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9

Aldehydes

CONTENTS

CONTENTS *(continued)*

A large number of methods exist for the preparation of aldehydes, many of which are very limited in their scope. The more general methods are given here. An excellent review on the synthesis of aromatic aldehydes has been published.[120]

140. Formylation with Carbon Monoxide (Gattermann-Koch)

$$ArH + CO + HCl \xrightarrow{AlCl_3\text{-}CuCl_2} ArCHO$$

Aromatic aldehydes are prepared by passing carbon monoxide and dry hydrogen chloride through an ether or nitrobenzene solution of an aromatic hydrocarbon in the presence of a catalyst, commonly aluminum chloride with cuprous chloride as a carrier. The process is illustrated by the synthesis of *p*-tolualdehyde (51%).[70] A convenient procedure for obtaining an equimolar mixture of anhydrous hydrogen chloride and carbon monoxide consists in dropping chlorosulfonic acid on formic acid,[266] viz.,

$$HSO_3Cl + HCO_2H \longrightarrow HCl + CO + H_2SO_4$$

In most reactions at atmospheric pressure the yields are about 30–50%, whereas at a high pressure of carbon monoxide the yields are 80–90%.[73] This method is particularly suitable for the reaction of mono- and polyalkylbenzenes. It is not applicable to phenols and aromatic ethers. The reaction has been considered in detail.[243]

141. Formylation with Cyano Compounds (Gattermann)

$$ArH + HCN + HCl \xrightarrow{ZnCl_2} ArCH{=}NH \cdot HCl \xrightarrow{H_2O} ArCHO$$

A mixture of hydrogen cyanide and hydrogen chloride in the presence of zinc chloride reacts with an aromatic compound to form an aldimine hydrochloride which on hydrolysis produces the corresponding aldehyde.

The reaction can be carried out more conveniently and in equally good yields by substituting zinc cyanide for the hydrogen cyanide (70–90%).[71,72] Potassium chloride impurity in this catalyst is necessary.[75] Sodium cyanide has also been used.[79] With these modifications, phenols[71] and ethers[72] as well as hydrocarbons[74,78,79] react (cf. method 140).

142. Formylation with N-Methylformanilide

$$ArH + C_6H_5N(CH_3)CHO \xrightarrow{POCl_3} ArCHO + C_6H_5NHCH_3$$

This synthesis is applicable to many aromatic compounds, including alkoxyl or N,N-dimethylamino derivatives of benzene[103] and naphthalene,[101] naphthols,[106] indole,[105] and certain reactive hydrocarbons, namely, anthracene,[101] 1,2-benzanthracene,[102] 3,4-benzpyrene,[102] and pyrene.[104] The high-melting polynuclear hydrocarbons react best in the presence of a solvent, such as *o*-dichlorobenzene. For example, a solution of anthracene, methyl formanilide, and phosphorus oxychloride in *o*-dichlorobenzene is heated 1 hour at 90–95°; then an aqueous solution of sodium acetate is added, and the solvent and N-methylaniline are removed by steam distillation. The solid residue is readily purified to yield 9-anthraldehyde (84%).[101] With liquid or low-melting compounds a solvent is not required.

The conversion of thiophene and its derivatives to the corresponding aldehydes by this procedure has been extensively studied, the yield of 2-thiophenealdehyde being 76%.[260]

unsym-Diarylethylenes react in a similar manner to yield unsaturated aldehydes, $Ar_2C{=}CHCHO$.[202]

Other catalysts and reagents have been used. In the presence of aluminum chloride, 2-naphthol reacts with formamide to give 2-naphthol-1-aldehyde (45%).[106]

143. Formylation of Phenols with Chloroform (Reimer-Tiemann)

$$C_6H_5OH + CHCl_3 \xrightarrow[HCl]{NaOH;} o\text{- and } p\text{-}HOC_6H_4CHO$$

Substituted phenols react with chloroform and alkali in alcohol solution to yield *o*- and *p*-hydroxybenzaldehydes. The yields are often less than 50%, the *para*- isomer predominating.[81] The procedure involves heating an alkaline ethanolic solution of the reactants for several hours, followed by acidification and isolation of the product by steam distillation or crystallization. An example is the synthesis of 2-hydroxy-1-naphthaldehyde (48%).[80]

144. Formylation of Phenols (or Amines) with Hexamine (Duff)

$$C_6H_5OH + (CH_2)_6N_4 \longrightarrow o\text{-}HOC_6H_4CH{=}NCH_3 \longrightarrow o\text{-}HOC_6H_4CHO$$

This reaction is readily accomplished by heating the phenolic compound at 150–160° for 10 to 30 minutes with a mixture of glycerol, boric acid, and hexamine. The phenolic aldehyde is liberated by acidification and steam distillation. By this general procedure, sixteen phenolic aldehydes have been prepared. Although the yields are only 15–20%, the method requires little time and furnishes a reasonably pure product which is the *ortho* isomer[96] (cf. method 143).

The method has been extended to the formation of *p*-dialkylaminobenzaldehydes in 35–45% yields.[99]

145. Hydroformylation of Unsaturated Compounds

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{Catalyst}]{\text{Pressure}} RCH_2CH_2CHO$$

Addition of carbon monoxide and hydrogen to an alkene linkage in the presence of cobalt catalysts gives aldehydes in an average yield of 50%.[190] The reactions may be carried out in the usual hydrogenation apparatus. The poisonous properties of carbon monoxide and cobalt carbonyls call for considerable care. Compounds made by hydroformylation include cyclopentanealdehyde from cyclopentene (65%), β-carbethoxypropionaldehyde from ethyl acrylate (74%), and ethyl β-formylbutyrate from ethyl crotonate (71%).

146. Formylation of Ketones with Formic Esters

$$CH_3COCH_2CH_3 \xrightarrow[\text{Na}]{HCO_2C_2H_5} CH_3COCH(CHO)CH_3$$

Acylation of ketones having reactive methylene groups by higher esters has been shown to be an excellent method for preparing β-diketones (method 203). If the acylating ester is an alkyl formate, then a keto aldehyde is formed (50–80%).[171–174] The formylation is simply brought about by adding sodium metal to a mixture of the ketone and ester in anhydrous ether. Oftentimes, the product is isolated as the sodium salt of the hydroxymethylene form. The point of attack is unpredictable in unsymmetrical ketones, CH_3COCH_2R.[173, 174]

147. Interaction of Halomethyl Compounds and Hexamine (Sommelet)

$$ArCH_2X \xrightarrow{(CH_2)_6N_4} [ArCH_2(CH_2)_6N_4]^+Cl^- \xrightarrow{H_2O} ArCHO$$

Substituted benzyl halides react with hexamine in boiling alcohol to form addition compounds which decompose on heating with water to give aldehydes.[85–90] An excellent discussion of the reaction has been presented, and improvements in the conditions have been made.[244] Aqueous acetic acid (1 : 1) is recommended as solvent for the entire process, and there is no need to isolate the intermediate salt. The procedure is illustrated by the synthesis of 1-naphthaldehyde (82%).[245] In other instances, the addition compound is first prepared in chloroform solution, isolated, and then decomposed with water or dilute acetic acid, as in the synthesis of 2-thiophenaldehyde (53%).[84]

The reaction is applicable to the formation of *m*- and *p*-dialdehydes, but not the *ortho* isomer, from the *bis*-(chloromethyl)-benzenes,[246] as well as aldehyde esters, e.g., *p*-carbomethoxybenzaldehyde,[85] and halo aldehydes, e.g., 1-bromo-2-naphthaldehyde.[87]

A somewhat similar reaction is the conversion of substituted benzylamines to the corresponding benzaldehydes by treating their formaldehyde condensation product with hexamine.[97]

148. Interaction of Benzyl Halides and Sodium 2-Propanenitronate

$$ArCH_2Br + [(CH_3)_2CNO_2]^-Na^+ \longrightarrow ArCHO + (CH_3)_2C{=}NOH + NaBr$$

A general procedure for the conversion of *p*-substituted benzyl halides to the corresponding benzaldehydes consists in treating the halide with sodium 2-propanenitronate suspended in absolute ethanol. The resulting instable nitronic ester breaks down into acetoxime and the carbonyl compound. The yields are in the range 68–77% for benzaldehydes having a methyl, bromo, carbomethoxyl, cyano, or trifluoromethyl group in the *para* position. However, *p*-nitrobenzyl chloride undergoes C-alkylation to furnish the stable substituted nitropropane, $p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2$.[261] The reaction has been extended to the synthesis of *o*-tolualdehyde (73%).[262]

149. Decomposition of Arylsulfonohydrazides

$$ArCONHNH_2 \xrightarrow{C_6H_5SO_2Cl} ArCONHNHSO_2C_6H_5 \xrightarrow{Na_2CO_3} ArCHO$$

Aromatic and heterocyclic aldehydes have been prepared from hydrazides, *via* the arylsulfonyl derivative, in 50–65%[123] and 20–40% yields,[124] respectively; the method fails in the aliphatic series. The hydrazide is treated with benzenesulfonyl chloride in pyridine, and the subsequent product is isolated by precipitation with water and decomposed by heating with sodium carbonate in ethylene glycol or glycerol at 160°.

Benzhydrazides in small quantities have been oxidized to the aldehydes with potassium ferricyanide in excess ammonium hydroxide (30–60%).[127]

150. Cleavage of Schiff Bases

$$ArCH{=}NR + H_2O \longrightarrow ArCHO + RNH_2$$

Several preparations of aldehydes have been developed that involve the formation and cleavage of Schiff bases. The condensation of anilines or phenols with formaldehyde and *p*-nitrosodimethylaniline leads to such intermediates. These substances can be isolated and converted by an exchange reaction with formaldehyde in acetic acid to the corresponding aldehydes. *p*-Dimethylaminobenzaldehyde is made in this manner in 59% yield.[187]

$$(CH_3)_2NC_6H_5 \xrightarrow[CH_2O]{p\text{-}(CH_3)_2NC_6H_4NO} p\text{-}(CH_3)_2NC_6H_4CH{=}NC_6H_4N(CH_3)_2 \xrightarrow{CH_2O}$$

$$p\text{-}(CH_3)_2NC_6H_4CHO$$

When a methyl group on an aromatic nucleus is activated by a nitro group in the *ortho* or *para* position, condensation with nitrosobenzenes can occur to give a Schiff base; subsequent hydrolysis furnishes the aldehyde. An example is the synthesis of 2,4-dinitrobenzaldehyde (32%).[186]

$$(NO_2)_2C_6H_3CH_3 \xrightarrow{p\text{-}(CH_3)_2NC_6H_4NO} (NO_2)_2C_6H_3CH{=}NC_6H_4N(CH_3)_2 \xrightarrow{H_2O}$$

$$(NO_2)_2C_6H_3CHO$$

Condensation of diethylaniline and formaldehyde in the presence of sulfanilic acid gives the structure

$$p\text{-}(CH_3CH_2)_2NC_6H_4CH_2NCH_6H_4SO_3H,$$

which can be isolated and oxidized with potassium dichromate to the benzylidene compound; the latter on alkaline hydrolysis gives *p*-diethylaminobenzaldehyde in 50% yield.[188]

Imino chlorides, which are readily prepared by the action of phosphorus pentachloride on anilides, are reduced by anhydrous stannous chloride to imino intermediates which on hydrolysis yield aromatic aldehydes (50–90%); applications in the aliphatic series are poorly described.[128–132]

$$RCONHC_6H_5 \xrightarrow{PCl_5} RC(Cl){=}NC_6H_5 \xrightarrow[HCl]{SnCl_2} RC(H){=}NC_6H_5 \xrightarrow{H_2O} RCHO$$

In most cases, the crude imino chloride is treated directly by adding it to a solution of stannous chloride saturated with dry hydrogen chloride; the aldehyde is then liberated by steam distillation. The procedure is illustrated by the synthesis of *o*-tolualdehyde (70%).[128] Imino chlorides have also been prepared by treatment of ketoximes with phosphorus pentachloride, viz., $RR'C{=}NOH \longrightarrow RCCl{=}NR'$, in preparations of benzaldehyde and *p*-chlorobenzaldehyde (70–85%).[133] As in the Stephen reaction (method 164), groups *ortho* to the imino chloride group hinder the reaction.

Schiff bases from other sources furnish aldehydes (methods 166 and 170).

151. Hydrolysis of *gem*-Dihalides

$$ArCH_3 \xrightarrow{X_2} ArCHX_2 \xrightarrow{H_2O} ArCHO$$

Toluenes substituted with chloro, bromo, fluoro, or cyano groups can be dichlorinated or dibrominated and the resulting benzal halides hydrolyzed directly to the corresponding aldehydes in the presence of calcium carbonate or sulfuric acid (50–70%).[135,136] *o*- and *p*-Xylene have been converted to the corresponding dialdehydes.[139,140] In the halogenation of certain cresols, the carbonate or acetate esters are used in order to prevent nuclear halogenation.[141,216]

Aliphatic *gem*-dihalides require more vigorous conditions for hydrolysis than do the benzal halides. Examples are found in the treatment of certain 1,1-dichloroalkanes, like 1,1-dichloro-3-methylbutane and 1,1-dichloro-3,3-dimethylbutane, with water and, in some cases, magnesium oxide for 4 hours at 200–300°. The aldehydes are formed in 60–96% yields (cf. method 222).

152. Interaction of Pyridinium Salts and *p*-Nitrosodimethylaniline

$$ArCH_2COCH_2Cl \xrightarrow{Pyridine} [ArCH_2COCH_2\overset{+}{N}C_5H_5]Br^-$$

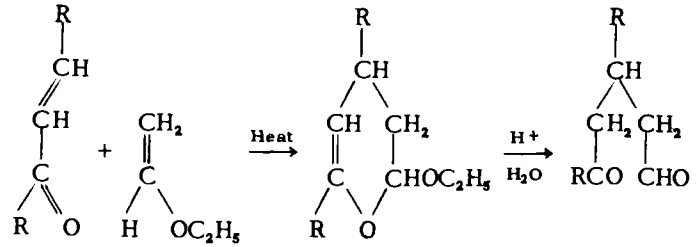
$$\downarrow (CH_3)_2NC_6H_4NO$$

$$ArCH_2COCHO \xleftarrow[H_2O]{H^+} ArCH_2COCH{=}NOC_6H_4N(CH_3)_2$$

Compounds containing reactive halogens ($ArCH{=}CHCH_2X$ or $ArCOCH_2X$) readily form pyridinium salts. Rearrangement of these prod-

ucts with *p*-nitrosodimethylaniline to a nitrone followed by hydrolysis with acid gives α,β-unsaturated aldehydes or substituted glyoxals.[189] Substituted benzyl halides, $ArCH_2X$, undergo the series of reactions to give the corresponding aldehydes, ArCHO. Terephthaldehyde is made in this way in a 70% over-all yield.[189]

153. Hydrolysis of 2-Alkoxy-3,4-dihydro-1,2-pyrans



Hydrolysis of 2-alkoxy-3,4-dihydro-1,2-pyrans with dilute hydrochloric acid furnishes a convenient synthesis of glutaraldehyde (R = H) and other 1,5-dicarbonyl compounds. The starting materials are obtained by the 1,4-addition of vinyl ethers to α,β-unsaturated carbonyl compounds. The wide selection of diene systems includes acrolein, crotonaldehyde, methacrolein, cinnamaldehyde, β-furylacrolein, methyl vinyl ketone, benzalacetone, and benzalacetophenone. Ethyl vinyl ether is preferred as the dienophile. The yields in the cyclization step are in the range of 25–87% and in the subsequent hydrolysis step, 59–85%.[265]

154. Hydrolysis of Aldehyde Derivatives

$$RCH{=}NOH + C_6H_5CHO \longrightarrow RCHO + C_6H_5CH{=}NOH$$

Oftentimes, aldehydes are isolated and purified as their derivatives, and their regeneration is then of importance (cf. method 195). The fission of the oxime, semicarbazone, hydrazone, etc., may be accomplished by acid hydrolysis or by an exchange of the nitrogenous moiety with another carbonyl compound, such as benzaldehyde, for which it has a greater affinity.

Semicarbazones of volatile aldehydes may be hydrolyzed by steam distillation in the presence of phthalic anhydride.[107] A synthetic route for aromatic aldehydes involves the hydrolysis of semicarbazones which have been prepared by the interaction of dithio acids and semicarbazide hydrochloride in pyridine solution.[17, 28]

$$ArCSSH \xrightarrow{H_2NNHCONH_2} ArCH{=}NNHCONH_2 \xrightarrow{H_2O} ArCHO$$

The hydrolysis of succinaldehyde dioxime must be carried out with care because of the instability of the dialdehyde. This step has been accomplished in 60% yield by treating the dioxime with ethyl nitrite in dioxane or with sodium nitrite in dilute sulfuric acid.[108]

The adducts formed from amine bisulfites and aldehydes are readily purified by crystallization from organic solvents and, like the sodium bisulfite addition products, are readily decomposed by the action of dilute acids.[122]

Acetals are readily hydrolyzed by dilute mineral acids; however, the yields are not always satisfactory. These substances are not affected by alkaline reagents. The sensitive *dl*-glyceraldehyde acetal is converted to its aldehyde in 80% yield by the action of dilute sulfuric acid under mild conditions.[238] Other procedures are illustrated by the treatment of acetals which are formed by the interaction of Grignard reagents and orthoformic esters (method 165).

Olefinic aldehydes have been prepared by bromination of the diethylacetal derivatives followed by dehydrobromination (cf. Acetals and Ketals); the unsaturated aldehydes are readily liberated by mild acid treatment of their acetals.[6] *Alkoxy aldehydes* have also been synthesized through acetal intermediates, which in turn are prepared from sodium alkoxides and bromoacetals.[111]

α-Hydroxy aldehydes have been prepared by hydrolysis of the oximes resulting from the action of Grignard reagents on certain isonitroso ketones.[175]

$$RCH_2COCH{=}NOH \xrightarrow{R'MgX} R'RCHC(OH)CH{=}NOH \xrightarrow{H_2O} R'RCHC(OH)CHO$$

155. Oxidation of Aromatic Side Chains

$$ArCH_3 \xrightarrow[(CH_3CO)_2O]{CrO_3} ArCH(OCOCH_3)_2 \xrightarrow[H_2O]{HCl} ArCHO$$

Oxidation of the methyl group in substituted toluenes with chromium trioxide in acetic anhydride forms crystalline diacetates, which are stable to further oxidation. These compounds are readily hydrolyzed in acid solution to the corresponding aldehydes (40–50% over-all).[149, 150] The procedure is generally applicable to the preparation of benzaldehydes carrying nitro, halo, and cyano substituents.

Other oxidative procedures have been described. The heterogeneous liquid-phase oxidation of toluene with manganese dioxide in 65% sulfuric acid is important in the production of benzaldehyde and salicylaldehyde. An example of its application in the laboratory is found in the preparation of 3,5-dimethylbenzaldehyde (48%) from mesitylene.[153] In a comparison

of other oxidants, chromyl chloride is outstanding; however, it must be employed with care. The hydrocarbon is added slowly to a chloroform solution of this reagent, and the addition complex is carefully decomposed with dilute sulfurous acid to give the aldehyde. Yields range up to 80% (Etard reaction).[215] The internal oxidation-reduction of nitrotoluenes can be brought about by refluxing with alkaline sodium polysulfide, e.g., *p*-aminobenzaldehyde from *p*-nitrotoluene (75%).[156]

Benzyl halides have been oxidized directly with selenium dioxide[91] or copper nitrate.[92]

156. Oxidation of Olefinic Compounds

$$RCH{=}CH_2 \xrightarrow[H_2O]{O_3;} RCHO + CH_2O$$

Aldehydes result from the decomposition of certain ozonides. The technique is similar to that used for the preparation of ketones (method 182). High yields are obtained by catalytic hydrogenation of the ozonides.[114] This step coupled with Grignard and dehydration reactions has been used as a procedure for the degradation of an aldehyde to its next lower homolog, viz.,

$$RCH_2CHO \xrightarrow[H_2O]{C_6H_5MgX;} RCH_2CHOHC_6H_5 \xrightarrow{-H_2O} RCH{=}CHC_6H_5 \xrightarrow[H_2]{O_3;} RCHO$$

Dialdehydes result when cyclic olefins are ozonized.[115] Improved directions for the ozonolysis of unsaturated esters in glacial acetic acid to yield aldehyde esters have been given.[116] The same procedure is applied to the preparation of aliphatic aldehydes containing halo,[117] hydroxyl,[118] and ether groups.[121]

Oxidation of olefinic side chains with ozone to form aromatic aldehydes gives erratic results and therefore other oxidants are employed.[120] For this purpose, the most widely used oxidant is nitrobenzene in dilute alkali; the mixture is allowed to react at moderate temperatures for several hours. Thus, hydroxy benzaldehydes may be obtained from propenylphenols, which in turn are readily prepared by the Claisen rearrangement of O-alkyl ethers (method 100). Sodium dichromate in the presence of sulfanilic acid, which removes the aldehyde as it is formed, gives yields as high as 86% in the oxidation of isoeugenol and isosafrole.[267]

157. Oxidation of Methyl Ketones by Selenium Dioxide

$$ArCOCH_3 \xrightarrow{SeO_2} ArCOCHO$$

The preparation of certain substituted benzils by treatment of aryl benzyl ketones with selenium dioxide is discussed later (method 183). If a methyl ketone is treated under these conditions, the methyl group is oxidized to an aldehyde group.[176] The reaction is carried out by refluxing a mixture of selenium dioxide and ketone in dioxane or alcohol for several hours. Preparative details are found in the procedures for phenylglyoxal (72%)[177] and glyoxal (74%);[178] the latter is isolated as its bisulfite derivative.

4-Methylquinoline and 1-methylisoquinoline, which have reactive methyl groups, are converted to quinoline-4-aldehyde (61%) and isoquinaldehyde (42%), respectively, by means of this reagent.[183,184]

158. Oxidation of Primary Alcohols

$$RCH_2OH \xrightarrow{(O)} RCHO$$

Controlled oxidation of a primary alcohol with a mixture of sulfuric and chromic acids gives the corresponding aldehyde. In the preparation of low-molecular-weight aldehydes, an aqueous medium is used and the product is removed by steam distillation, thus preventing further oxidation. This procedure is well illustrated by the preparation of propionaldehyde (49%)[1] and isovaleraldehyde (60%).[2] Certain benzyl alcohols are dissolved in aqueous acetic acid for chromic acid oxidation.[4] *Olefinic aldehydes* are produced by a rapid low-temperature (5–20°) oxidative procedure, as illustrated by the preparation of 2-heptenal (75%) from 2-heptenol.[10] *Aldehyde ethers* such as methoxyacetaldehyde and ethoxyacetaldehyde have been prepared by the chromic acid oxidation of the corresponding alcohols in 17% and 10% yields, respectively.[11]

Aldehydes have been formed from alcohols by the use of other oxidizing agents. Dihydroxyacetone has been oxidized with excess cupric acetate to *hydroxypyruvic aldehyde* in 87% yield.[12] *p*-Cyanobenzyl alcohol treated at 0° with a chloroform solution of nitrogen tetroxide gives practically pure *p*-cyanobenzaldehyde (90%).[13] Aromatic alcohols containing nitro groups have been oxidized to the corresponding *nitro aldehydes* with concentrated nitric acid, e.g., *o*- and *p*-nitrobenzaldehydes (80–85%).[14] *m*-Nitrobenzenesulfonic acid in basic media has been used for the oxidation of substituted benzyl alcohols, most satisfactorily for the water-soluble phenolic benzyl alcohols.[217] Selenium dioxide, or less effectively tellurium dioxide, oxidizes benzyl alcohol slowly to benzaldehyde.[218]

The Oppenauer reaction has been applied in the conversion of aliphatic and aromatic alcohols.[269] The alcohol, a high-boiling aldehyde (such as cinnamaldehyde), and aluminum alkoxide catalyst are heated, and the volatile aldehyde is removed as it is formed.

$$RCH_2OH + R'CHO \xrightarrow[\text{alkoxide}]{\text{Aluminum}} RCHO\uparrow + R'CH_2OH$$

In this manner, benzaldehyde and *n*-butyraldehyde have been obtained in 95% and 72% yields, respectively.[15] This procedure is employed more extensively in the preparation of ketones (method 180).

159. Dehydrogenation of Primary Alcohols

$$RCH_2OH \xrightarrow{\text{Catalyst}} RCHO + H_2$$

Catalytic dehydrogenation of primary alcohols in the vapor phase has been studied in detail.[226] Formerly, a copper catalyst[32] was used; however, it has been found that this catalyst is easily poisoned.[39] A copper chromite catalyst at 300–345° and atmospheric pressure gives improved and consistent yields (50–70%) and retains its activity over long periods.[33, 34, 38] Side reactions, such as dehydration, condensation, and ester formation, do not occur appreciably under these conditions.[38] Preparation of the catalyst and the apparatus have been described.[34–36, 38]

Catalytic dehydrogenation of alcohols has been conducted with yields as high as 90% by passing the vapor mixed with air over silver or copper-silver catalysts.[41, 195, 225] A three-step synthesis of DL-glyceraldehyde from glycerol consists in protecting two of the hydroxyl groups by ketal formation with acetone, followed by air oxidation over a silver catalyst and then hydrolysis of the ketal (59% over-all yield).[221] Methacrolein, $H_2C{=}C(CH_3)CHO$, is made by the air oxidation of methallyl alcohol (95%).[227] A laboratory-scale model for the air oxidation of tetrahydrofurfuryl alcohol over a silver gauze catalyst has been described.[228]

Liquid-phase dehydrogenation is carried out under a pressure of ethylene, which serves as a hydrogen acceptor.[40]

Ethoxyacetaldehyde, an *aldehyde ether*, is readily prepared in 35% yield from Cellosolve by the vapor-phase dehydrogenation technique.[36]

Similar techniques are employed for the catalytic dehydrogenation of secondary alcohols (method 181).

160. Oxidative Cleavage of Glycols

$$RCHOHCHOHR' \xrightarrow[Pb(OOCCH_3)_4]{HIO_4 \text{ or}} RCHO + R'CHO$$

Certain β-amino alcohols and glycols and their dehydroderivatives, i.e., α-ketols, α-ketals, and diketones, are readily oxidized with periodic acid or lead tetraacetate to aldehydes. A review of the method has been made.[144]

The reactions are usually carried out at a moderate temperature, using water as the solvent for periodic acid and organic solvents for lead tetraacetate; however, both reagents can be used in aqueous solvents. Addition of the oxidizing reagent to the glycol instead of the reverse gives an improved yield.[169] The yields are high, and the method has found extensive application in both analytical and preparative procedures. It has been applied in the preparation of aldehydes containing a double bond or hydroxyl, carboxyl, ester, or ether groups.[147, 148, 169] Oxidation of 1,2-cyclohexanediols with lead tetraacetate leads to substituted adipic aldehydes in 68% yields.[249]

Several small-scale synthetic routes for obtaining intermediates for cleavage to aldehydes by lead tetraacetate have been proposed.[145, 146]

(*a*) $$RMgX \xrightarrow[80\%]{CH_2{=}CHCH_2Br} RCH_2CH{=}CH_2 \xrightarrow[\substack{KOAc\\60\%}]{Br_2;} RCH_2CHOHCH_2OH \xrightarrow{(O)} RCH_2CHO$$

(*b*) $$RCOCl \xrightarrow[90\%]{CH_2N_2} RCOCHN_2 \xrightarrow[90\%]{HOAc} RCOCH_2OAc \xrightarrow[80\%]{H^+} RCOCH_2OH \xrightarrow{(O)} RCHO$$

161. Selective Reduction of Olefinic Aldehydes

$$RCH{=}CHCHO \xrightarrow[\text{Catalyst}]{H_2} RCH_2CH_2CHO$$

Aldehydes may be prepared by selective hydrogenation of substituted acroleins in much the same manner as the selective reduction of unsaturated ketones (method 196); however, there are few examples adequately described.[93–95, 100, 236]

162. Reduction of Acyl Chlorides (Rosenmund)

$$RCOCl \xrightarrow[\text{Catalyst}]{H_2} RCHO + HCl$$

Selective catalytic hydrogenation of an acyl chloride to an aldehyde can be accomplished with varying yields; the method has been reviewed.[58] The preferred catalyst is palladium suspended on barium sulfate. The reaction may be carried out in the liquid phase by bubbling hydrogen through a hot solution of the acyl chloride in xylene or tetralin in which

the catalyst is suspended, or in the vapor phase by passing the acyl chloride over palladinized asbestos at about 200°.[64] In the former procedure, the reduction has been arrested at the aldehyde stage by careful control of the temperature[62] (lowest point at which hydrogen chloride is evolved) or by use of a catalyst "regulator" which inactivates the catalyst for reduction of the aldehyde. Typical reductions with and without catalyst poisons are found in the preparation of β-naphthaldehyde (81%)[56] and 2,4,6-trimethylbenzaldehyde (80%),[57] respectively. The reaction is applicable to acyl chlorides carrying halogen, nitro, or ester groups,[65, 67, 233] and even a double bond although this may migrate during the reaction.[66] Hydroxyl groups should be protected by acetylation.

