

THE SYNTHESIS OF AROMATIC ALDEHYDES

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I. INTRODUCTION

This review is a survey of the literature for methods used to synthesize aromatic aldehydes and will be limited to a discussion of those compounds in which the formyl group is directly attached to the aromatic nucleus. Processes by which aldehydes are obtained from natural sources or by fermentation will not be considered.

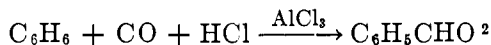
Examination of the literature reveals the fact that most investigations have been carried out on benzene and its substitution products. In only a few instances have the reactions been extended to other aromatic nuclei. Unfortunately, per cent yields or limitations for some of the methods have not been reported.

There are two general routes for the synthesis of aromatic aldehydes (110): (1) *Direct methods*. These procedures involve the direct introduction of the formyl group, or groups directly changeable into it, into the aromatic nucleus. (2) *Indirect methods*. By this term is meant the conversion of groups already in the nucleus into aldehyde groups.

In choosing any one of the methods to produce an aromatic aldehyde it is important to consider the effect of groups already in the nucleus, since these influence orientation, activation, or deactivation of the ring and side reactions with the reagents.

II. DIRECT METHODS

A(1). Gattermann and Koch reaction



Gattermann and Koch (75) first reported the method of preparing aromatic aldehydes by reacting benzene (and its substitution products) with carbon monoxide and hydrogen chloride, using anhydrous aluminum chloride as a catalyst.

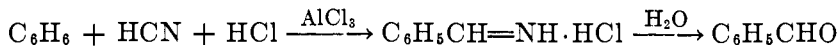
The two gases, carbon monoxide and hydrogen chloride, are bubbled for a suitable period through an ether or nitrobenzene solution containing the aromatic compound, cuprous chloride, and aluminum chloride. Ice is then added and the aldehyde steam-distilled from the reaction mixture (171). If the reaction is run under elevated pressures of carbon monoxide, the hydrogen chloride and the aluminum chloride activators (chlorides of copper, iron, or nickel) are not required (102, 123). In this case, to shorten the induction period, a trace of water or hydrogen chloride is added, or better, a residue of aldehyde-aluminum chloride complex is left in the reaction chamber (127). Nickel and iron carbonyls have been used as sources of carbon monoxide, but the resulting yields of aldehydes were less than 40 per cent (98, 293).

Under normal pressures the yields average only 30–50 per cent, but with high carbon monoxide pressures they run 80–90 per cent. The reaction is not

² The equations used throughout this paper are not balanced, but merely indicate reactants and important products.

applicable to phenols or their alkyl ethers. Only monosubstitution takes place, usually in the para-position (171, 201). If the para-position is occupied, migration from this position is known to occur (63). Thus, *p*-xylene will give 2,4-dimethylbenzaldehyde.

A(2). Gattermann reaction



In 1906 Gattermann altered the Gattermann-Koch reaction by using dry hydrogen cyanide in place of carbon monoxide (70). This modification produces the aldimine hydrochloride as an intermediate which must then be hydrolyzed to the aldehyde.

The Gattermann reaction, unlike the Gattermann and Koch reaction, can be applied to phenols and aromatic ethers. With only one hydroxyl or alkoxy group in the ring, anhydrous aluminum chloride is recommended for the catalyst, but meta-substituted di- and tri-hydric phenols, or their alkyl ethers, react when a milder catalyst such as anhydrous zinc chloride is used, and a few will react even without a catalyst (71, 72, 73, 75, 242). Monohydric phenols will react with hydrogen cyanide to yield aryl formidate hydrochlorides, $\text{C}_6\text{H}_5\text{OCH}=\text{NH} \cdot \text{HCl}$, but without a catalyst rearrangement to the aldimine will not occur (105). The Gattermann reaction has been extended to mono- and di-hydroxynaphthalenes.

Adams (1, 2) introduced a more convenient method for carrying out this reaction by using zinc cyanide in place of hydrogen cyanide. Pure zinc cyanide is ineffective. However, with a trace of added potassium or sodium chloride zinc cyanide works very satisfactorily (8).

B. Reimer-Tiemann reaction



The production of aromatic hydroxy aldehydes from phenols, chloroform, and aqueous alkali was described by Reimer and Tiemann in 1876 (216).

The phenol, chloroform, and aqueous alkali are refluxed at a moderate temperature for several hours. Then the reddish-violet reaction mixture is acidified, and the aldehyde isolated by steam distillation or crystallization (7, 225). A milder base such as sodium carbonate is sometimes used in place of the sodium hydroxide (101). If pyridine is substituted for the aqueous alkali, only the ortho-isomer is obtained (241, 271). Bromoform, iodoform, or trichloroacetic acid will serve equally as well as the chloroform but are more expensive. Side-products containing chlorine or ketone groups are known to be produced (7, 10, 133, 271).

The ortho:para ratio is usually less than unity (101) and occasionally traces of dialdehydes are recovered. Yields seldom run over 50 per cent and are less than 25 per cent when the ring contains such negative groups as sulfo, nitrile, carboxyl, or nitro, which deactivate the nucleus (271).

Chaudhuri (31) has found that chloroform, potassium hydroxide, and benzaldehyde will react to give *o*- and *m*-dichloromethylbenzaldehydes, which can be hydrolyzed to the corresponding phthalaldehydes. Rapson, Saunder, and Stewart (215) were unable to repeat Chaudhuri's work.

C. Duff's hexamethylenetetramine reaction



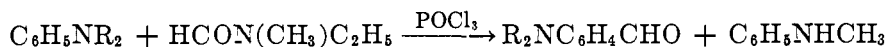
Hexamethylenetetramine will condense with phenols to form intermediate products which, when hydrolyzed in mineral acids, will give small amounts of aromatic hydroxy aldehydes (50). Duff has worked out a general procedure resulting in slightly improved yields (48).

The phenol is heated at elevated temperatures for 10–30 min. in a mixture of hexamethylenetetramine, boric acid, and glycerol. The resulting dark brown viscous liquid is acidified with dilute sulfuric acid, and the aldehyde isolated by steam distillation.

Only ortho substitution, or a small amount of ortho–para disubstitution, takes place. The yields, averaging only 15–20 per cent, are lower than those from the Reimer–Tiemann reaction, but this method offers the advantage of producing a much purer product and requires less time. Negative groups hinder or prevent the reaction from taking place, while resorcinol and phloroglucinol rapidly form resins under the conditions of the reaction (271). This method does not apply for hydroxypyridines and hydroxyquinolines (131, 271).

Duff (49) found that the above procedure does not succeed with *N,N*-dialkylanilines, but that with a slight modification satisfactory results may be obtained. In place of the glyceroboric acid, which was found unsuitable, a mixture of formic acid and acetic acid is used. Either acid alone is unsatisfactory. Duff believes that the formic acid has reducing action, as indicated by the evolution of carbon dioxide during the reaction. The yields of *p-N,N*-dialkylamino- or *p-N,N*-alkylaryl-amino-benzaldehydes average 35–45 per cent.

