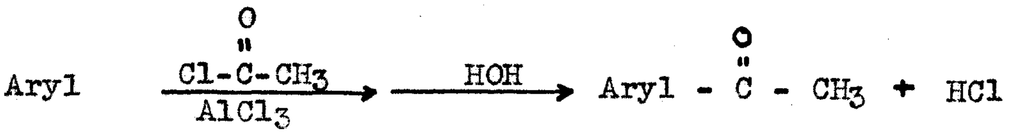


$$Ar - \overset{\overset{\textstyle O}{\|}}{C} - \overset{\overset{\textstyle O}{\|}}{C} - H \xrightarrow{OH^-} Ar - \overset{\overset{\textstyle O}{\|}}{C} - \underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle OH}{|}}{C}} -O^- \longrightarrow Ar - \underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle OH}{|}}{C}} - \overset{\overset{\textstyle O^-}{|}}{C}{=}O$$

For simplicity in classification this is referred to here as the KETO-ALDEHYDE SYNTHESIS (II).

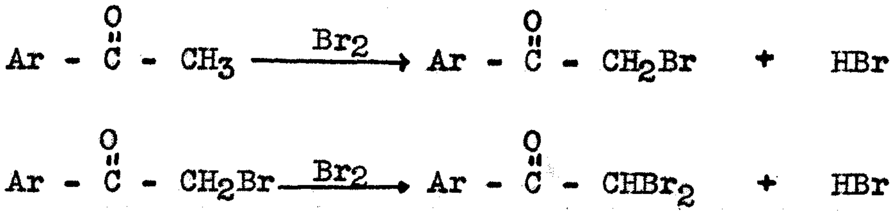
Several ways of obtaining the necessary keto-aldehyde or diketo structure are possible:

II A. Omega-halogenation synthesis. This synthesis requires three steps. The first consists in an acetylation of an aromatic nucleus by means of the Friedel-Craft reaction.



$$Aryl \xrightarrow[AlCl_3]{Cl-\overset{\overset{\textstyle O}{\|}}{C}-CH_3} \xrightarrow{HOH} Aryl - \overset{\overset{\textstyle O}{\|}}{C} - CH_3 + HCl$$

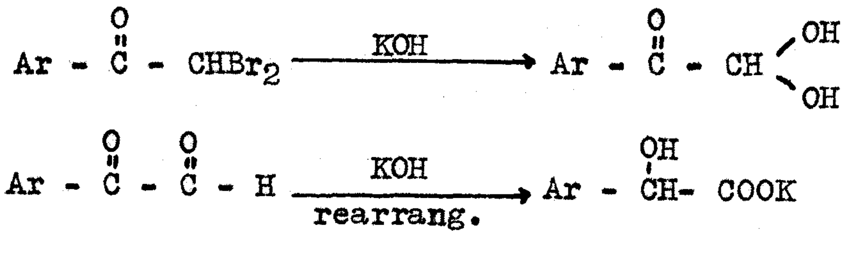
This phase of the synthesis is subject to the ordinary limitations of the Friedel-Craft reaction, the most serious restriction being that nitrobenzene cannot be used. Purification of the product, a methyl ketone, is usually accomplished by a vacuum distillation. The second step consists in omega-halogenation of the methyl ketone. In most cases bromine is used as the halogenating agent:



$$Ar - \overset{\overset{O}{\|}}{C} - CH_3 \xrightarrow{Br_2} Ar - \overset{\overset{O}{\|}}{C} - CH_2Br \quad + \quad HBr$$

$$Ar - \overset{\overset{O}{\|}}{C} - CH_2Br \xrightarrow{Br_2} Ar - \overset{\overset{O}{\|}}{C} - CHBr_2 \quad + \quad HBr$$

This reaction proceeds readily and in good yield. Acetic acid was found to be the most suitable solvent. Although the dibromination can be carried out in one step it was usually advantageous to proceed in two stages as shown above. This makes possible a purification of the intermediate product which can be readily done by crystallization from alcohol. The final product is then obtained in a better and more readily purified form. The third step consists in hydrolysis of the di-omega-brominated ketone in alkaline solution followed by immediate rearrangement to the desired glycolic acid derivative. The keto-aldehyde is not isolated.



$$Ar - \overset{\overset{O}{\|}}{C} - CHBr_2 \xrightarrow{KOH} Ar - \overset{\overset{O}{\|}}{C} - CH\begin{matrix} / OH \\ \backslash OH \end{matrix}$$

$$Ar - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - H \xrightarrow[\text{rearrang.}]{KOH} Ar - \overset{\overset{OH}{|}}{CH} - COOK$$

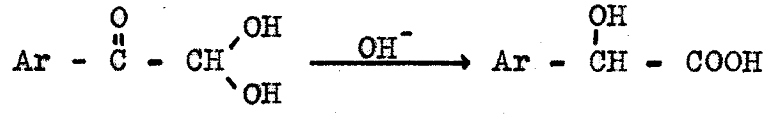
This reaction proceeds well and with satisfactory yields in almost all cases. The free acid is best isolated by ether extraction of the acidified product followed by recrystallization from benzene. The following compounds have been made by this method:

Glycolic acid,	1-naphthyl	(198, 270)
	2-naphthyl	(270)
Mandelic acid,		(215)
	p-bromo	(61, 283)
	p-chloro	(61)
	2,4-dimethyl	(101, 283)
	3,5-dinitro	(101)
	p-iodo	(270)
	p-methyl	(283)
	o-nitro	(89, 90)
	m-nitro	(89, 94)
	p-nitro	(90)
	2,4,5-trimethyl	(101)

In addition to the foregoing method there are several other ways of obtaining the desired alpha-keto aldehyde. These differ from the omega-halogenation method in that the alpha-keto aldehyde can be isolated. However, they are more tedious and give lower yields. Consequently they are important only as alternate methods of synthesis which might serve in cases where the omega-halogenation method fails.

II B. Carbinol-acetate Synthesis. The appropriate methyl ketone is monobrominated and the product is then refluxed with acetic acid to produce a carbinol-acetate. This is then brominated, the bromine atom attaching itself to the carbon atom between the keto and acetate group. Alkaline hydrolysis of this product results in the glycolic acid.