Phosphorus- or sulfur-containing compounds formed in the preparation of the acyl chlorides hinder the reaction and therefore must be removed.[223]

163. Reduction of Thiol Esters

$$RCOSR' \xrightarrow[Ni]{(H)} RCHO + H_2S + R'H$$

The reduction of a carboxyl group to an aldehyde group can be effected by a reductive desulfurization of the thiol ester with Raney nickel. The thiol esters are prepared by the reaction of the acyl chloride with an excess of ethyl mercaptan in pyridine or by reaction with lead mercaptide in dry ether. The hydrogenolysis is then carried out by refluxing an ethanolic solution of the thiol ester with Raney nickel for 6 hours. By this new synthesis, propionaldehyde and benzaldehyde have been prepared in 73% and 62% yields, respectively.[160]

164. Reduction of Nitriles (Stephen)

$$RCN \xrightarrow{HCl} RC(Cl)=NH \cdot HCl \xrightarrow[HCl]{SnCl_2} (RCH=NH)_2SnCl_4 \xrightarrow{H_2O} RCHO$$

Nitriles may be converted to their imino chloride salts by the action of dry hydrogen chloride in ether. These intermediates are reduced by anhydrous stannous chloride to stannic aldimonium chlorides, which on hydrolysis yield aldehydes. Chloroform may be added to facilitate the solution of the nitrile. The quality of the stannous chloride catalyst is important; the preparation of an active and dependable form has been described.[49] The yields are usually high for many aromatic nitriles, as in the preparation of β-naphthaldehyde (95%).[49] The reaction has also been employed in the heterocyclic series, as in the synthesis of 4-methylthiazole-5-aldehyde (40%).[51] The reduction of the cyano group in the

presence of an ester group leads to an aldehyde ester, e.g., methyl cyanobenzoate to methyl *p*-formylbenzoate (90%).[53]

However, it has been shown that the method may not be as general as originally supposed, especially in the preparation of the aliphatic aldehydes.[50, 52, 55] Also, groups *ortho* to the nitrile group hinder the reaction.

Instead of reducing the imino chloride with stannous chloride, as indicated above, sodium amalgam may be used in the presence of phenylhydrazine. The resulting phenylhydrazone is then hydrolyzed.[54]

165. Interaction of Grignard Reagents and Orthoformic Esters

$$RMgX + HC(OC_2H_5)_3 \longrightarrow RCH(OC_2H_5)_2 \xrightarrow{H^+} RCHO$$

The reaction of ethyl orthoformate and Grignard reagents gives acetals which are hydrolyzed readily by dilute acid to aldehydes. This method has been employed extensively for the preparation of aliphatic and aromatic aldehydes. A study of the optimum conditions has been made, using the conversion of bromobenzene to benzaldehyde as a model synthesis (90%).[17, 21] Comparative studies of various aldehyde syntheses that employ Grignard reagents (methods 154, 166, and 167) show that this one is the most practical;[16, 17] however, the possibility of a sudden exothermic reaction limits the size of the run. Longer reaction times at room or reflux temperature help overcome this difficulty.[16, 18] Examples of the better preparative procedures are found in those for *n*-hexaldehyde (50%),[18] *p*-tolualdehyde (79%),[17] and phenanthrene-9-aldehyde (42%).[224]

N,N-Dialkylformamide[16, 19] or ethyl formate[20] and Grignard reagents have been used with some success; however, the former reaction is complicated and frequently produces tertiary amines as the chief product, and the latter forms secondary alcohols by further reaction of the aldehyde. Substituted benzaldehydes have been prepared from aryllithium compounds and N-methylformanilide in good yields.[122]

166. Interaction of Grignard Reagents and Ethoxymethyleneaniline

$$ArMgX + C_6H_5N=CHOC_2H_5 \longrightarrow ArCH=NC_6H_5 \xrightarrow{H^+} ArCHO$$

Aromatic Grignard reagents react smoothly with ethoxymethyleneaniline to give imines which are easily hydrolyzed to aldehydes. The reaction is easy to cary out, is adaptable to large-scale preparations, and gives high yields (65–82%).[17] Its use is limited by the availability of the ethoxymethyleneaniline, which may be prepared in a pure condition from the dry silver salt of formanilide and ethyl iodide.

167. Decomposition of Glycol Monoalkyl Ethers

$$2RMgX + C_2H_5OCH_2CO_2C_2H_5 \longrightarrow C_2H_5OCH_2C(OH)R_2$$

$$\downarrow H_2SO_4$$

$$R_2CHCHO \leftarrow [R_2C{=}CHOH] \leftarrow [C_2H_5OCH{=}CR_2]$$

A large number of symmetrical diaryl- or dialkyl-acetaldehydes, difficult to obtain by other means, have been prepared by the reaction of ethyl ethoxyacetate, or ethyl phenoxyacetate, with Grignard reagents followed by treatment of the resulting glycol monoalkyl ether with anhydrous oxalic acid or dilute sulfuric acid.[29] The yield in the first step is 40–80%, and the yield in the subsequent transformation is 50–80%.

Unsymmetrical dialkylacetaldehydes may be obtained by starting with an α-keto ether.[30]

$$RMgX + R'COCH_2OC_2H_5 \longrightarrow RR'C(OH)CH_2OC_2H_5 \longrightarrow RR'CHCHO$$

By this procedure, 2-(α-naphthyl)-propionaldehyde has been obtained in a 74% yield.[31]

The method has been further studied in its application for the synthesis of ketones (method 202).

168. Thermal Decomposition of Acids

$$RCOOH + HCOOH \xrightarrow{ThO_2} RCHO + CO_2 + H_2O$$

The old method of heating the calcium salts of formic and a second carboxylic acid for aldehyde formation has been modified by the use of a catalytic decomposition technique. By this scheme, the acid vapors are passed over thorium oxide, titanium oxide, or magnesium oxide at 300°;[213] or the acids are heated under pressure at 260° in the presence of titanium dioxide.[214] In the latter procedure, non-volatile acids can be used. With aliphatic acids over titanium oxide, reaction occurs only when more than seven carbon atoms are present, the yields increasing with increase in the molecular weight (78–90%). Aromatic acids having halo and phenolic groups are converted in high yields to aldehydes, e.g., salicylaldehyde (92%) and *p*-chlorobenzaldehyde (89%). Preparation of a thorium oxide catalyst has been described[268] (cf. method 186).

169. Decomposition of α-Hydroxy Acids

$$RCHOHCO_2H \xrightarrow{Heat} RCHO + CO + H_2O$$

High-molecular-weight aliphatic aldehydes have been made by the distillation of α-hydroxy acids, which are prepared by the hydrolysis of the corresponding α-bromo acids. The reaction is carried out under diminished pressure or in an atmosphere of carbon dioxide. Details for the procedure are found in the preparation of octanal (57%)[43] and undecanal (96%).[44] Preparation of the α-bromo acid and its subsequent hydrolysis are also described. A later modification has been the distillation of the α-methoxy acid in the presence of copper. This procedure gives an almost quantitative yield in the preparation of heptadecanal.[45]

Aldehydes have also been prepared from α-hydroxy acids by oxidation with lead tetraacetate in glacial acetic acid, e.g., tridecanal (55%) and pentadecanal (58%)[46] (cf. method 160).

170. Decarboxylation of α-Keto Acids

$$RCOCOOH \xrightarrow[Heat]{C_6H_5NH_2} RCH{=}NC_6H_5 \xrightarrow{H_2O} RCHO$$

α-Keto acids are readily decomposed to aldehydes and carbon dioxide. The decarboxylation may be brought about by heating the α-keto acid or its arylimino derivative. By the latter procedure, a solution of the keto acid in aniline is boiled, which causes the formation of water, carbon dioxide, and a Schiff base, $RCH{=}NC_6H_5$; hydrolysis of this product gives the aldehyde.[164] Oftentimes, decarboxylation is accomplished in higher yields by heating the glyoxylic acid in N,N-dimethyl-*p*-toluidine at 170°[170] or in diphenylamine at 150–200°.[256]

Another modification is the decomposition of the bisulfite-addition compound of the keto acid as illustrated by the synthesis of phthalaldehydic acid (41%).[166]

171. Decarboxylation of Glycidic Acids

$$RR'C\underset{O}{\diagdown\!\diagup}CCO_2H \xrightarrow{HCl} RR'CHCHO$$

Aromatic and aliphatic aldehydes have been prepared in good yields by the decarboxylation and isomerization of the corresponding glycidic acids. Esters of the latter are obtained by treating a ketone with ethyl chloroacetate in the presence of sodium amide (method 127). The glycidic esters are first converted to the sodium salts with sodium ethoxide and then treated with aqueous hydrochloric acid under gentle reflux. By this procedure, α-phenylpropionaldehyde has been prepared from acetophenone in an over-all yield of 38%.[157] Other details have been discussed.[161]

A similar route is the formation and isomerization of substituted ethylene oxides.[159] This synthesis has been carried out without isolating the intermediates.[30]

$$RCOCH_2Cl \xrightarrow{R'MgX} RR'COHCH_2Cl \xrightarrow{KOH} RR'C\underset{\diagdown\,O\,\diagup}{\!-\!}CH_2 \xrightarrow{HCl} RR'CHCHO$$

172. Hydrolysis of Olefin Dibromides[113]

$$(CH_3)_3COH \xrightarrow{Br_2} (CH_3)_2CBrCH_2Br \xrightarrow{H_2O} (CH_3)_2CHCHO$$

Over-all yield 75%

173. Degradation of Acid Amides and Azides

(*a*) α-Bromo Azides[112] (cf. method 220).

$$RCHBrCON_3 \xrightarrow{Heat} RCHBrNCO \xrightarrow{H_2O} (RCHBrNH_2) \xrightarrow{H_2O} RCHO$$

(*b*) Monosubstituted Malonyl Azides.[240]

$$RCH_2CH(CON_3)_2 \xrightarrow{C_2H_5OH} RCH_2CH(NHCO_2C_2H_5)_2 \xrightarrow{H_2O} RCH_2CHO$$

(*c*) α,β-Olefinic Amides.[168]

$$RCH{=}CHCONH_2 \xrightarrow[CH_3OH]{NaOCl} RCH{=}CHNHCO_2CH_3 \xrightarrow{H_2O} RCH_2CHO$$

174. Acid Treatment of Primary *Aci*nitroparaffins[194]

$$RCH_2NO_2 \xrightarrow{NaOH} RCH{=}\underset{\displaystyle O}{\overset{\displaystyle \downarrow}{N}}ONa \xrightarrow[80\text{–}85\%]{H^+} RCHO$$

R = methyl, ethyl, isopropyl, and *n*-butyl.

175. Isomerization of Unsaturated Alcohols[195]

$$H_2C{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}CH_2OH \xrightarrow[96\%]{H_2SO_4} (CH_3)_2CHCHO$$

176. Condensation of Aromatic Hydrocarbons with Chloral[120,197]

$$ArCH_3 + Cl_3CCHO \xrightarrow{OH^-} ArCH_2CHOHCCl_3 \xrightarrow{(O)} ArCH_2CHO$$

177. Formylation of Acetylenes[211,228]

(*a*) $$C_6H_5C{\equiv}CNa + HCO_2R \xrightarrow[18\%]{} C_6H_5C{\equiv}C{-}CHO$$

(*b*) $$CH_3(CH_2)_3C{\equiv}CNa + HCO_2R \xrightarrow[24\%]{-20^\circ} CH_3(CH_2)_3C{\equiv}C{-}CHO$$

TABLE 25. ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Aldehydes				
C_1	Formaldehyde	159	35	9[142]	-21/760, 169Se, 166Dn *
C_2	Acetaldehyde	158	72	9[3]	162Se *
		158	50	9[142]	147Dn *
		....	74	9[207]	20/760, 1.3353[12.5], 168Dn *
C_3	Propionaldehyde	158	49	9[1]	55, 1.364, 99Se *
		159	67	9[33]	154Se *
		163	73	9[160]	154Dn
		165	82	9[21]	49
		174	80	9[194]	
C_4	*n*-Butyraldehyde	158	72	9[15]	82/760, 1.3843 *, 104Se *
		159	62	9[33]	77, 122Dn *
		165	76	9[21]	75
		174	85	9[194]	
	Isobutyraldehyde	158	64	9[8]	63/741, 125Se *
		172	75 †	9[113]	65/740, 182Dn *
		175	96	9[195]	64, 1.3730
C_5	*n*-Valeraldehyde	158	50	9[6]	102, 1.3947 *, 106Dn *
		159	72	9[37]	
		159	58	9[33]	
		165	50	9[25]	
	Isovaleraldehyde	158	60	9[2]	95, 1.3902 *, 107Se *
		159	61	9[33]	123Dn *
		162	100	9[64]	92
	Methylethylacetaldehyde	158	52	9[9]	92, 1.3942 *, 120Dn *
		159	63	9[33]	
		165	25 †	9[26]	93, 103Se
		171	35	9[9]	91/751
	Trimethylacetaldehyde	159	66	9[39]	76, 191Se *
		165	35	9[20]	74/730, 1.3791, 210Dn *
		170	40	9[236]	78
C_6	*n*-Hexaldehyde (caproic aldehyde)	159	53	9[33]	128 *, 106Se *
		165	50	9[18]	128/747, 1.4068 *, 104Dn *
	Methyl-*n*-propylacetaldehyde	161	68	9[100]	116/737, 102Se *, 103Dn *
	Isobutylacetaldehyde	165	86	9[23]	127Se, 99Dn
		168	86	9[213]	121/743
	Diethylacetaldehyde	159	55	9[33]	
		167	60 †	9[29]	118, 94Se
	Dimethylethylacetaldehyde	159	66	9[39]	104
	t-Butylacetaldehyde	151	60	9[248]	103, 1.4150, 147Dn
	Methylisopropylacetaldehyde	167	61	9[30]	114, 1.3998[25], 124Dn
		....	14 †	9[30]	114

TABLE 25 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Aldehydes (*continued*)				
C_6	Cyclopentylaldehyde	161	60	9[94]	136/758, 34/10, 124Se
C_7	*n*-Heptaldehyde (oenanthol) (from castor oil)	....	....	9[208]	155/760, 1.4125 *, 109Se * 108Dn *
	5-Methylhexanal	156	62	9[114]	144/750, 1.4114, 117Dn, 117Se
	3,3-Dimethylpentanal	151	80	9[248]	134, 1.4292, 102Dn
	Ethylpropylacetaldehyde	167	60 †	9[29]	141
	Ethylisopropylacetaldehyde	167	60	9[30]	133.5, 1.4086[25], 121Dn
	Cyclohexanealdehyde	161	86	9[236]	63/24, 1.4503[18], 172Dn
C_8	*n*-Octaldehyde	164	100	9[50]	65/11, 60-Ox, 98Se, 80*p*N
		168	90	9[213]	1.4217 *
		169	57	9[43]	81/32, 59-Ox, 101Se
	Ethyl-*n*-butylacetaldehyde	159	58	9[33]	163 *, 254dSe *, 121Dn *
	Di-*n*-propylacetaldehyde	167	60 †	9[29]	161, 1.4142[15], 101Se
	Ethylisobutylacetaldehyde	167	60 †	9[29]	155, 98Se
	Cyclohexylacetaldehyde	165	47	9[22]	58/10, 1.4509[25], 159Se, 125Dn
C_9	Nonanal (pelargonic aldehyde)	159	90	9[42]	78/3, 1.4273 *
		160	33 †	9[147]	100/15, 64-Ox, 106Dn
		168	78	9[214]	
		168	85	9[213]	80/13, 64-Ox, 100Se
	Methyl-*n*-hexylacetaldehyde	167	60 †	9[29]	83/20, 80Se
	7-Methyloctanal	156	67	9[114]	103/140, 94/120, 100Dn, 80Se
	3,5-Dimethylhexahydrobenzaldehyde	171	65	9[253]	71/14, 171Se
C_{10}	Decanal	169	40	9[48]	98/13, 102Se *
C_{11}	Undecanal	169	96	9[44]	120/20, 1.4324[23], 103Se *, 104Dn *
C_{12}	Dodecanal (lauric aldehyde)	168	90	9[214]	238, (39.5), 78-Ox *, 106Dn *
C_{13}	Tridecanal	169	55	9[46]	136/8, (15), 106Se, 108Dn
C_{14}	Tetradecanal (myristaldehyde	164	100	9[50]	155/10, (23), 83-Ox, 107Se, 95*p*N
		169	35	9[47]	166/24, (24), 106Se, 83-Ox
C_{15}	Pentadecanal	169	58	9[46]	160/14, (25), 109Se, 108Dn

For explanations and symbols see pp. xi-xii.

TABLE 25 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Aldehydes (*continued*)				
C_{16}	Hexadecanal (palmitaldehyde	164	100	9[50]	(34), 88-Ox, 107Se, 97*p*N
		169	47	9[47]	202/29, (34), 107Se, 88-Ox
C_{17}	Heptadecanal (margaric aldehyde)	160	80	9[146]	(63)
		169	52	9[47]	204/26, (36), 108Se, 90-Ox
C_{18}	Octadecanal (stearaldehyde	164	100	9[50]	(38), 89-Ox, 109Se, 101*p*N
	Aromatic Aldehydes				
C_7	Benzaldehyde	147	70	9[98]	
		148	73	9[261]	64/13, 1.5446, 235Dn
		149	73	9[123]	222Se **
		150	85	9[133]	88/40, 158Ph *
		151	70	9[142]	179
		155	44	9[215]	
		158	95	9[15]	
		162	96	9[64]	
		163	62	9[160]	235Dn
		165	89	9[16]	
		168	93	9[214]	
		....	97	9[52]	
C_8	Phenylacetaldehyde	160	72	9[145]	84/14, 97-Ox
		162	80	9[65]	156Se **
		164	33	9[52]	
		165	58	9[21]	195, 99-Ox
		171	50	9[158]	95/22, 121Dn *
		173	75	9[240]	82/12, 58Ph *
	o-Tolualdehyde	147	70	9[89]	88/19, 111Ph
		148	73	9[262]	72/6, 1.5430[25], 193Dn *
		150	70	9[128]	93/19, 101Ph **
		155	65	9[215]	
		165	73	9[17]	
		166	81	9[27]	
	m-Tolualdehyde	155	60	9[215]	84Ph *
		164	50	9[230]	198/756, 212Dn
	p-Tolualdehyde	140	51	9[70]	205
		140	65	9[74]	114Ph **
		148	70	9[261]	72/6, 1.5420, 234Se
		149	60	9[127]	198*p*N
		155	80	9[215]	
		164	77	9[52]	106/10, 200*p*N **
		165	74	9[17]	
		166	82	9[27]	
C_9	α-Phenylpropionaldehyde	171	38 †	9[157]	93/10, 76/4, 135Dn

TABLE 25 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Aldehydes (*continued*)				
C_9	β-Phenylpropionaldehyde	162	62	9[232]	119/11
		165	67	9[24]	100/13, 127Se
	2,6-Dimethylbenzaldehyde	162	67	9[63]	228/742, 158Se
	3,5-Dimethylbenzaldehyde	155	48	9[153]	78/3.5, 1.5385, 201Se
C_{10}	3-Phenyl-2-methylpropanal	171	55	9[159]	90/6, 123Se
	p-*n*-Propylbenzaldehyde	170	65	9[167]	114/13
	p-Isopropylbenzaldehyde	140	60	9[243]	133/35, 1.5301 *, 211Se *
	2,3,6-Trimethylbenzaldehyde	165	61	9[17]	114/10, 126-Ox, 169Se
	2,4,5-Trimethylbenzaldehyde	165	72	9[17]	121/10, (44) *, 243Se *, 127Ph *
	2,4,6-Trimethylbenzaldehyde	140	83	9[78]	128/15, 1.5524
		162	80	9[57]	98/6
		162	80	9[164]	98/6
		165	57	9[17]	188Se
		170	50	9[164]	98/6
	1,2,3,4-Tetrahydro-2-naphthaldehyde	162	67	9[231]	92/0.5, 197Se
C_{11}	*p*-*s*-Butylbenzaldehyde	165	66	9[122]	118/15, 1.5240[25]
	2,3,5,6-Tetramethylbenzaldehyde	165	61	9[17]	135/11, (20), 270dSe, 125-Ox
	α-Naphthaldehyde	147	68	9[88]	152/13, 98-Ox, 219Se
		147	82	9[245]	107/0.2, 162/18, (2.5)
		158	42	9[5]	
	β-Naphthaldehyde	147	50	9[90]	150/15
		162	81	9[56]	(60)
		164	95	9[49]	(58), 154-Ox *
		165	70	9[27]	(61), 245dSe
C_{13}	2,4,6-Triethylbenzaldehyde	140	69	9[78]	149/21
	p-Phenylbenzaldehyde	140	73	9[243]	(60), 189dPh *
	o-Phenylbenzaldehyde	149	55 †	9[241]	162/12
	2-(α-Naphthyl)-propionaldehyde	167	74	9[31]	132/2, 204Se
	1-Acenaphthaldehyde	162	72	9[59]	(100.5)
C_{14}	Diphenylacetaldehyde	171	90	9[255]	146/5, 114-Ox
	9-Formylfluorene	....	71	9[199]	172/2
C_{15}	α,β-Diphenylpropionaldehyde	150	50	9[129]	170/11, (54), 125Se,
	9-Anthraldehyde	142	84	9[101]	(105), 187-Ox *, 207Ph *
	1-Phenanthraldehyde	150	75	9[134]	(111.5), 189-Ox

For explanations and symbols see pp. xi–xii.

TABLE 25 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
		Aromatic Aldehydes (*continued*)			
C_{15}	2-Phenanthraldehyde	150	85	9[130]	(59) *, 195-Ox *
		162	70	9[60]	(59.5), 282Se *
	3-Phenanthraldehyde	150	85	9[130]	275Se *
		162	90	9[60]	(80), 145-Ox *
	9-Phenanthraldehyde	150	90	9[131]	(101), 223Se
		162	90	9[60]	(101)
		165	42 †	9[224]	(101)
	1,2,3,4-Tetrahydrophenanthrene-9-aldehyde	150	68	9[133]	(129)
C_{16}	2,4,6-Triisopropylbenzaldehyde	140	65	9[78]	126/4
C_{17}	Pyrene-3-aldehyde	142	53	9[104]	(126)
C_{19}	1,2-Benzanthracene-10-aldehyde	142	64	9[102]	(148)
C_{21}	3,4-Benzpyrene-5-aldehyde	142	90	9[102]	(203)
		Heterocyclic Aldehydes			
C_5	Furfural	560	....	39[6]	90/65, 159/745
	3-Furaldehyde	162	62	9[61]	68/39, 1.4945 *, 211Se
	Tetrahydrofurfuraldehyde	159	60	9[228]	43/15, 1.4473, 134Dn
	2-Thiophenealdehyde	142	76	9[260]	92/25, 1.5888^{25}, 139Ph
		147	53 †	9[84]	91/21, 1.5880^{25}, 242Dn
		158	65	9[223]	79/12, 1.5880^{25}
		165	70	9[257]	78/20, 1.5950^{16}
		170	45 †	9[162]	198, 119Ph
	3-Thenaldehyde	147	32 †	9[86]	199/744, 1.5860, 137Ph
	α-Pyrrole aldehyde	143	33	9[83]	109/14, (50)
	4-Methylthiazole-5-aldehyde	149	40	9[124]	118/21, (75), 159Ph
		164	65	9[51]	(72.5), 161Ph
C_6	5-Methylfurfural	7	22 †	39[210]	85/15
		560	22	39[5]	85/15
	3-Methyl-2-thiophenealdehyde	142	83	9[260]	114/25, 1.5833^{25}, 149Ph
	5-Methyl-2-thiophenealdehyde	142	81	9[260]	114/25, 1.5782^{29}, 126Ph
	Nicotinaldehyde	149	23	9[125]	99/26, 158Ph
C_7	β-Furylpropionaldehyde	161	46	9[95]	70/14, 1.4470, 80Se
C_9	Thianaphthene-3-aldehyde	147	31	9[247]	(58)
		162	43	9[235]	(54)
	Indole-3-aldehyde	142	54	9[105]	(195)
		143		9[82]	198Ph *
		170	74	9[163]	(198)
	Coumarin-3-aldehyde	162	75	9[62]	(132)

TABLE 25 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
		Heterocyclic Aldehydes (*continued*)			
C_{10}	Quinoline-2-aldehyde	176	50	9[198]	(69)
	Quinoline-4-aldehyde	157	61	9[164]	(84.5), 182-Ox
		176	36 †	9[197]	123/4, (51), 179Pi
	Isoquinaldaldehyde	157	42	9[183]	(55.5), 197Se
C_{13}	Dibenzofuran-2-aldehyde	140	81	9[77]	(68), 162Ph

For explanations and symbols see pp. xi-xii.

TABLE 26. DIALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
C_2	Glyoxal	157	74	9[178]	51 *, 178-Ox *
C_3	Malonaldehyde	154	45 †	9[206]	(74)
C_4	Succinaldehyde	154	60	9[106]	67/13, 172-Ox, 280Dn
C_5	Glutaraldehyde	153	59	9[265]	75-81/15, 1.4330^{25}, 169*p*N
C_6	Adipic dialdehyde	156	60	9[115]	94/12, 186-Ox *
		160	68	9[249]	70/3, 1.4350, 206Se *
C_8	Phthaldehyde	151	58	9[139]	(55.5), 191Ph *
	Isophthaldehyde	155	31 †	9[151]	(89), 242Ph *, 180-Ox *
	Terephthalaldehyde	147	34	9[244]	(114), 278dPh *
		151	84	9[140]	(116), 200-Ox *
		152	70 †	9[169]	(118)
		158	80	9[14]	(116)

For explanations and symbols see pp. xi-xii.

TABLE 27. OLEFINIC ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
		Aliphatic and Alicyclic Olefinic Aldehydes			
C_3	Acrolein	....	48	9[191]	55.5, 171Se *
		....	85	9[192]	54, 1.4025, 165Dn *
C_4	Methacrolein (2-Methyl-2-propenal)	159	95	9[227]	73.5/760, 1.4191 *, 198Se *
		159	90	9[195]	206Dn *
C_5	2-Pentenal	158	50	9[10]	125, 1.4350^{21}, 180Se
		154	70	9[6]	125, 123*p*N *
	2-Methyl-2-butenal	36	30	2[315]	116-119, 216Se
	β-Methylcrotonaldehyde	19	40	2[439]	130-135, 1.4526 *, 223Se

For explanations and symbols see pp. xi-xii.