D. Reactions with N-methylformanilide



Vilsmeier and Haack (273) found *N,N*-dialkylanilines and *N*-methylformanilide to condense in the presence of phosphorus oxychloride, producing intermediates which, when hydrolyzed in acid solution, will give *p*-(*N,N*-dialkylamino)benzaldehydes in 80 per cent yields. *N*-Methylformanilide alone, when reacted with phosphorus oxychloride and phosphorus pentachloride, will give a 37 per cent yield of *p*-(*N*-methylamino)benzaldehyde.

As a result of their work an excellent method for the preparation of aldehydes has been developed, but it is limited in its applicability (57, 188, 207). Benzene and naphthalene will not react; however, their alkoxy or *N,N*-dimethylamino derivatives, naphthols, and certain hydrocarbons which contain active hydrogen atoms will give yields averaging 70–85 per cent.

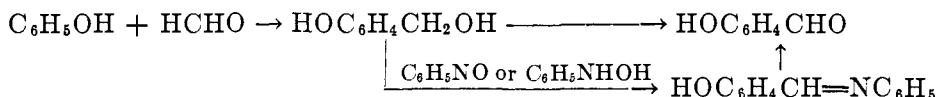
The aromatic derivative, *N*-methylformanilide, and phosphorus oxychloride are allowed to react at a suitable temperature; then an aqueous solution of sodium acetate is added and the mixture steam-distilled to liberate the aldehyde. Table 1 will serve to illustrate the behavior of several compounds in this reaction (56, 58, 271, 274).

Compounds other than phosphorus oxychloride which will serve as catalysts are halogen acid anhydrides, such as thionyl chloride, oxalyl chloride, or phosgene (271). In the presence of aluminum chloride or the above oxychlorides of phosphorus and sulfur, *N,N*-dimethylaniline will react with a large excess of formamide to give *p*-(*N,N*-dimethylamino)benzaldehyde (113, 114, 177).

TABLE 1
Reaction with N-methylformanilide

COMPOUND	POSITION OF SUBSTITUTION	YIELD
		<i>per cent</i>
Anthracene.....	9	80-92
Acenaphthene.....	3	85
β -Ethoxynaphthalene.....	1	74-85
<i>o</i> -Chloroanisole.....	?	3
Resorcinol dimethyl ether.....	2	95
<i>N,N</i> -Diethylaniline.....	4	80
1,2-Benzanthracene.....	10	64
Pyrene.....	3	53
1,2,5,6-Benzanthracene.....		No reaction
3,4-Benzpyrene.....	5	90
Hydrindene.....		No reaction
α -Methylnaphthalene.....		No reaction
Phenanthrene.....		No reaction
Crysene.....		No reaction

E. Formaldehyde condensations



Anilines and phenols condense with formaldehyde in dilute acid or base to give substituted derivatives of benzyl alcohol, which may be isolated or oxidized in the same reaction mixture to the corresponding aldehydes (47, 78, 96, 178, 238, 268, 278). This method has been used largely for the technical preparation of amino- and hydroxy-benzaldehydes.

The aniline or phenol, dilute formaldehyde, aqueous acid or alkali, and the oxidant are mixed, allowed to react for several hours at a suitable temperature, acidified, and the aldehyde isolated by steam distillation (175). Nitrosobenzene or phenylhydroxylamine is used for the oxidizing agent and cupric oxide as a catalyst.

Para substitution predominates, with yields running as high as 85 per cent but

averaging only 40–50 per cent. Some processes use iron, aluminum, or electrolytic reduction to reduce nitro- and nitroso-benzenes to phenylhydroxylamines, and the reduction is carried out simultaneously with the formaldehyde condensation (118, 239, 275). This reduction–condensation technique gives lower yields than the straight condensation method.

F. Chloral condensations



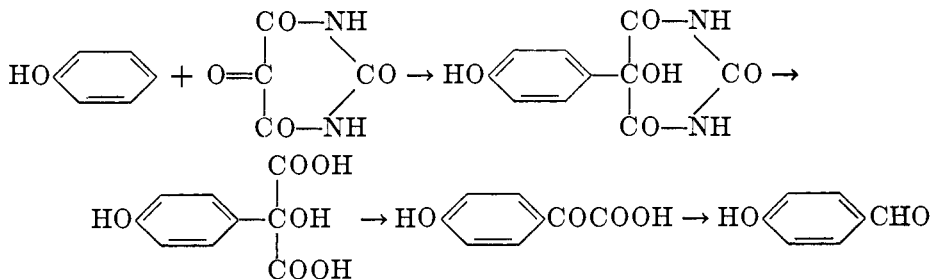
Phenols condense with chloral hydrate in dilute base to give, along with small amounts of further condensation products, hydroxyphenyltrichloromethylcarbinols which can be oxidized to the corresponding hydroxybenzaldehydes (185, 190, 199, 209). The phenols and chloral hydrate are kept alkaline with potassium carbonate for six to twelve weeks, whereupon the carbinols are produced in 60–80 per cent yields. The latter are either treated with zinc dust in aqueous alcohol and the product oxidized with chromium trioxide, or oxidized directly to the aldehydes with dilute alkaline sodium dichromate. The hydroxybenzaldehydes are obtained in 40–60 per cent yields on the basis of the amount of phenol used.

Substitution takes place in the para-position unless it is occupied and then ortho substitution occurs, but to a lesser extent.

G. Condensation with alloxan, mesoxalates, oxalyl ester acid chlorides, and sodium glyoxylate

Alloxan, mesoxalates, oxalyl ester acid chlorides, 1,2-diketo esters, and sodium glyoxylate condense with phenols to produce intermediates which can be converted into phenylglyoxylic acids, and the latter can be decarboxylated to the corresponding benzaldehydes.

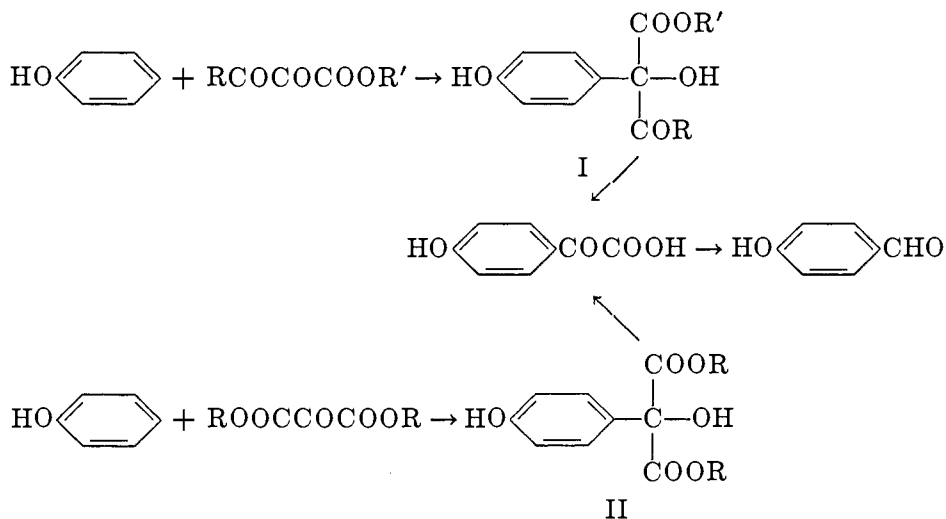
(1) Alloxan



Phenols and alloxan, in the presence of hydrogen chloride, concentrated sulfuric acid, or anhydrous zinc chloride, condense similarly to an aldol condensation (22, 238). The products are hydrolyzed in dilute alkali and the hydroxymalonic acid derivatives, which are freed by acidification, are heated in acid solution, whereupon they lose carbon monoxide and water to produce the phenylglyoxylic

acids. These are decarboxylated in boiling *p*-toluidine to produce the corresponding hydroxybenzaldehydes.