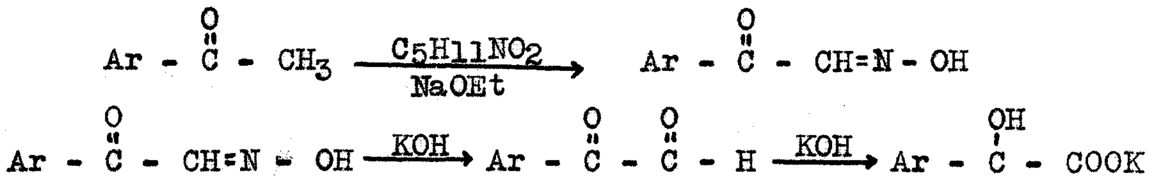
derivative. The various steps can be represented:

1. $\mathrm{Ar - COCH_3 \xrightarrow{Br2} Ar - COCH_2Br}$
2. $\mathrm{Ar - COCH_2Br \xrightarrow{KOAc} Ar - COCH_2OCOCH_3}$
3. $\mathrm{Ar - COCH_2OCOCH_3 \xrightarrow{Br2} Ar - COCHBrOCOCH_3}$
4. $\mathrm{Ar - COCHBrOCOCH_3 \xrightarrow[H^+]{HOH} Ar - COCH(OH)_2}$
5. 

$$\mathrm{Ar - \overset{\overset{O}{\|}}{C} - CH\!\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix} \xrightarrow{OH^-} Ar - \overset{\overset{OH}{|}}{CH} - COOH}$$

Mandelic acid and beta-naphthylglycolic acid have been made by this method (192).

II C. Isonitroso synthesis. A nitroso derivative is formed by the action of amyl nitrite on a methyl ketone. Hydrolysis of this product in alkaline medium gives a keto-aldehyde which then rearranges to the glycolic acid (220, 221, 223, 283).

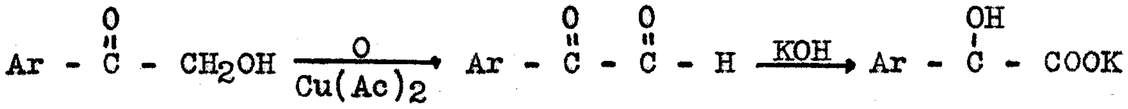


$$\mathrm{Ar - \overset{\overset{O}{\|}}{C} - CH_3 \xrightarrow[NaOEt]{C_5H_{11}NO_2} Ar - \overset{\overset{O}{\|}}{C} - CH{=}N - OH}$$

$$\mathrm{Ar - \overset{\overset{O}{\|}}{C} - CH{=}N - OH \xrightarrow{KOH} Ar - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - H \xrightarrow{KOH} Ar - \overset{\overset{OH}{|}}{C} - COOK}$$

There are many side reactions so that the maximum yield of acid is about 25% in the most favorable cases.

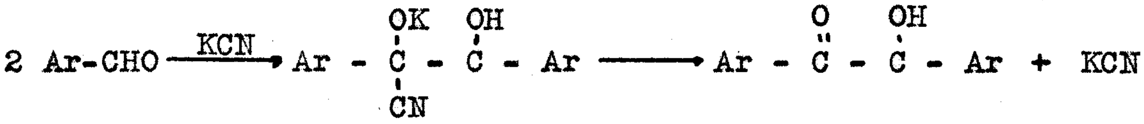
II D. Keto-alcohol oxidation. Nef, Evans, and coworkers have shown that keto-alcohols can be selectively oxidized to the aldehyde in the presence of copper acetate. The resulting keto-aldehyde rearranges to the glycolic acid in the presence of alkali:



$$Ar - \overset{O}{\overset{\|}{C}} - CH_2OH \xrightarrow[Cu(Ac)_2]{O} Ar - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - H \xrightarrow{KOH} Ar - \overset{OH}{\overset{|}{C}} - COOK$$

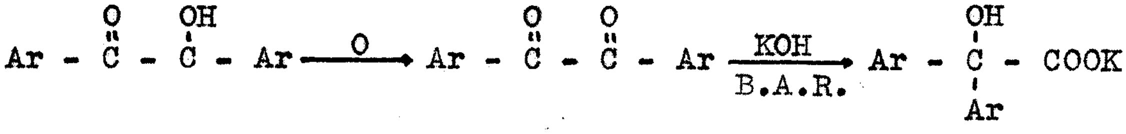
Good yields are obtainable but the synthesis must be carried out under carefully controlled conditions and the method involves time-consuming steps.

II E. Benzilic Acid Synthesis. Aromatic aldehydes, in the presence of potassium cyanide, undergo a reaction known as the benzoin condensation:



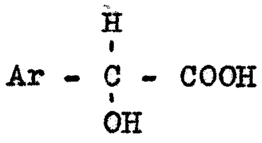
$$2\ Ar-CHO \xrightarrow{KCN} Ar - \underset{CN}{\underset{|}{\overset{OK}{\overset{|}{C}}}} - \overset{OH}{\overset{|}{C}} - Ar \longrightarrow Ar - \overset{O}{\overset{\|}{C}} - \overset{OH}{\overset{|}{C}} - Ar + KCN$$

The product can be readily oxidized to the diketone. The diketone, in the presence of alkali undergoes the benzilic acid rearrangement to produce the alpha-disubstituted hydroxyacetic acid derivative.



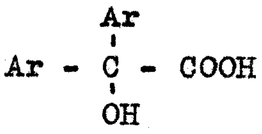
$$Ar - \overset{O}{\overset{\|}{C}} - \overset{OH}{\overset{|}{C}} - Ar \xrightarrow{O} Ar - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - Ar \xrightarrow[B.A.R.]{KOH} Ar - \underset{Ar}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - COOK$$

This synthesis, like the preceding ones, is applicable in the aromatic series only. It differs from the previous syntheses in that two aryl groups are introduced on the alpha carbon instead of one.



$$Ar - \underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}} - COOH$$

Syntheses II A-D.



$$Ar - \underset{OH}{\underset{|}{\overset{Ar}{\overset{|}{C}}}} - COOH$$

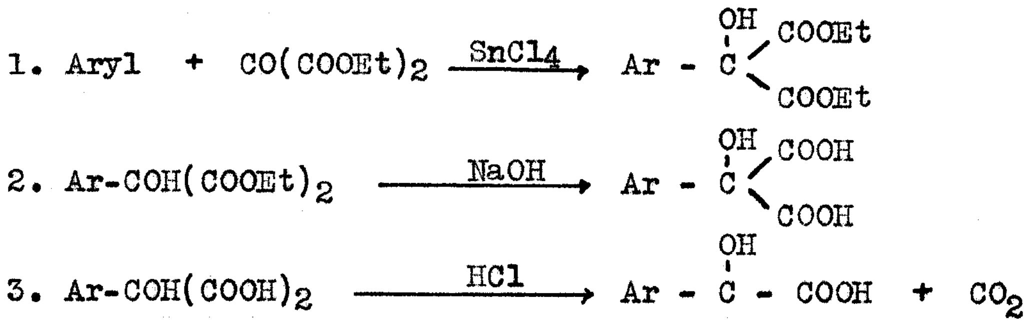
Synthesis IIE.

This synthesis can be carried out with any aldehyde which will give the benzoin condensation (214, 266).