TABLE 27 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Olefinic Aldehydes (*continued*)				
C_6	2-Hexenal	158	50	9[10]	150, 1.4470[13], 176Se, 139*p*N
	3-Hexenal	160	40	9[146]	150, 147Dn
	Hexadienal	36	50	2[317]	65/11, 160-Ox, 102Ph
	α-Isopropylacrolein	24	50	2[167]	109, 1.4223
		26	53	2[167]	107, 1.4223, 165Dn
	1-Cyclopentenylformaldehyde	....	28 †	9[94]	146/760, 48/11, 1.4828[21]
C_7	2-Heptenal	158	75	9[10]	85/14, 1.4314, 169Se, 116*p*N
	1-Cyclohexenealdehyde	20	77	2[451]	70/13, 1.4921[17], 213Se, 99-Ox *
	2-Cyclopentenylacetaldehyde	159	85	9[229]	50/15
C_8	4-Octenal	158	35	9[219]	84/13, 1.4463[25], 108Dn
	Octatrienal	36	40	2[317]	(55)
	2-Ethyl-2-hexenal	36	58	2[73]	73/30, 152Se, 125Dn
	2-Ethyl-3-hexenal	...	78	9[196]	84/52, 156Se
	3,6-Dihydro-o-tolualdehyde	34	31	2[520]	66/2, 1.5248[28], 219Dn, 230Se
C_9	2-Nonenal	158	50	9[10]	126/21, 1.4426, 165Se, 113*p*N
		160	67	9[147]	58/0.1, 1.4502[25], 165Se, 126Dn
C_{11}	11-Undecenal	160	64	9[146]	103/10, 91Dn
	Aromatic and Heterocyclic Olefinic Aldehydes				
C_7	β-Furylacrolein	36	54	2[313]	95/9, (52)
C_9	*p*-Formylstyrene (*p*-Vinylbenzaldehyde	27	52	2[493]	93/14, 1.5960[25], 131Ph
C_{10}	α-Methylcinnamaldehyde	36	67	2[314]	124/14, 208Se *
C_{11}	5-Phenylpentadienal	36	20	2[318]	161/12
	α-Ethylcinnamaldehyde	36	58	2[312]	112/7, 1.5822[25]
C_{15}	Stilbene-2-aldehyde	149	80	9[126]	(83)
	α-Phenylcinnamaldehyde	36	25	2[316]	200/16, (95), 141Ph, 195Se
	β-Phenylcinnamaldehyde	142	60	9[202]	210/14, 196Dn, 173Ph *

For explanations and symbols see pp. xi-xii.

TABLE 28. ACETYLENIC ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, Deriv.
C_3	Propargyl aldehyde	158	46	9[220]	55
C_4	2-Butynal	177	28 †	9[225]	105-110/755, 1.446[19] 136Dn
C_7	2-Heptynal	177	24	9[225]	54/13, 1.4521[17], 74Dn
C_9	Phenylpropargyl aldehyde	43	70 †	3[33]	116/17, 1.6032[25], 108-Ox *
		154	81	9[238]	117/17, 1.6032[25]

For explanations and symbols see pp. xi-xii.

TABLE 29. HALO ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Halo Aldehydes				
C_2	Trifluoroacetaldehyde	....	46	9[222]	-20, 151Dn
	Tribromoacetaldehyde (bromal)	66	57	4[513]	74/18
C_3	β-Chloropropionaldehyde	73	43	4[197]	130, 50/10 *
	β,β,β-Trifluoropropionaldehyde	158	57	9[222]	56/745, 1.3168[22], 151Dn
C_4	α-Bromoisobutyraldehyde	66	18 †	4[642]	115, 1.4518[25]
		154	47	9[239]	108-113
C_5	α-Bromo-*n*-valeraldehyde	66	70	4[514]	54/13
	2,3-Dibromo-2-methylbutanal	74	70	4[430]	73/3.5, 1.5228
C_6	Bromoparacetaldehyde	66	32	4[516]	(104)
	2-Methyl-2,3-dichloropentanal	74	81	4[438]	67/13, 1.4586[19,5]
C_7	α-Bromoheptaldehyde	66	40 †	4[642]	92/17, 1.4580-1.4600[25]
	1-Bromocyclohexanealdehyde	66	80	4[639]	91/20, 1.500[18]
C_9	9-Chlorononaldehyde	156	66	9[117]	100/3, 1.4501[25]
	Aromatic Halo Aldehydes				
C_7	*o*-Fluorobenzaldehyde	151	71	9[137]	91/45, 90Ph *, 63-Ox *
	o-Chlorobenzaldehyde	149	61	9[242]	98/20, 209Dn *
		162	70	9[65]	
	o-Iodobenzaldehyde	150	80	9[132]	129/14, 108-Ox *, 79Ph *
	m-Fluorobenzaldehyde	151	44	9[137]	93/45, 114Ph *
		162	60	9[67]	173/760, 63-Ox
	m-Chlorobenzaldehyde	56	79	4[329]	86/8, 107/26, 135Ph *
	m-Bromobenzaldehyde	56	67	4[329]	92/4, 205Se *
	p-Fluorobenzaldehyde	151	49	9[137]	94/45, 147Ph *
	p-Chlorobenzaldehyde	149	77	9[123]	75/3, (47) *, 232Se *
		150	81	9[133]	(47), 220*p*N *

For explanations and symbols see pp. xi-xii.

TABLE 29 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Halo Aldehydes (*continued*)				
C_7	*p*-Chlorobenzaldehyde	151	60	9[136]	111/25, (47)
		168	89	9[214]	
	p-Bromobenzaldehyde	148	75	9[261]	(57), 229Se
		151	69	9[135]	(57)
		155	51 †	9[140]	(57)
		164	62	9[230]	(57), 257Dn
	p-Iodobenzaldehyde	56	100	4[330]	(77), 121Ph *
		164	56	9[230]	(77), 257Dn
C_8	*p*-Trifluoromethylbenzaldehyde	148	77	9[261]	67/13, 1.4630
C_9	α-Bromobenzylacetaldehyde hydrate	66	90	4[515]	(82)
C_{11}	1-Bromo-2-naphthaldehyde	147	40	9[87]	(118)

For explanations and symbols see pp. xi–xii.

TABLE 30. HYDROXY ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Hydroxy Aldehydes				
C_2	Glycolaldehyde	156	25	9[118]	(76), 162Ph *
		....	25	9[205]	(87)
		....	96	9[212]	
C_3	α-Hydroxypropionaldehyde	96	35	5[557]	114/9, 127*p*N
	dl-Glyceraldehyde	154	80	9[237]	139
		159	59 †	9[221]	(133)
	Hydroxypyruvic aldehyde	158	87	9[12]	(160), 135-Ox
C_4	4-Hydroxybutanal	160	42	9[250]	60/8, 1.4403, 118Dn
C_5	5-Hydroxypentanal	99	79	5[625]	55/3, 1.4514^{25}
	Methylethylglycolic aldehyde	154	50	9[175]	
	3-Methyl-3-hydroxybutanal	156	75	9[119]	67/13, 142*p*N
	α,α-Dimethyl-β-hydroxypropionaldehyde	102	80	5[200]	85/15, (97)
C_6	2-Methyl-3-hydroxypentanal	102	86	5[206]	86/12, 1.4373
	2-Isopropyl-3-hydroxypropionaldehyde	102	52	5[201]	84/10, 1.4603, 126Dn

TABLE 30 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Hydroxy Aldehydes (*continued*)				
C_7	Methyl-*n*-butylglycolic aldehyde	89	15 †	5[396]	87/35, 143Se
		154	50	9[175]	88/35, 143Se
C_8	2,2,4-Trimethyl-3-hydroxypentanal	102	....	5[202]	110/13, 1.4443
C_9	9-Hydroxynonanal	160	23 †	9[147]	120/0.1, (54)
	Aromatic Hydroxy Aldehydes				
C_7	Salicylaldehyde	143	50	9[109]	196, 59-Ox *
		144	20	9[96]	197, 142Ph
		149	55	9[123]	230Se *
		151	50	9[141]	248Dn *
		168	92	9[214]	
	m-Hydroxybenzaldehyde	93	56	5[489]	(104), 88-Ox, 130Ph *
	Resorcyl aldehyde	141	95	9[71]	(136)
	3,4-Dihydroxybenzaldehyde	154	61 †	9[264]	(154d), 230dSe *
		97	61	5[714]	(154), 157d-Ox *
C_9	Benzylglycolic aldehyde	96	50	5[555]	121/4, (52), 70Bz, 137Se
	Methylphenylglycolic aldehyde	89	19 †	5[398]	101/4, 182Se
		154	36	9[175]	101/4, 183Se
	2-Ethyl-4-hydroxybenzaldehyde	141	21	9[76]	145/1, (53)
C_{10}	Ethylphenylglycolic aldehyde	89	11 †	5[396]	110/5, 188Se
		154	28	9[175]	111/5, 188Se
C_{11}	1-Naphthol-2-aldehyde	141	72	9[71]	(178)
	2-Naphthol-1-aldehyde	141	85	9[71]	(81)
		142	45	9[106]	161/11, (84)
		143	48	9[80]	(80)
		144	20	9[96]	(82), 157-Ox
C_{14}	Diphenylglycolic aldehyde	89	25 †	5[398]	(163), 124-Ox
		154	65	9[175]	(163), 242Se

For explanations and symbols see pp. xi–xii.

TABLE 31. ALDO ETHERS

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Aldo Ethers				
C_3	Methoxyacetaldehyde	158	17	9[11]	92, 125Dn
		160	51	9[148]	89, 124Dn

For explanations and symbols see pp. xi–xii.

TABLE 31 (*continued*)

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Aldo Ethers (*continued*)				
C_4	γ-Methoxypropionaldehyde	121	63	6[140]	
	Ethoxyacetaldehyde	158	10	9[11]	106, 117Dn
		159	35	9[36]	106/760*, 1.3956*
		160	40	9[148]	91, 116Dn
C_5	β-Methoxyisobutyraldehyde	121	51	6[140]	129, 1.4030^{27}, 102Dn
	n-Propoxyacetaldehyde	160	28	9[148]	68/100, 119/748, 86Dn
C_6	5-Methoxyvaleraldehyde	156	78	9[121]	59/14.5
	α-Methyl-γ-methoxybutyraldehyde	171	59	9[154]	$66/55, 1.4280^{25}$, 88Dn
C_8	2-Methyl-2,3-dimethoxypentanal	115	85	6[80]	$67/12, 1.4196^{19}$
	Aromatic Aldo Ethers				
C_8	Phenoxyacetaldehyde	154	60	9[111]	105/10, 95-Ox*
		160	45	9[148]	94/6, 146Se, 138Dn
		160	60	9[169]	83/5, 1.5360
	o-Methoxybenzaldehyde	116	92	6[91]	(37), 205*p*N*
	m-Methoxybenzaldehyde	116	72†	6[90]	90/3, 171*p*N*
	p-Methoxybenzaldehyde	141	100	9[72]	248, 203Se*
		149	77	9[123]	161*p*N*
C_9	*o*-Ethoxybenzaldehyde	116	90	6[93]	125/15, 59-Ox, 219Se*
	3,4-Dimethoxybenzaldehyde (veratraldehyde)	116	87	6[94]	153/8, (46), 90-Ox
C_{10}	2-Ethyl-4-methoxybenzaldehyde	141	53	9[76]	$134/12, 1.5543^{28}$
	3-Ethoxy-4-methoxybenzaldehyde	116	93	6[161]	155/10
	3-Methoxy-4-ethoxybenzaldehyde	116	79	6[161]	(64)
	3,4,5-Trimethoxybenzaldehyde	162	64	9[148]	(75)
C_{11}	3,4-Diethoxybenzaldehyde	116	95	6[95]	130/2
C_{13}	*o*-Phenoxybenzaldehyde	115	22	6[154]	153/1, 215Se
	2-Ethoxy-1-naphthaldehyde	142	84	9[101]	(112), 258Dn*
C_{14}	*m*-Benzyloxybenzaldehyde	115	97	6[40]	218/20, (54)

For explanations and symbols see pp. xi-xii.

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10

Ketones

CONTENTS

CONTENTS *(continued)*

178. Acylation of Hydrocarbons (Friedel-Crafts)

$$ArH + RCOCl \xrightarrow{Catalyst} ArCOR + HCl$$

Many organic compounds react with carboxylic acids, acyl halides, or anhydrides in the presence of certain metallic halides, metallic oxides, iodine, or inorganic acids to form carbonyl compounds. The reaction is generally applicable to aromatic hydrocarbons. Benzene, alkylbenzenes, biphenyl, fluorene, naphthalene, anthracene, acenaphthene, phenanthrene, higher aromatic ring systems, and many derivatives undergo the reaction. In addition, olefinic and heterocyclic compounds have been converted to ketonic compounds. Therefore, a large number of ketones have been prepared by this reaction. Excellent reviews are available.[10]

Benzene is usually acylated by the addition of anhydrous aluminum chloride to a benzene or carbon disulfide-benzene solution of the aliphatic

or aromatic acyl halide, as in the preparation of phenyl benzyl ketone (83%),[1] benzophenone (90%),[2] and stearoylbenzene (65%).[3]

The mono- and poly-alkylated benzenes are treated using modifications of the above procedure. Monoalkylbenzenes are added to a preformed complex of acyl halides and aluminum chloride in carbon tetrachloride[4] (Perrier modification). In this manner, the manipulation is easier, no tars are encountered, and the yields are improved (85–90%). The procedure shows no advantage, however, in the acylation of alkoxy- or chloro-aromatic compounds. The addition of benzoyl chloride to *p*-alkylbenzenes in the presence of aluminum chloride in cold carbon disulfide is a good procedure for making *p*-alkylbenzophenones (67–87%).[5] The condensation of homologs of benzene with oxalyl chloride under similar conditions yields *p,p'*-dialkylbenzophenones (30–55%).[27] Polyalkylbenzenes have been acylated with acetic anhydride and aluminum chloride (2.1:1 molar ratio) in carbon disulfide in 54–80% yields.[6,7] Ferric chloride catalyst has been used under similar conditions.[8] Acetylation of *p*-cymene with acetyl chloride and aluminum chloride in carbon disulfide yields 2-methyl-5-isopropylacetophenone (55%).[9]

Studies on the conditions of the reaction have been made using simple compounds as model substances. A comparison of thirty-nine metallic chlorides shows aluminum chloride to be the most effective in the preparation of *p*-methylacetophenone.[11] Optimum yields result when the molar ratios of aluminum chloride to anhydride, acyl chloride, and acid are 3.3, 1.0, and 2.5, respectively. Halogen and oxyhalogen carriers are not helpful.[12] Inconsistent yields in the Friedel-Crafts reaction have been attributed to the presence of ferric chloride or moisture in the aluminum chloride catalyst.[13] Prolonged heating causes condensation of the ketone product. It has been shown that cessation of hydrogen chloride evolution may not be a satisfactory criterion for judging completeness or optimum period of reaction.[14] For the most part, the success of the reaction depends on the use of mild conditions and pure reagents.[15-17]

Other aromatic compounds have been acylated by varying procedures. A general procedure for the preparation of alkyl biphenyl ketones has been described whereby the acyl halide is added to a mixture of biphenyl, aluminum chloride, and carbon disulfide (62–90%).[18] Nitrobenzene or carbon disulfide is used as the solvent in the preparation of 2-acetylfluorene (83%)[19,31] and the isomeric 2- and 3-acylphenanthrenes.[20,21] A convenient method for obtaining pure 2-acylphenanthrene is the acylation of 9,10-dihydrophenanthrene followed by sulfur dehydrogenation. In this case, only the 2-position is attacked; the over-all yield is about 48%.[22] Anthracene is acylated in the 9-position (60%).[32] The isomeric acetylacenaphthenes have been prepared from the hydrocarbon and acetic

acid, using hydrogen fluoride as catalyst.[23,24] Substituted tetralins have been prepared by the Friedel-Crafts reaction under mild conditions. Thus, tetralin or its 7-alkylated derivative reacts with acid anhydrides in the presence of aluminum chloride and nitrobenzene solvent at 0° (60–80%).[25] Naphthalene is acetylated or benzoylated almost exclusively in the alpha position by the action of an acyl chloride and aluminum chloride in methylene or ethylene chloride solution.[30] Also, on treatment with benzoyl chloride in the presence of iodine, it is converted predominantly to the α-benzoyl isomer (52%).[26] Aroyl halides respond better than anhydrides to this treatment.

Heterocyclic ketones derived from furan or thiophene have been prepared similarly using an iodine catalyst. Short reaction time and low temperature are used. Thus, thiophene and acetic anhydride heated for 1 hour with a small quantity of iodine at about 100° yields 2-acetylthiophene (86%); similarly, furan yields 2-acetylfuran (75%).[59] Other catalysts for the acylation of furan and thiophene have been used, namely, zinc chloride,[60] silica-metal oxides,[61] stannic chloride,[62] aluminum chloride,[63] boron trifluoride,[64,65,68] and orthophosphoric acid.[66] The last-named catalyst has been employed for the preparation of eleven compounds including 2-acetylthiophene (94%), 2-benzoylthiophene (99%), and 2-acetyl-5-methylthiophene (91%). Other oxygenated acids have been studied, but orthophosphoric acid is the most effective and produces the fewest side reactions. In general, the acid anhydride as acylating agent is preferred over the acyl halide. In introducing large acyl groups, it is convenient to use merely the organic acid and phosphorus pentoxide. Yields of acylated thiophene range from 45% with acetic acid to 97% with oleic acid.[66]

γ-Aryl-substituted acids, $Ar(CH_2)_3COOH$, or their halides undergo an internal Friedel-Crafts reaction to give 1-tetralones.[15] The acids may be cyclized directly with 85–95% sulfuric acid as in the preparation of 4-methyl-1-tetralone (74%).[80] However, sulfonation by-products may occur. Thus, 1-tetralone from γ-phenylbutyric and sulfuric acid mixture is obtained in 49% yield, whereas it is prepared from the acyl chloride and aluminum chloride in 92% yield.[79] A better catalyst for direct cyclization is hydrofluoric acid. The organic acid is simply treated at room temperature with 10 parts hydrofluoric acid for several hours. In this manner, 1-tetralone (92%), 1-hydrindone (73%), 1,2-benz-10-anthrone (75%), and other difficultly obtained anthrones have been prepared.[24] In preparing acyl chlorides with thionyl chloride for the Friedel-Crafts reaction, care must be taken to remove this reagent completely since it may lead to side reactions. Better results have been obtained by employing phosphorus pentachloride for formation of the acyl halide, but again the harmful phosphorus oxychloride

must be removed. This is readily accomplished by codistillation with benzene. The acyl chloride may be cyclized without further purification. A solution in benzene, nitrobenzene, or chlorobenzene *is added to* aluminum chloride below 25°.[17] Polyphosphoric acid has also been applied in the synthesis of cyclic ketones.[75]

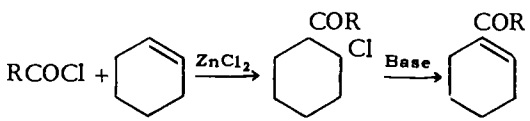
Ring closure of this type has been brought about by the reaction of a lactone, namely, γ,γ-dimethylbutyrolactone, with benzene and aluminum chloride to give 4,4-dimethyl-1-tetralone (70%).[86] Tetralones containing halogen atoms[87] or alkoxyl groups[17,88] have been prepared. Also, β-haloalkyl ketones of the type $ArCOCH_2CH_2Cl$ undergo intramolecular condensation to furnish 1-indanones.[74]

Diketones have been prepared by the Friedel-Crafts method. Both acyl chloride groups in adipyl chloride react with benzene in the presence of aluminum chloride to form the diketo compound, 1,4-dibenzoylbutane (81%).[89] When diketene is treated with benzene under the conditions of the Friedel-Crafts reaction, benzoylacetone, $C_6H_5COCH_2COCH_3$, is formed (73%).[90]

$$CH_2=C(-O-C=O)-CH_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCH_2COCH_3$$

This synthesis of 1,3-diketones may be extended by the use of other available diketenes.

Olefinic ketones have been obtained from the reaction of acyl chlorides or anhydrides with olefins using the conditions of the Friedel-Crafts reaction. The intermediate chloro ketones are oftentimes stable and must be treated with sodium bicarbonate or dimethylaniline to complete the dehydrohalogenation. In this manner, 1-acetyl-1-cyclohexene (62%)[92,103] and 1-butyryl-1-cyclohexene (60%)[93] are prepared.



More recently, it has been shown that acetylation of cyclohexene with acetic anhydride in the presence of stannic chloride is less troublesome and does not necessitate dehydrohalogenation.[97]

The reaction has been investigated in detail using diisobutylene and acetic anhydride whereby methyl octenyl ketones are formed in yields as high as 60%. Studies of catalysts show zinc chloride to be the most effective. It is used in relatively small concentrations compared with

the catalyst requirements for aromatic hydrocarbons. A low temperature (40°) is maintained to prevent polymerization of the olefin. On a small scale, a preformed complex of the anhydride and zinc chloride is prepared and treated with the olefin.[94,95]

Under these conditions, the addition of acyl chlorides to acetylene leads to β-chlorovinyl ketones (62–80%).[99]

$$RCOCl + HC\equiv CH \xrightarrow{AlCl_3} RCOCH=CHCl$$

Ketones containing a double bond have also been prepared by the reaction of unsaturated acyl halides with aromatic hydrocarbons[96] in the usual Friedel-Crafts manner. Acylation of benzene and its homologs with β,β-dimethylacroyl chloride leads to dimethylvinyl aryl ketones, $(CH_3)_2C=CHCOAr$ (75–90%).[100] The latter compounds are stable and do not undergo intramolecular condensation.

Three types of *halo ketones,* differing in the position of the halogen atom, have been prepared by the Friedel-Crafts reaction: (1) a halogenated acyl chloride and an aromatic hydrocarbon give a haloalkyl aryl ketone, e.g., β-bromopropiophenone, $C_6H_5COCH_2CH_2Br$, (93%)[112] from benzene and β-bromoacetyl chloride; (2) an aryl halide upon acylation gives a haloaryl alkyl ketone, e.g., *p*-fluoroacetophenone (74%) from fluorobenzene and a preformed acetic anhydride-aluminum chloride complex[110] or *p*-bromoacetophenone (79%)[113] from bromobenzene and acetic anhydride; and (3) an aryl-substituted alkyl halide on acylation gives an aryl alkyl ketone containing a halogenated side chain, e.g., β-(*p*-acetylphenyl)-ethyl bromide, $p\text{-}CH_3COC_6H_4CH_2CH_2Br$ (83%),[112] from β-phenylethyl bromide and acetyl chloride. In general, the reactions are carried out in carbon disulfide with aluminum chloride catalyst.

Phenolic ketones have been prepared by modifications of the Friedel-Crafts reaction. In preparing acyl derivatives of phenol, a preformed complex of phenol and aluminum chloride is treated with an acyl chloride. *Ortho* and *para* isomers are formed with the latter predominating.[123] On the other hand, in preparing acyl derivatives of the polyhydric phenols and naphthols, a preheated solution of zinc chloride and acylating acid is treated with the hydroxy compound (Nencki reaction).[124-126] This procedure gives poor yields when applied to the monohydroxy phenols.[127] Phloroglucinol, $sym\text{-}C_6H_3(OH)_3$, condenses with acetonitrile in the presence of zinc chloride and hydrochloric acid to give phloroacetophenone (87%) (Hoesch-Houben reaction).[128,129] An imino chloride is probably formed, viz., $CH_3CN + HCl \rightarrow CH_3C(Cl)=NH$, which reacts with the phenol to give an intermediate ketimine hydrochloride.

$$sym\text{-}(HO)_3C_6H_3 + CH_3C(Cl)=NH \xrightarrow[HCl]{ZnCl_2} sym\text{-}(HO)_3C_6H_2C(=NH\cdot HCl)CH_3 \xrightarrow{H_2O} sym\text{-}(HO)_3C_6H_2COCH_3$$

Acylation of aromatic ethers yields the corresponding *keto ethers.*[131] Typical examples are found in the conversion of anisole with aluminum chloride and appropriate acyl halide to *p*-methoxybutyrophenone (85%)[132] and *p*-methoxyphenyl benzyl ketone (84%).[133] Mild catalysts like iodine[26] and phosphorus pentoxide[29] are also effective.

Aryl-substituted *γ-keto acids* are readily obtained by acylation of aromatic compounds with succinic anhydride, e.g., *β*-benzoylpropionic acid (85%).[135]

$$C_6H_6 + \begin{matrix} CH_2CO \\ | \quad\quad O \\ CH_2CO \end{matrix} \rightarrow C_6H_5CO(CH_2)_2CO_2H$$

Phenol,[136] bromobenzene,[87] *t*-butylbenzene,[137] and acenaphthene[138] give keto acids in good yields. The reaction is applicable to other aliphatic dibasic acid anhydrides like glutaric anhydride,[139] adipic polyanhydride,[140] and maleic anhydride,[141] furnishing *ω*-aroyl acids. An excellent discussion including experimental conditions and procedures has been given.[142]

Optimum conditions for the reaction of naphthalene,[670] biphenyl,[144] and chlorobenzene[145] with phthalic anhydride have been determined. The corresponding keto acids are obtained in 90–98% yields. In this type of condensation, nitrobenzene is stated to be far superior to other solvents with respect to solvent power and ability to slow side reactions.[146]

Another variation consists in the reaction between an aromatic nucleus and the ester-acyl chloride of a dibasic acid followed by hydrolysis of the resulting keto ester. This synthesis affords *ω*-aroyl aliphatic acids in 85–95% yields and is applicable to benzene, its alkyl, halo, alkoxy, and alkylalkoxy derivatives as well as to thiophene and naphthalene.[139,147]

When the interaction of an ester-acyl chloride and an aromatic nucleus is employed for the synthesis of a *keto ester,* then a reesterification step is recommended.[147] Certain *α-keto esters* have been prepared by using ethyl oxalyl chloride, $CO_2ClCO_2C_2H_5$, as the acylating agent, e.g., ethyl *α*-thienyl glyoxylate (50%),[150] ethyl *α*-naphthylglyoxylate (46%),[151] and ethyl *p*-biphenylylglyoxylate (70%).[152] An example of acylation of an aromatic ester is found in the preparation of the *para* and *meta* isomers of ethyl acetylphenylacetate (80%).[153]

Nitro- and *amino*-aromatic compounds do not respond favorably. However, acylations of acetanilide with acetic anhydride using iodine catalyst[26] or with acetyl chloride and aluminum chloride catalyst[154] have been reported. *o*-Nitrophenyl 2-thienyl ketone has been prepared.[155]

Use of *α*-cyanopropionyl chloride results in a *cyano ketone,* e.g., *α*-cyanopropiomesitylene, $C_6H_2(CH_3)_3COCHCNCH_3$ (20%).[156]

179. Oxidation of Secondary Alcohols

$$R_2CHOH \xrightarrow{(O)} R_2CO$$

Oxidation of secondary alcohols to ketones with sulfuric-chromic acid mixture proceeds readily. In general, the reaction is carried out in an aqueous medium keeping the temperature at 20–40°. Occasionally, the reaction temperature is elevated to 50–80° for additional periods.[157,158] Vigorous stirring is required for slightly soluble alcohols. The yields vary from 60% to 80% for the C_5–C_{10} aliphatic ketones. Isopropyl *s*-butyl ketone is prepared by carrying out the oxidation of the alcohol at 40° for 36 hours (68%).[159] Substituted cyclohexanones have been prepared in good yields (70–93%) with widely varying reaction times and temperatures.[169–172,675] Oxidation of insoluble aromatic carbinols is carried out with acetic acid as the solvent. Thus, *m*-biphenylmethylcarbinol and 2-phenylcyclohexanol are oxidized at 45–50° to the corresponding ketones in 80% yield.[173,47] Concentrated nitric acid at reflux temperature for 20 minutes has been used for the preparation of hexamethylacetone (81%).[174] The mechanism of chromic acid oxidation of alcohols has been discussed.[168,175,186]

Among the *diketones* prepared by oxidation of an alcohol group are the the benzils from the corresponding benzoins and aliphatic *α*-diketones from the acyloins. The oxidation of the former is accomplished with copper sulfate in pyridine, e.g., benzoin to benzil (86%),[190] and the latter with cupric acetate in 70% acetic acid, e.g., 4-hydroxy-3-hexanone to dipropionyl (70%).[191] Ferric chloride in a boiling ether-water mixture is also used as an oxidant.[191] Certain alicyclic 1,2-diketones are prepared by oxidation of the acyloins with chromic anhydride in glacial acetic acid, e.g., 3,3,6,6-tetramethyl-1,2-cyclohexanedione (64%).[201] Improvements in carrying out oxidations of benzoins and in processing the reaction mixtures have been described.[192–194] In one oxidation procedure, a catalytic quantity of cupric acetate is employed, which is continuously regenerated by the action of ammonium nitrate. The reduction product of the latter is ammonium nitrite, which is decomposed simultaneously to nitrogen and water.[194] Benzoins carrying halo,[195] methoxyl,[198,212] and dialkylamino[199] groups have been oxidized.