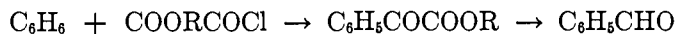
(2) 1,2-Diketo esters and mesoxalates



Phenols and anilines condense with 1,2-diketo esters or mesoxalates in acetic acid, anhydrous zinc chloride being used as catalyst, to give aldol-type condensation products, I and II, in 75–85 per cent yields (86). To obtain the phenylglyoxylic acids, compounds of type I are refluxed with an aqueous solution of cupric acetate, while those of type II are first hydrolyzed in dilute potassium hydroxide, neutralized, and then refluxed with aqueous cupric sulfate. The phenylglyoxylic acids give 68 per cent yields of the corresponding aldehydes when heated with *N,N*-dimethylaniline and up to 97 per cent yields when heated at 170°C. in *p*-(*N,N*-dimethyl)toluidine.

Diketosuccinic acid, HOCCOCOCOOH, when substituted for its diester in the condensation with phenol, gives only a 15 per cent yield of the *p*-hydroxyphenylglyoxylic acid.

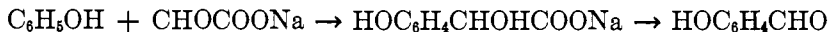
(3) Oxalyl ester acid chlorides



Bouveault discovered that ethyl oxalate acid chloride condenses with benzene and its substitution products in the presence of anhydrous aluminum chloride to give the esters of phenylglyoxylic acids in yields, usually, above 70 per cent (24). The phenylglyoxylates have also been obtained in small yields from diphenylmercury and ethyl oxalate acid chloride. Besides the methods given above for the decarboxylation of the phenylglyoxylic acids, Bouveault frequently prepared the hydrazine, hydroxylamine, or aniline Schiff's base of the phenylglyoxylic acid and then heated this to bring about decarboxylation to the corresponding

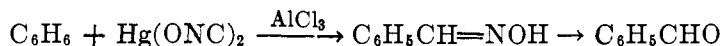
aldehyde Schiff's base. Derivatives of toluene and anisole are especially suitable for this method of preparing the corresponding aldehydes.

(4) Sodium glyoxylate



Monoalkyl ethers of catechol will condense with sodium glyoxylate, and the products may be converted into the corresponding substituted benzaldehydes by refluxing with aqueous cupric sulfate or nitrobenzene (32, 179, 186, 220). Yields up to 80 per cent are obtained, but the method has only been extended to a few derivatives of catechol.

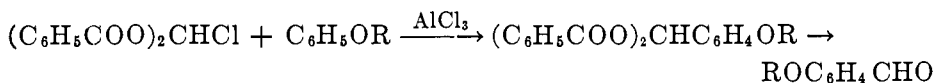
H. Mercury fulminate condensations



Benzene and its alkyl derivatives react with mercury fulminate in the presence of aluminum chloride to give moderate yields of oximes which may then be hydrolyzed to the corresponding aldehydes (235, 236). The reaction is run at 45°C. (mercury fulminate explodes when heated to about 180°C.). If a solvent is necessary it is usually nitrobenzene; carbon disulfide and ligroin are unsatisfactory.

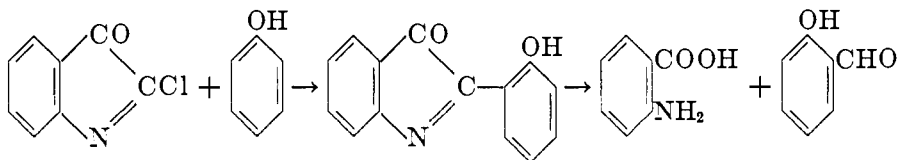
Scholl discovered that if sublimed aluminum chloride is used as the catalyst substituted benzonitriles are the main products, while traces of substituted benzaldehydes and benzamides are formed as side products. But, by using a mixture of sublimed aluminum chloride, crystallized aluminum chloride hexahydrate, and dried aluminum hydroxide, a 65-70 per cent yield of the oxime is obtained. Polyhydric phenols give excellent yields, phloroglucinol giving almost a quantitative yield. Ortho and para substitution are both found to take place.

I. Chloromethylene dibenzoate condensations



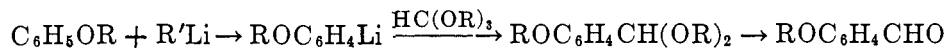
Wenzel found that when chloromethylene dibenzoate and anhydrous aluminum chloride are added to a benzene solution of mesitylene an intermediate is formed which, upon hydrolysis in hydrochloric acid, produces mesitylaldehyde (285). Likewise, anisole reacts with chloromethylene dibenzoate to give an 80 per cent yield of anisaldehyde, while benzene only produces a diphenylcarbinol benzoate.

J. Isatin chloride condensations



Upon refluxing in benzene solution, phenols and naphthols condense with isatin chloride to give the corresponding 2-indolindigo derivatives which may be hydrolyzed in 10 per cent sodium hydroxide to produce anthranilic acid and the *o*-hydroxybenzaldehyde or naphthaldehyde in 20–40 per cent over-all yields (18, 65, 231).

K. Reactions with organolithium compounds

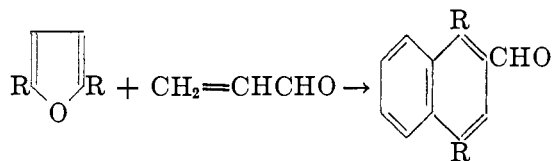


When phenyllithium derivatives are heated with *N*-methylformanilide or ethyl orthoformate, intermediates are formed which, upon acid hydrolysis, produce substituted benzaldehydes in 70 per cent yields (270, 291, 292).

The hydrogen atoms which are ortho to an alkoxy group in the benzene nucleus are sufficiently active to be readily replaced by lithium. A convenient method is to effect an exchange with phenyl- or butyl-lithium. Thus anisole, after several hours heating at 100°C. with phenyllithium, gives a 70 per cent yield of 2-methoxyphenyllithium (291, 292).

Should the phenyllithium derivative be prepared through an exchange of lithium for a halogen atom in an aromatic ring, the method would fall into the "indirect method" classification and would then parallel the Grignard method, for which magnesium is used.

L. Naphthaldehydes from benzofurans and acrolein

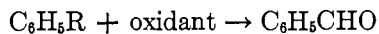


Substituted benzofurans have been reacted with acrolein by refluxing in ethyl alcohol; after addition of hydrochloric acid, substituted naphthaldehydes were isolated in 50 per cent yields (283, 284).

III. INDIRECT METHODS

As stated above, the processes whereby groups on the aromatic nucleus are converted into aldehyde groups have been classified as indirect methods. Most of these consist of oxidation or reduction of side chains to the formyl group. Thus, the $-\text{CH}_2\text{Y}$ group, where Y represents a hydrogen, hydroxyl, halogen, nitro, or carboxyl group, may be oxidized and the COOH , COCl , COOR , CN , CONR_2 , and CHNNR_2 groups may each be reduced to the aldehyde group.