For the present purposes methods (I) and (II) have usually been sufficient to prepare the desired derivatives. A number of other methods are available: These will be briefly reviewed to illustrate the wide variety of approaches to the synthesis of glycolic acid derivatives.

III. OXYMALONIC ESTER CONDENSATION.

This reaction consists in the condensation of substituted aromatic hydrocarbons with oxymalonic acid in the presence of stannic chloride. The aryl, hydroxy-substituted malonic ester which results is decomposed to the sodium salt of the acid with sodium hydroxide. Treatment of the sodium salt with hydrochloric acid produces the free acid which then decarboxylates to the mandelic acid derivative.



$$1.\ \text{Aryl} + \text{CO(COOEt)}_2 \xrightarrow{\text{SnCl}_4} \text{Ar} - \overset{\text{OH}}{\text{C}}\left\langle\begin{matrix}\text{COOEt}\\ \text{COOEt}\end{matrix}\right.$$

$$2.\ \text{Ar-COH(COOEt)}_2 \xrightarrow{\text{NaOH}} \text{Ar} - \overset{\text{OH}}{\text{C}}\left\langle\begin{matrix}\text{COOH}\\ \text{COOH}\end{matrix}\right.$$

$$3.\ \text{Ar-COH(COOH)}_2 \xrightarrow{\text{HCl}} \text{Ar} - \overset{\text{OH}}{\text{C}} - \text{COOH} + \text{CO}_2$$

This synthesis is especially suited for the preparation of alkyl substituted mandelic acids and hence a large number of derivatives of this type have been prepared:

Mandelic acid,	(5, 241)
p-bromo	(244)
p-butyl	(244)
2,3-dimethyl	(5)
2,5-dimethyl	(216)
2,6-dimethyl	(5)

Mandelic acid,	p-ethyl	(243)
	p-iodo	(244)
	p-isoamyl	(244)
	p-isopropyl	(243)
	p-methyl	(5, 243)
	2,3,4,5,6-pentamethyl	(244)
	p-phenyl	(244)
	p-propyl	(244)
	p-secbutyl	(243)
	p-tertamyl	(244)
	p-tertbutyl	(243)
	2,3,5,6-tetramethyl	(244)
	2,4,6-trimethyl	(243)

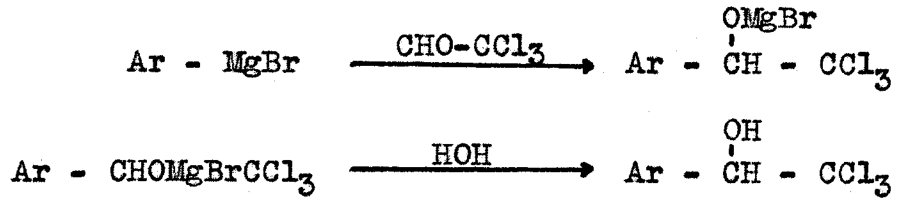
IV. HYDROLYSIS OF TRICHLOROCARBINOLS.

Trichlorocarbinols readily hydrolyze to mandelic acid derivatives.

$$\mathrm{Ar - \overset{OH}{CH} - CCl_3 \xrightarrow{3KOH} Ar - \overset{OH}{CH} - COOH + 3KCl + H_2O}$$

These trichlorocarbinols have been obtained in three ways:

A. Action of a Grignard Reagent on Chloral.



$$\mathrm{Ar - MgBr \xrightarrow{CHO-CCl_3} Ar - \overset{OMgBr}{CH} - CCl_3}$$

$$\mathrm{Ar - CHOMgBrCCl_3 \xrightarrow{HOH} Ar - \overset{OH}{CH} - CCl_3}$$

B. Condensation of Chloroform with an Aldehyde.

$$\mathrm{Ar{-}CHO + CHCl_3 \xrightarrow[ether]{KOH} Ar - \overset{OH}{CH} - CCl_3}$$

C. Condensation of Chloral with an Aldehyde.

$$\mathrm{Ar{-}CHO + CCl_3CHO \longrightarrow Ar - \overset{OH}{CH} - CCl_3}$$

Of these the use of the Grignard reagent is the more dependable as the number and variety of derivatives prepared by this synthesis indicates.

IV. A.	Glycolic Acid,	cyclohexyl	(139)
		alpha-naphthyl	(139, 198)
	Mandelic acid,		(139, 161, 237)
		p-bromo	(139)
		2,5-dimethyl	(254)
		3,4-dimethyl	(139)
		p-dimethylamino	(139)
		p-ethyl	(139)
		p-hydroxy	(127)
		p-methyl	(139)
IV. B.	Mandelic acid,		(161, 237)
IV. C.	Glycolic acid,	alpha-naphthyl	(198)
	Mandelic acid,	2-ethoxy-5-nitro	(49)
		2-ethyl-4-methyl-5-nitro	(50)
		p-hydroxy	(127)

V. <u>ETHYL</u> <u>OXALATE</u> <u>CONDENSATION</u>.

An aryl magnesium bromide is brought to react with diethyloxalate in ether solution. Hydrolysis of the reaction product yields the mandelic acid derivative. Lapkin obtained 2,4,6-trimethylmandelic acid by this method (180).

VI. <u>HYDROLYSIS</u> <u>OF</u> <u>AN</u> <u>ALPHA-HALO</u> <u>ACID</u>.

Alpha-halo acids readily hydrolyze in the presence of weak alkalies to form mandelic acids. p-Nitro and p-aminomandelic acid were prepared in this manner (106).

VII. <u>GLYOXALIC</u> <u>ACID</u> <u>REDUCTION</u>.

Alpha-keto acids can be reduced to alpha-hydroxy acids using sodium amalgam, aluminum amalgam, or catalytically.

$$\text{Aryl} - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{COOH} \xrightarrow{\text{H}} \text{Aryl} - \overset{\text{OH}}{\overset{|}{\text{C}}} - \text{COOH}$$

Suitable glyoxalic (alpha-keto) acids have been made by oxidation of methyl ketones with potassium permanganate or selenium dioxide. Four derivatives are reported:

Glycolic acid,	alpha-naphthyl	(59, 324)
	beta-naphthyl	(59)
Mandelic acid,	o-methyl	(249)
	p-phenyl	(31)

VIII. ACTION OF NITROUS ACID ON AMINO ACIDS.

Alpha-amino acids can be changed to alpha-hydroxy acids by the action of nitrous acid. Mandelic acid (103) and its m-nitro derivative (225) have been made in this manner.

$$\text{Aryl} - \overset{NH_2}{C} - COOH \xrightarrow{HONO} \text{Aryl} - \overset{OH}{C} - COOH + N_2 + H_2O$$