Secondary acetylenic alcohols, prepared in good yields from acetylenic Grignard reagents and aldehydes, are oxidized to *acetylenic ketones*

(40–80%).[203,204] The oxidation is carried out at 0–20° by means of chromic acid with acetone as solvent. An acetone layer of the unsaturated ketone separates, preventing further oxidation.

Preparations of *halo ketones*, such as α,α′-dichloroacetone (75%)[205] and 1-chloro-4-phenyl-2-butanone (82%),[143] and *keto ethers*, such as 4-methoxycyclohexanone (65%)[207] and *sym*-dialkoxyacetones (40–70%),[208] have been carried out by the oxidation of the corresponding alcohols with chromic-sulfuric acid mixture. Methyl esters of certain α-hydroxy acids can be oxidized to the *α-keto esters* with lead tetraacetate in boiling benzene as in the preparation of methyl phenylglyoxylate (84%).[213] Also, esters of lactic acid, $CH_3CHOHCO_2R$, have been converted to pyruvic esters by the action of potassium permanganate.[218,692] This same reagent has been employed for changing mandelic acid to the *α-keto acid*, benzoylformic acid (72%).[214]

A general synthesis for γ-keto acids involves the oxidation of γ-lactones with bromine in the presence of magnesium hydroxide.[216,217] The lactones are readily obtained by interaction of oxides and sodiomalonic esters with subsequent hydrolysis and decarboxylation (method 323). The over-all yields are excellent.

Nitro alcohols from the condensation of aromatic aldehydes with sodium salts of nitroparaffins are oxidized to *α-nitro ketones* with chromic-acetic acids, as illustrated by the preparation of α-nitroacetophenone, $C_6H_5COCH_2NO_2$ (80%).[219]

180. Oxidation of Alcohols by Ketones (Oppenauer)

$$R_2CHOH + R'_2CO \underset{\text{alkoxide}}{\overset{\text{Metal}}{\rightleftharpoons}} R_2CO + R'_2CHOH$$

Oxidation of alcohols by ketones in the presence of a metallic alkoxide has proved especially valuable in the steroid field.[221,222] The literature to 1951 has been reviewed.[693] An extensive investigation of experimental conditions using aluminum *t*-butoxide has been carried out.[223] The merits of various ketones as hydrogen acceptors have been considered. In general, methyl ethyl ketone and cyclohexanone are best for high-molecular-weight alcohols. The condensation products from these ketones may be removed by steam distillation. Benzil is recommended for preparing aldehydes and ketones capable of being distilled from the reaction mixture below 100°. Benzil or quinone may be used for ketone products boiling from 100° to 200°, especially if they are likely to condense. The optimum temperature, duration of reaction, and concentration of reactants may vary for the alcohol oxidized. In general, 0.5 mole of alkoxide per mole of alcohol gives good results; however, an additional 0.5 mole of alkoxide is recommended to remove any water present in the reaction mixture. A high ratio of 40 to 80 moles of ketone for 1 mole of a steroid is desirable. For simpler alcohols, 20 moles of acetone or methyl ethyl ketone, 3–10 moles of cyclohexanone, or 1–3 moles of quinone or benzil are satisfactory. The equilibrium is displaced by the large excess of the ketone reactant to give the desired product. It is preferable to carry out the oxidation at 55–60°. The use of an inert diluent, such as benzene, toluene, or dioxane, minimizes ketone condensation products.

The reaction has been extended to nitrogen-containing compounds by the use of an alkali alkoxide, such as potassium *t*-butoxide.[224]

181. Catalytic Dehydrogenation of Secondary Alcohols

$$R_2CHOH \xrightarrow[\text{Catalyst}]{-H_2} R_2CO$$

Ketones are formed in good yields by vapor-phase dehydrogenation of secondary alcohols over copper chromite catalyst. An example is the conversion of cyclohexanol to cyclohexanone (60%).[225] A liquid-phase dehydrogenation using Raney nickel catalyst at 170° has proved successful for preparing C_4–C_9 aliphatic ketones (79–95%).[226] The catalyst can be reused. The procedure has been modified by employing a hydrogen acceptor, such as cyclohexanone. The mixture of catalyst, hydrogen acceptor, alcohol, and toluene is merely refluxed for short periods.[227]

The reaction may also be performed over a mixed-oxide catalyst at 280° and 100 atm. of ethylene, which serves as the hydrogen acceptor,[363] as illustrated by the preparation of β-tetralone from 1,2,3,4-tetrahydro-2-naphthol.[485] By the same procedure, diisobutyryl, a *diketone*, has been prepared from the acyloin (27%).[228]

Dehydrogenation of 1,4-pentanediol over a copper chromite catalyst in the liquid phase yields the corresponding *hydroxy ketone*, 5-hydroxy-2-pentanone (30%).[229]

182. Oxidation of Olefinic Compounds (Ozonolysis)

$$R_2C{=}CHR \xrightarrow[H_2O]{O_3;} R_2CO + RCHO$$

Ozonolysis of olefins has found little application in the preparation of ketones for synthetic purposes. Since the ozonides may be explosive, the method has been limited to the reaction of small quantities of olefins, mostly for degradation studies and location of double bonds.

Improved conditions for the oxidation of olefins with ozone to ketones (60–70%) have been described.[231-233] The use of Dry Ice temperature and methylene chloride as solvent lessens the loss of volatile olefins in the

oxygen stream. The ozonides are decomposed by zinc and water in the presence of acetic acid or by catalytic hydrogenation with 1% palladium-calcium carbonate catalyst. Ozonides also react with Raney nickel to give aldehydes and ketones.[234] A new ozonizer has been described.[231]

Several olefinic compounds have been oxidized with potassium permanganate or chromic acid to furnish ketones. An example is the oxidation of diisobutylene to methyl neopentyl ketone (56%).[235]

Methylenecyclobutane has been converted to cyclobutanone by oxidation to the corresponding glycol with performic acid and subsequent cleavage of the glycol with lead tetraacetate (75% over-all).[237]

183. Oxidation of Methylene Groups

$$ArCOCH_2Ar \xrightarrow[\text{or Nitrogen oxides}]{SeO_2} ArCOCOAr$$

Compounds containing reactive methylene groups are readily converted by suitable oxidizing agents to carbonyl derivatives. Reviews of the reaction employing selenium dioxide [564] or nitrogen oxides [565] are given.

Selenium dioxide is commonly applied to a methylene group activated by a carbonyl group, although an adjacent double bond, aromatic ring, or heterocyclic ring may also subject it to attack. The conversion of aldehydes and methyl ketones leads to glyoxals (method 157). Best results are obtained when only one methylene group is present. For example, aryl benzyl ketones have been oxidized almost quantitatively to substituted benzils by treatment with selenium dioxide and acetic anhydride at 140–150° for 3 to 4 hours.[566] Dioxane has been used as solvent with this oxidizing agent. The products are purified by activated-charcoal treatment. Other experimental details are illustrated in the preparation of methyl phenyl diketone (60%)[567] and 2,4,6-trimethylbenzil (83%).[568]

Cyclic ketones like cyclohexanone[569] and cycloheptanone[570] yield the corresponding α-diketones in 35% and 90% yields, respectively.

Compounds having methylene groups situated between two activating groups—ketone, acid, or ester—are readily oxidized with selenium dioxide to furnish *triketones,*[571] *keto diesters,*[572] *α,β-diketo esters,*[573] or *α-keto acids.*[574]

Another procedure utilizes oxides of nitrogen. An example is the oxidation of diethyl malonate to diethyl oxomalonate, $CO(CO_2C_2H_5)_2$, with nitrous anhydride (76%).[575] Synthesis of alkyl aryl α-diketones has been accomplished under similar conditions (30–40%).[576]

A benzyl side chain is changed to a benzoyl group by vigorous oxidation. For example, 4,4′-diacetylaminodiphenylmethane[248] is converted with chromic acid to the benzophenone in 70% yield. Also, 2-benzoylpyridine is made from 2-benzylpyridine in 86% yield by the action of potassium permanganate.[244]

Oxidation of cyclohexene with chromic anhydride in acetic acid gives a 37% yield of 2-cyclohexenone; likewise, 1-methylcyclohexene goes to 3-methyl-2-cyclohexen-1-one (20%).[441]

Certain aromatic compounds containing alkyl groups have been converted to carbonyl derivatives by liquid-phase oxidation of these groups with air in the presence of chromium oxide catalysts.

$$ArCH_2CH_3 \xrightarrow[\text{Catalyst}]{O_2} ArCOCH_3$$

By the simple procedure of passing dispersed air through a suspension of *m*-diethylbenzene, 1% chromia, and 4% calcium carbonate at 130° for 40 hours, a 50% yield of *m*-ethylacetophenone is obtained.[238] Likewise, aromatic esters,[239,246,247] acetophenones,[4] and halogenated benzenes[245] containing alkyl groups yield the corresponding *keto esters, diketones,* and *halo ketones,* respectively. Manganese dioxide catalyst has also been used.[240] Tetralin can be oxidized to α-tetralone with dispersed air in the absence of a catalyst (56%).[241]

184. Cleavage of β-Keto Esters

The formation of β-keto esters and their cleavage represents an important synthesis for many types of ketones. The methods of synthesis of various β-keto esters are considered under methods 211 to 215 and have been reviewed.[614] Quite often the intermediate β-keto esters are not isolated but are cleaved directly to ketones. With few exceptions (methods 266 and 308), the cleavage always results in the formation of a ketone. Syntheses involving these cleavages are considered here.

Monoalkylation of ethyl acetoacetate and subsequent ketonic hydrolysis gives methyl ketones of the type CH_3COCH_2R (acetoacetic ester synthesis).

$$CH_3COCH_2CO_2C_2H_5 \xrightarrow[RX]{NaOC_2H_5;} CH_3COCHRCO_2C_2H_5 \xrightarrow{H^+} CH_3COCH_2R$$

$$CH_3COCHRCO_2C_2H_5 \xrightarrow{NaOC_2H_5;R'X} CH_3COCRR'CO_2C_2H_5$$

$$CH_3COCRR'CO_2C_2H_5 \xrightarrow{H^+} CH_3COCHRR' + CO_2 + C_2H_5OH$$

The over-all yields resulting from the use of primary alkyl bromides are 50–70%. The method is illustrated by the preparation of methyl *n*-amyl ketone. (61%).[256] Monoalkylation with secondary alkyl bromides is less complete, and the over-all yields are lower (20–30%).

Dialkylation followed by hydrolysis gives methyl ketones of the type $CH_3COCHRR'$ The over-all yields are 30–40%, often depending on which

alkyl group is introduced first when R and R′ are different.[250,251] For example, in the preparation of methyl methylisopropylacetoacetate, better results are obtained if the methyl group is substituted first (60% ester yield)[252] (cf. method 213). Hydrolysis of disubstituted acetoacetic esters, $CH_3COCRR'CO_2C_2H_5$, in which R and R′ are methyl or ethyl groups usually gives ketones in 60 to 80% yields.[253,254] When R is a *n*-butyl group and R′ is either a *n*- or *s*-butyl group, the ketones are formed in low yields, ester formation being favored (cf. method 308); however, these particular ketones are available in good yields by cleaving the corresponding *t*-butyl acetoacetates.[255]

Sulfuric[256] or phosphoric[257] acids are used for the ketonic hydrolysis, as in the preparation of methyl *n*-amyl ketone. Also, the hydrolysis is brought about by boiling with acetic-sulfuric acid mixture,[258] hot 5% potassium hydroxide solution,[259] or hydriodic acid if the hydrolysis is especially difficult.[260] Benzylacetone, $C_6H_5CH_2CH_2COCH_3$, is formed by hydrolysis of the corresponding β-keto ester with water at 150–250° and 200 atm. Dialkylated β-keto esters are stable to this treatment; therefore, a single ketone can be obtained from a mixture of mono- and di-alkylated β-keto esters.[253]

Difunctional compounds have been prepared by this series of reactions. Alkylation with unsaturated halides[284-287] or alkylation of unsaturated β-keto esters[262] leads to *olefinic ketones*. Halogenation of a substituted acetoacetate followed by acetic-sulfuric acid hydrolysis gives *α-halo ketones*. An example of this transformation is the chlorination of ethyl benzylacetoacetate with sulfuryl chloride (69%) followed by hydrolysis and decarboxylation to give α-benzyl-α-chloroacetone (84%).[288] If alkoxy halides are used, *keto ethers* result. In this manner, δ-ethoxybutyl methyl ketone (35% over-all)[291] and δ-phenoxybutyl methyl ketone (61%)[292] have been prepared. Similarly, alkylation using dialkylamino halides yields *dialkylamino ketones* in about 60% over-all yield,[306] as illustrated by the conversion of γ-diethylaminopropyl chloride and ethyl sodioacetoacetate to 1-diethylamino-5-hexanone (60%).[307] An example of the reaction of a halogenated ester leading to a *keto acid* is found in the preparation of 8-ketononoic acid (68%).[297] γ-Keto-α-alkyl acids have been prepared by a one-step hydrolysis and decarboxylation of certain cyanoacetoacetic esters.[296]

$$RCHCNCH(COCH_3)CO_2C_2H_5 \xrightarrow{H^+} RCH(COOH)CH_2COCH_3 + CO_2 + C_2H_5OH$$

α-Keto acids have also been obtained by treating α-oxalyl esters with boiling dilute sulfuric acid for 6 hours (8–94%).[295] These starting materials are prepared by condensation of ethyl oxalate and a second ester (method 211).

$$(CO_2C_2H_5)_2 + RCH_2CO_2C_2H_5 \xrightarrow{NaOC_2H_5} C_2H_5O_2CCOCHRCO_2C_2H_5$$
$$\downarrow H^+$$
$$RCH_2COCO_2H + CO_2 + C_2H_5OH$$

β-Keto esters prepared by additional methods (methods 211–215) are cleaved to give other types of ketones. (1) Acylation of the sodium enolates of disubstituted acetic esters followed by hydrolysis and decarboxylation gives ketones of the type $R'COCHR_2$.

$$HCR_2CO_2C_2H_5 \xrightarrow{(C_6H_5)_3CNa} Na^+(CR_2CO_2C_2H_5)^-$$
$$\downarrow R'COCl$$
$$R'COCHR_2 + CO_2 + C_2H_5OH \xleftarrow{H^+} R'COCR_2CO_2C_2H_5$$

The over-all yield from ester and acid chloride is 38–58%.[262] (2) Self-condensation of high-molecular-weight esters and hydrolysis of the resulting β-keto esters gives symmetrical ketones of the type RCH_2COCH_2R.

$$RCH_2CO_2C_2H_5 \xrightarrow{NaOC_2H_5} RCH_2COCHRCO_2C_2H_5 \xrightarrow{H^+} RCH_2COCH_2R$$

The over-all yields (R equals *n*-C_3–C_8, *n*-C_{11}, and *n*-C_{12}) from the esters vary from 55% to 78%.[259] Certain heterocyclic ketones, namely, 8-acetylquinoline and β-acetylpyridine, have been prepared through a mixed ester condensation.[279,280] (3) If acetoacetic ester is acylated in the form of its sodium enolate and carefully hydrolyzed, a new β-keto ester is formed. Alkylation of this keto ester followed by hydrolysis gives ketones of the type $RCOCH_2R'$.

$$CH_3COCH_2CO_2C_2H_5 \xrightarrow[RCOCl]{NaOC_2H_5;} CH_3COCH(COR)CO_2C_2H_5$$
$$\downarrow NH_3$$
$$RCOCHR'CO_2C_2H_5 \xleftarrow[R'X]{NaOC_2H_5;} RCOCH_2CO_2C_2H_5$$
$$\downarrow H^+$$
$$RCOCH_2R'$$

The over-all yields are stated to be 13–20% from the acid chloride;[303] however, the directions are not clear.[304,305] If the chloride of a dibasic acid is used, a *diketone* results. Thus, terephthalic acid chloride gives *p*-diacetylbenzene (15% over-all).[283] *o*-Chloroacetophenone, a *halo ketone*, has been prepared from ethyl acetoacetate and *o*-chlorobenzoyl chloride (54%).[290]

Aminomethyl ketones have been prepared by the α-oximination of β-keto esters followed by reduction and cleavage.[310]

$$RCOCH_2CO_2C_2H_5 \xrightarrow{HNO_2} RCOC(NOH)CO_2C_2H_5 \xrightarrow[(CH_3CO)_2O]{Zn}$$

$$RCOCH(NHAc)CO_2C_2H_5 \xrightarrow{HCl} RCOCH_2NH_2 \cdot HCl$$

Symmetrical ketones are sometimes prepared from acyl chlorides by way of diketenes and β-keto acids.[691]

$$2RCH_2COCl \xrightarrow{(C_2H_5)_3N} RCH_2COC(R)=C=O \xrightarrow{H_2O} (RCH_2)_2CO + CO_2$$

The addition of ethyl sodiomalonate to olefinic ketones followed by ring closure and β-keto ester cleavage leads to 1,3-cyclohexanediones. The reaction has been applied to the formation of 2-alkyl-5-phenyl-1,3-cyclohexanediones[583] and is typified by the preparation of 5,5-dimethyl-1,3-cyclohexanedione (85%).[584] Other cyclizations for formation of four- and five-membered rings have been described.[585,586]

185. Decarboxylation of Acylmalonic Acids

$$RCOCl + C_2H_5OMgCH(CO_2C_2H_5)_2 \longrightarrow RCOCH(CO_2C_2H_5)_2 \xrightarrow{H^+} RCOCH_3$$

A convenient method for preparing alicyclic or aromatic methyl ketones consists in the acylation of the ethoxymagnesium derivative of diethyl malonate with the appropriate acyl chloride, followed by acid hydrolysis and decarboxylation of the resulting β-keto diester.[312-314] The last step is carried out like the ketonic cleavage of β-keto esters.[262] The over-all yields are 60–85%.

The method is especially valuable for the preparation of certain substituted acetophenones, namely, *o*- and *p*-nitroacetophenone and *o*-chloroacetophenone.[314] Methods involving Grignard, Friedel-Crafts, or nitration reactions are apparently not applicable for the preparation of these nitro compounds, and the Friedel-Crafts reaction is not applicable to the preparation of *o*-chloroacetophenone. Although the acetoacetic ester synthesis has been used for the preparation of these and other substituted acetophenones, it may be complicated by O-acylation and also by cleavage at either acyl group (cf. method 212).

High-molecular-weight aliphatic ketones of the type $RCOCH_2R'$ are made by acylation of substituted dibenzyl esters of malonic acid followed by hydrogenolysis and decarboxylation.[316]

$$R'CH(CO_2CH_2C_6H_5)_2 \xrightarrow[RCOCl]{NaOC_2H_5;} RCOCR'(CO_2CH_2C_6H_5)_2$$

$$\xrightarrow[Pd]{H_2} RCOCR'(CO_2H)_2 \xrightarrow{-CO_2} RCOCH_2R'$$

Decomposition of acylated malonic esters over aromatic sulfonic acids leads to β-keto esters (method 214).

186. Thermal Decarboxylation of Acids

$$RCO_2H \xrightarrow[Heat]{Catalyst} R_2CO + CO_2$$

Symmetrical ketones (R equals ethyl, propyl, isopropyl, *n*-butyl, isobutyl, and *n*-heptyl) have been prepared in nearly "quantitative" yields by passing the acid vapors over thoria at high temperatures. Studies have been made of metallic oxide catalysts and temperature of reaction. In general, a thoria catalyst has been favored at temperatures of 400–500°.[318] The apparatus and catalyst preparation have been described.[319]

More recently, it has been shown that a thoria "aerogel" catalyst is superior to the thoria-hydrogel and thoria-on-pumice catalysts. High yields at a lower temperature (310°) and high flow rates are obtained.[320]

The distillation of lauric acid (or other high-boiling acids) over the catalyst bed is difficult and gives poor yields; however, when the lower-boiling methyl ester is used, laurone is obtained in a 93% yield.[321] Similarly, the ethyl ester of 9-undecenoic acid gives undecylenone (86%).

A large number of unsymmetrical ketones have been prepared by the thermal decarboxylation method;[322,323] however, the yields are not recorded. In general, by using a large excess of the short-chain acid (which minimizes formation of the long-chain symmetrical ketone) over thoria at 400°, yields of about 50% are obtained.[35,303] Methyl benzyl ketone and other alkyl aryl ketones have been synthesized in this manner (65%).[319] The use of manganese oxide catalyst at 400° gives about the same results.[324]

The thermal decarboxylation of a mixture of barium salts has been used to prepare unsymmetrical ketones; the yields are not stated.[325] The earlier procedure has been modified by carrying out the reaction *in vacuo*[326] in an iron flask. Glass reaction vessels are inferior. In this manner, a large number of the high-molecular-weight methyl ketones, C_9, C_{10}, C_{12}–C_{17}, and C_{19}, are prepared in 54–67% yields. Cyclopentanone has been synthesized in 80% yield by distillation of adipic acid from barium hydroxide at 295°.[327] In a study of metallic oxides and carbonates, magnesium oxide is preferred for the liquid-phase ketonization of stearic acid at 330–360° (95%).[328] A convenient method for the preparation of dibenzyl ketone is the reaction of phenylacetic acid, acetic anhydride,

and fused potassium acetate at 150° (41%).[330] Several pyridyl ketones have been made in a similar way.[339,340]

Acids which have no α-hydrogen atoms may yield unsymmetrical ketones on decarboxylation instead of the anticipated symmetrical compounds.[331]

187. Interaction of Grignard Reagents and Nitriles

$$R'MgX + RCN \longrightarrow RR'C{=}NMgX \xrightarrow{H_2O} RCOR'$$

Grignard reagents react with nitriles to form ketimine salts which on hydrolysis give ketones. For the most part, the procedure is successful only for high-molecular-weight aliphatic and aromatic nitriles, although the lower-membered aliphatic nitriles respond favorably with aromatic Grignard reagents.[353,354,388] Poor results have been associated with a competing reaction of the Grignard reagent at the α-hydrogen of the nitrile to form a hydrocarbon and a magnesium derivative which may react further at the nitrile group, viz., $RCH_2CN + R'MgX \longrightarrow R'H + (RCHCN)MgX$.[677]

Alkyl α-naphthyl ketones from α-cyanonaphthalene and RMgX are prepared when R is methyl through *n*-hexyl, cyclohexyl, or phenyl (35–60%).[346] The Grignard reagents are treated with the cyanide for 5 hours in boiling toluene or benzene-ether mixture. The intermediate ketimine salt is then hydrolyzed with aqueous ammonium chloride. Acylated aromatic compounds can be prepared readily in this way, avoiding isomeric mixtures encountered by the Friedel-Crafts method. Thus, the pure acetyl-, propionyl-, and benzoyl-phenanthrenes have been synthesized (50–87%).[21,347,348]

Ketones from fatty acid nitriles and high-molecular-weight Grignard reagents are often contaminated with hydrocarbons.[349,350] This difficulty can be avoided by discarding the ethereal solution containing the hydrocarbon products before the hydrolysis of the ketimine salt.[351] The ketone-hydrocarbon mixture has been separated by dissolving the ketone in warm concentrated sulfuric acid, removing the insoluble hydrocarbons, and then reclaiming the ketone by diluting the acid solution with water.[303]

The reaction of olefinic Grignard reagents with nitriles to give *olefinic ketones* is not common. An example is the preparation of 4-hexen-3-one from allylmagnesium bromide and propionitrile (25%).[371]

Nitriles carrying relatively unreactive halogen atoms have been used to prepare *halo ketones*. Thus, 4-chloro-2-ethoxybutyronitrile, $CH_2ClCH_2CH(OC_2H_5)CN$, has been converted to 3-chloro-1-ethoxypropyl alkyl ketones in 40–75% yields.[369] Reaction of methyl Grignard reagent and o-bromophenyl cyanide gives o-bromoacetophenone (80%).[470]

Diphenylacetoin, a *hydroxy ketone*, has been prepared in 45–60% yield by the action of benzyl Grignard reagent on phenylacetaldehyde cyanohydrin.[372]

An important method for the preparation of *keto ethers* is the reaction of cyano ethers with Grignard reagents. In this manner, a large number of α-alkoxy aliphatic ketones have been made (30–70%).[208,373–377] Likewise, phenoxymethyl alkyl ketones have been prepared (20–64%).[380] When the Grignard reagent contains an ω-alkoxy group, ω-alkoxy ketones are formed.[379]

Ethyl β-oxovalerate, a *β-keto ester*, is prepared from ethyl Grignard reagent and ethyl cyanoacetate (58%).[386,387] *Amino ketones* are conveniently made by the action of aromatic Grignard reagents on γ-diethylaminobutyronitrile, $(C_2H_5)_2NCH_2CH_2CH_2CN$, in 80–90% yields.[388]

188. Interaction of Organometallic Reagents and Anhydrides

$$(RCO)_2O \xrightarrow{R'MgX} RC(OMgX)(R')OCOR \xrightarrow{H_2O} RCOR'$$

A large number of ketones have been prepared by treating anhydrides with Grignard reagents. It has been shown that the yields are best at low temperatures (−75°). Primary, secondary, and tertiary aliphatic or aromatic Grignard reagents give high yields when treated with acetic, propionic, or butyric anhydrides.[389–391]

A variety of ketones may be made using cadmium alkyls (50–70%). In the preparation of alkyl aryl ketones, reaction of the aliphatic rather than the aromatic anhydride is preferred.[392] *Keto acids* result when phthalic anhydride[392–394] or dimethylsuccinic anhydride (60–70%)[395] is used.

Acetylenic ketones of the type $RC{\equiv}CCOCH_3$ are prepared by the reaction of acetic anhydride and acetylenic Grignard reagents. The latter compounds are readily made from acetylenic hydrocarbons and ethylmagnesium chloride, and are added slowly to the anhydride at a low temperature. This procedure prevents a secondary reaction of the desired product with a second molecule of Grignard reagent. In this manner, 3-octyn-2-one (58%) and 3-nonyn-2-one (55%) are prepared.[396] Sodium phenylacetylide has been treated with various anhydrides, including acetic, benzoic, cinnamic, and crotonic, to give the corresponding phenylacetylenic ketones.[397]

189. Interaction of Organometallic Reagents and Acyl Chlorides

$$2RCOCl + R'_2Cd \longrightarrow 2RCOR' + CdCl_2$$

Addition of cadmium alkyls to acyl chlorides yields the corresponding ketones. The method has been reviewed,[400] and the experimental condi-

tions have been studied.[401] The cadmium reagents are readily prepared by adding anhydrous cadmium chloride to Grignard reagents. It is advisable to check the completeness of the cadmium alkyl formation by the standard Gilman test for Grignard reagent. The use of an alkyl bromide for formation of the cadmium reagent and of benzene as solvent during the coupling reaction has improved the yield. A variety of ketones have been prepared, and yields of 50–80% may be expected if highly reactive ketones are not formed and if the cadmium alkyl is not secondary or tertiary.[401,402] In the preparation of methyl *n*-butyl ketone (74%), *n*-propyl-*n*-heptadecyl ketone (65%), acetophenone (85%), and ethyl α-furyl ketone (61%), the smaller alkyl fragment comes from the cadmium alkyl. Either the aryl or alkyl cadmium compound is satisfactory for formation of alkyl aryl ketones.