A. Oxidation of saturated side chains



(1) *Electrolytic oxidation*: There have been many attempts to oxidize side-chain alkyl groups to aldehyde groups, but few have met with success (157).

The products from the electrolysis of toluene, as reported by several authors, are chiefly ethyl benzoate, benzoic acid, *p*-sulfobenzoic acid, quinone, hydroquinone, and benzaldehyde, depending upon the experimental conditions (54, 109, 151, 218).

Following their experiments with toluene emulsified in sulfuric acid, Fichter and Stocker proposed that the ring is attacked more rapidly than the side chain, giving rise to polyhydroxybenzenes and subsequent decomposition (55). Mann and Paulson, using platinum sheet electrodes (140), attempted to determine the conditions for a maximum yield of benzaldehyde from toluene regardless of side products. With yields below 19 per cent their results indicate that a diaphragm around the anode is necessary and that solvents such as acetone, alcohol, or chloroform are unsatisfactory. Kawada investigated the conditions for a maximum yield of benzaldehyde from toluene, using manganous sulfate in sulfuric acid for an electrolyte and lead-plate electrodes; he concluded that a diaphragm and vigorous stirring are necessary (115). Law and Perkin obtained aldehydes from alkylbenzenes in yields up to 35 per cent, using platinum electrodes and acetone-sulfuric acid solutions for an electrolyte (128). Ethylbenzene gave mainly methylphenylcarbinol.

(2) *Chemical oxidation*: Most investigations of the vapor-phase oxidation of toluene have been directed toward the technical production of benzaldehyde (108, 124, 125, 141, 143, 180, 202). Air, diluted usually with nitrogen to prevent total destruction of the hydrocarbon, is most frequently used as the oxidant, while occasionally substances such as methanol, which are more readily oxidized than the toluene, are added to serve as protective agents. Experiments have largely made use of recirculating continuous processes with varied contact periods, temperature ranges up to 550°C., and catalyst carriers of asbestos, pumice, zeolites, talc, or porcelain. The relative proportions of benzyl alcohol, benzaldehyde, and benzoic acid produced are determined by the conditions. In general, oxides of molybdenum, tungsten, zirconium, and tantalum catalyze oxidations to benzaldehyde and are not active to promote further oxidation to any great extent. Oxides of manganese, copper, nickel, chromium, and uranium are more powerful and favor formation of aldehydes, but they also promote further oxidation to complete combustion of the toluene, while oxides of cobalt and cerium lead to complete combustion. Oxides of titanium, bismuth, and tin are only slightly active and require such high temperatures to initiate reaction that the toluene ignites. Vanadium pentoxide is particularly active in the oxidation of aldehydes to acids (146). Certain salts catalyze the oxidation of benzaldehyde to benzoic acid at a faster rate than the oxidation of toluene to benzaldehyde and naturally only a small yield of the aldehyde can be expected.

Oxidation of side chains consisting of straight-chain alkyl groups containing two or more carbon atoms produces chiefly ketones, since it is the carbon atom adjacent to the ring which is most readily attacked.

The heterogeneous liquid-phase oxidation of substituted toluene derivatives to the corresponding benzaldehydes has been very successful. One of the important technical methods of producing benzaldehyde consists in the treatment of toluene

with manganese dioxide in 65 per cent sulfuric acid at 40°C. Salicylaldehyde also is produced on a large scale from *o*-cresol by this method, the hydroxyl group being protected from oxidation by ester formation with sulfonic or carbonic acids (6, 64, 191, 245). The oxides of lead, nickel, cobalt, cerium, selenium, and tellurium and ammonium persulfate have all been used more or less successfully as oxidants (129, 192).

A good laboratory method for oxidizing methyl groups to aldehyde groups in 40–50 per cent yields is the use of chromium trioxide in acetic anhydride (170). The diacetates are formed, preventing further oxidation, and crystallize out as sharp-melting products which may then easily be hydrolyzed in acid solution to the corresponding aldehydes (193, 260). Xylenes will give phthalaldehydes by this method.

The Étard reaction makes use of chromyl chloride, an oxidant which is reported to have just the potential required to oxidize a methyl group to a formyl group (52, 53). The chromyl chloride is added slowly to a carbon disulfide or carbon tetrachloride solution of the substituted toluene derivative, from which a dark brown, insoluble, explosive intermediate is precipitated. This is decomposed in dilute sulfurous acid to give the aldehyde. Yields up to 80 per cent are sometimes obtained. Alkyl groups other than the methyl group lead to various products. Thus, ethylbenzene gives phenylacetaldehyde; propylbenzene gives benzaldehyde, benzyl methyl ketone, and chlorinated products; and cymol gives cuminaldehyde plus an unidentified ketone (23, 129, 156, 208, 219, 220).

The methyl group of substituted toluenes may be dichlorinated or dibrominated and the benzal chloride or bromide hydrolyzed to the corresponding aldehyde (253). Large amounts of benzaldehyde are produced technically by illuminated chlorination of toluene until a certain density is reached, treatment of the mixture of mono-, di-, and tri-chlorotoluenes with aqueous calcium hydroxide or carbonate, and isolation of the aldehyde by steam distillation. Small amounts of benzoic acid are recovered from the distilling liquid after cooling (64, 139, 172). In the case of cresols, the carbonate or acetate esters are first prepared in order to prevent nuclear halogenation (38, 240, 271).

By treating nitrotoluenes with either a solution of alcoholic-aqueous sodium sulfide, a solution of sulfur in concentrated alcoholic-aqueous sodium hydroxide, or fuming sulfuric acid, oxidation and reduction within the same molecule will occur and produce aminobenzaldehydes and aminonaphthaldehydes in yields up to 70 per cent (16, 101, 194, 263). Occasionally aldehydes are not produced and sometimes toluidines and aminobenzoic acids are formed as the main products; hence the method is not general (271).

Methyl groups which are activated by ortho- or para-situated nitro groups are smoothly condensed with nitrosobenzenes, and the resulting Schiff's bases are hydrolyzed to the corresponding aldehydes in over-all yields up to 88 per cent (158, 173, 195, 228).

o-Nitrotoluene reacts with mercuric oxide in dilute sodium hydroxide to produce a mercury salt which may be oxidized directly to *o*-nitrobenzaldehyde, or

halogenated to give *o*-nitrobenzal halide and the latter hydrolyzed to liberate *o*-nitrobenzaldehyde. The over-all yields of *o*-nitrobenzaldehyde are reported to be as high as 84 per cent (216a).

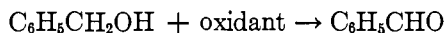
Toluene derivatives react with alkyl nitrites in alcoholic solutions of sodium alkoxide to convert the methyl group to an aldehyde group in 50–70 per cent yields (5, 137, 261). In the case of nitrotoluenes, the corresponding oxime is isolated and must then be hydrolyzed to the aldehyde.

Dibenzyl, prepared from benzene and 1,2-dichloroethane using anhydrous aluminum chloride as catalyst, has been oxidized to benzaldehyde by molecular oxygen at 150–280°C. (40, 234).

The oxidation of β -(5-chloro-6-methoxy-2-naphthoyl)propionic acid with alkaline sodium hypochlorite gives a 39 per cent yield of 5-chloro-6-methoxy-2-naphthaldehyde (120).