From among the compounds described in the literature those chosen for testing are listed below, together with the method of preparation and some of their physical properties:

Acid	Method of Preparation	M.W.	M.P.	Color
Glycolic acid	comm. avail.	76	76-7°	Color's
Lactic acid	" "	90	17	Color's
α-Hydroxydecanoic a.	" "	188	-	Amber
Mandelic acid	" "	152	118	White
p-Chloromandelic acid	IIA	187	119	"
p-Bromomandelic acid	IIA	231	117-8	"
p-Iodomandelic acid	IIA	278	135-6	"
p-Methylmandelic acid	IIA	166	146	"
o-Nitromandelic acid	I	197	140-3	"
p-Nitromandelic acid	I	197	126-7	Lt. Yel.
m-Nitromandelic acid	I	197	119-20	White
Benzilic acid	IIE	228	150	"
2-Naphthylglycolic acid	IIA, B	202	156	"
2-azo-β-naphtholman. a.	IIA	322	205-6	Red
3-azo-β-naphtholman. a.	IIA	322	210	"

CHAPTER IV

EXPERIMENTAL RESULTS

I. QUALITATIVE TESTING OF REAGENTS.

The first step in determining the precipitating action of glycolic acid derivatives on zirconium was the qualitative testing of the selected reagents. The following procedure was used:

> To 2.5 ml. of a standard zirconyl chloride solution, representing approximately 0.04 gram of zirconium oxide, are added 7.5 ml. of concentrated hydrochloric acid and 15 ml. of water. This solution is then heated to approximately 85°C. on a water bath and 25 ml. of the reagent added dropwise from a buret with constant stirring. (Water solutions of the free acids are used when the free acids are sufficiently soluble in water. When not sufficiently soluble the sodium salt of the acid is dissolved in water.) The appearance of a precipitate is taken as a positive test. This is confirmed by filtering off the precipitate and igniting it to the oxide.

A rough estimate of the weighting effect of the various substituents was obtained by carrying out the precipitation in 50 ml. graduated flasks. The results are summarized in Table 1 and are visually presented on the accompanying photographs.

These qualitative tests indicate that the ability to precipitate zirconium is retained (as expected) in compounds other than mandelic acid containing the grouping -CHOH-COOH. In the aliphatic series no significant improvement over mandelic acid was observed. Alpha-hydroxydecanoic acid does produce a large amount of precipitate per unit

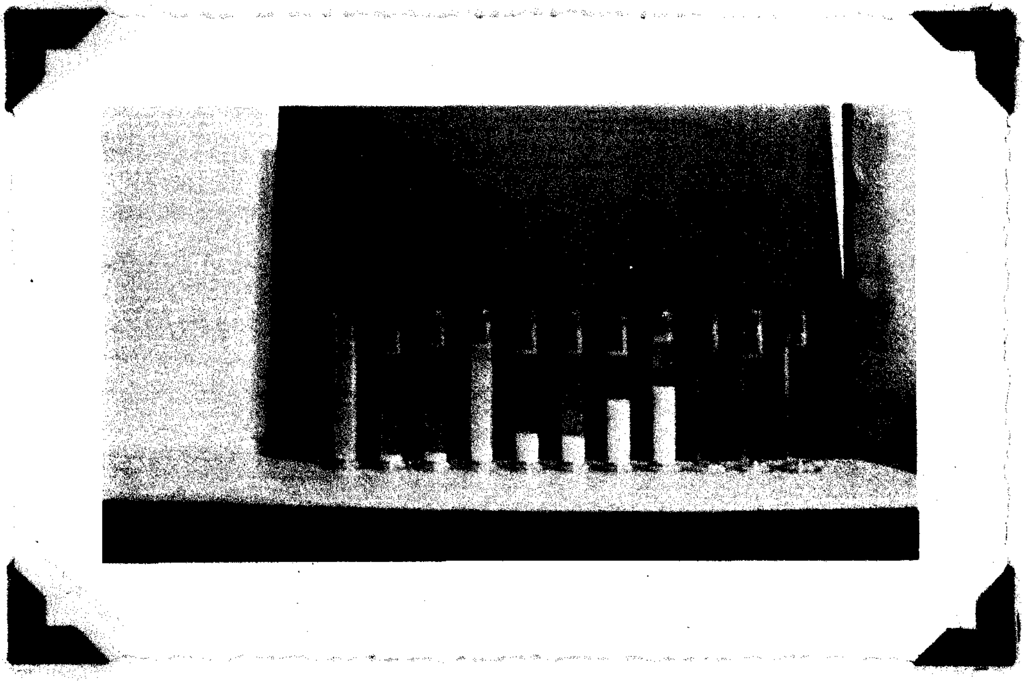
Table 1

Qualitative Tests of Glycolic Acid Derivatives with Zirconium.

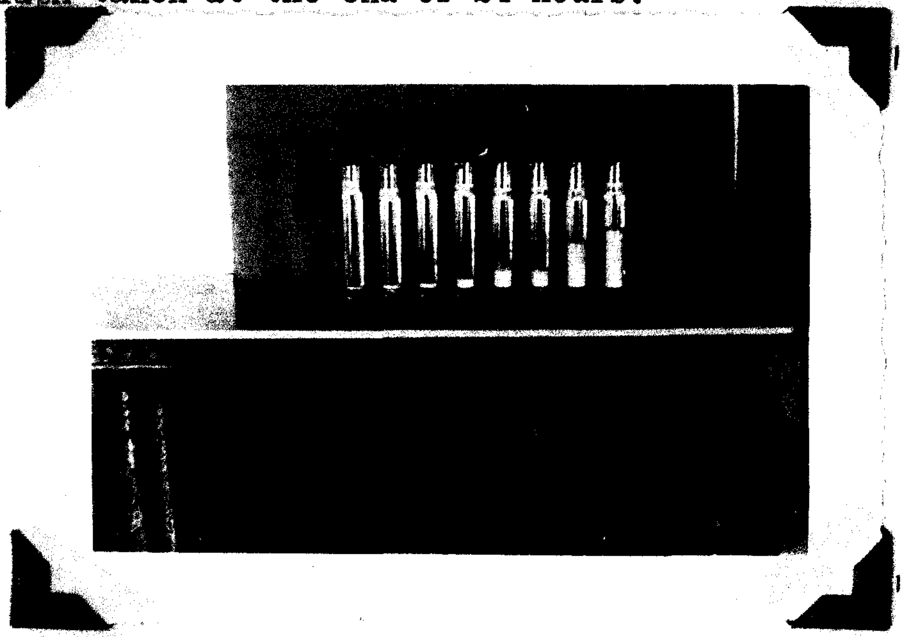
Acid Used	Concn.	Test	Color of Ppt.	Volume of Ppt. in Flask Elapsed time (days)					
				1/6	1	2	7	8	13
1. Mandelic	1.0 m.	pos.	white	1	1	1	1	1	1
2. p-Methylmand.	0.1	pos.	white	2	2	2	2	2	2
3. p-Bromomand.	0.1	pos.	white	3½	3	3	2½	2½	2½
4. p-Chloromand.	0.1	pos.	white	5½	5	4	3	3	3
5. p-Iodomand.	0.06	pos.	white	12	7	6	6	6	6
6. α-Hydroxydecanoic	unk.	pos.	white	11	9	7	7	6	5½
7. Benzilic	0.04	pos.	white	25	24	23	23	23	23
8. 2-Naphthylglycolic	0.08	pos.	white	30	29	29	26	25	24
9. o-Nitromand.	0.1	neg.	-	-	-	-	-	-	-
10. m-Nitromand.	0.1	neg.	-	-	-	-	-	-	-
11. Lactic	1.0	neg.	-	-	-	-	-	-	-
12. Glycolic	1.0	neg.	-	-	-	-	-	-	-
13. p-Nitromand.	0.1	pos.	pale yellow	3	2	2	2	2	2
14. o-azo-β-naphtholmand.	unk.	pos.	red	-	5	5	5	5	5
15. m-azo-β-naphtholmand.	unk.	pos.	red	-	9	9	9	9	9