The reaction has been extended to the formation of difunctional compounds. High-molecular-weight *keto esters* and *halo ketones* are formed by using carbalkoxy acyl chlorides and halogenated acyl chlorides, respectively. Methyl 4-keto-7-methyloctanoate (75%) and 1-chloro-2-hexanone (51%) have been prepared in this way.[401,403] Also, β-aroylpropionic esters are made by the reaction of diarylcadmium reagents with β-carbomethoxypropionyl chloride.[678] In the preparation of a carbalkoxy acyl chloride having a branched carbon skeleton, an ester interchange may occur to give a mixture of the two possible carbalkoxy acyl chlorides.[581] Alkoxy acyl chlorides react with cadmium alkyls to give *keto ethers*, as in the preparation of γ-phenoxypropyl methyl ketone (78%) from γ-phenoxybutyryl chloride and methylcadmium[292] and of certain 2-alkoxyethyl phenyl ketones from β-alkoxypropionyl chloride and diphenylcadmium.[404]

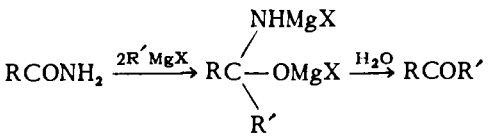
A large number of methyl and ethyl ketones have been prepared in about 70% yields by employing zinc alkyls; however, full directions are not given.[405] Reaction of zinc alkyls and unsaturated acyl chlorides in the presence of a zinc-copper couple gives *olefinic ketones* in 75–90% yields. By this procedure, 5-ethyl-4-hepten-3-one (74%) and 3,4-diethyl-4-hexen-2-one (83%) are made.[406] High-molecular-weight *keto acids* (C_{28}–C_{35}) have been prepared in good yields (77–92%) by adding ethereal Grignard reagents to anhydrous zinc chloride, replacing the ether with benzene as solvent, and then treating with carbethoxy acyl chlorides under reflux.[407,408]

In general, the cadmium reagent is preferred to the zinc reagent because it is more readily prepared and is less reactive toward the carbonyl group.

Grignard reagents have been used directly in mono-[409,410,539] and diketone[415] formation. More recently, it has been found that a catalytic quantity of cuprous chloride greatly increases the yields.[416,419] An example is the formation of hexamethylacetone in 70–80% yield from *t*-butylmagnesium chloride and trimethylacetyl chloride. Diketones have

also been prepared by coupling magnesium enolates of certain ketones with high-molecular-weight acyl chlorides.[539]

190. Interaction of Grignard Reagents and Amides



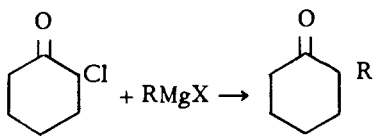
This reaction has been used extensively for the preparation of neopentyl and *t*-butyl ketones from *n*-alkyl Grignard reagents and *t*-butylacetamide and trimethylacetamide, respectively, (52–78%).[427,428] In addition, a large number of *halo ketones* have been prepared by the reaction of aromatic Grignard reagents with chloro-substituted aromatic amides (60–80%).[429–432] For example, benzyl Grignard reagent and *m*-chlorophenylacetamide react to give benzyl *m*-chlorophenyl ketone (80%). In a similar manner, the use of mandelamide or *p*-methoxyphenylacetamide leads to *hydroxy ketones* or *keto ethers*, respectively.[429]

191. Interaction of Grignard Reagents and α,β-Olefinic Ketones

$$RCH{=}CHCOR + R'MgX \longrightarrow RR'CHCH{=}C(OMgX)R \xrightarrow{H_2O} RR'CHCH_2COR$$

Aliphatic and aromatic ketones have been prepared by this method. The Grignard reagent adds 1:4 to the conjugated ketone system. This is illustrated by the addition of ethyl Grignard reagent to ethylideneacetone, $CH_3CH{=}CHCOCH_3$, to give a 75% yield of 4-methyl-2-hexanone.[437] Highly branched ketones have been prepared in small yields.[438,439] The amount of 1:4 addition varies considerably with the Grignard reagent[440,441] (cf. method 89). Certain methoxy-substituted chalcones, $ArCH{=}CHCOAr$, have been treated successfully.[132]

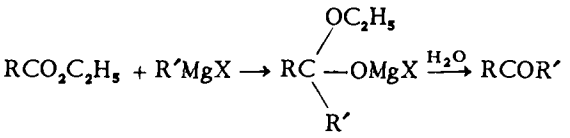
192. Interaction of Grignard Reagents and Halo Ketones



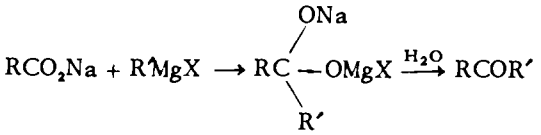
The most successful application of this method has been the synthesis of 2-substituted cyclohexanones by the action of either aliphatic[444] or aromatic[445] Grignard reagents on 2-chlorocyclohexanone. An example is the formation of 2-phenylcyclohexanone (R = C_6H_5) in 60% yield.[443] The

aromatic moiety may also be substituted with alkyl or alkoxyl groups. The method has been extended to the preparation of 2-phenylcyclopentanone (50%).[446]

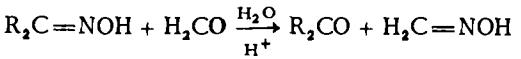
193. Interaction of Organometallic Reagents and Esters[447-450]
(cf. method 91)



194. Interaction of Organometallic Reagents and Salts of Carboxylic Acids[449,451]

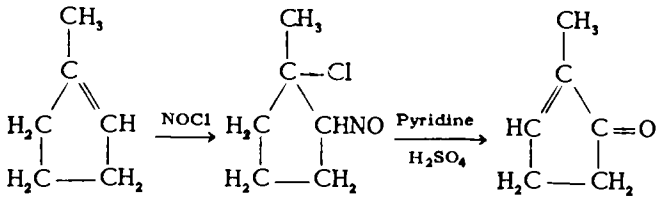


195. Hydrolysis of Ketone Derivatives



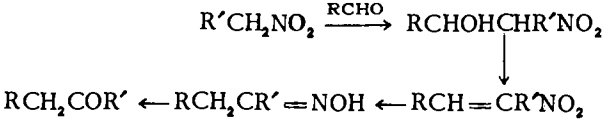
Oximes, which are produced by several synthetic routes (cf. Chapter 27), are readily hydrolyzed to carbonyl compounds. Thus, the acetylbenzoyl monoxime, prepared by the nitrosation of propiophenone, has been converted to the diketone by hydrolysis with dilute sulfuric acid.[452]

In another instance, the action of aliphatic Grignard reagents on methyl α-nitrosoethyl ketone with subsequent acid hydrolysis furnishes α-hydroxy ketones of the type $CH_3(R)COHCOCH_3$.[456] The oxime of 1-methylcyclopenten-5-one is hydrolyzed by dilute sulfuric acid (54%). It is prepared by the action of nitrosyl chloride on 1-methylcyclopentene with subsequent dehydrohalogenation with pyridine.[598]



A method for hydrolyzing *p*-quinone oximes with the aid of cuprous chloride has been described; the yields are excellent.[459]

Aliphatic ketones have been prepared by a five-step synthesis from nitroparaffins.

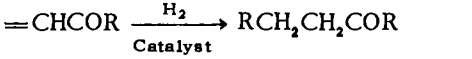


The nitroparaffins are condensed with aldehydes to yield nitro alcohols (70–80%), which on acetylation and treatment with an aqueous methanolic solution of sodium bicarbonate are converted to nitroölefins (80–84%). These compounds are reduced to the corresponding ketoximes by zinc and acetic acid (50–60%).[453] Reduction with iron and dilute hydrochloric acid gives good yields of either ketones or ketoximes, depending upon the amount of hydrochloric acid used.[679] The ketoximes can be hydrolyzed to ketones by refluxing with dilute sulfuric acid in the presence of formalin, which acts as a hydroxylamine acceptor (80%). The over-all yields from the nitroölefins are 40–60%. In this manner, certain otherwise difficultly obtainable ketones are prepared. Semicarbazones have been converted to ketones by treatment with sodium nitrite in glacial acetic acid,[454] with aqueous oxalic acid,[455] or with phthalic anhydride.[490]

α-Keto acids or *esters* may be prepared by the hydrolysis of the corresponding oximino esters with 85% formic acid and nitrosylsulfuric acid at 0°.[457] Although α-oximino acids can be obtained in excellent yield from α-halo acids or substituted acetoacetic or malonic esters,[458] their hydrolysis may proceed poorly.[295]

Elimination of carbon dioxide from a carboxylic acid in the presence of a diazonium salt leads to an aryl hydrazone (Japp-Klingemann). Subsequent hydrolysis in the presence of pyruvic acid furnishes the carbonyl compound, as illustrated by the preparation of 2-*n*-butyrylpyridine (81%).[535]

196. Selective Reduction of α,β-Olefinic Ketones

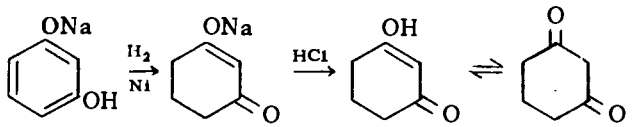


Selective hydrogenation of α,β-olefinic ketones to saturated ketones can be accomplished through careful control of the temperature, duration of reaction, and use of a catalyst active enough to permit low-temperature hydrogenation.[464] Thus, mesityl oxide, benzalacetone, and benzalacetophenone have been reduced in 90–100% yields to the corresponding saturated ketones.[465] Preparations of nickel catalysts used in these reductions are described.[465,466]

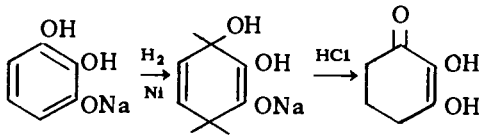
Other olefinic ketones have been reduced selectively at room temperature and atmospheric pressure over a platinum or palladium catalyst to give good yields of the ketones, namely, 5-methyl-3-heptanone (94%),[467,468] diisobutyl ketone (100%),[469] and α-benzylacetophenone (81–95%).[688] Selective hydrogenations of some 3-alkyl-2-cyclohexenones have been carried out over palladinized charcoal in essentially quantitative yields.[475] Preparation of platinum catalyst has been described.[470] Many olefinic ketones prepared by the aldol condensation or by acylation of olefins have been hydrogenated; however, the yields are not always stated.[471] Benzalacetone, $C_6H_5CH{=}CHCOCH_3$, is selectively reduced to benzylacetone in a 63% yield by the action of sodium amalgam in acetic acid-alcohol solution.[476]

Unsaturated keto esters obtained by the Knoevenagel condensation have been selectively hydrogenated in good yields with Raney nickel catalyst at room temperature and 45 atm. to saturated *keto esters*, e.g., ethyl α-heptylacetoacetate (97%) from ethyl α-heptylideneacetoacetate.[689]

197. Partial Reduction of Phenols



Phenols can be partially hydrogenated in the presence of alkali to cyclohexanones. An example is the synthesis of dihydroresorcinol, or 1,3-cyclohexanedione, by hydrogenation of resorcinol in the presence of Raney nickel and an equimolar quantity of sodium hydroxide (95%).[481] Under these same conditions, pyrogallol furnishes a stable enediolone.[482]



Hydrogenation of 2-naphthol in the presence of palladium and an organic base like N-ethylmorpholine gives 2-tetralone (40%);[483] other conditions for its reduction lead to other products.[484,485] By means of Raney nickel and alkali, 1,6-dihydroxynaphthalene has been partially reduced to 6-hydroxy-1-tetralone.[484]

Reductions of this type may also be carried out by the action of sodium and ammonia, sodium and alcohol,[486] or Raney nickel-aluminum alloy and alkali.[484]

198. Alkylation of Ketones

$$RCH_2COCH_2R \xrightarrow[R'X]{NaNH_2;} RCH_2COCHRR'$$

Many highly branched ketones have been prepared by the alkylation of simpler ketones, sodium amide or sodium alkoxides generally being used to form the enolate ion. For example, ketones of the type RCOR′, where R and R′ represent many combinations of methyl (Me), ethyl (Et), *n*-propyl (Pr), isopropyl, *n*-butyl, *s*-butyl, *t*-butyl, isoamyl, Et_2CH—, Et_3C—, *n*-Pr_2CH—, *n*-PrMeCH—, isoPrCH_2—, and *n*-$PrMe_2C$—, have been prepared; however, the yields are not always reported.[488] Alkylation of alicyclic ketones like cyclopentanone and cyclohexanone has also been studied. In these reactions all available α-hydrogens may be replaced, disubstitution on one side of the carbonyl group occurring first.[489-493] Alkyl aryl ketones of the types $ArCOCH_2R$, ArCOCHR′R″, and ArCOCR′R″R‴ are made by alkylating acetophenone and its derivatives with allyl or benzyl halides.[495] In general, the reactivity of the alkyl halide decreases with increasing carbon content and complexity. Oftentimes, an alkyl sulfate is employed as the alkylating agent. A review of the earlier work has been presented.[494] The method is illustrated by the conversion of diisopropyl ketone to hexamethylacetone in the presence of sodium amide (52%).[165]

Methyl γ-chloropropyl ketone, $CH_3CO(CH_2)_3Cl$, undergoes intramolecular cyclization to methyl cyclopropyl ketone under the influence of 50% aqueous sodium hydroxide.[694]

The effect of the basic reagent has been studied in the methylation of phenylacetone. Monomethylation proceeds better with sodium isopropoxide than with sodium ethoxide. Introduction of a second alkyl group is accomplished best with potassium *t*-butoxide. Sodium *t*-amylate allows many alkylations that fail or give poor results when carried out with sodium amide.[493] 1,1-Disubstituted 2-tetralones are conveniently prepared by alkylation in the presence of sodium hydride, no monosubstituted products being formed with this reagent.[496]

The temperature of the reaction has been shown to be important. For example, in the alkylation of 2-methylcyclopentyl phenyl ketone, the reaction carried out at the temperature of the refluxing benzene solution gives the desired product; however, the use of boiling xylene leads to O-alkylated products, and boiling toluene gives mixtures.[668]

Diketones have been alkylated by a modified procedure.[500,501] The monosodio derivative is prepared in ether by treating the diketone with powdered sodium. It is then allowed to react with the alkyl iodide in acetone or dioxane solution. This scheme has been applied in the prep-

aration of *n*-butylbenzoylacetone, $PhCOCH(n\text{-}Bu)COCH_3$, ethylacetylacetone, $CH_3COCH(C_2H_5)COCH_3$, and other high-molecular-weight compounds. In a similar manner, acyloin enolates are alkylated with primary halides in ethyl ether or toluene to furnish *α,α-dialkyl-α′-hydroxy ketones.*[502]

Alkylation with allyl bromide leads to *olefinic ketones,* e.g., 2-allylcyclohexanone (62%) and α-allylethyl ethyl ketone (56%) from the corresponding ketones.[286,503] Desoxybenzoin, $C_6H_5CH_2COC_6H_5$, and β-diethylaminoethyl chloride, $(C_2H_5)_2NCH_2CH_2Cl$, combine to form the corresponding *amino ketone.*[504]

199. Interaction of Diazomethane and Carbonyl Compounds

$$RCHO + CH_2N_2 \longrightarrow RCOCH_3 + N_2$$

Diazomethane reacts with carbonyl compounds to introduce methylene groups.[505] In the case of aldehydes, nitrogen is lost and the corresponding epoxide, methyl ketone, or higher homolog of the starting aldehyde is formed, depending on the nature of the R group and catalytic influences. Similarly, ketones yield epoxides and homologous ketones. The latter may react further with additional diazomethane. For these reasons, the reaction may be complicated.

Cyclic ketones react to form the higher homologs; for example, cyclohexanone is converted to cycloheptanone (63%).[506]

An extension of this reaction has been the use of other aliphatic diazoalkanes. Benzaldehyde and the appropriate diazo compound give propiophenone, butyrophenone, and valerophenone in almost quantitative yield.[507] Furylaldehyde also reacts to form furyl alkyl ketones[526]

200. Catalytic Hydration of Acetylenic Compounds

$$RC{\equiv}CH + H_2O \xrightarrow{\text{Catalyst}} RCOCH_3$$

This method finds commercial application in the production of acetaldehyde from acetylene. Mercuric salts in the presence of dilute sulfuric acid act as the catalyst. The reaction has been extended to higher alkylacetylenes, which are obtained in about 60% yield from sodium acetylide and alkyl halides. These compounds are readily hydrated in aqueous solutions of acetone, methanol, or acetic acid to give 80–90% yields of the corresponding methyl ketones, for example, methyl butyl, methyl amyl, and methyl hexyl ketones.[508] Hydration has been accomplished by passing the acetylenic hydrocarbon and steam over a phosphoric acid catalyst at 150–204° and atmospheric pressure.[509]

Acetylenic carbinols (from sodium acetylide and a ketone) are readily hydrated in the presence of mercuric sulfate to give the corresponding

hydroxy ketones in high yields.[510,511] *β-Keto acids* have been prepared by hydration of acetylenic acids.[512] α-Acyloxy ketones, $R_2C(OCOCH_3)COCH_3$, are made by the action of carboxylic acids on acetylenic carbinols.[657]

201. Dehydration and Rearrangement of α-Diols

$$R_2COHCOHR_2 \xrightarrow{H^+} R_3CCOR + H_2O$$

The classical example of this method is the rearrangement of pinacol to pinacolone (72%).[513] The reaction is usually brought about by dilute sulfuric acid. A second procedure is the passage of a mixture of the pinacol and steam over silica-phosphoric acid at 275–300°; the yield of pinacolone is 94%.[514] Benzopinacol, $(C_6H_5)_2COHCOH(C_6H_5)_2$, is dehydrated and rearranged by iodine in acetic acid (96%).[515] Under the same conditions, diphenyl-(1-hydroxy-1-cyclopentyl)-carbinol undergoes rearrangement accompanied by ring expansion to form 2,2-diphenylcyclohexanone (98%).[516]

The reaction has been extended to other pinacols; however, their preparation may involve lengthy procedures.[517] Certain benzoins on reduction with metals and acids yield diols which are then converted to desoxybenzoins.[518–520] These conversions involve the migration of a hydrogen atom rather than an alkyl group. Similarly, aromatic *keto ethers* and *amino ketones* have been prepared.[520,521]

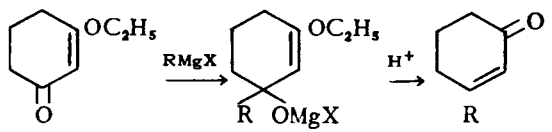
A modification of this reaction is the hydrolysis and rearrangement of olefin dibromides.[522] The most successful of these conversions is the preparation of methylisopropyl ketone (59%) from trimethylethylene dibromide.[523]

202. Decomposition of Glycol Monoalkyl Ethers

$$RCHBrCO_2C_2H_5 \xrightarrow[65\%]{NaOC_2H_5} RCH(OC_2H_5)CO_2C_2H_5 \xrightarrow[75\%]{R'MgX} RCH(OC_2H_5)COHR'_2 \xrightarrow[90\%]{H^+} RC(OC_2H_5){=}CR'_2 \xrightarrow[68\text{–}96\%]{H^+} RCOCHR'_2$$

Ketones of the type $RCOCHR'_2$, where R represents methyl, ethyl, isopropyl, *n*-butyl, *n*-hexyl, or phenyl, and R′ represents ethyl, *n*-propyl, *n*-butyl, or phenyl, have been prepared by a series of reactions similar to that used in the preparation of aldehydes (method 167).[525]

In an analogous manner, the monoethyl ether of dihydroresorcinol reacts with alkylmagnesium halides to form 3-alkyl-2-cyclohexenones.[475]



203. β-Diketones by Acylation of Ketones

$$CH_3COCH_2R \xrightarrow[BF_3]{(R'CO)_2O} R'COCH_2COCH_2R \quad \text{(Type I)}$$

$$CH_3COCH_2R \xrightarrow[\text{Base}]{R'CO_2C_2H_5} R'COCHRCOCH_3 \quad \text{(Type II)}$$

The acylation of ketones having reactive methylene groups by esters[501,541] or anhydrides[542,543] is a common and convenient method for preparing β-diketones. An ester is used in the presence of a base, and an anhydride with boron trifluoride. From an unsymmetrical ketone two types of ketones result, depending on which α-hydrogen atom reacts. In general, the boron trifluoride method leads to the formation of type I ketones, $R'COCH_2COCH_2R$, whereas the basic reagent method favors type II ketones, $R'COCHRCOCH_3$. Either sodium amide[544,549] or sodium hydride[545,549] is preferred as the basic reagent. Unsymmetrical ketones having only one reactive side (such as acetophenone) respond the same by either method.[542] Also, symmetrical ketones take the same course by both methods, e.g., acetone to acetylacetone.[546,547] Many representative ketones—methyl ethyl, methyl isopropyl, methyl isobutyl, methyl *t*-butyl, diisobutyl, methyl *n*-amyl, cyclohexanone, and acetophenone—have been converted to diketones. The acylating agents are varied and include ethyl esters or anhydrides of acetic, propionic, *n*-butyric, isobutyric, *n*-valeric, *n*-caproic, benzoic, anisic, phenylacetic, lauric, and nicotinic acids. Thus, a large number of β-diketones have been prepared in varying yields, mostly in the range of 30–60%.

β-Diketones are also formed by acylation of the enol esters of ketones with anhydrides in the presence of boron trifluoride.[673]

$$(RCO)_2O + R'C(OCOR)=CHR'' \xrightarrow[CH_3CO_2Na]{BF_3 \text{ then}} RCOCHR''COR'$$

If the acylating ester is diethyl oxalate, then an *α,γ-diketo ester,* or a substituted glyoxalate, is formed.[555-557] These substances are important intermediates in the synthesis of certain β-keto esters (method 307).

$$RCOCH_3 + (CO_2C_2H_5)_2 \xrightarrow{NaOC_2H_5} RCOCH_2COCO_2C_2H_5$$

204. α,β-Olefinic Ketones from Acetylenic Carbinols

$$RCH_2COH(R')C{\equiv}CH \xrightarrow{HCO_2H} RCH{=}C(R')COCH_3$$

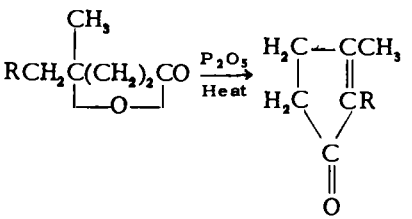
Ethynyl carbinols on heating with formic acid are isomerized to α,β-olefinic ketones; for example, isohexylmethylethynylcarbinol is taken to 3,7-dimethyl-3-octen-2-one (48%)[264] and 1-ethynyl-1-cyclohexanol to 1-acetyl-1-cyclohexene (70%).[594] Small amounts of unsaturated aldehydes may contaminate the product.

205. γ,δ-Olefinic Ketones from Alkenyl Esters of β-Keto Acids

$$CH_3COCH_2CO_2CH_2CH{=}CH_2 \xrightarrow{170\text{–}250^\circ} CH_3COCH_2CH_2CH{=}CH_2 + CO_2$$

Acetoacetates or benzoylacetates of β,γ-unsaturated alcohols—methallyl alcohol, crotyl alcohol, methylvinylcarbinol, cinnamyl alcohol, etc.—on heating at 170–250° evolve carbon dioxide and produce γ,δ-olefinic ketones (23–88%).[595] The unsaturated acetoacetates are readily prepared by the action of diketene on the corresponding unsaturated alcohols.

206. Cyclopentenones from Lactones



γ-Methyl-γ-lactones having a methylene group adjacent to the γ-carbon are converted conveniently to 2-alkyl-3-methyl-2-cyclopentenones (30–50%). The method is not applicable, however, to the preparation of 2-cyclopentenone and 3-methyl-2-cyclopentenone. The lactone is simply warmed over phosphorus pentoxide, and the product is distilled from the reaction mixture.[596]

207. β-Halo Ketones from Acyl Chlorides and Olefins

$$R'COCl + RCH{=}CHR \xrightarrow{\text{Catalyst}} RCHClCHRCOR'$$

Addition of acyl halides to olefins in the presence of catalytic amounts of aluminum chloride, stannic chloride, or zinc chloride gives β-halo ketones.[599] An example is the addition of propionyl chloride to ethylene

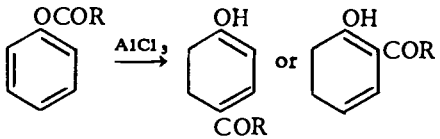
to form ethyl β-chloroethyl ketone (45%).[98] Sometimes the addition products are very unstable and undergo spontaneous dehydrohalogenation to olefinic ketones[101] (cf. methods 20 and 178).

208. α-Halo Ketones from Alkenyl Esters

$$RCO_2CR'{=}CH_2 \xrightarrow{Br_2} RCO_2CR'BrCH_2Br \longrightarrow RCOBr + R'COCH_2Br$$

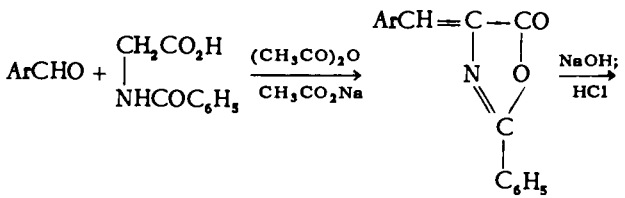
The dibromide derivatives of alkenyl esters spontaneously cleave in the cold to form α-bromo ketones and acyl halides. In this manner, 1-bromo-2-hexanone (67%) and 1-bromo-2-heptanone (80%) are prepared. The alkenyl esters are prepared by the catalytic addition of organic acids to alkylacetylenes (30–35%).[601]

209. Hydroxy Ketones from Phenolic Esters (Fries)



An ester of a phenol may be converted to the isomeric *o* or *p*-hydroxy ketone, or a mixture of both, by treatment with aluminum chloride. Critical discussions of the reaction have been presented[602] with respect to the influence of temperature, solvents, ester-reagent ratio, and the structure of the acyl[603] and phenoxy groups.[604] By varying the first three factors, it is often possible to prepare predominantly either of the isomeric ketones. The reaction is exemplified in the preparation of *o*- and *p*-propiophenol (35% and 40%, respectively)[605] and 2-hydroxy-4,6-dimethylacetophenone (80%).[606]

210. α-Keto Acids from Azlactones



$$ArCH_2COCO_2H + C_6H_5CO_2H + NH_4Cl$$

Hydrolysis of certain unsaturated azlactones with aqueous sodium hydroxide followed by treatment with dilute hydrochloric acid yields

α-keto acids. The azlactones are readily prepared from substituted benzaldehydes and hippuric acid.[608,609] In this manner, phenylpyruvic acid (72% over-all)[610] and *m*-chlorophenylpyruvic acid (52% over-all)[611] have been prepared. Other applications have been described.[608,612,613]

211. β-Keto Esters by Condensation of Esters

$$2RCH_2CO_2C_2H_5 \overset{NaOC_2H_5}{\rightleftharpoons} RCH_2COCHRCO_2C_2H_5 + C_2H_5OH$$

The acetoacetic ester condensation consists of a base-catalyzed reaction of two esters (at least one having an α-hydrogen atom) to form a β-keto ester. The scope, limitations, experimental procedures, and applications have been reviewed.[614,615,626]

Variations of the reaction include condensation of the same ester, a mixed ester condensation, and ester cyclizations. Improvement in yield of the self-condensation reaction is obtained by removing the alcohol produced, the reaction being forced to completion. In this manner, methyl esters[616] catalyzed by sodium methoxide and ethyl esters[148] catalyzed by sodium ethoxide are self-condensed (50–85%). Ethyl isobutyrate and ethyl isovalerate do not respond to sodium alkoxide catalysis; however, these compounds are readily self-condensed with the aid of diisopropylaminomagnesium bromide.[626] Another promising reagent is sodium hydride.[545] Mixed ester condensations in which only one ester has an α-hydrogen atom are satisfactory. These are less complicated than a condensation of two different esters each having reactive α-hydrogens. Thus methyl benzoate condensed under "forcing" conditions with methyl acetate, propionate, or butyrate forms the α-alkylbenzoylacetates, $C_6H_5COCHRCO_2CH_3$, in 45%, 61%, and 41% yields, respectively.[616] Similarly, condensation between ethyl oxalate and these esters produces α-ethoxalyl esters.[295,617]

$$RCH_2CO_2C_2H_5 + (CO_2C_2H_5)_2 \xrightarrow{NaOC_2H_5} RCH(COCO_2C_2H_5)CO_2C_2H_5 + C_2H_5OH$$

An example is the synthesis of ethyl α-ethoxalylpropionate (R = CH_3) in 70% yield.[618] Ethyl oxalate and ethyl succinate form ethyl α-ethoxalylsuccinate (83%).[624] In a mixed ester condensation, the use of a more reactive ester, such as the phenyl or biphenyl ester, helps to prevent side reactions.[619,620] Simple heterocyclic esters, namely, ethyl nicotinate and ethyl 8-quinolinecarboxylate, undergo the mixed ester condensation in good yields.[280,281,630] The internal condensation of ethyl adipate to give 2-carbethoxycyclopentanone (Dieckmann reaction) is an example of cyclization (81%).[627]

212. β-Keto Esters by Selective Cleavage of α,α-Diacyl Esters

$$CH_3COCH_2CO_2C_2H_5 \xrightarrow[RCOCl]{NaOC_2H_5;} RCOCH(COCH_3)CO_2C_2H_5 \xrightarrow{NH_3} RCOCH_2CO_2C_2H_5 + CH_3CONH_2$$

The acylation of simple β-keto esters with acyl chlorides to form diacylacetic esters proceeds readily; however, the subsequent cleavage for removing the smaller acyl group is complicated in that the original keto ester may be regenerated. The optimum conditions for the conversion of benzoylacetoacetic ester to benzoylacetic ester with ammonium chloride and ammonium hydroxide have been studied.[631] The over-all synthesis of this ester has been described (57%).[632] An improved procedure for the ammonolysis of ethyl α-acetyl-β-oxocaproate using gaseous ammonia has been described.[386] By a similar process, a series of alicyclic β-keto esters has been prepared in over-all yields of 20-40%.[633]

Variations of the above procedures are sometimes employed. β-Keto esters may be obtained by alcoholysis of the intermediate diacyl esters by sodium methoxide in methanol,[634] as in the preparation of methyl β-oxocaprylate (88%).[635] The starting β-keto ester can be converted to the new β-keto ester in a single step. Thus, in the synthesis of ethyl benzoylacetate (55%), ethyl acetoacetate and ethyl benzoate are converted directly to this keto ester by distilling the lower-boiling product, ethyl acetate, thereby forcing the reaction to completion.[636]

$$CH_3COCH_2CO_2C_2H_5 + C_6H_5CO_2C_2H_5 \xrightarrow{NaOCH_3} C_6H_5COCH_2CO_2C_2H_5 + CH_3CO_2C_2H_5\uparrow$$

Finally, the sodium enolate of the new β-keto ester may be alkylated directly to give β-keto esters of the type $RCOCHRCO_2C_2H_5$.[637]

213. β-Keto Esters by Alkylation of β-Keto Esters

$$RCOCH_2CO_2C_2H_5 \xrightarrow[R'X]{NaOC_2H_5;} RCOCHR'CO_2C_2H_5$$

This reaction has been considered above (method 184) with respect to ease of mono- and di-alkylation. A large number of condensing agents have been compared, including sodium and potassium ethoxide, sodium in dioxane or toluene, sodium hydride, sodium amide, and sodium or potassium *t*-butoxide.[642] In general, sodium ethoxide is recommended in the alkylation of acetoacetic ester with primary halides (73%); potassium ethoxide with branched halides, such as isobutyl and *s*-butyl halides

(61% and 55%); and potassium *t*-butoxide for introducing a second alkyl group in α-substituted acetoacetic esters (60-80%). The other reagents are successful in certain cases. Alkylation of 2-carbethoxycyclopentanone with methyl, ethyl, or isopropyl iodides gives the corresponding β-keto esters in 82%, 74%, and 59% yields, respectively.[268,643] Other examples are found in the preparation of ethyl monomethyl- (71%) and dimethylacetoacetic esters (54%)[644] and ethyl *n*-butylacetoacetate (72%).[645] Alkylations by ethyl benzenesulfonate,[623] isopropyl acetate or isopropyl alcohol in the presence of boron trifluoride,[646,647] and dimethyl sulfate[648] have proved more successful than those by the corresponding alkyl halides.