Phenylbromoacetamides, upon treatment with sodium hydroxide, will give the corresponding derivatives of benzaldehyde. The procedure has not been worked out for the general preparation of aromatic aldehydes (169).

B. Oxidation of benzyl alcohols



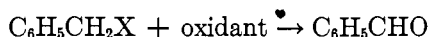
A clean-cut laboratory method for oxidizing hydroxymethyl groups to aldehyde groups in yields up to 90 per cent is through the use of chromium trioxide in acetic acid or anhydride (250).

A cheaper method and one that is used more often as a technical process makes use of sulfonic or carbon acids of *m*-nitrobenzene in basic media (89, 181, 203, 270, 278). This method has shown more applicability when there are also hydroxyl groups attached to the nucleus of the benzyl alcohol since, through solution in the aqueous alkali, there results a homogeneous reaction mixture.

Dichromates in dilute sulfuric acid have been used to oxidize hydroxymethyl to formyl groups in 80–95 per cent yields (134, 300). Alkaline sodium hypochlorite has been used as an oxidant, with simultaneous steam distillation of the aldehyde as it is produced (204). Selenium dioxide (9), tellurium dioxide (62), and chloroform solutions of nitrogen trioxide or tetroxide (34) will oxidize benzyl alcohol to benzaldehyde in yields of 40 per cent or less.

A schematic method for converting a substituted benzyl alcohol into the corresponding benzaldehyde is to reflux the alcohol with a less volatile aldehyde, using an aluminum alkoxide catalyst. The equilibrium which is set up is displaced by removing the resulting less volatile aldehyde as it is formed. Thus, benzaldehyde was prepared from benzyl alcohol and cinnamaldehyde in 95 per cent yield, while the cinnamyl alcohol was recovered in 87 per cent yield (43). Anisaldehyde has also been used to prepare benzaldehyde from benzyl alcohol (227).

The vapor-phase oxidation of benzyl alcohol by air or oxygen under reduced pressures has been conducted with yields up to 90 per cent by using such catalysts as silver metal, cupric oxide, or vanadium pentoxide at temperatures of 100–350°C. (4, 44a, 163, 206, 245).

C. Oxidation of benzyl halides

A simple reaction for converting substituted benzyl halides to the corresponding benzaldehyde derivatives, and one that is quite general, is Sommelet's reaction, which consists in refluxing the benzyl halide with hexamethylenetetramine in dilute alcohol, acidifying, and isolating the aldehyde by steam distillation (36, 196, 254, 271). The yields average 60–70 per cent.

Nitrates of copper, lead, or calcium in dilute nitric acid have often been used to oxidize benzyl halides to the corresponding benzaldehydes, usually resulting in low yields (60, 214, 237, 246, 271). Oxidation with alkaline dichromates will sometimes give yields up to 90 per cent (20, 134). The refluxing of selenium dioxide with substituted benzyl chlorides produces a 45–55 per cent yield of the substituted benzaldehyde (61).

Vapor-phase oxidation of benzyl chlorides to the corresponding benzaldehydes has been carried out to give 70–90 per cent yields (245, 248).

D. Oxidation of benzylanilines, benzylamines, N-alkylanilines, phenylnitromethanes, and phenylacetic acids

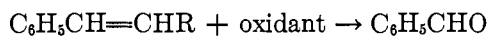
The oxidation of benzylanilines in acetone solution with dichromates or permanganates produces benzalanilines, which may be hydrolyzed in mineral acid to liberate the substituted benzaldehydes (35, 197, 228).

In alkaline media, hydroxybenzylamines have been oxidized by air to hydroxybenzaldehydes, using isatin or potassium isatin-5-sulfonate as a catalyst (182, 187).

Prolonged oxidation of tribenzylamines with such oxidants as aqueous bromine, chromic acid, or thionyl chloride has been found to produce benzaldehydes (37, 132, 149, 153). Various substituted benzaldehydes and naphthaldehydes have been prepared when an arylalkylamine was heated with a chlorobenzene containing an active chlorine atom and the intermediate product oxidized in acid solution (183). The chlorinated reagents used were 2,4-dinitrochlorobenzene, 2-nitrochlorobenzene-4-sulfonic acid, or 4-nitrochlorobenzene-2-sulfonic acid.

Substituted toluenes have been carefully nitrated to give nitrophenylmethanes which were then converted into the corresponding benzaldehydes upon treatment with manganese salts in neutral or faintly alkaline solutions (161).

Phenylacetic acids may be oxidized in small yields directly to the corresponding benzaldehydes (148, 159, 266); however, it is better to oxidize them with selenium dioxide in boiling xylene to the phenylglyoxylic acids and then decarboxylate these to the benzaldehydes (30).

E. Oxidation of olefinic side chains

Olefins, particularly propenylbenzenes, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$, are easily converted into benzaldehydes. Chemical methods have been more successful than elec-

trolytic processes. Propenylphenols are the most common type used in this method, since they are conveniently prepared by the allyl rearrangement of the *O*-allyl ethers and subsequent isomerization of the allylphenols to the propenylphenols (3, 286). The most widely employed oxidant and the one which is used for the technical production of substituted *o*- and *p*-hydroxybenzaldehydes is nitrobenzene in dilute alkali (28, 184, 199, 270).

The propenylbenzene, dilute sodium hydroxide solution, and nitrobenzene are mixed, allowed to react for several hours at moderate temperatures with or without pressure, and then the aldehyde is isolated by acidification and steam distillation, or by precipitation.

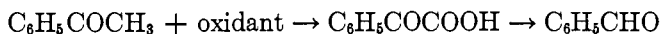
Several other substances have been used for the oxidation of the propenylbenzenes to aldehydes. Aqueous alkaline peroxides have given only small yields (87). Fair yields may be obtained with anhydrous *tert*-butyl alcohol or *n*-amyl alcohol solutions of hydrogen peroxide, using a catalyst of vanadium pentoxide or chromium trioxide (154). The use of an aqueous alkaline suspension of mercuric oxide in dilute alkali produces a 23 per cent yield of vanillin from eugenol (213). Good yields are attainable by using air with catalysts such as ultraviolet light or terpenes, but the process is slow and has not been developed for general use (46, 80). Sodium dichromate, in the presence of sulfanilic acid, gives 50–70 per cent yields (243). Oxidations with nitric acid, chromyl chloride, or by electrolysis have only resulted in low yields (88, 137, 164, 168, 212, 239).

Ozone, which has been employed by many workers, is not a practical agent for laboratory or technical use, since good yields are often obtained but are not reproducible (270). Hexane or acetic acid solutions of the substituted propenylbenzenes are treated with dilute ozone, whereby an explosive insoluble ozonide is produced, which is then reduced with potassium ferrocyanide or zinc dust in glacial acetic acid (90, 92, 176, 256). By forming an emulsion between the propenylbenzene and aqueous bisulfite tar formation is sometimes minimized and too, the bisulfite addition compound is isolated directly.

Bert has prepared various substituted ω -alkoxypropenylbenzenes in good yields by reacting 1,3-dichloropropene with substituted benzenes in the presence of aluminum chloride and isomerizing the ω -chloroallyl derivatives to cinnamyl ethers by the action of alcoholic potassium hydroxide. He then oxidized these ethers to the substituted benzaldehydes with ozone, a mixture of chromium trioxide plus potassium permanganate, or nitric acid (17).