Note - Samples 9, 10, 11, 12 gave positive tests under conditions of less acidity.

Photograph taken at the end of 4 hours:



Photograph taken at the end of 24 hours:



Order of reagents reading from left to right:

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 (See Table 1.)

weight of zirconium but the reagent is a viscous, sticky, water-insoluble liquid, which is so difficult to handle that it hardly warrants further consideration.

In the aromatic series, however, the volume of precipitate produced per unit weight of zirconium is increased over mandelic acid from twice as much for p-methylmandelic acid to twenty five times as much for 2-naphthylglycolic acid. (See Table 1.) A possible increase in sensitivity of the reaction is thus indicated. In addition, while most of the reagents are white and give white precipitates with zirconium, p-nitromandelic acid is yellow and produces a pale yellow zirconium precipitate. The ortho- and meta- azo-beta-naphthol derivatives of mandelic acid are red in color and give red precipitates with zirconium. Another increase in sensitivity is thus possible through production of colored precipitates.

It was concluded from these tests that certain of the aromatic derivatives of mandelic acid show sufficient promise to merit further study as possible reagents for zirconium. These reagents are:

p-methylmandelic acid
p-chloromandelic acid
p-bromomandelic acid
p-iodomandelic acid
p-nitromandelic acid
benzilic acid
2-naphthylglycolic acid
o-azo-beta-naphtholmandelic acid
m-azo-beta-naphtholmandelic acid

Of these the p-nitro, o-azo-beta-naphthol, and m-azo-beta-naphthol derivatives of mandelic acid were considered too difficult to prepare to merit further consideration over the other compounds, although they do possess the advantage of being colored. A study of the suitability of these and similar reagents for sensitive qualitative tests for the detection of zirconium seems advisable.

II. <u>QUANTITATIVE TESTING OF SELECTED REAGENTS</u>.

The following procedure was developed for quantitative testing:

5 ml. of a standard solution of zirconyl chloride containing the equivalent of 0.1 gram of zirconium oxide is diluted with 15 ml. of concentrated hydrochloric acid and 30 ml. water. The solution is then heated to approximately 85°C. and 50 ml. of reagent added slowly from a buret to the hot solution. A precipitate generally develops after about 10-20 ml. of reagent has been added. The sample is allowed to digest for 15-20 min., cooled, allowed to settle, filtered in a Selas crucible, washed with three or four 8 ml. portions of distilled water, dried at 130°C., ignited to zirconium oxide and weighed.

In cases where the reagent is not sufficiently water-soluble it is added as the sodium salt in amount calculated just slightly more than sufficient to produce quantitative precipitation. In addition, the volume of solution is increased to about 200 ml.and the solution is filtered hot.

Results from these tests are given in Table 2.

None of these reagents could be eliminated from further consideration on the basis of these analyses. However, p-bromomandelic acid and p-chloromandelic acid gave more favorable results than any of the other reagents. They also possess the advantage of being water soluble and relatively easy to prepare. In addition, by inclusion of

Table 2

Quantitative Tests - Glycolic Acid Derivatives with Zirconium.

Reagent	Zr. Pres. gm.	Zr. found gm.	Dev'n. gm.	Dev'n %
Benzilic Acid	0.0782	0.0767	-0.0015	1.9
		0.0710	-0.0072	9.2
2-Naphthylglycolic Acid	0.0782	0.0771	-0.0011	1.4
		0.0791	0.0009	1.1
p-Methylmandelic Acid	0.0782	0.0786	0.0004	0.5
		0.0764	-0.0018	2.3
p-Iodomandelic Acid	0.0782	0.0599	-0.0283	36.0
		0.0671	-0.0111	14.0
		0.0787	0.0005	0.6
p-Chloromandelic Acid	0.0782	0.0785	0.0003	0.4
		0.0769	-0.0013	1.7
		0.0791	0.0009	1.1
p-Bromomandelic Acid	0.0782	0.0787	0.0005	0.6
		0.0784	0.0002	0.3
		0.0788	0.0006	0.8
Mandelic Acid	0.0782	0.0783	0.0001	0.1
		0.0781	-0.0001	0.1
		0.0782	0.0000	0.0

p-iodomandelic acid where appropriate, these reagents show the gradation in properties best suited to demonstrate the effect of weighting in the reagent on zirconium precipitation. Hence further experimental work was confined to halo-substituted mandelic acids.

First, these reagents were subjected to more exhaustive tests for quantitative precipitation of zirconium from pure zirconyl chloride solutions. The results are summarized in Table 3.

Table 3. Analysis of Pure Zirconyl Chloride Solutions.

Reagent	Number of Determinations	Result	Dev'n.
Zirconium Solution 1			
Cupferron	11	0.0783 gm.	--
Ammonia	8	0.0784	0.0001
Phosphate	5	0.0776	-0.0007
Mandelic Acid	8	0.0771	-0.0012
p-Chloromandelic Acid	14	0.0770	-0.0013
p-Bromomandelic Acid	4	0.0772	-0.0011
Zirconium Solution 2			
Cupferron	10	0.0782	--
Ammonia	4	0.0784	0.0002
Mandelic Acid	3	0.0782	0.0000
p-Chloromandelic Acid	3	0.0782	0.0000
p-Bromomandelic Acid	3	0.0786	0.0004
p-Iodomandelic Acid	1	0.0787	0.0005

Examination of the results obtained with zirconium solution 1 show disagreement of about 1.5% between the data secured with cupferron or ammonia and the mandelic acid reagents. The mandelic acid method was approximately 0.6% low in comparison with the phosphate method. The mandelic acid reagents give results which agree well with each other. It is believed that the cupferron-ammonia results are slightly high and the mandelic acid results slightly low possibly due to the inclusion of several low values incurred during development of the technique. Subsequent testing of the mandelic acid reagents in the presence of ions other than zirconium (see Table 4) gave an average value of about 0.0775 gram of zirconium oxide which agrees with the phosphate value in Table 3 and lies between the cupferron-ammonia and mandelate values. In any event very satisfactory checks were obtained with zirconium solution 2.