β-Keto esters containing a double bond,[284-287] an alkoxyl group,[291,292] or an amino group[306,307] are formed by alkylating acetoacetic ester with a substituted alkyl halide.

214. β-Keto Esters from Ethyl *t*-Butyl Acylmalonic Esters

$$C_2H_5OMgCH(CO_2C_2H_5)CO_2C(CH_3)_3 \xrightarrow{RCOCl} RCOCH(CO_2C_2H_5)CO_2C(CH_3)_3 \longrightarrow RCOCH_2CO_2C_2H_5 + CH_2{=}C(CH_3)_2 + CO_2$$

Olefin elimination and decarboxylation of ethyl *t*-butyl acylmalonates proceeds easily on treatment with toluenesulfonic acid to form β-keto esters of the type $RCOCH_2CO_2C_2H_5$.[650,651] By this procedure, acyl acetates where R is ethyl (63%), cyclohexyl (65%), 2-furyl (70%), benzyl (46%), or propenyl (35%) have been prepared. The limiting factor in this excellent method is the availability of ethyl *t*-butyl malonate; its synthesis has been described.[651]

A reaction similar to the above involves the acylation of malonic ester through its magnesium enolate. Thus, the reaction of propionyl chloride with the ester enolate leads to diethyl propionylmalonate. Thermal decomposition of this compound with β-naphthalenesulfonic acid yields ethyl propionylacetate (57%). This modification appears to be general in that it has been extended to the use of aliphatic, aromatic, and carbalkoxy acyl chlorides.[652]

215. β-Keto Esters by Acylation of Ester Enolates

$$RCOCl + Na^+[CR'_2CO_2C_2H_5]^- \longrightarrow RCOCR'_2CO_2C_2H_5 + NaCl$$

The acylation of the sodium enolates of esters (prepared by sodium triphenylmethide) with acyl chlorides gives the corresponding α,α-disubstituted β-keto esters, $RCOCR'_2CO_2C_2H_5$. The synthesis is direct, and the product is free from monoalkylation products usually encountered

by the dialkylation of β-keto esters. By this procedure, ethyl dimethylacetoacetate (51%), ethyl *n*-butyryldimethylacetate (58%), and ethyl benzoyldimethylacetate (65%) have been prepared.[523,653] In a similar manner, the acylation of malonic ester is performed through its magnesium enolate.[652,653,655]

216. β-Keto Nitriles by Acylation of Nitriles

$$RCH_2CN + R'CO_2C_2H_5 \xrightarrow{Base} R'COCHRCN + C_2H_5OH$$

In the presence of sodium ethoxide, nitriles having reactive α-methylene groups may be acylated with esters to form β-keto nitriles. The method is general and is illustrated by the reaction of alkyl cyanides, where R is C_1 to *n*-C_4, with ethyl benzoate to form the corresponding alkylbenzoylacetonitriles in 53–60% yield.[659] Aliphatic esters also react; for example, phenylacetonitrile with ethyl acetate gives α-phenylacetoacetonitrile, $C_6H_5CH(CN)COCH_3$ (64%).[660] In the case of the higher-boiling nitriles, the alcohol product is removed by distillation, thereby increasing the yield and decreasing the reaction time.[661]

The method has been extended to the preparation of numerous acylacetonitriles in the benzene, naphthalene, furan, and the thiophene series. Modifications of the procedure including the substitution of commercial sodium methoxide for sodium ethoxide and the use of an inert solvent to facilitate stirring have been employed.[662]

If the acylating ester is capable of undergoing self-condensation in the presence of sodium ethoxide, sodium triphenylmethide is substituted for the latter. An example is the reaction of acetonitrile with ethyl *n*-butyrate to give *n*-butyrylacetonitrile (52%).[663]

217. Hydrogenolysis of 1,3-Diketones[487]

$$CH_3COCH_2COCH_2CH(CH_3)_2 \xrightarrow[42\%]{H_2,\ Catalyst} CH_3CH_2CH_2COCH_2CH(CH_3)_2$$

218. Acid Treatment of *Aci*nitroparaffins[540]

$$R_2CHNO_2 \xrightarrow{NaOH} R_2C{=}N(\rightarrow O){-}ONa \xrightarrow[80\text{–}85\%]{H^+} R_2CO$$

219. Pyrolysis of Glycidic Acids[341,342,367]

$$R_2C(\text{O})CR'CO_2H \xrightarrow[-CO_2]{Heat} R_2CHCOR'$$

220. Rearrangement of α-Bromo Azides[83,343,344]

$$R_2CBrCON_3 \xrightarrow{Heat} R_2CBrNCO \xrightarrow{H_2O} (R_2CBrNH_2) \xrightarrow{H_2O} R_2CO$$

Where R equals ethyl, *n*-butyl, or cyclopentyl, over-all yields of 35%, 77%, and 60%, respectively, have been obtained.

221. Degradation of Disubstituted Glycolic Acids[345]

$$R_2COHCO_2H \xrightarrow{Pb(OAc)_4} R_2CO + H_2O + CO$$

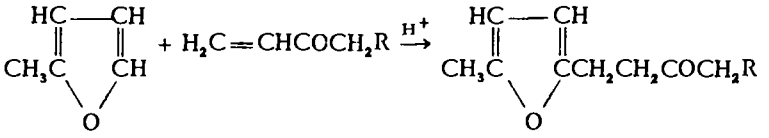
222. Hydrolysis of *gem*-Dihalides[460-463] (cf. method 151)

$$R_2CX_2 \xrightarrow{H_2O} R_2CO$$

223. Isomerization of Vinyl Carbinols[528]

$$CH_2{=}CHCHO \xrightarrow[30\text{–}50\%]{RMgX} CH_2{=}CHCHOHR \xrightarrow[50\text{–}70\%]{Cu} CH_3CH_2COR$$

224. Condensation of Furans with Unsaturated Ketones

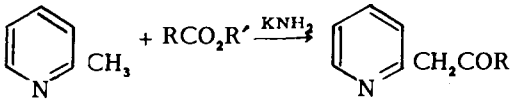


Furans and unsaturated ketones undergo a condensation similar to the Diels-Alder type (cf. method 34) to give furyl-substituted ketones; for example, α-methylfuran and methyl vinyl ketone react under mild acidic conditions to yield 5-methylfurfurylacetone (65%).[529]

225. Condensation of Anhydrides[533]

$$2(RCH_2CO)_2O \xrightarrow{BF_3} (RCH_2COCHRCO)_2O \xrightarrow[-CO_2]{H_2O} RCH_2COCH_2R$$

226. Acylation of Certain Heterocyclic Compounds[534]



227. Addition of Aldehydes to Olefins[536]

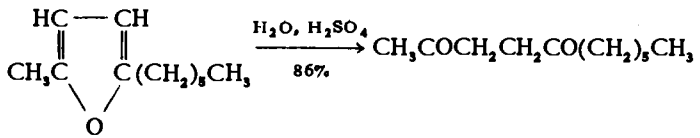
$$RCHO + R'CH{=}CH_2 \xrightarrow[\text{peroxide}]{\text{Diacetyl}} RCOCH_2CH_2R'$$

Typical compounds prepared include 4-decanone (41%), 4-dodecanone (57%), and 7-pentadecanone (75%).

228. Interaction of Hydriodic Acid and Diazo Ketones[537,538]

$$RCOCHN_2 + HI \longrightarrow RCOCH_3 + N_2 + I_2$$

229. γ-Diketones from Substituted Furans[589-591]



230. α-Diketones by Oxidation of Aryl Acetylenes[592]

$$ArC{\equiv}CAr \xrightarrow[60\%]{CrO_3 - CH_3CO_2H} ArCOCOAr$$

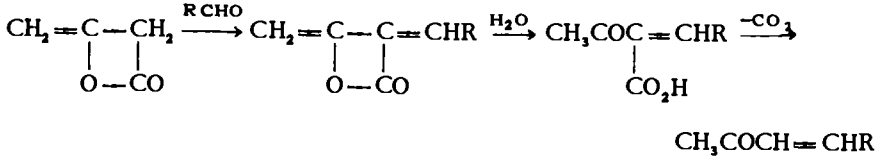
231. γ-Diketones from Ketones[593]

$$2RR'CHCOCHRR' \xrightarrow{\text{Diacetyl peroxide}} \begin{matrix} RR'CCOCHRR' \\ | \\ RR'CCOCHRR' \end{matrix}$$

232. Olefinic Ketones from Hydrocarbons and Carbon Monoxide[597]

$$3CH_3CH_2CH_3 + CO \xrightarrow[23\%]{AlCl_3,\ 125\ atm.,\ 12\ hr.} (CH_3)_2CH{=}CHCH_2COCH(CH_3)_2$$

233. α,β-Olefinic Ketones from Diketene and Aldehydes[90]



234. β-Keto Esters by the Reformatsky Reaction[658,666]

$$C_6H_5CO_2C_6H_5 + (CH_3)_2CBrCO_2C_2H_5 \xrightarrow[(52\%)]{Zn} C_6H_5COC(CH_3)_2CO_2C_2H_5$$

235. Hydrolysis of β-Iminonitriles[682]

$$ArCN + CH_3CN \xrightarrow[40-60\%]{NaNH_2} ArC(=NH)CH_2CN \xrightarrow[60-70\%]{H_2O} ArCOCH_2CN$$

TABLE 32. MONOKETONES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Ketones				
C_3	Acetone	186	61	10[317]	56, 1.3592*, 187Se*
	(purification only)	....		10[667]	56*, 1.3592*, 187Se*
C_4	Methyl ethyl ketone	181	79	10[226]	82, 1.3791*, 135Se*
C_5	Methyl *n*-propyl ketone	179	74	10[157]	102
		184	70	10[254]	102/747, 110Se
		186	44	10[324]	102/756, 1.3902, 110Se
	Methyl isopropyl ketone	201	59	10[523]	94, 1.3879*, 113Se*
	Diethyl ketone	179	57	10[157]	103, 156Dn*
		186	59	10[324]	102/751, 1.3922, 139Se
C_6	Methyl *n*-butyl ketone	179	64	10[160]	127
		179	80	10[161]	127
		182	60	10[233]	124/738, 1.4002, 107Dn
		184	50†	10[256]	128
		188	56†	10[392]	126/760, 121Se
		188	83	10[389]	
		189	74	10[402]	127, 125Se
		200	80	10[508]	127
	Methyl isobutyl ketone	184	20†	10[256]	119, 1.3956*, 135Se*, 95Dn*
		188	80	10[389]	119
		196	100	10[465]	116/740
	Methyl *s*-butyl ketone	179	81	10[163]	116/734, 1.4002
		188	78†	10[390]	118
	Methyl *t*-butyl ketone	188	78	10[389]	106
		189	40	10[409]	106, 158Se*
		190	52	10[427]	105/746, 1.3960, 127Dn, 80-Ox
		201	72	10[513]	107
		201	94	10[514]	106, 1.4019[25], 124Dn
	Ethyl *n*-propyl ketone	179	85	10[162]	123, 130Dn*
		181	86	10[226]	126, 113Se
		186	62	10[324]	125/760, 1.4007, 113Se
		190	45	10[433]	124
		223	57	10[528]	124
C_7	Methyl *n*-amyl ketone	179	70	10[158]	150/750, 123Se
		179	83	10[168]	1.4073[25]*, 74Dn
		184	61†	10[256]	151/750, 127Se*
		184	95	10[257]	150
		200	87	10[508]	149
	Methyl isoamyl ketone	184	60	10[254]	142/746, 143Se
		194	50	10[451]	144
	4-Methyl-2-hexanone	184	30†	10[256]	142
		184	52	10[261]	139, 1.4057[25], 120Se
		191	75	10[437]	139/762, 128Se*
	3-Methyl-2-hexanone	184	30†	10[251]	137, 70Se*
	3-Ethyl-2-pentanone	184	45	10[254]	139/746, 1.4073*, 99Se

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Ketones *(continued)*				
C_7	Methyl neopentyl ketone	182	56	10[235]	125/760, 1.4018[25]
		222	96	10[463]	122, 100Dn
	Methyl *t*-amyl ketone	179	36	10[164]	130/733, 1.4100, 112Dn
	3,4-Dimethyl-2-pentanone	184	36†	10[252]	138, 1.4094*, 113Se*
	Ethyl *n*-butyl ketone	179	70	10[158]	148/756, 103Se
		181	89	10[226]	148, 101Se
		186	46	10[35]	146/767, 1.4092*
		195	48†	10[453]	
	Ethyl isobutyl ketone	189	70	10[405]	135/735, 1.407*, 152Se*
		195	48†	10[453]	
	Ethyl *s*-butyl ketone	179	63	10[168]	78Dn
		184	78	10[262]	136/760, 1.402*, 137Se*
	Ethyl *t*-butyl ketone	190	78	10[427]	125/729, 1.4052, 144Dn
	Di-*n*-propyl ketone	179	70	10[158]	144/756, 132Se
		186	50	10[324]	145/767, 1.4069, 134Se
		225	60	10[533]	145
	n-Propyl isopropyl ketone	184	79	10[262]	136/760, 1.4075, 119Se
		189	60	10[402]	132, 119Se
	Diisopropyl ketone	179	74	10[165]	125/742, 1.4001, 98Dn*
		184	78	10[262]	125/760, 160Se
		187	58	10[356]	125, 160Se
C_8	Methyl *n*-hexyl ketone	179	96	10[166]	173, 1.4154
		181	95	10[226]	172, 121Se
		184	70	10[263]	172, 122Se*
		200	91	10[508]	170
	Methyl isohexyl ketone	184	47†	10[264]	171, 1.4146
		184	77	10[254]	164/746, 154Se
		....	....	10[455]	164/757, 1.4144[19], 77Dn
	3-Methyl-2-heptanone	179	68	10[167]	162/760, 1.415, 82Se
	3,4-Dimethyl-2-hexanone	191	20	10[439]	158, 120Se
		196	80	10[472]	155, 118Se
		196	90	10[468]	158, 126Se
	4-Ethyl-2-hexanone	195	48†	10[453]	
	3-Methyl-3-ethyl-2-pentanone	189	48	10[164]	79/20, 1.4206*, 74Dn
	Ethyl isoamyl ketone	189	40	10[410]	163, 132Se
		196	92	10[472]	160, 132Se
	5-Methyl-3-heptanone	196	94	10[467]	161
	Ethyl neopentyl ketone	189	51	10[421]	92/150, 1.4160*, 136Dn
	n-Propyl *n*-butyl ketone	201	25	10[527]	170, 96Se
	n-Propyl isobutyl ketone	217	42	10[487]	150/750, 124Se
	n-Propyl *t*-butyl ketone	179	41	10[168]	124Dn
		190	67	10[427]	145/738, 1.4107, 116Dn
	Isopropyl *s*-butyl ketone	179	68	10[159]	65/50, 1.4080, 71Dn
		189	70	10[424]	145, 1.4059

For explanations and symbols see pp. xi–xii.

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Ketones *(continued)*				
C_8	Isopropyl *t*-butyl ketone	190	20	10[427]	135/744, 1.4065, 144-Ox
		198	54	10[497]	135, 132Se*
C_9	Methyl *n*-heptyl ketone	181	83	10[226]	118Se
		185	93	10[313]	80/10, 118Se
		186	54	10[326]	192/743, 120Se*
	4-Methyl-2-octanone	182	69	10[233]	94/40, 70Se
	3-Methyl-3-ethyl-2-hexanone	189	47	10[420]	110/86, 1.4222[30], 81Dn
	Ethyl *n*-hexyl ketone	186	41	10[35]	187/751, 112Se*
		195	48†	10[453]	
	5-Ethyl-3-heptanone	187	40	10[387]	173, 134Se
		195	48†	10[453]	
	Di-*n*-butyl ketone	184	72	10[259]	88/22
		186	99	10[320]	93/24, 90Se*
	n-Butyl isobutyl ketone	188	20	10[398]	168, 132Se
	n-Butyl *t*-butyl ketone	190	68	10[427]	166/745, 1.4167, 145Se
		198	38	10[498]	166/745
	Diisobutyl ketone	196	100	10[469]	56/11, 122Se
	Isobutyl *s*-butyl ketone	184	75	10[262]	167/760, 133Se
		188	21	10[399]	169, 132Se
	Isobutyl *t*-butyl ketone	198	35	10[498]	158, 145Se*
	Isopropyl neopentyl ketone	193	55	10[447]	107/180, 129Dn
	Isopropyl *t*-amyl ketone	189	87	10[419]	87/35, 1.4214
	Di-*t*-butyl ketone	179	81	10[249]	154, 1.4188[22]
		185	81	10[174]	154
		189	80	10[416]	153, 1.4392
		198	52	10[165]	150/740, 1.4194
C_{10}	Methyl *n*-octyl ketone	196	92	10[473]	142/100, (14), 126Se
C_{11}	*sym*-Tetraethylacetone	225	57	10[533]	104/30
	Di-*n*-amyl ketone	225	64	10[533]	125/35
		184	81	10[259]	106/13, (15)
		184	72†	10[692]	100/15
		186	69	10[35]	223/760
C_{12}	Methyl *n*-decyl ketone	185	94	10[313]	107/5, 123Se
C_{13}	Di-*n*-hexyl ketone	184	82	10[259]	264, (30)
	Methyl *n*-undecyl ketone	185	97	10[313]	(28), 117Se
C_{15}	Di-*n*-heptyl ketone	184	93	10[259]	178, (42), 120-Ox*
C_{17}	Di-*n*-octyl ketone	184	93	10[259]	(53), 112-Ox*
C_{19}	Methyl *n*-heptadecyl ketone	185	96	10[313]	(56), 77-Ox
	Di-*n*-nonyl ketone	184	95	10[259]	(59)
C_{21}	Di-*n*-decyl ketone	184	90	10[268]	(64)

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Ketones *(continued)*				
C_{23}	Di-*n*-undecyl ketone (laurone)	184	98	10[289]	(69), 40-Ox*
		184	55†	10[692]	(69)
		186	93	10[321]	(69)
C_{27}	Di-*n*-tridecyl ketone (myristone)	184	97	10[289]	(79), 51-Ox*
C_{35}	Di-*n*-heptadecyl ketone (stearone)	186	95	10[328]	(89), 63-Ox*
	Alicyclic Ketones				
C_4	Cyclobutanone	182	91	10[237]	100, 1.4189[28], 146Dn
C_5	Methyl cyclopropyl ketone	198	83	10[694]	111, 1.4226[25]
	Cyclopentanone	186	80	10[327]	131, 1.4370, 203Se*
C_6	Methyl cyclobutyl ketone	186	60	10[332]	137/767, 149Se
		189	66	10[423]	136, 1.4283[28], 149Se
	2-Methylcyclopentanone	184	80	10[267]	140, 182Se
		184	56†	10[266]	140/758
	3-Methylcyclopentanone	186	76	10[333]	145/755, 1.4329, 185Se
	Cyclohexanone	179	85	10[176]	155, 160Dn*
		181	60	10[225]	156, 165Se
C_7	Methyl cyclopentyl ketone	179	54†	10[177]	155, 143Se
	3,3-Dimethyl-1-cyclopentanone	186	30	10[334]	153/748, 178Se
	1-Ethylcyclopentanone	184	64	10[268]	161/755, 189Se
	2-Methylcyclohexanone	179	85	10[169]	165, 1.4487, 191Se
	3-Methylcyclohexanone	179	90	10[170]	65/30
		179	78	10[169]	169, 1.4463, 182Se
		179	88	10[675]	64/20, 1.4460
		196	100	10[475]	93/15, 1.4446, 185Se
	4-Methylcyclohexanone	179	74	10[171]	168, 1.4448, 193Se
		179	70	10[169]	172, 1.4462, 196Se
		179	70	10[172]	170
	Cycloheptanone	186	40	10[333]	66/15, 163Se
		199	63	10[506]	182
C_8	2-Isopropylcyclopentanone	196	88	10[178]	174, 1.4395[29], 202Se
	2-Methyl-5-ethylcyclopentanone	184	88	10[269]	165/750
	Methyl cyclohexyl ketone	179	85	10[163]	67/12, 1.4514
		185	66†	10[312]	65/12
	2-Ethylcyclohexanone	179	86	10[675]	76/20, 1.4522
		184	74	10[271]	74/35, 162Dn
		192	41	10[444]	42/2, 1.4530[16], 162Se
		198	43	10[493]	67/12, 1.4543[15], 163Se

For explanations and symbols see pp. xi–xii.

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Alicyclic Ketones *(continued)*				
C_8	3-Ethylcyclohexanone	179	84	10[171]	192, 1.4511, 182Se
		196	100	10[475]	41/0.8, 1.4537, 175Se
	2,2-Dimethylcyclohexanone	198	30	10[490]	170/761, 1.4482, 201Se
		198	26†	10[493]	171/760, 1.4499^{18}, 193Se
	2,4-Dimethylcyclohexanone	179	79	10[178]	176, 1.4430^{25}, 200Se
	2,6-Dimethylcyclohexanone	179	93	10[675]	69/20, 1.4470
		179	49	10[179]	174, 1.4500
		184	91	10[270]	58/10
	3,4-Dimethylcyclohexanone	179	93	10[675]	81/20, 1.4520
	3,5-Dimethylcyclohexanone	179	92	10[675]	75/20, 1.4434
		196	78	10[474]	182/750, 1.4427, 201Se
C_9	α-Methyl-α-cyclopentylacetone	184	69	10[272]	79/17, 1.4470, 98Se
	2,2,5,5-Tetramethylcyclopentanone	198	35	10[493]	155/760, 1.4280
	2-*n*-Propylcyclohexanone	192	30	10[444]	88/17, 120Se
	3-*n*-Propylcyclohexanone	196	100	10[475]	42/0.7, 1.4530, 169Se
	3-Isopropylcyclohexanone	196	100	10[475]	51/1, 1.4540, 195Se
	4-*n*-Propylcyclohexanone	179	82	10[180]	212/740, 1.4514^{25}, 180Se
	4-Isopropylcyclohexanone	179	82	10[181]	91/13, 1.4560, 188Se
	3-Methyl-5-ethylcyclohexanone	196	94	10[474]	205/747, 1.4452
	2,2,6-Trimethylcyclohexanone	198	27	10[491]	179/767, 1.4480, 209Se, 141Dn
C_{10}	2,2,6,6-Tetramethylcyclohexanone	198	26	10[492]	184/772, 1.4473, (15)
	cis-α-Decalone	180	80	10[693]	116/18, 1.4939, 220dSe
	2-Decalone	179	94	10[182]	114/15
C_{11}	Dicyclopentyl ketone	220	60	10[344]	112/12, 162Se
	1-Methyl-2-decalone	179	80	10[185]	107/7
C_{12}	4-Cyclohexylcyclohexanone	179	87	10[184]	100/0.1, (31), 216Se
	Aromatic Ketones				
C_8	Acetophenone	178	83	10[6]	88/16, (20)
		178	86	10[12]	(19), 60-Ox*
		183	63	10[240]	
		187	70	10[553]	205/760, 1.541, 199Se

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_8	Acetophenone *(continued)*	188	75	10[389]	202
		188	75†	10[392]	104/31, 199Se
		189	85	10[402]	91/16, 203Se
C_9	Methyl benzyl ketone	178	32	10[33]	114/22, 188Se
		184	86	10[273]	112/24
		185	71†	10[312]	98/13, 190Se
		186	65	10[319]	120/22
		188	52†	10[390]	
		190	65	10[434]	125/50, 153Dn
		195	77	10[679]	216
	Phenyl ethyl ketone	178	58	10[35]	215/763
		178	84	10[34]	220, 189Dn*
		187	83	10[354]	106/17, 1.5270, 173Se
		189	81†	10[401]	103/16, 179Se
	o-Methylacetophenone	179	60†	10[185]	105/20, 203Se
		184	35	10[274]	95/15, 210Se
		189	60	10[413]	108/25
		189	85	10[412]	94/13, 206Se
	m-Methylacetophenone	189	83	10[402]	108/19, 203Se
	p-Methylacetophenone	178	88	10[28]	108/18, 1.5348, 88-Ox
		178	89	10[6]	93/7, 87-Ox*
		178	93	10[12]	227/764
		179	50†	10[185]	109/12, 197Se
		189	84	10[402]	138/13, 198Se
	1-Indanone (α-hydrindone)	178	55	10[74]	(41)
		178	84	10[76]	120/13, 146-Ox*
		178	93	10[77]	(38)
		....	60	10[78]	126/17, (41), 233Se*
	2-Indanone	201	75	10[76]	(57), 153-Ox
C_{10}	Phenyl *n*-propyl ketone	178	65	10[36]	115/17
		187	82	10[354]	123/20, 1.5203
	Phenyl isopropyl ketone	179	75	10[186]	....
		184	81	10[262]	102/15, 181Se*
		188	72†	10[392]	217/760, 57-Ox
	Ethyl benzyl ketone	195	68	10[679]	102/10
	Benzylacetone	184	35†	10[276]	110/7, 142Se
		184	88	10[275]	124/16
		184	97	10[253]	
		196	63	10[476]	235, 87-Ox*
		196	67	10[477]	236/748, 142Se
		196	96	10[468]	133/15
	3-Phenyl-2-butanone	198	74	10[499]	107/22, 1.5092
		187	28	10[338]	78/1.5, 1.5088^{25}, 158Se

For explanations and symbols see pp. xi–xii.