Stilbenes, cinnamic acids, and other derivatives with olefinic side chains have been oxidized to benzaldehydes in yields which varied and ran as high as 86 per cent when sulfanilic acid was used to remove the aldehyde as it was formed (45, 91, 94, 130, 217, 265).

F. Oxidation of acetophenones



Acetophenones may be oxidized to phenylglyoxylic acids and these decarboxylated to the corresponding aldehydes by heating in *p*-(*N,N*-dimethyl)-

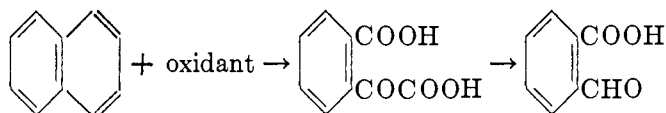
toluidine. This procedure is well illustrated by Mottern's preparation of vanillin from guaiacol (162).

Guaiacol was acetylated, and the ester was subjected to the Fries rearrangement to yield apocynin. This was oxidized with nitrobenzene in dilute alkali to vanilloylformic acid in 85 per cent yield, and the latter was decarboxylated to vanillin (as described above for phenylglyoxylic acids) in 98 per cent yield.

Other authors (244) have not been successful in repeating Mottern's synthesis. Thus, Barch failed to oxidize the apocynin with nitrobenzene to vanilloylformic acid, while Sharygrin and Bogacheva were unable to repeat Mottern's preparation of apocynin or its oxidation to vanilloylformic acid.

A 50 per cent yield of mesitylaldehyde has been obtained from acetylmesitylene by using cold alkaline permanganate (14).

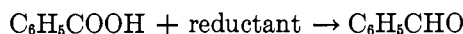
G. Oxidation of naphthalenes



A schematic method for the preparation of substituted *o*-carboxybenzaldehydes is to oxidize a chosen naphthalene derivative to a substituted phthalonic acid and decarboxylate this to the phthalaldehydic acid. The oxidation step is carried out in 40–50 per cent yields, using alkaline permanganate (29, 69, 82, 166, 174), and the resulting phthalonic acids are decarboxylated in 65 per cent yields by boiling in xylene, aqueous bisulfite solutions (33, 174, 279), or as described by Bouveault above (24). Charkravarti and Swaminathan (30) state that derivatives of homophthalic acid are more readily obtained than the required substituted naphthalenes and can be converted into the substituted phthalonic acids with selenium dioxide in xylene in 50–80 per cent yields.

Phthalaldehydic acid has also been obtained by the hydrolysis of 2-bromo- or 2-chloro-phthalide, which may be prepared by the halogenation of phthalide (205, 249). The yield of the phthalaldehydic acid from the phthalide runs up to 65 per cent.

H. Reduction of acids



(1) *Electrolytic reduction*: The electrolytic reduction of the carboxyl group to the formyl group has been carried out, but the process is not developed to give reproducible results. Mittler (152) reduced benzoic and salicylic acids to the aldehydes in 30–50 per cent yields, using a pool of mercury for a cathode and water–benzene emulsions to dissolve the aldehyde as it is formed. Tesh and Lowy (259) were able to obtain only a 20 per cent yield with this technique. Since the reduction of the aldehyde apparently occurs more easily than the reduction of the acid, some means should always be used to remove the aldehyde as it is produced. To do this Tesh and Lowy tried simultaneous steam distilla-

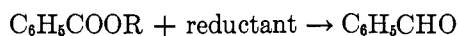
tion, extraction with benzene, or addition of *p*-toluidine, β -naphthylamine, or sodium bisulfite. Using sodium bisulfite in sodium sulfate solutions and a mercury-pool cathode they were able to attain 55 per cent yields of salicylaldehyde from salicylic acid. Cathodes of copper or lead were unsatisfactory, and sodium acetate, sodium chloride, calcium chloride, or potassium sulfate as electrolyte gave poorer results than sodium sulfate. The authors concluded that the process consisted in an electrolytic preparation of sodium amalgam with subsequent chemical reduction. Rutovskii and Korolev (225) repeated Tesh and Lowy's work but obtained only a 34 per cent yield. Kawada and Yosida (116) report an 80 per cent yield of salicylaldehyde from sodium salicylate as a result of a detailed study of electrode material, current density, electrolyte, added reagents, and diaphragm materials. They obtained the best yield when using a mercury-pool cathode, sodium sulfate as the electrolyte, and sodium bisulfite as the agent to remove the aldehyde from solution.

(2) *Chemical reduction*: Formic acid, under elevated pressures and temperatures and with the aid of proper catalysts, will reduce carboxylic acids to aldehydes in good yields (44, 225). Davies and Hodgson (44) used titanium dioxide at temperatures of 250–260°C. and obtained yields of aldehydes up to 92 per cent from substituted benzoic acids. If copper or nickel metal is used as the catalyst, further reduction takes place on the side chain or in the ring.

o-Hydroxybenzene- and *o*-hydroxynaphthalene-carboxylic acids are readily reduced to the corresponding aldehydes in 50–60 per cent yields with 2–3 per cent sodium amalgam in the presence of boric acid and a large excess of sodium chloride (280, 281). As in the electrolytic reductions, bisulfite or amine is added to remove the aldehyde as it is formed. Reduction will not take place without the addition of boric acid and sodium chloride. Complex salts of boron are thought to be formed between the adjacent hydroxyl and carboxyl groups, since *p*-hydroxybenzoic acids are not reduced in the process (271). Weil, Traun, and Marcel found that polyhydroxybenzoic acids give small yields of aldehydes, if any, while in the case of 5-aminosalicylic acid the amino group is removed from the nucleus and the ring and carboxyl group are reduced (281). Without the addition of an agent to remove the salicylaldehyde as it is formed, salicylic acid gives a 10 per cent yield of *o,o'*-dihydroxystilbene.

Very early Kolbe obtained traces of benzaldehyde from the treatment of benzoic acid with sodium amalgam (121). Baeyer (11) produced small amounts of benzaldehyde by the action of zinc dust on benzoic acid or phthalic acid. Calcium salts of carboxylic acids produce aldehydes when heated with calcium formate, but in the aromatic series only traces of the aldehyde are recovered (138). Thus, vanillin was produced in a 2 per cent yield from vanillic acid (211, 264)

I. Reduction of esters

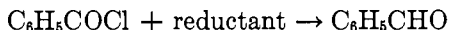


The electrolytic and chemical reduction of aromatic esters to aldehydes has shown little success, leading usually to the alcohol. Kharasch, Sternfeld, and

Mayo did obtain a 50 per cent yield of benzaldehyde, along with other products, from ethyl benzoate, using sodium dissolved in liquid ammonia (117).

The usual practice is to convert the esters to the acid hydrazides and reduce these as described below.

J. Reduction of acid chlorides

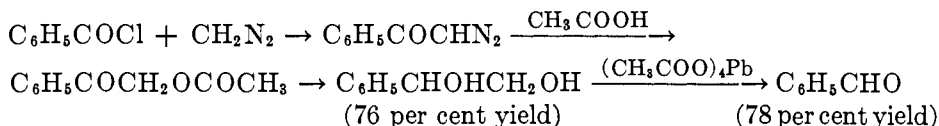


Baeyer attempted the reduction of acid chlorides to aldehydes with sodium amalgam in acetic acid and isolated only a small amount of the aldehydes, in addition to several other products (12). Since then, others have tried various means of reduction but always with unsatisfactory results (122, 210, 233). Later, Rosenmund succeeded in obtaining high yields, sometimes quantitative, by using hydrogen with a palladium or nickel catalyst (221, 223).