III. EFFECT OF COSOLUTES.

Solutions containing iron, aluminum, tin, copper, barium, calcium, bismuth, antimony, cerium, thorium, vanadium, titanium, chromium, cadmium, and magnesium were added to a standard zirconyl chloride solution and the zirconium determined by the method previously described. Results from these determinations are given in Tables 4 and 5.

The agreement is good in almost all cases and never exceeds 1.3% in spite of the high ratio of cosolutes to zirconium. Such unfavorable ratios are seldom if ever encountered in practical analyses.

Table 4

The Effect of Added Cations on Mandelate Detn. of Zirconium.

Cat.	Amount Added gm.	Reagent	Zirconium Present gm.	Zirconium Found gm.	Diff. gm.	Devn. %
Fe^{+++}	.500	M.A.	0.0775	0.0783	0.0008	1.0
	.500	p-Cl-M.A.	0.0775	0.0776	0.0001	.13
	.500	p-Br-M.A.	0.0775	0.0778	0.0003	.4
Al^{+++}	.250	M.A.	0.0782	0.0788	0.0006	.8
	.250	p-Cl-M.A.	0.0775	0.0768	-0.0007	- .9
	.250	p-Br-M.A.	0.0775	0.0769	-0.0006	- .8
Sn^{++++}	.250	M.A.	0.0782	0.0789	0.0007	.9
	.500	p-Cl-M.A.	0.0775	0.0777	0.0002	.3
	.250	p-Br-M.A.	0.0782	0.0785	0.0003	.4
Cu^{++}	.500	M.A.	0.0775	0.0775	0.0000	.0
	.500	p-Cl-M.A.	0.0775	0.0778	0.0003	.4
	.500	p-Br-M.A.	0.0775	0.0774	-0.0001	- .1
Ba^{++}	.500					
Ca^{++}	.500	M.A.	0.0775	0.0770	-0.0005	- .6
Ba^{++}	.500					
Ca^{++}	.500	p-Cl-M.A.	0.0775	0.0771	-0.0004	- .5
Ba^{++}	.500					
Ca^{++}	.500	p-Br-M.A.	0.0775	0.0779	0.0004	.5
Bi^{+++}	.500	M.A.	0.0775	0.0775	0.0000	.0
	.500	p-Cl-M.A.	0.0775	0.0771	-0.0004	.5
	.500	p-Br-M.A.	0.0775	0.0782	0.0007	.9
Sb^{+++}	.500	M.A.	0.0775	0.0776	0.0001	.1
	.500	p-Cl-M.A.	0.0775	0.0779	0.0004	.5
	.500	p-Br-M.A.	0.0775	0.0781	0.0006	.8
Ce^{++++}	.035	M.A.	0.0782	0.0792	0.0010	1.3
	.175	p-Cl-M.A.	0.0782	0.0786	0.0004	.5
	.175	p-Br-M.A.	0.0775	0.0775	0.0000	.0
Th^{++++}	.650	M.A.	0.0782	0.0792	0.0010	1.3
	.136	p-Cl-M.A.	0.0775	0.0777	0.0002	.3
	.136	p-Br-M.A.	0.0775	0.0771	-0.0004	- .5
V^{+++++}	.001	M.A.	0.0775	0.0769	-0.0006	- .8
	.001	p-Cl-M.A.	0.0782	0.0780	-0.0002	- .3
	.001	p-Br-M.A.	0.0775	0.0774	-0.0001	- .1
Ti^{++++}	.425	M.A.	0.0782	0.0792	0.0010	1.3
	.850	p-Cl-M.A.	0.0775	0.0770	-0.0005	- .6
	.425	p-Br-M.A.	0.0782	0.0786	-0.0004	- .5
Cr^{+++}	.500	M.A.	0.0782	0.0784	0.0004	.5
	.500	p-Cl-M.A.	0.0782	0.0786	0.0004	.5
	.500	p-Br-M.A.	0.0775	0.0775	0.0000	.0
Cd^{++}	.500	M.A.	0.0782	0.0785	0.0003	.4
	.500	p-Cl-M.A.	0.0782	0.0784	0.0002	.3
	.500	p-Br-M.A.	0.0782	0.0786	0.0004	.5

Table 5. Effect of Mixtures of Cations on Zr. Precipitation.

Cations Added gm.	Reagent	No. of Det'ns.	Zirconium Present gm.	Zirconium Found gm.	Diff. gm.
Fe^{+++} 0.70					
Al^{+++} 0.47	p-Cl-M.A.	5	0.0782	0.0783	0.0001
Ti^{++++} 0.02					
V^{+++++} 0.002	p-Br-M.A.	3	0.0782	0.0788	0.0006
Ca^{++} 0.10					
Mg^{++} 0.10	p-Cl-M.A.	2	0.0782	0.0782	0.0000
Cr^{+++} 0.10	p-Br-M.A.	2	0.0782	0.0791	0.0009

IV. APPLICATION TO COMMERCIAL PRODUCTS.

The zirconium in commercial samples of zirconyl chloride, an Fe-Zr-Al alloy, and a zirconium silicate ore generously furnished by the Titanium Alloy Manufacturing Division of the National Lead Company was determined by use of the mandelate reagents as follows:

A. $ZrOCl_2 \cdot 8H_2O$.

A sample of commercial zirconyl chloride of known zirconium content was dissolved in water and diluted to 500 ml. The zirconium present in aliquots of this solution was then determined as described for pure zirconyl chloride solutions. Results are tabulated in Table 6.

B. Fe-Zr-Al Alloy.

After considerable experimentation the following procedure was found to give acceptable results:

Table 6

Analysis of Commercial Zr Compounds by the Mandelate Method.