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_{10}	*p*-Methylpropiophenone	178	86	10[6]	106/8
	o-Ethylacetophenone	186	74	10[337]	108/18, 180Se
		187	62	10[336]	118/29, 1.5249
	m-Ethylacetophenone	183	50	10[238]	116/14, 1.5232^{25}
	p-Ethylacetophenone	178	98	10[4]	117/13, 1.5275^{25}
		186	38†	10[336]	125/20, 1.5298
	2,4-Dimethylaceto-phenone	178	48	10[8]	97/4, 1.5381, 234Se*
		178	54	10[7]	113/18, 64-Ox*
		178	74	10[8]	94/5, 1.5340, 187Se*
	2,5-Dimethylaceto-phenone	178	68	10[8]	94/8, 1.5291, 169Se*
		186	69	10[336]	127/31, 1.5306
	3,4-Dimethylaceto-phenone	186	58	10[336]	132/19, 1.5400
	3,5-Dimethylaceto-phenone	187	63	10[336]	$129/22, 1.5276^{25}$
	α-Tetralone	178	91	10[17]	170/49
		178	91†	10[79]	107/2, 102-Ox
		178	92	10[24]	123/8, 217Se
		183	56	10[241]	124/9
	β-Tetralone	181	42	10[485]	$121\text{-}132/8, 1.5555^{25}$, (18)
		197	40	10[483]	194Se
		197	56	10[486]	131/11, 88-Ox*
C_{11}	Phenyl *n*-butyl ketone	179	93	10[186]	
		187	83	10[354]	141/24, 1.5146, 166Se*
		195	50	10[679]	107/10
	3-Phenyl-2-pentanone	198	55	10[499]	110/18, 1.5051, 191Se
	4-Phenyl-2-pentanone	178	39	10[530]	115/13, 1.5124, 137Se
	5-Phenyl-2-pentanone	184	25†	10[276]	122/6, 130Se
	Phenyl isobutyl ketone	178	62	10[36]	235, 210Se*
	Phenyl *s*-butyl ketone	184	69	10[262]	109/10
	Phenyl *t*-butyl ketone	179	64	10[187]	108/16, 150Se*
		189	67	10[417]	84/3, 1.5102, 195Dn
		198	77	10[187]	104/14, 166-Ox
	5-Phenyl-3-pentanone	196	82	10[479]	244/760, 1.5125, 80Se
	Pivalophenone	187	82	10[355]	224/750, 1.5082
	3-Methyl-3-phenyl-2-butanone	187	61	10[358]	$77/15, 1.5078^{25}$, 186Se
		198	50	10[499]	99/12, 1.5083, 186Se
	3-Methyl-4-phenyl-2-butanone	....	65	10[681]	$106/9, 1.5065^{18}$, 114Se
		196	83	10[479]	$130/17, 1.5090^{19}$, 112Se
	2,4,5-Trimethylaceto-phenone	178	75	10[37]	124/5, 204Se*
		178	80	10[7]	123/10, 86-Ox*
	2,4,6-Trimethylaceto-phenone	178	72	10[7]	123/18
		178	83	10[29]	102/1
	2-Phenylcyclopentanone	192	50	10[446]	135-140/9, (37), 214Se

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_{11}	2-Methyl-1-tetralone	178	71	10[82]	$138/16, 1.5538^{25}$
		178	92	10[81]	80/1, 1.5447, 195Se
		184	95	10[80]	116/2.5, 205Se
	3-Methyl-1-tetralone	178	73†	10[84]	96/0.3, 123-Ox
		178	86	10[83]	136/14, 242Dn
	4-Methyl-1-tetralone	178	74	10[80]	111/1, 211Se
	7-Methyl-1-tetralone	178	89†	10[88]	109/1.5-2, (33)
C_{12}	Phenyl neopentyl ketone	178	87	10[478]	116/11, 1.5078, 218Se, 114-Ox
	m-Propylpropiophenone	187	82	10[360]	145/20, 128Se
	Mesitylacetone	185	83†	10[312]	(60), 205Se
		187	50	10[359]	130/10, (60), 197Se
	p-*n*-Butylacetophenone	178	78	10[38]	141/14, 185Se
	p-Isobutylacetophenone	178	38	10[38]	135/16
	p-*s*-Butylacetophenone	178	74	10[39]	135/11, 1.5195
	p-*t*-Butylacetophenone	178	83	10[4]	$138/16, 1.5195^{25}$
	2-Methyl-5-isopropylaceto-phenone	178	55	10[9]	125/12
	Acetodurene	178	80	10[7]	131/10
		178	86	10[40]	(73)
	Acetoisodurene	178	81	10[7]	137/16
	Acetoprehnitene	178	70	10[7]	124/8
	2-Phenylcyclohexanone	179	80	10[173]	160/15, (63), 190Se
		192	60	10[443]	155/13, (60), 139Dn
		201	80	10[532]	150/9, (59)
	4-Phenylcyclohexanone	179	40	10[188]	(78), 212Se
	Methyl α-naphthyl ketone	178	35	10[42]	151/7, 237Se*
		178	93	10[30]	163/15, (9.0)
		187	52	10[346]	150/8, 1.6257, 116Pi*
	Methyl β-naphthyl ketone	178	40	10[43]	(53), 82Pi
	6-Acetyltetralin	178	74	10[41]	115/2
		178	93	10[4]	$121/2.0, 1.5591^{25}$
		178	60	10[25]	$156/10, 1.5593^{29}$, 234Se
	1,1-Dimethyl-2-tetralone	198	80	10[496]	96/0.5, 1.538, 204Se
	7-Acenaphthenone	179	65	10[189]	(121)
		....	45	10[531]	(121)
C_{13}	Benzylpinacolone	196	75	10[478]	261/746, 1.4972, 158Se
	p-*n*-Amylacetophenone	178	73	10[38]	159/17
	p-Isoamylacetophenone	178	73	10[38]	153/16
	p-*s*-Amylacetophenone	178	58	10[39]	145/11, 1.5150
	p-*t*-Amylacetophenone	178	59	10[38]	146/13
	Acetopentamethyl-benzene	178	80	10[7]	145/8, (84)
	Benzophenone	178	76	10[44]	(49), 167Se*
		178	90	10[2]	(48), 144-Ox*
		183	87	10[577]	140-Ox

For explanations and symbols see pp. xi-xii.

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_{13}	Benzophenone *(continued)*	186	87	10[329]	(48)
		189	57	10[402]	172/19
		222	89	10[460]	190/15, (48)
	Ethyl α-naphthyl ketone	187	37	10[346]	170/11, 1.6109, 58-Ox*
		187	89	10[685]	146/1, 79Pi
	6-Propionyltetralin	178	68	10[25]	163/11, 1.5508[29], 209Se
	Fluorenone	183	70	10[242]	(83.5)
		186	82	10[242]	(84), 195-Ox*
		222	90	10[462]	(83.5)
C_{14}	Phenyl benzyl ketone (desoxybenzoin)	178	83	10[1]	160/5, (56), 148Se*
		190	77	10[429]	(57), 98-Ox
		201	88	10[519]	(58)
	p-Methylbenzophenone	178	55	10[46]	185/17, 122Se*
	4-Phenylhexahydroacetophenone	178	60	10[48]	121/1-2, 191Se
	p-Cyclohexylacetophenone	178	91	10[4]	129/1.5, (69)
	2-Acetylbiphenyl	188	48†	10[391]	105/1, 197Se
	3-Acetylbiphenyl	179	81	10[47]	138/1, 1.6140[28]
		188	46†	10[391]	151/1, 223Se
	4-Acetylbiphenyl	178	70	10[47]	150/2, (121)
		178	80	10[48]	(121)
		178	90	10[18]	(121)
	1-Acetoacenaphthene	178	45	10[49]	(105)
	Anthrone	178	28	10[30]	(154)
		....	83	10[83]	(153)
C_{15}	Benzylacetophenone	196	95	10[688]	(73), 144Se*
	Dibenzyl ketone	186	41	10[330]	320, (30), 146Se*
		186	85	10[338]	187/15
		187	11	10[210]	(35)
	α,α-Diphenylacetone	....	57†	10[680]	(61)
	Di-*o*-tolyl ketone	189	40	10[667]	(67), 105-Ox
	o-Ethylbenzophenone	178	83†	10[82]	165/18
	p-Ethylbenzophenone	178	80	10[5]	144/0.2, 315/730
	p,p'-Dimethylbenzophenone	178	55	10[27]	(95), 140Se
	Ethyl 4-biphenylyl ketone	178	79	10[18]	(89)
	2-Acetylfluorene	178	63	10[31]	192/4, (130)
		178	83	10[19]	(129)
	9-Acetylfluorene	....	60	10[199]	(75.5), 139Ph
		....	60	10[53]	(75)
C_{16}	*p*-*n*-Propylbenzophenone	178	67	10[5]	114/0.05

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_{16}	*p*-Isopropylbenzophenone	178	55	10[46]	197/16
		187	40	10[361]	118/0.04
	Mesityl phenyl ketone	183	83	10[868]	(137), 232Dn
	1-Acetylphenanthrene	187	85	10[347]	(113)
	2-Acetylphenanthrene	178	15	10[20]	(143), 260Se
		178	53†	10[22]	(143)
	3-Acetylphenanthrene	178	64	10[20]	(72), 230Se
	9-Acetylphenanthrene	184	83†	10[277]	(74), 201Se
		187	59	10[347]	170/1, (74)
	9-Acetylanthracene	178	60	10[32]	(76)
C_{17}	*p*-*n*-Butylbenzophenone	178	69	10[5]	164/0.65
	p-*s*-Butylbenzophenone	178	88	10[39]	188/9, 1.5760
		187	50	10[361]	139/0.04
	p-*t*-Butylbenzophenone	178	74	10[6]	205/15, (37.5)
	Benzoylisodurene	178	78	10[84]	164/4, (61)
	Phenyl α-naphthyl ketone	178	52	10[26]	169/1, (75), 161-Ox
		178	86	10[30]	225/15, (73)
	2-Propionylphenanthrene	178	23	10[21]	(105), 107Pi
		178	45†	10[22]	(104)
		187	77	10[21]	(105), 107Pi
	3-Propionylphenanthrene	178	23	10[21]	(57), 113Pi
		187	22	10[21]	(57), 113Pi
	9-Propionylphenanthrene	187	86	10[21]	(57), 107Pi
	9-Propionylanthracene	178	11	10[35]	(75)
C_{18}	Laurophenone	187	90	10[362]	(44), 63-Ox
	p-*s*-Amylbenzophenone	178	60	10[39]	190/5, 1.5672
	2,2-Diphenylcyclohexanone	201	98	10[516]	(99)
C_{19}	Dimesityl ketone	189	56	10[418]	(137)
	Phenyl 3-biphenylyl ketone	187	46	10[686]	(79)
	Phenyl 4-biphenylyl ketone	178	75	10[18]	(106)
	1-Benzoylacenaphthene	190	95	10[23]	(92)
	3-Benzoylacenaphthene	178	70	10[24]	(99)
C_{21}					
	β,β-Diphenylpropiophenone	178	85	10[56]	(92), 133-Ox
		191	90	10[442]	(96)
	Di-α-naphthyl ketone	187	75	10[351]	(100), 200-Ox*
	1-Benzoylphenanthrene	178	8	10[58]	(149)
	2-Benzoylphenanthrene	187	85	10[58]	(118)
	3-Benzoylphenanthrene	178	20	10[58]	(112)
		187	60	10[58]	(112)

For explanations and symbols see pp. xi-xii.

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Ketones *(continued)*				
C_{21}	9-Benzoylphenanthrene	187	65	10^{346}	(90)
	9-Anthraphenone	178	65	10^{57}	(148)
	2,3-Diphenyl-1-indenone	19	71	2^{78}	238/6, (151)
C_{24}	Stearoylbenzene	178	65	10^{3}	(65)
C_{26}	Phenyl triphenylmethyl ketone	201	96	10^{315}	(180)
C_{27}	*sym*-Tetraphenylacetone	189	52	10^{422}	(134)
		189	36	10^{278}	
		...	39	10^{278}	(134)
C_{33}	Pentaphenylacetone	189	70	10^{422}	(181)
	Heterocyclic Ketones				
C_4	3-Thiophanone	560	22	39^{7}	85/24, 192Se
C_6	2-Acetylfuran	178	66	10^{60}	48/5, (32), 150Se*
		178	48	10^{65}	90/43, 1.5015^{30}, (32)
		178	77	10^{64}	48/5
		178	76	10^{59}	48/5, 220Dn
		189	28	10^{421}	58/3
		199	75	10^{526}	169-173, 148Se
	2-Acetylthiophene	178	70	10^{68}	88/8, 1.5666
		178	83	10^{62}	91/9, 1.566
		178	79	10^{66}	90/10, (10.5), 1.5662
		178	73	10^{64}	81/7
		178	86	10^{59}	78/4, 1.5666
C_7	α-Furylacetone	195	40	10^{579}	180
	Ethyl 2-furyl ketone	178	52	10^{67}	77/17, (28), 189Se
		178	81	10^{64}	63/6
		189	61	10^{402}	82/15, 189Se
		199	100	10^{526}	183, (30), 189Se
	2-Acetyl-5-methylfuran	178	42	10^{68}	73/8, 191Se
	α-Thienylacetone	219	87	10^{367}	106/12, 1.5366^{24}, 195Se
	Ethyl 2-thienyl ketone	178	79	10^{64}	89/6
	2-Acetyl-5-methylthiophene	178	91	10^{66}	83/2, 1.5622, 217Se
	Methyl 2-pyridyl ketone	184	50	10^{279}	190, 121-Ox*
	Methyl 3-pyridyl ketone	184	81	10^{279}	218, 137Ph*
		184	96	10^{280}	92/5, (14), 177HCl
		186	36	10^{399}	108/23
		187	50	10^{364}	220, 113-Ox
	Methyl 4-pyridyl ketone	184	80	10^{279}	212, 142-Ox*
C_8	*n*-Propyl 2-furyl ketone	178	93	10^{64}	78/7
	1-(α-Furyl)-2-butanone	195	70	10^{579}	76/12, 1.4680^{25}
	1-(α-Tetrahydrofuryl)-3-butanone	196	73	10^{583}	81/2, 1.4459^{19}

TABLE 32 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Heterocyclic Ketones *(continued)*				
C_8	5-Methyl-2-propiofuran	199	100	10^{526}	96/14, 164Se
	n-Propyl 2-thienyl ketone	178	89	10^{64}	96/4
	n-Propyl 3-pyridyl ketone	189	30	10^{365}	98/3, 1.5128, 104Pi
	3-Pyridylacetone	186	40	10^{340}	123/1, 185Se
C_9	2-Furyl 2-thienyl ketone	178	66	10^{69}	136/3, 1.6694^{24}
	2-Furyl 2-pyrryl ketone	189	42	10^{69}	144/1.5, (70)
	n-Propyl 3-pyridyl ketone	187	40	10^{365}	98/3, 1.5136, 130Ph
	2-*n*-Butyrylpyridine	195	81	10^{535}	217, 1.5078, 75Pi
C_{10}	Methyl 2-benzofuryl ketone	178	37	10^{71}	119/5, (72), 207Se
		570	80	39^{60}	136/11, (76), 154Ph
	3-Acetylthianaphthene	178	70	10^{70}	137/3, 250Se
C_{11}	2-Benzoylfuran	178	70	10^{66}	150/3, (44), 122-Ox
	Phenyl 2-thienyl ketone	178	90	10^{63}	209/40, (56), 93-Ox
	2-Acetylquinoline	201	62	10^{518}	(46), 54Ph
	3-acetylquinoline	184	95	10^{511}	(98.5)
	8-Acetylquinoline	184	52	10^{281}	116/0.7, (43.5), 253Dn
C_{12}	2-Benzoylpyridine	183	86	10^{244}	133/2, 1.6056, 199Dn
C_{13}	2-Phenacylpyridine	226	57	10^{534}	150-160/4, (54)
C_{14}	2-Acetyldibenzofuran	178	57	10^{73}	220/18
	2-Acetyldibenzothiophene	178	25	10^{72}	(112), 235Se

For explanations and symbols see pp. xi-xii.

TABLE 33. DIKETONES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Diketones				
C_5	Acetylacetone	203	45	10^{547}	136
		203	54	10^{544}	141/758
		203	85	10^{545}	136, 150-Ox*
C_6	Dipropionyl	179	70	10^{191}	35/10, 185-Ox*
	Propionylacetone	203	35	10^{500}	157
		203	46	10^{542}	157/754, 199Cu
		203	60	10^{541}	158, 198Cu
	Acetonylacetone	229	90	10^{595}	79/15, 89/25
	Methyldiacetylmethane	203	32	10^{542}	79/30
C_7	Dipropionylmethane	203	51	10^{545}	80/30
		203	57	10^{544}	80/30, 210Cu

For explanations and symbols see pp. xi-xii.

TABLE 33 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Diketones *(continued)*				
C_7	*n*-Butyrylacetone	203	45	10[500]	90/38
		203	48	10[542]	73/20, 165Cu
	Isobutyrylacetone	203	30	10[541]	67/20, 172Cu
		203	41	10[545]	64/19
		203	54	10[500]	164
	3-Methyl-2,4-hexanedione	203	31	10[542]	91/30, 177Cu
		203	45	10[541]	183, 177Cu
		203	60	10[545]	184
	3-Methyl-2,5-hexanedione	184	83	10[282]	71/10, 1.4260, 220Se
	Diacetylethylmethane	198	30	10[500]	178/740
C_8	*n*-Valerylacetone	203	62	10[500]	81/17
	Propionyl-*n*-butyrylmethane	203	70	10[544]	86/20, 158Cu
	3-Methyl-2,4-heptanedione	203	44	10[542]	96/20, 163Cu
		203	47	10[500]	100/45
	Isovalerylacetone	203	64	10[500]	77/17
	Pivaloylacetone	203	43	10[544]	71/20, 192Cu
	Diisobutyryl	181	27	10[228]	148, 172-Ox*
	Isopropyldiacetylmethane	198	35	10[501]	183/740
C_9	Caproylacetone	203	54	10[549]	98/11, 1.4222^{25}
		203	61	10[541]	105/20, 138Cu
	Di-*n*-butyrylmethane	203	76	10[544]	102/20, 157Cu
	Methylpropionylbutytylmethane	203	46	10[542]	108/20, 152Cu
	Propionyl-isovaleryl-methane	203	75	10[545]	93/19
	Diisobutyrylmethane	203	28	10[546]	63/3
	n-Butyldiacetylmethane	198	38	10[501]	94/10
		203	53	10[542]	106/20
		203	67	10[673]	106/20
	Diacetyldiethylmethane	198	32	10[501]	100/10
C_{10}	Dipivaloyl	179	36	10[196]	73/24
		179	50	10[201]	62/14, 1.4144
C_{11}	2,5-Undecandione	229	86	10[590]	(33)
	Diisovalerylmethane	203	76	10[549]	116/20, 1.4565^{25}
	Alicyclic Diketones				
C_5	Cyclopentan-1,2-dione	184	67	10[561]	97/20
C_6	4-Methyl-cyclopentan-1,2-dione	184	65	10[562]	98/17
	1,2-Cyclohexanedione	183	30	10[569]	97/25, 188-Ox

TABLE 33 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Alicyclic Diketones *(continued)*				
C_6	1,3-Cyclohexanedione	197	95	10[481]	(104), 156-Ox*
	1,4-Cyclohexanedione	184	85	10[587]	132/20, (79), 188-Ox*
C_7	1,2-Cycloheptanedione	183	90	10[570]	109/17, 182-Ox
C_8	Tetramethyl-1,3-cyclobutanedione	....	38	10[585]	161, (116)
	2-Acetylcyclohexanone	203	35	10[541]	115/20
		203	35	10[542]	97/10
		203	56	10[548]	101/11
	5,5-Dimethyl-1,3-cyclohexanedione	184	85	10[584]	(148), 176-Ox*
C_9	5-Isopropyl-1,3-cyclohexanedione	184	80	10[588]	(62)
	2-Propionylcyclohexanone	203	29	10[545]	125/20
		203	35	10[542]	125/20, 185Cu
C_{10}	2-Ethyl-4-*n*-propyl-1,3-cyclopentanedione	....	32	10[586]	176/1, (120)
	Aromatic Diketones				
C_9	Acetylbenzoyl	183	20	10[576]	128/20, 232Se*
		183	60	10[567]	115/15
		195	70	10[482]	116/20, 240-Ox*
	Ninhydrin (triketohydrindene)	183	35	10[571]	(243), 201-Ox
C_{10}	1-Phenyl-1,2-butanedione	183	35	10[576]	132/20
	Benzoylacetone	178	73	10[90]	141/15, (59)
		203	50	10[542]	141/18
		203	66	10[545]	(61)
		203	68	10[573]	146/20
		203	70	10[500]	136/16, (60)
		203	83	10[548]	(60)
	o-Diacetylbenzene	183	71	10[248]	147/16, (38.5)
	p-Diacetylbenzene	183	76	10[4]	130/3, (114)
		184	15	10[283]	(114), 240-Ox*
C_{11}	*w*-Propionylacetophenone	203	30	10[542]	152/10, 153Cu
		203	55	10[541]	127/5, 149Cu
		203	61	10[580]	122/5, 1.5837, 151Cu
	3-Phenyl-2,4-pentanedione	203	41	10[542]	134/20, (60), 224Cu
C_{12}	1,3,5-Triacetylbenzene	....	51	10[568]	(161)
C_{14}	Benzil	179	86	10[190]	(95), 244Se*
		179	95	10[193]	(95), 225Ph*
		179	100	10[194]	(95)
		183	93	10[566]	

For explanations and symbols see pp. xi–xii.

TABLE 33 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Diketones *(continued)*				
C_{15}	Dibenzoylmethane	203	71	10[552]	(78)
		202	80	10[551]	(78)
	Diphenyl triketone	222	59†	10[461]	(70)
	4-Methylbenzil	183	75	10[566]	221/15
	Mesityl *t*-butyl ketone	179	83	10[197]	118/2, 1.5068, 139-Ox*
C_{16}	1,2-Dibenzoylethane	196	76	10[480]	(147), 204-Ox*
	p-Tolil	179	47	10[194]	(102), 225-Ox*
	p,p'-Diacetylbiphenyl	178	45	10[18]	(191)
C_{18}	1,4-Dibenzoylbutane	178	81	10[89]	(107)
	Heterocyclic Diketones				
C_8	Acetyl-2-furoylmethane	203	43	10[553]	110/10, 222Cu
		203	45	10[500]	110/10
	Tetrahydrofuroylacetone	203	60	10[500]	97/8
	Acetyl-2-thenoylmethane	203	81	10[554]	131/8, 230Cu
C_9	Propionyl-2-thenoylmethane	203	62	10[554]	126/4, 194Cu
	Nicotinylacetylmethane	203	63	10[690]	135/6, (83.5)
C_{10}	Furil	179	63	10[200]	(166)
		179	91	10[194]	(165)
C_{11}	Di-2-thenoylmethane	203	64	10[554]	(100), 263Cu
	2-Furoyl-2-thenoylmethane	203	75	10[553]	195/6, (55.5), 274Cu
C_{13}	Benzoyl-2-furoylmethane	203	55	10[500]	165/3, (68)
		203	87	10[553]	169/3, 248Cu
	Benzoyl-2-thenoylmethane	203	58	10[554]	201/4, (78), 278Cu

For explanations and symbols see pp. xi-xii.

TABLE 34. OLEFINIC KETONES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Olefinic Ketones				
C_4	Methyl vinyl ketone	26	81†	2[478]	81/734
		36	15†	2[70]	81, 1.4095[22]
			15	10[665]	81, 1.4095[22], 140Se*
		181	63	10[230]	
C_5	Methyl propenyl ketone	36	42	2[76]	119-125
	Ethyl vinyl ketone	178	22	10[95]	102/740, 1.4192, 129Dn
	Methyl isopropenyl ketone	24	98	2[488]	38/85, 1.4235, 173Se, 181Dn
		26	92	2[478]	97/734

TABLE 34 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Olefinic Ketones *(continued)*				
C_5	Methyl isopropenyl ketone *(continued)*	36	80	2[291]	58/200, 1.4232
		200	91	10[98]	
C_6	5-Hexen-2-one-(allylacetone)	184	48†	10[284]	132/760, 1.4170[27]
		205	31	10[595]	128/ 1.4174[25], 108Dn, 102Se*
		188	42	10[590]	
	4-Hexen-3-one	187	25	10[571]	139, 1.4388, 157Se
	1,2-Diacetylethylene	....	15	2[521]	90/15, (77)
	2-Methyl-1-penten-3-one	20	65	2[149]	119/751, 1.4270[24], 161Se
	3-Methyl-3-penten-2-one	36	87	2[487]	97/200, 1.4489
		36	90	2[71]	140
	4-Methyl-3-penten-2-one	36	80	2[67]	128
	(mesityl oxide)	36	100	2[69]	129
C_7	*trans*-3-Hepten-2-one	36	33	2[72]	60/16, 1.4421, 125Se
	5-Hepten-2-one (crotylacetone)	184	81†	10[284]	154/770, 1.4280[25]
		205	80	10[595]	153, 1.4272[25], 105Se
	3-Methyl-1-hexen-5-one	205	37	10[595]	138, 1.4197[25], 112Se
	5-Methyl-4-hexen-3-one	20	30	2[150]	148/760, 1.4496[15], 163Se
		178	30†	10[101]	148/760, 163Se
	5-Methyl-5-hexen-2-one	184	69	10[284]	145-150/760, 1.4278[27], 137Se
	(methallylacetone)	205	26	10[595]	149, 1.4285[25], 137Se
	3,4-Dimethyl-3-penten-2-one	178	54†	10[101]	147, 200Se
	3,4-Dimethyl-3-penten-2-one	20	54	2[150]	147, 1.4506[14], 200Se
	3,4-Dimethyl-4-penten-2-one				144, 114Se
	3,4-Dimethyl-4-penten-2-one	178	54†	10[101]	144, 114Se
	4,4-Dimethyl-1-penten-3-one	20	60	2[149]	66/105, 1.4219[14]
C_8	3-Methyl-3-hepten-2-one	36	93	2[71]	175, 164Se
	3-Methyl-3-hepten-5-one	36	72	2[319]	82-86/42, 1.4488[25], 114Se
	4-Methyl-6-hepten-3-one	198	56	10[286]	156, 80Dn
	2-Methyl-2,5-heptadien-4-one	194	30	10[449]	72/16, 1.4922[21], 141Dn
	3-Ethyl-5-hexen-2-one	184	48	10[286]	152, 1.4260[25], 53Dn
	2-Ethyl-1-hexen-3-one	20	55	2[149]	158/742, 1.4408[16], 119Se
	3,4-Dimethyl-3-hexen-2-one	36	....	2[322]	158, 1.4476[18], 142Se
	5,5-Dimethyl-3-hexen-2-one	36	40	2[292]	79/40, 1.4430, 178Se
	4,5-Dimethyl-4-hexen-3-one	178	57†	10[101]	166/750, 209Se
	4,5-Dimethyl-5-hexen-3-one	178	57†	10[101]	162/750, 110Se

For explanations and symbols see pp. xi-xii.