Hydrogen is bubbled through a refluxing solution of the acid chloride and the catalyst until the theoretical amount of hydrogen chloride has been evolved; then the mixture is acidified and the aldehyde isolated by steam distillation (98).

To arrest the reduction at the aldehyde stage, a quinoline-sulfur poison is added. Xylene or tetralin is found to serve best as the solvent (299), while without a solvent the yields are seldom greater than 10 per cent. Hydroxyl groups must be protected; this is usually done by acetylation or carbomethoxylation. Phosphorus- and sulfur-containing side products that are formed in the preparation of the acid chlorides prevent or greatly hinder the reaction, and therefore must be removed (68, 298). Dialdehydes are easily obtainable from diacid chlorides.

Grundman describes a procedure for going from acid chlorides to aldehydes in about 50 per cent yields (84). The acid chlorides are treated with diazomethane



in a dry solvent, and the products refluxed with acetic acid to split off nitrogen and produce ω -acetoxybenzophenones in 80–90 per cent yields. These are reduced with sodium amalgam or aluminum amalgam in ether or, preferably, with aluminum isopropoxide in isopropyl alcohol, and the substituted β -hydroxy- β -phenylethanols are oxidized with lead tetraacetate to the substituted aldehydes.

Another indirect route of preparing aldehydes from acid chlorides was used by Mauthner, who thereby obtained yields up to 70 per cent (142). He transformed the acid chlorides into the acid cyanides, hydrolyzed the acid cyanides to the phenylglyoxylic acids, and then decarboxylated the latter to the aldehydes by heating them in aniline.

K. Reduction of nitriles



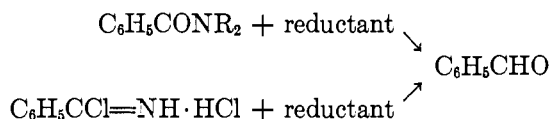
Stephen worked out a method for preparing aldehydes from nitriles in yields that are usually greater than 90 per cent (258, 289). Hydrogen chloride is

bubbled through a dry ether solution of the nitrile and anhydrous stannous chloride during a period of several hours. The resulting imidochloride may be isolated, or reduced directly to the aldehyde. If necessary, chloroform may be added to the ether to aid solution of the nitrile.

The reaction is general except for steric hindrance due to groups ortho to the nitrile group. Thus, α -naphthonitrile, *o*-tolunitrile, and *o*-nitrobenzonitrile give negligible yields of the aldehydes (258, 288, 289). Nitro groups do not interfere with the success of the reaction; however, they may be reduced if sufficient stannous chloride is used.

Another method for reducing benzonitriles to the corresponding aldehydes is that of Henle, which gives yields up to 95 per cent (95). It consists in converting the nitriles into the imido-esters, reducing the latter with sodium amalgam in the presence of phenylhydrazine, and hydrolyzing the resulting phenylhydrazones to liberate the aldehydes. Semicarbazide or substituted hydrazines may be used in place of phenylhydrazine, but aniline gives rise to many side products; without the addition of the amines the yields are very low. Other reducing agents, such as zinc dust, tin, stannous chloride, or magnesium, are unsatisfactory.

L. Reduction of amides and imidochlorides



The direct reduction of amides to aldehydes has always given poor results (85, 107, 290), the best yield being only 20–30 per cent (150). An alternative scheme for changing amide groups into formyl groups is through the reduction of the imidochloride which is prepared from the amide by treatment with phosphorus pentachloride or thionyl chloride. Staudinger (257) used magnesium in ethyl acetate to reduce the imidochloride and obtained 40–50 per cent yields. Later, Sonn and Muller reported the method of bubbling hydrogen chloride through an ether solution of the imidochloride and anhydrous stannous chloride to reduce the imidochloride and then hydrolyzing the product to isolate the aldehyde (255). Over-all yields from the amides averaged 50–60 per cent. Hydroxyl groups are protected by carbomethoxylation. As in Stephen's reaction above, groups ortho to the imidochloride group hinder the reaction. Anhydrous chromous chloride may be substituted for the stannous chloride, but it is more difficult to prepare and, unless it is dry, hydrolysis of the imidochloride takes place faster than its reduction (26).

M. Reduction of hydrazides

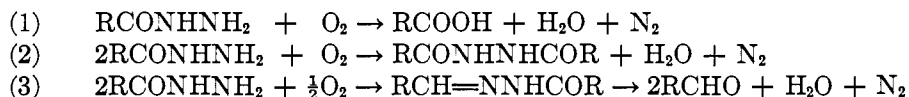


As stated above, esters are not reduced to aldehydes directly but may be converted into their hydrazides, which may then be reduced to the aldehydes.

McFadyen and Stevens (147) worked out a general procedure, giving 50–65 per cent yields, and the method is found to apply to most substituted benzhydrazides (93, 165, 167, 269).

The ester is converted into the hydrazone, which is then treated with benzenesulfonyl or *p*-toluenesulfonyl chloride, and the product is decomposed by heating with sodium carbonate in ethylene glycol at 160°C. to produce the aldehyde.

According to Kalb and Gross (112), acid hydrazides react in three ways:

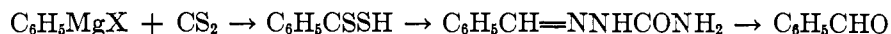


As indicated in equations 2 and 3, Curtius and Struve (41) oxidized benzhydrazide with iodine or mercuric oxide to produce dibenzoylhydrazine and benzalbenzoylhydrazine, and Darapsky (42) used sodium hypochlorite to obtain a low yield of benzaldehyde. Kalb and Gross tried several oxidants and found that, by treating various substituted benzhydrazides with potassium ferricyanide in excess ammonium hydroxide, the corresponding aldehydes are produced in yields up to 65 per cent.

N. Aldehydes from Grignard reagents

At least ten types of compounds which react with aromatic Grignard reagents to produce aldehydes are recorded in the literature. These include hydrogen cyanide, alkyl orthoformates, formate esters, formic acid, copper formate, disubstituted formamides, methyl isocyanide, ethoxymethylaniline, carbon disulfide, and chloral.

Wuyts developed the method of using carbon disulfide. The Grignard reagents are treated with carbon disulfide to produce the dithio acids, these are digested with a pyridine solution of semicarbazide hydrochloride, and the resulting semicarbazone is hydrolyzed to liberate the aldehyde (294, 295, 296).



When phenylhydrazine or hydroxylamine was tried in place of the semicarbazide, several side reactions were found to occur. Wuyts's only mention of the yield from the aromatic halide was for *p*-dibromobenzene, in which case the yield was 46 per cent. The yields based on the amount of aldehyde produced from the dithio acid average about 80 per cent.

Savariau reacted chloral with Grignard reagents to produce phenyltrichloromethylcarbinols, hydrolyzed these with aqueous alkali to liberate mandelic acids, and decarboxylated the latter by heating them with dilute potassium carbonate, producing the substituted benzaldehydes (232).