Reagent	No. of Det'ns.	Zirconium Present	Zirconium Found	Diff.
A. Zirconyl Chloride.				
Mandelic Acid	3	0.0825 gm.	0.0827 gm.	0.0002 gm.
p-Chloromandelic A.	6	0.0825	0.0823	-0.0002
p-Bromomandelic A.	3	0.0825	0.0832	0.0007
B. Fe-Zr-Al Alloy.				
Mandelic Acid	2	46.44%	47.59%	1.15%
p-Chloromandelic A.	3	46.44	46.67	0.23
p-Bromomandelic A.	2	46.44	47.06	0.62
p-Iodomandelic A.	1	46.44	46.19	-0.25
C. Zirconium Silicate.				
Mandelic Acid	2	64.68%	64.14	-0.54
p-Chloromandelic A.	5	64.68	64.55	-0.13
p-Bromomandelic A.	7	64.68	64.66	-0.02

Approximately 0.15 gram of the finely ground alloy sample is placed in a 150 ml. beaker and treated with 5 ml. water, 2 ml. sulfuric acid, and 3 drops of hydrofluoric acid (more, if necessary to effect solution). The beaker is kept covered with a watch glass. Toward the end of the reaction 1 ml. of nitric acid is added. The solution is evaporated to dryness on a sand bath. The residue is dissolved in 50 ml. of water containing 0.5 ml. of concentrated hydrochloric acid. 50 ml. of the mandelic reagent is added. A white precipitate readily develops. This is digested for 10-20 minutes, cooled, filtered, dried and ignited as previously.

The results obtained are given in Table 6.

Both hydrofluoric and nitric acid must be eliminated before addition of the reagent. The amount of sulfuric acid used should be kept to a minimum. Unexpected difficulty was experienced with mandelic acid. The best values were more than 1% high with this reagent. No reason is known for the high results obtained.

C. Zirconium Silicate Ore (Zircon).

The powdered zirconium silicate ore, weighed so as to contain approximately 0.1 gram of zirconium oxide, is fused with 2 grams of borax in a platinum crucible for 1-6 hours. The cooled melt is dissolved by digestion (preferably overnight) with 200 ml. of 1:5 hydrochloric acid solution. After removal of the crucible, the solution is made alkaline and the precipitate washed by decanting the solution through filter paper to remove silica. The residue is dissolved by addition of hydrochloric acid and poured through the same filter paper. Finally the paper is washed with hot dilute acid solution. The filtrate is analyzed for zirconium as previously described.

It was found necessary to remove silica in the manner described before carrying out the zirconium determination of the zircon. If this was not done, the colloidal silicic acid clogged the Selas crucibles to such an extent that filtration stopped. Furthermore, analyses obtained by using paper filters instead of Selas crucibles gave high results. This interference is not serious since, in a complete analysis, the silica present would be removed during the silicon determination.

V. EFFECT OF SULFURIC ACID.

The effect of the presence of sulfuric acid on the mandelate precipitation was determined by running analyses on zirconyl chloride solutions as before but with varied amounts of added sulfuric acid. The results are compiled in Table 7.

These results show that, as with mandelic acid, up to 5% sulfuric acid by weight can be tolerated. In addition, it was observed that dilution of solutions from which precipitation had been inhibited by the presence of sulfuric acid was followed by production of additional mandelate precipitate. The same effect is observed on partial neutralization of the acid with sodium hydroxide. In general, it is advisable to hold the sulfuric acid content to a minimum.

Table 7. The Effect of Sulfuric Acid on Zr. Precipitation.

H_2SO_4 Added ml.	% by wt.	Zirconium Present gm.	Zirconium Found gm.	Diff. gm.	Dev'n. %
Reagent - p-bromomandelic acid.					
1	2	0.0782	0.0786	0.0004	0.5
2	4	0.0782	0.0786	0.0005	0.6
3	5	0.0782	0.0754	-0.0028	-3.6
3	5	0.0782	0.0733	-0.0029	-3.7
4	7	0.0782	0.0689	-0.0093	-11.9
4	7	0.0782	0.0771	-0.0011	- 1.4
5	9	0.0782	0.0483	-0.0299	-38.
10	18	0.0782	0.0317	-0.0465	-59.
Reagent - p-chloromandelic acid.					
2.5	4	0.0782	0.0788	0.0006	0.8
2.5	4	0.0782	0.0753	-0.0029	-4.0
3	5	0.0782	0.0787	0.0005	0.6
3	5	0.0782	0.0782	0.0000	0.0
3.5	6	0.0782	0.0152	-0.0630	-80.
4	7	0.0782	0.0210	-0.0572	-73.

Table 8. The Effect of Acidity on Zr. Mandelate Pptn.

Samp.	Stand. Zr. Soln. ml.	H_2O ml.	Acid ml.	p-Cl-M.A. ml.	pH ml.	Zirconium Pres. gm.	Found gm.
1.	5	45	-	50	1.5	0.0782	0.0783
2.	5	45	-	50	1.2	0.0782	0.0782
3.	5	35	10	50	0	0.0782	0.0788
4.	5	30	15	50	0	0.0782	0.0790
5.	5	25	20	50	0	0.0782	0.0779

VI. EFFECT OF ACIDITY ON PRECIPITATION OF ZIRCONIUM.

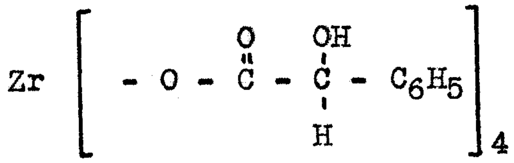
Samples of standard zirconyl chloride (0.01564 g. zirconium oxide per ml.) were analyzed as in section II except that the amount of concentrated hydrochloric acid added was varied. Table 8 lists the results.

The samples described as 1 and 2 in Table 8 produced precipitates immediately upon addition of the reagent but the precipitates were bulky and gelatinous and the solutions passed through the Selas crucibles exceedingly slowly. This behavior indicates that these precipitates may have been zirconyl hydroxide. On ignition there was only a slight production of carbon, indicating that the precipitate contained little organic matter. The precipitate in samples 3 and 4 developed more slowly and in a coarse, readily filterable form. The precipitate in sample 5 developed very slowly and appeared in chunks or flakes which tended to cling to the sides of the beakers.

The acidity apparently has little effect on the quantitative nature of the precipitation but does affect its form. About 10-15 ml. hydrochloric acid per 100 ml. of solution seems to be optimum.

VII. THEORETICAL CONSIDERATIONS. THE POSSIBILITY OF DIRECT WEIGHING OF ZIRCONIUM MANDELATES.

Kumins analyzed a carefully washed and dried sample of zirconium mandelate, and on the basis of his results proposed the formulation of the compound as:



$$\mathrm{Zr}\left[-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{C_6H_5}\right]_4$$

The possibility of determining zirconium by "direct weighing" of the zirconium mandelate precipitate produced is worth considering both from the standpoint of the saving in time in not having to conduct the ignition to zirconium oxide and the increased weight of the molecule per unit weight of zirconium oxide.