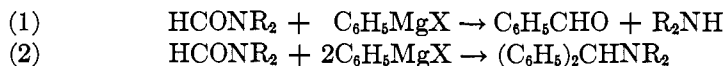
Sachs and Loewy (229) treated Grignard reagents with methyl isocyanide to produce aldehydes; later, Gilman and Hechert found that of the alkyl isocyanides, only methyl isocyanide will serve for the reaction (81). Hinkel and Dunn prepared benzaldehyde by addition of phenylmagnesium bromide to an ether solution of bimolecular hydrogen cyanide and subsequent hydrolysis (100). Methyl

and amyl formates (15), formic acid (103, 297), and copper formate (103) have been used to convert Grignard reagents into aldehydes in yields of 30 per cent or less.

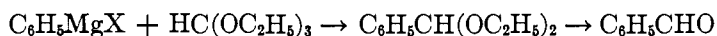
Bouveault introduced the use of aryl- or alkyl-disubstituted formamides to convert Grignard reagents to aldehydes in yields varying between 30 and 70 per cent (24, 25).



It is found that, depending upon the substituted amide, the reaction follows one of two different courses (105, 144, 145, 272):

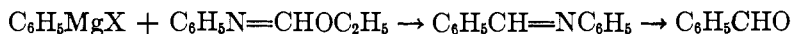


Bodroux (21), Tschitschibabin and Gattermann (267), and Maffezzoli (76) independently observed that ethyl orthoformate reacts with Grignard reagents to produce aldehydes and secondary alcohols.



If excess ethyl orthoformate is used, the product consists mainly of the aldehyde. The pure acetal may be recovered by fractionation or hydrolyzed directly to the aldehyde. Methyl orthoformate has also been used to convert Grignard reagents to the corresponding aldehyde in 55-70 per cent yields (228). Yields reported by different authors varied so widely that Smith and Bayliss experimented to determine the conditions for obtaining the maximum yield, which averaged about 60-70 per cent (251).

Monier and Williams obtained aldehydes from Grignard reagents in yields of 30-60 per cent by using ethoxymethyleneaniline (160).



Of the above methods, Smith and Nichols assumed that those which use ethyl orthoformate, ethoxymethyleneaniline, and carbon disulfide give the most reproducible results and proceeded to compare these three (252). Their results indicated that carbon disulfide, ethyl orthoformate, and ethoxymethyleneaniline give increasing yields, respectively; owing to the unavailability of the last substance, they concluded that ethyl orthoformate is the best reagent to use with Grignard reagents for the preparation of aldehydes.

O. Aldehydes from benzophenone oxime



Cuisa (39) used a unique procedure of obtaining benzaldehyde from benzophenone oxime by refluxing it with phosphorus pentasulfide in carbon disulfide, boiling the resulting thiobenzanilide in aqueous alkaline silver nitrate to produce benzanilide, and treating the latter with zinc dust in 20 per cent potassium hydroxide solution. He isolated benzaldehyde in a 42 per cent over-all yield.

TABLE 2
Yields in the preparation of aldehydes

METHOD	HALO-GEN	NITRO	SULFO	CYANO	HYDRO-XYL	ALKO-XYL	ALKYL OR HYDRO-GEN	POLY-CYCLIC	ACYL	AMINO
Gattermann and Koch reaction.....							60-80			
Gattermann reaction.....					50-100	70-100	75-85	60-90		
Reimer-Tiemann reaction....					30-50			50-80		
Reactions with hexamethylene tetramine.....					15-20			20-25		35-45
Reactions with <i>N</i> -methylformanilide.....						70-85		60-90		50-80
Reactions with formaldehyde..					40-50			40-60		40-50
Reactions with chloral.....					40-60					
Reactions with alloxan.....	Yields were not located									
Reactions with mesoxalates...					50-80					50-80
Reactions with oxalyl ester acid chlorides.....					40-60	40-60	40-60			
Reactions with sodium glyoxylate.....					50-70					
Reactions with mercury fulminate.....					60-80		50-60			
Reactions with chloromethylene dibenzoate.....						60-80	30-50			
Reactions with isatin chloride..					30			30		
Reactions with organolithium compounds.....						50-60	50-60			
Naphthaldehydes from benzofurans and acrolein.....								50		
Oxidation of saturated side chains.....	50									80
Oxidation of benzyl alcohols...	60									90
Oxidation of benzyl halides....	50									80
Oxidation of benzylanilines, benzylamines, <i>N</i> -alkylanilines, phenylnitromethanes, and phenylacetic acids.....	30									50
Oxidation of olefinic side chains.....	50									70
Oxidation of acetophenones...	Method not standardized									
Oxidation of naphthalenes....	25									35
Reduction of acids.....					50-60		50-90	50-90		
Reduction of esters.....	Method not standardized									
Reduction of acid chlorides....	60-90	40-50				60-90	60-90	60-90	60-90	
Reduction of nitriles.....	60									90
Reduction of amides and imidochlorides.....	50									60
Reduction of hydrazides.....	50									65
Aldehydes from Grignard reagents.....	30									50
Aldehydes from benzophenone oxime.....	Method not standardized									

IV. NON-PREPARATIVE REACTIONS

There are a number of reactions by which small amounts of aldehydes are produced, but they should not be considered as preparative methods. Among these are the following:

Benzil, when reacted with alcoholic potassium cyanide, produces the ester of benzoic acid and benzaldehyde (111).

Benzyl sulfoxide, when treated with a chloroform solution of hydrogen chloride, produces traces of benzaldehyde (97).

Aldehydes have been isolated by refluxing phenols with ethyl orthoformate and a non-aqueous base and hydrolyzing the acetal produced with mineral acid. Upon refluxing *o*-hydroxyphenylmercuric chloride with ethyl orthoformate and then hydrolyzing the product in dilute acid, a small amount of salicylaldehyde is obtained (271).

Aluminum chloride-catalyzed condensations of substituted benzenes with alkyl and aryl carboxylic acids produce derivatives of acetophenone and benzophenone, respectively, in good yields. In accordance with this, formic acid should lead to the aldehyde but only a 1-2 per cent yield has been attained (83). Probably the aldehyde reacts further as soon as it is formed.

Aldehydes are among the pyrolysis products of several compounds (19, 66, 67, 119, 126, 135).

Electrolytic processes are known to yield traces of aldehydes (13, 27, 155, 277).

V. YIELDS IN THE SYNTHESIS OF ALDEHYDES

In table 2 are listed the average per cent yields that may be expected from the different methods when the various substituents listed at the top are attached to the benzene ring. Under the heading "polycyclic" are listed the yields from any of the methods when applied to polycyclic compounds in general, without regard to substituents. Methods which can be employed only for phenol and its substitution products are listed under the column headed "hydroxyl." With this exception, blank spaces indicate that the method is not recommended in the case of such substituents. Extended yields imply that the method is general and inapplicable only where obvious chemical reactions will occur between the reactants and the substituents.

The author wishes to acknowledge his indebtedness to Professor Melvin Calvin, of the University of California, whose numerous suggestions were followed in carrying out investigations of several of the methods described in this paper, and also to Professor R. Percy Barnes, of Howard University, for his kindness in reviewing the manuscript.

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