	M.W.	Ratio
ZrO_2	132	1
$Zr(Ma)_4$	696	5.2
$Zr(MaCl)_4$	833	6.3
$Zr(MaBr)_4$	1011	7.7
$Zr(MaI)_4$	1199	9.1

The slight solubility of zirconium mandelate in pure water as well as the high concentration of mandelic acid used in the determination by Kumin's procedure makes it impossible to obtain zirconium mandelate free of mandelic acid. The halo-derivatives are free of these disadvantages; the zirconium halo-mandelates produced can be washed with distilled water and thus freed from excess reagent. Consequently a series of experiments were performed in which the zirconium mandelate precipitates were first dried at 125-130°C. for several hours, weighed, ignited, and weighed again. Results are given in Table 9.

Table 9. Comparison - Direct Weighed vs Ignited

Reagent	Direct Weighed gm.	Ignited gm.	Dev'n gm.
Mandelic Acid	0.0769	0.0764	-0.0005
	0.0784	0.0760	-0.0024
	0.0787	0.0762	-0.0025
p-Chloromandelic Acid	0.0774	0.0768	-0.0006
	0.0764	0.0766	0.0002
	0.0776	0.0773	0.0003
	0.0767	0.0772	0.0005
p-Bromomandelic Acid	0.0778	0.0779	0.0001
	0.0769	0.0765	-0.0004
	0.0774	0.0774	0.0000

Note: The amount of ZrO_2 present in samples analyzed was 0.0775 gm.

Table 10. Further Comparison - Direct Weighed vs Ignited

Solution Used	Reagent	No. of Det'ns.	Direct Weighed gm. ZrO_2	Ignited gm. ZrO_2	Dev'n gm.
Pure $ZrOCl_2$	M.A.	3	0.0780	0.0771	-0.0009
	p-Cl M.A.	4	0.0770	0.0770	0.0000
	p-Br M.A.	3	0.0775	0.0772	-0.0002
$ZrOCl_2$ in Presence Other Ions	M.A.	13	0.0780	0.0775	-0.0005
	p-Cl M.A.	20	0.0770	0.0774	0.0004
	p-Br M.A.	15	0.0773	0.0775	0.0002

Note: Amount ZrO_2 present - 0.0775 gram.

The results were so encouraging that these direct weighings were carried out on all samples used in testing the selective action of the mandelic acid reagents (See section III and Table 4.) The averages of the values obtained in these tests are listed in Table 10.

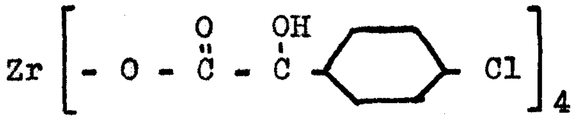
As expected, mandelic acid gave high direct weighed results due to inability to remove excess mandelic acid completely without at the same time losing some zirconium mandelate to the filtrate. In fact, it is rather surprising that the results are as close as they are. This is probably due to the compensation of errors due to the above factors which are opposite in effect.

Unfortunately, when it was attempted to apply the direct weighing technique to the analysis of the alloy and ore samples, results became erratic and unreliable even when ignited results were correct. It was necessary to discontinue further work on this phase of the problem. However, the advantages of such a procedure are sufficiently great to warrant further investigation of the problem.

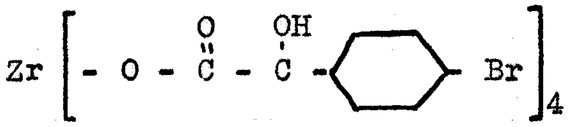
These results also may be taken as evidence for the formulation of the zirconium mandelates as suggested by Kumins since the procedure amounts to an analysis of the zirconium present in the precipitate.

$$Zr\ (MaX)_4 \longrightarrow ZrO_2$$

Consequently the halo-mandelates can be formulated:



and



It was found also that, like zirconium mandelate, the halo-mandelates dissolved in sodium hydroxide with the production of zirconium hydroxide, and in ammonium hydroxide without production of any precipitate. This latter reaction indicates a possible masking action of ammonia in the presence of mandelates with zirconium and should be investigated further.

VIII. COMPARISON OF REAGENTS.

The question arises as to which of the mandelic acid reagents is to be preferred in a zirconium determination. This question cannot be answered unequivocally as no one reagent has decided advantages over the others. Their differences are of degree rather than of kind.

Mandelic acid is cheaper; but since ten times as much mandelic acid is used per determination the price differential is considerably lessened. The zirconium mandelate precipitate is dense and easily handled and therefore can be readily transferred to Selas crucibles during filtration. The halo-mandelate precipitates have some tendency to creep during filtration and are a little more difficult to transfer. This disadvantage is compensated by the fact that the zirconium mandelate is slightly soluble in water and specified washing techniques must be strictly followed. The washing of the halo-mandelates is simple and convenient. The increased amount of precipitate per given weight of zirconium (weighting effect) provided by the halo-mandelic acids is a factor in their favor. This will be especially valuable if a direct weighing procedure proves to be possible. Active oxidizing agents attack mandelic acid compounds and this causes some trouble since the reagents are consumed and, in the case of the halo-mandelic acids, the oxidation products are compounds which are not soluble in cold water. With mandelic acid a similar reaction occurs but the product is water soluble.

These minor differences are not sufficient to make one reagent superior to the others. However, if given a choice of reagent, the author would select these zirconium precipitants in the order: p-bromomandelic acid, p-chloromandelic acid, mandelic acid.

The mandelate method offers distinct advantages in comparison with other methods. No other procedure can match it in selectivity, and in the rapidity and ease with which the determination can be carried out. There is every reason to believe that, in the near future, the mandelate method will become the preferred and accepted method for determining zirconium.

CHAPTER V

SUMMARY

1. The zirconium-precipitating action of the -CHOH-COOH group is retained in compounds other than mandelic acid. Bulkier precipitates and colored precipitates are obtained by use of appropriate glycolic acid derivatives.

2. The halo-mandelic acid derivatives (p-chloromandelic acid and p-bromomandelic acid) were found to be completely analogous to mandelic acid in their ability to precipitate zirconium selectively and quantitatively.

3. p-Chloromandelic acid and p-bromomandelic acid were applied successfully as reagents in the mandelate determination of the zirconium in zirconyl chloride, an Fe-Zr-Al alloy, and a zirconium silicate ore.

4. Precipitation of zirconium halomandelates is inhibited by the presence of sulfuric acid in amount greater than 5% by weight. Oxidizing agents also interfere by attacking the reagent.

5. The possibility of determining zirconium by direct weighing of the mandelate precipitate obtained was investigated.

6. The preferred reagent for the determination of zirconium by the mandelate method was found to be: p-bromomandelic acid, then p-chloromandelic acid, and finally mandelic

acid although the distinction between them is small.

7. The mandelate method offers distinct and important advantages over the generally accepted methods of determining zirconium.

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