TABLE 34 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic Olefinic Ketones *(continued)*				
C_9	7-Methyl-5-octen-4-one	36	45	2[74]	86/25, 1.4413
	5-Ethyl-4-hepten-3-one	189	74	10[406]	179/740, 105Se
	2,3-Dimethyl-2-hepten-6-one	184	86	10[285]	76/13, 163Se
	3-Propyl-3-hexen-2-one	19	68	2[75]	72/9, 142Se
	2,4,5-Trimethyl-4-hexen-3-one	178	40†	10[101]	174/755
	Alicyclic Olefinic Ketones				
C_6	2-Methyl-2-cyclopentenone	179	67	10[202]	53/12, 220Se
		195	54	10[598]	161/760, 1.4771, 127-Ox
	2-Cyclohexenone	19	35	2[79]	68/22, 172Se, 163Dn
		183	38	10[441]	67/25, 1.4879, 168Se, 117Dn
C_7	1-Acetyl-1-cyclopentene	178	50†	10[102]	74/12, 211Se
	2,3-Dimethyl-2-cyclopentenone	206	30	10[596]	92/25, 1.4830, 250Se
	3-Methyl-2-cyclohexen-1-one	183	20	10[441]	78/14, 1.4938, 201Se, 176Dn
		202	34	10[475]	40/0.8, 1.4945, 178Dn, 199Se
C_8	1-Cyclopentenylacetone	184	90	10[287]	67/12, 150Se
	α-Propylidenecyclopentanone	36	65	2[77]	80/10, 225Se
	2,2,3-Trimethyl-4-cyclopentenone	206	6	10[596]	66/19, 1.4601, 190Se
	3-Ethyl-2-cyclohexenone	202	75	10[475]	57/0.9, 1.4913, 160Dn, 136Se
	3,5-Dimethyl-2-cyclohexen-1-one	36	55	2[409]	85/9
	1-Acetyl-1-cyclohexene	178	50†	10[103]	93/14
		178	54	10[97]	69/5, 1.4883[25], 220Se, 59-Ox
		178	62†	10[92]	200, 221Se
		204	70	10[594]	88/22, 1.4892
C_9	3-Methyl-2-*n*-propyl-1-cyclopentenone	206	32	10[596]	58/2, 1.4778, 210Se
	1-Propionyl-1-cyclohexene	178	36†	10[104]	102/14, 189Se, 78-Ox
		178	40†	10[93]	90/10, 195Se
	2-Allylcyclohexanone	184	66	10[286]	79/11, 1.4662[25], 70-Ox
		198	62	10[503]	92/17
	3-*n*-Propyl-2-cyclohexenone	202	75	10[478]	60/0.4, 1.4876[25], 156Dn, 175Se
	3-Isopropyl-2-cyclohexenone	202	12	10[475]	60/0.3, 1.4842, 155Dn, 179Se
	3-Methyl-5-ethyl-2-cyclohexen-1-one	36	66	2[409]	100/9, 1.4880*

TABLE 34 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Alicyclic Olefinic Ketones *(continued)*				
C_{10}	2,2-Dimethyl-1-acetyl-1-cyclohexene	204	56	10[490]	118/49, 1.4810[25], 201Se
C_{12}	2-Cyclohexylidenecyclohexanone	36	70	2[320]	150/22, 1.5084[25], 188Se
	Aromatic Olefinic Ketones				
C_9	Phenyl vinyl ketone	20	78	2[146]	
C_{10}	Phenyl propenyl ketone	178	61	10[96]	95/2
	Benzalacetone	36	78	2[294]	128/8, (42)
	α-Methylacrylophenone	26	70	2[288]	60/3, 1.5354
C_{11}	Isopropylideneacetophenone	178	35	10[580]	106/5, 1.5579[25]
		178	40	10[100]	
		194	40	10[449]	121/4, 1.5598[19], 168*p*N
C_{12}	1-Phenyl-1-hexen-5-one	205	88	10[595]	99/0.30, 1.5458[25], 132Se
	1-Phenyl-4-hexen-1-one	205	83	10[595]	97/1, 1.5270[25], 130Se
	3-Phenyl-1-hexen-5-one	205	74	10[595]	86/1, 1.5193[25], 103Dn
	Phenyl 2-methyl-3-butenyl ketone	205	76	10[595]	100/2.1, 1.5223[25], 177Se
	o-Methylstyryl ethyl ketone	36	26	2[302]	152/14, 178Se
C_{13}	Benzalpinacolone	36	93	2[296]	146/10, (43)
	1-Benzoyl-1-cyclohexene	178	40†	10[92]	147/8
C_{14}	1-Naphthalacetone	36	75	2[297]	170/1, 1.6665
	2-Naphthalacetone	36	69	2[297]	(104)
C_{15}	Benzalacetophenone (chalcone)	36	82	2[295]	(55-57)
C_{16}	*trans*-Dibenzoylethylene	178	83	10[91]	(110), 211-Ox*
	2,4-Diphenyl-2-buten-4-one	36	82	2[321]	139/1, 1.6273[25], 135-Ox
C_{17}	Dibenzalacetone	36	94	2[295]	(111)
	Heterocyclic Olefinic Ketones				
C_8	Furfuralacetone	36	66	2[307]	116/10, (38)
C_{11}	Furfuralacetofuran	36	89	2[309]	(90)
C_{13}	Furfuralacetophenone	36	90	2[308]	179/7, (26)
	2-Thenalacetophenone	36	96	2[482]	(59)

For explanations and symbols see pp. xi–xii.

TABLE 35. ACETYLENIC KETONES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n^t_D, (M.p.), Deriv.
C_4	Methyl ethynyl ketone	179	40	10[208]	86, 181Dn, 143pN
C_5	3-Pentyn-2-one	179	67	10[204]	74/95, 1.4380[23], 149Dn
C_6	*n*-Propyl ethynyl ketone	179	70	10[208]	66/100, 137Dn
C_8	3-Octyn-2-one	179	80	10[208]	76/15, 88Dn, 109Se
		188	58†	10[396]	76/15, 1.4446[28]
C_9	3-Nonyn-2-one	188	55†	10[396]	87/13, 1.4463[25]
	Phenyl ethynyl ketone	179	80	10[203]	(51), 214Dn
C_{10}	4-Phenyl-3-butyn-2-one	188	45†	10[396]	102/3, 1.5735[25]
		188	55	10[397]	125/14
C_{15}	Phenyl phenylethynyl ketone	189	74	10[424]	(55)
		193	85	10[424]	(66)

For explanations and symbols see pp. xi–xii.

TABLE 36. HALO KETONES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n^t_D, (M.p.), Deriv.
	Aliphatic and Alicyclic Halo Ketones				
C_3	Chloroacetone	66	72	4[495]	120
		184		10[90]	
	Bromacetone	66	44	4[483]	42/13
	α,α′-Dibromoacetone	66	60	4[634]	98/22, (26.5)
	α,γ-Dichloroacetone	179	75	10[205]	175, (45)*
	α,α,α′-Tribromoacetone	66	60	4[634]	116/14, (29)
	Hexafluoroacetone hydrate	182	60	10[236]	57/93, 1.3288
C_4	Methyl α-chloroethyl ketone	66	62	4[496]	113, 1.4171
	Methyl α-bromoethyl ketone	66	50	4[484]	34/12, 1.4571
	Methyl β-chloroethyl ketone	73	67	4[124]	50/15
		207	40	10[599]	48/15
	Chloromethyl ethyl ketone	66	21	4[496]	138, 1.4372
	Bromomethyl ethyl ketone	57	55	4[519]	155, 1.4670
		66	17	4[484]	50/12, 1.4670
	Chloromethyl β-chloroethyl ketone	207	45	10[599]	81/2.5
	Chloromethyl β-iodoethyl ketone	57	84	4[823]	(55)
	α,α′-Dibromodiacetyl	66	71	4[493]	(117)

TABLE 36 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n^t_D, (M.p.), Deriv.
	Aliphatic and Alicyclic Halo Ketones *(continued)*				
C_5	Methyl α-chloro-*n*-propyl ketone	66	44	4[494]	66/56
		66	37	4[488]	38/12
	Methyl γ-chloro-*n*-propyl ketone	184	91	10[694]	71/20, 1.4375[28]
	Methyl α-bromo-*n*-propyl ketone	66	50	4[485]	78/50, 1.4563[22]
		66	53	4[488]	53/14, 1.4629
	Chloromethyl *n*-propyl ketone	179	83	10[205]	66/26
	Bromomethyl *n*-propyl ketone	57	27	4[519]	92/50, 1.4575
		66	33	4[485]	92/50, 1.4620[23]
	Methyl α-chloroisopropyl ketone	66	58	4[496]	146, 1.4390, 116Dn
	Methyl α-bromoisopropyl ketone	66	35	4[485]	84/150, 1.4590[16]
	Bromomethyl isopropyl ketone	57	46	4[519]	86/50, 1.4467[14.5]
	1-Bromo-5-chloro-2-pentanone	57	80	4[519]	114/13, 1.5009[19.5]
	Ethyl β-chloroethyl ketone	207	45	10[98]	33/2.5, 1.4361
	α-Chloroethyl β-chloroethyl ketone	207	60	10[599]	65/1.5, 1.4631
	Di-β-chloroethyl ketone	207	48	10[600]	77/2, 1.4710[16]
	Bromoethyl β-bromoethyl ketone	207	60	10[599]	77/0.1
	2,3-Dibromo-3-methyl-2-butanone	74	97	4[442]	53/1
	1,5-Dibromoacetyl-acetone	184	67	10[289]	(7), 152Cu
	Acetyltrifluoroacetone	203	80	10[360]	107/760, 1.3893[21], 189Cu
C_6	6-Bromo-2-hexanone	54	58	4[125]	105/15, 1.4713, 81Dn
	1-Chloro-2-hexanone	189	51†	10[401]	72.5/15, 1.4370[24.5]
	1-Bromo-2-hexanone	57	50	4[519]	108/50, 1.4486[15.5]
		208	67†	10[601]	88/30
	Bromomethyl isobutyl ketone	57	70	4[519]	102/50, 1.4595[17]
	2-Methyl-1-chloro-3-pentanone	70	50	4[348]	64/9, 70Se
	2-Chloro-2-methyl-4-pentanone	53	74	4[187]	52/14
	2,3-Dibromo-3-methyl-2-pentanone	74	90	4[442]	82/5
	1-Chloro-3,3-dimethyl-2-butanone	66	85	4[496]	76/15, 1.4422, 144Dn
	1-Bromo-3,3-dimethyl-2-butanone	66	68	4[489]	49/1, 72/10

For explanations and symbols see pp. xi–xii.

TABLE 36 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Halo Ketones *(continued)*				
C_6	2-Chlorocyclohexanone	66	57	4[498]	79/7, (23), 1.4825
		66	66	4[497]	91/15
	2-Bromocyclohexanone	66	31†	4[643]	113/20, 1.5085[25]
C_7	1-Chloro-2-heptanone	57	90	4[522]	84/16
	1-Bromo-2-heptanone	208	85†	10[601]	110/30, 1.4644[25]
		57	70	4[519]	96/14, 1.4645[18]
	3-Bromo-2-heptanone	66	21†	4[643]	88/20, 1.4620[25]
		66	43	4[487]	80/9, 1.4613
	2-Chloro-3-heptanone	189	43†	10[401]	68/15
	1-Bromo-6-heptanone	51	47	4[67]	108/8
	3-Methyl-6-bromo-2-hexanone	54	44	4[370]	74/1.5
	3,4-Dimethyl-4-chloro 2-pentanone	207	42	10[101]	64/14
C_8	Chloromethyl *n*-hexyl ketone	57	92	4[522]	103/16
	3-Bromo-3-methyl-4-heptanone	66	45	4[486]	88/22, 1.4630
	2-Ethyl-1-chloro-3-hexanone	70	50	4[548]	92/12, 115Se
	4,5-Dimethyl-5-chloro-3-hexanone	207	57	10[101]	78/17
	Methyl α-bromocyclohexyl ketone	66	54	4[635]	58-65/3, 1.5027, (-8)
	Bromomethyl cyclohexyl ketone	57	95	4[635]	1.5033, (-2), 131Dn
	1-Acetyl-1,2-dibromocyclohexane	74	60	4[442]	(48)
	1-(Dibromoacetyl)-1-bromocyclohexane	66	80	4[645]	(74)
C_{13}	1-Bromo-2-tridecanone	57	92	4[524]	(53)
	Aromatic Halo Ketones				
C_8	ω-Fluoroacetophenone	178	46	10[105]	95/12, (28)
	ω-Bromoacetophenone	66	96	4[499]	(51)
	ω-Dichloroacetophenone	66	97	4[637]	134/13, 144/25
	ω-Dibromoacetophenone	66	50	4[502]	160/13, (37)
	ω-Trifluoroacetophenone	178	64	10[108]	67/37, 1.4576
	ω-Trichloroacetophenone	66	95	4[636]	102/3.5, 1.5685
		178	70	10[115]	121/15
	m-Bromophenacyl bromide	64	40	4[332]	174/14, (51), 164Se
	p-Bromophenacyl bromide	66	72	4[500]	(109)
	o-Chloroacetophenone	184	54†	10[290]	229/758
		185	81†	10[312]	87/5, 160Se*

TABLE 36 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Halo Ketones *(continued)*				
C_8	o-Bromoacetophenone	56	80	4[332]	112/10, 177Se
		187	80	10[370]	189Dn
		212	65	10[684]	117/12, 177Se*
	m-Chloroacetophenone	56	83	4[334]	113/11, 1.5494*
		183	76	10[245]	92/3, 232Se*
	m-Bromoacetophenone	56	56	4[331]	132/17, 1.5755, 233Se
	m-Iodoacetophenone	56	53	4[334]	117/4, 1.6220
	p-Fluoroacetophenone	178	74	10[110]	79/10, 1.5081[25]
		178	76	10[111]	196, 219Se
	p-Chloroacetophenone	178	78	10[113]	126/24
		178	83	10[12]	(12), 204Se*
	p-Bromoacetophenone	178	79	10[113]	117/7, (50.5), 129-Ox*
	p-Iodoacetophenone	56	52	4[335]	140/9, (84)
		178	95	10[114]	(85)
C_9	α-Chloro-α-phenylacetone	66	84	4[510]	118/16, 1.5373
	α-Bromo-α-phenylacetone	66	69	4[504]	127/7
	Chloromethyl benzyl ketone	57	85	4[520]	135/19, 98/1
	Bromomethyl benzyl ketone	57	62	4[519]	106/0.2, 1.5593[19*5]
	α-Chloropropiophenone	178	66	10[109]	133/26
	α-Bromopropiophenone	66	42†	4[643]	139/20, 1.5686[25]
	β-Chloropropiophenone	178	65	10[107]	(50)
		178	85	10[106]	(48)
	β-Bromopropiophenone	178	93	10[112]	(59)
	α,α-Dibromopropiophenone	66	83	4[651]	180/64, (30.5)
	α,β-Dibromopropiophenone	178	98	10[116]	(56)
	o-Chlorobenzyl methyl ketone	189	60	10[669]	130/15, 120-Ox
	p-Chlorobenzyl methyl ketone	178	16	10[117]	86/1
	o-Chloropropiophenone	56	85	4[333]	106/12, 173Se
	o-Bromopropiophenone	56	77	4[333]	118/11, 179Se
	m-Chloropropiophenone	56	73	4[333]	(46), 180Se
	m-Bromopropiophenone	56	44	4[333]	(40), 183Se
	p-Chloropropiophenone	56	76	4[333]	118/2, (35), 177Se
	p-Bromopropiophenone	56	58	4[335]	140/2, (46), 171Se
	p-Methylphenacyl bromide	66	94	4[501]	(50)
	p-Acetobenzyl bromide	54	46	4[369]	136/5
	m-Trifluoromethylacetophenone	187	50	10[368]	202
		189	91	10[368]	202

For explanations and symbols see pp. xi-xii.

TABLE 36 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Halo Ketones *(continued)*				
C_{10}	α-Bromo-*n*-propyl phenyl ketone	66	98	4 [503]	154/23
	Chloromethyl β-phenylethyl ketone	57	85	4 [510]	(40), 146Dn
		179	82	10 [143]	111/5, (41), 147Dn
	4-Phenyl-3-chloro-2-butanone	184	60†	10 [288]	99/4, 1.5268, 139Dn
	4-Phenyl-3-bromo-2-butanone	66	81	4 [503]	155–160/30
	Benzalacetone dichloride	74	34	4 [440]	(93)
	Benzalacetone dibromide	74	57	4 [439]	(125)
	1,3-*bis*-Chloroacetylbenzene	57	83	4 [526]	(98)
C_{11}	α-Bromoisobutyl phenyl ketone	66	80	4 [503]	145–155/20, (52)
C_{12}	α-Bromoacetylnaphthalene	66	80	4 [638]	215/15
C_{13}	α-Bromoisobutyrylmesitylene	178	70	10 [122]	170/24
	o-Chlorobenzophenone	178	86†	10 [118]	180/15, (44)
	o-Bromobenzophenone	178	52	10 [120]	153/0.05, 133-Ox*
		178	80	10 [121]	190/14
	p-Chlorobenzophenone	178	82	10 [119]	(78), 106Ph*, 185Dn*
C_{14}	Phenyl α-chlorobenzyl ketone	53	79	4 [183]	(67)
		62	65	4 [407]	(68)
	o-Chlorobenzyl phenyl ketone	190	73	10 [430]	(71), 86-Ox
	m-Chlorobenzyl phenyl ketone	190	42	10 [432]	(43), 102-Ox
	p-Chlorobenzyl phenyl ketone	190	70	10 [431]	(138), 96-Ox
	o-Chlorophenyl benzyl ketone	190	71	10 [430]	178/5, 132-Ox
	m-Chlorophenyl benzyl ketone	190	72	10 [429]	(62), 120-Ox*
	p-Chlorophenyl benzyl ketone	190	77	10 [431]	(108), 123-Ox
	4-Chlorobenzil	183	93	10 [566]	(73)
	4-Bromobenzil	183	94	10 [566]	(87)
	2,2′-Dichlorobenzil	179	39†	10 [195]	(129)
C_{15}	α-Chlorodibenzyl ketone	66	80	4 [511]	195/12, (68.5)
	α-Bromodibenzyl ketone	66	99	4 [506]	(49)
	Benzalacetophenone dichloride	74	96	4 [441]	(113)

TABLE 36 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Halo Ketones *(continued)*				
C_{15}	α-Bromo-4-propionylbiphenyl	66	75	4 [505]	(79)
C_{16}	9-ω-Bromoacetylanthracene	66	50	4 [508]	(107)
	Heterocyclic Halo Ketones				
C_6	2-Chloroacetylfuran	57	88†	4 [527]	93–108/4
	2-Chloroacetylthiophene	66	77	4 [512]	113/5, (48)
	2-Bromoacetylthiophene	66	80	4 [509]	98/1.5, 1.6258
C_{10}	2-Chloroacetylbenzofuran	57	95	4 [644]	(105)
C_{11}	4-Quinolyl chloromethyl ketone	57	50	4 [525]	(101)

For explanations and symbols see pp. xi–xii.

TABLE 37. HYDROXY KETONES

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Hydroxy Ketones				
C_3	Acetol (1-hydroxy-2-propanone)	95	58	5 [522]	42/12
C_4	1-Hydroxy-3-butanone	84	44†	5 [669]	74/13, 1.4302^{15}
		102	28	5 [207]	71/12, 1.435^{15}
C_5	1-Hydroxy-2-pentanone	95	15	5 [711]	152/760
	4-Hydroxy-2-pentanone	79	35	5 [158]	94/43, 1.4238^{25}, 104Ph
	5-Hydroxy-2-pentanone	99	31	5 [623]	75/3, 1.4350^{25}
		181	30	10 [229]	86/10, 155Se
	3-Methyl-4-hydroxy-2-butanone	102	93	5 [208]	84/19
	Dimethylacetylcarbinol	89	26†	5 [398]	140, 87-Ox, 165Se
	2-Hydroxycyclopentanone	104	16	5 [761]	74/10, 1.4701^{25}
C_6	5-Hydroxy-2-hexanone	184	69	5 [732]	61/2, 1.4312^{25}, 151Se
	4-Hydroxy-3-hexanone (propionoin)	104	55	5 [636]	60–65/12
	5-Hydroxy-3-hexanone	79	51	5 [158]	76/12, 1.4280^{25}
	3-Methyl-3-hydroxy-2-pentanone	200	60	10 [511]	73/50, 1.4200, 150Se

For explanations and symbols see pp. xi–xii.

TABLE 37 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Hydroxy Ketones *(continued)*				
C_6	3-Methyl-4-hydroxy-2-pentanone	102	67	5 [738]	76/10, 1.4350
	4-Methyl-4-hydroxy-2-pentanone (diacetone alcohol)	102	71	5 [204]	73/23
	2-Methyl-1-hydroxy-3-pentanone	102	57	5 [740]	94/15, 1.4346
	3-Ethyl-4-hydroxy-2-butanone	102	55	5 [740]	96/17, 1.4362 [18]
	2-Hydroxycyclohexanone	96	76	5 [187]	
		104	55	5 [761]	(117)
C_7	4-Hydroxy-2-heptanone	102	80	5 [210]	95/12, 1.4357
	2-Hydroxy-4-heptanone	79	58	5 [158]	101/24, 1.4300 [25]
	3-Methyl-4-hydroxy-2-hexanone	102	61	5 [211]	95/20, 1.435 [24]
	2-Methyl-5-hydroxy-3-hexanone	79	50	5 [158]	73/9, 1.4278 [25]
	2-Hydroxymethyl-1-cyclohexanone	102	20	5 [216]	115/16, 129Ph, 145*p*N
C_8	2-Hydroxy-4-octanone	79	66	5 [158]	91/8, 1.4333 [25]
	5-Hydroxy-4-octanone (butyroin)	104	70	5 [636]	80–86/12
	3-Methyl-3-hydroxy-2-heptanone	89	46†	5 [398]	84/19, 152Se
	3-Methyl-4-hydroxy-2-heptanone	102	45	5 [212]	110/16, 1.442
		102	82	5 [209]	115/30
	5-Methyl-5-hydroxy-3-heptanone	102	67	5 [205]	86/14, 1.4386 [14], 125Se
	5-Methyl-2-hydroxy-4-heptanone	79	64	5 [158]	114/36, 1.4318 [25]
	6-Methyl-2-hydroxy-4-heptanone	79	49	5 [158]	86/9, 1.4294 [25], 112Ph
	4-Ethyl-4-hydroxy-3-hexanone	193	54	10 [502]	178/742
		198	59	10 [502]	89/35, 177Se
	2,2-Dimethyl-5-hydroxy-3-hexanone	79	68	5 [158]	73/10, 1.4243 [25]
	2,5-Dimethyl-4-hydroxy-3-hexanone (isobutyroin)	104	75	5 [636]	70–75/14
	2-(α-Hydroxy-*n*-propyl)-cyclopentanone	102	45	5 [215]	105/9
C_9	3-Methyl-4-hydroxy-2-octanone	102	35	5 [211]	98/16, 1.4404 [29]

TABLE 37 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Hydroxy Ketones *(continued)*				
C_{10}	2,2,5,5-Tetramethyl-4-hydroxy-3-hexanone (pivaloin)	104	60	5 [636]	85–95/12
	2-(1′-Hydroxycyclopentyl)-cyclopentanone	102	40	5 [205]	99/3, (31), 78-Ox
	Aromatic Hydroxy Ketones				
C_8	*m*-Hydroxyacetophenone	93	48	5 [493]	(95)
	2,4-Dihydroxyacetophenone	178	65	10 [124]	(144)
	2,5-Dihydroxyacetophenone	209	77	10 [607]	(203)
	2,3,4-Trihydroxyacetophenone	178	57	10 [125]	(172)
	2,4,6-Trihydroxyacetophenone	178	87	10 [129]	(219)
C_9	Acetylphenylcarbinol	95	72	5 [523]	123/13, 113-Ox, 126Dn
		190	50	10 [435]	137/24, 194Se, 170Dn
	Methylbenzoylcarbinol	95	87	5 [523]	123/14, 134-Ox
	α,β-Dihydroxypropiophenone	98	90	5 [619]	(82)
	o-Propiophenol	209	35	10 [605]	115/6
	p-Propiophenol	178	82	10 [130]	(149), 170Se
		209	50	10 [605]	(148)
C_{10}	Acetylphenylmethylcarbinol	105	48	5 [650]	132/10
C_{12}	Phenyltrimethylacetylcarbinol	105	49	5 [649]	(47)
C_{13}	2-Hydroxybenzophenone	97	96	5 [536]	(153)
	3-Hydroxybenzophenone	97	88	5 [536]	(116)
	4-Hydroxybenzophenone	97	95	5 [536]	(134)
C_{14}	Benzoin	79	93	5 [156]	(134)
		79	97	5 [157]	
		104	92	5 [640]	(129)
		105	90	5 [648]	(133)
	o,o′-Dichlorobenzoin	104	40	5 [646]	(57)
	m,m′-Dichlorobenzoin	104	22	5 [646]	(76)
	p,p′-Dichlorobenzoin	104	88	5 [646]	(88)
	4,4′-Dihydroxybenzil	97	89	5 [541]	(235)
C_{15}	*p*-Methoxybenzoin (benzanisoin)	104	31	5 [644]	(106)

For explanations and symbols see pp. xi–xii.

TABLE 37 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref].	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Hydroxy Ketones *(continued)*				
C_{16}	Diphenylacetoin	187	45	10[372]	(52), 169 Se, 84NBz
	p,p'-Dimethoxybenzoin (anisoin)	104	73	5[643]	(113)
C_{17}	2',4',6'-Trimethylbenzoin	105	63	5[646]	(103)
C_{22}	β-Naphthoin	104	78	5[642]	(126), 172-Ox
	Heterocyclic Hydroxy Ketones				
C_6	2-Hydroxyacetylfuran	114	74	5[764]	(82)
C_{10}	α-Furoin	104	38	5[647]	(135)
	2,2'-Thenoin	104	30	5[763]	(109)

For explanations and symbols see pp. xi–xii.

TABLE 38. KETO ETHERS

C_n	Compound	Method	Yield (%)	Chapter[ref].	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Keto Ethers				
C_4	Mexthoxymethyl methyl ketone	179	29	10[209]	115/756, 1.3982, 111*p*N, 163Dn
		187	48	10[373]	114/746, 1.3980, 159Dn*, 109*p*N*
C_5	1-Methoxyethyl methyl ketone	187	37	10[375]	116/739, 1.3936, 141Se
	4-Methoxy-2-butanone	121	73	6[110]	66/50, 138/745, 1.4050
		195	75	10[578]	140/745
	Methoxymethyl ethyl ketone	187	49	10[373]	133/757, 1.4063
		187	59	10[379]	132, 198Dn*
	sym-Dimethoxyacetone	187	45	10[208]	78/18, 1.4174, 120Se
	Ethoxyacetone	187	65	10[381]	36/28, 1.4000, 96Se*
C_6	1-Methoxypropyl methyl ketone	187	29	10[378]	71/95, 1.4015[25], 147Se
	Methoxymethyl *n*-propyl ketone	187	51	10[373]	153/745, 1.4119
	Methoxymethyl isopropyl ketone	187	30	10[374]	144, 163Dn
		187	44	10[373]	145/748, 1.4078
	1-Methoxyethyl ethyl ketone	187	22	10[375]	136/750, 1.4019, 120Se
	4-Ethoxy-2-butanone	121	77	6[111]	150/764, 74/50
	Ethoxymethyl ethyl ketone	187	84	10[377]	147/752, 1.4068
	n-Propoxymethyl methyl ketone	187	52	10[376]	49/6, 1.4052

TABLE 38 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref].	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Keto Ethers *(continued)*				
C_6	Isopropoxymethyl methyl ketone	187	48	10[376]	35/10, 1.4004, 144Dn
		187	53	10[374]	142, 142Dn
C_7	1-Methoxy-5-hexanone	187	23	10[379]	67/8, 1.4180[25], 70Dn
	Methoxymethyl *n*-butyl ketone	187	34	10[373]	169/744, 1.4173
	Methoxymethyl isobutyl ketone	187	30	10[373]	164/751, 1.4140
	Methoxymethyl *s*-butyl ketone	187	32	10[373]	164/757, 1.4162
	Methoxymethyl *t*-butyl ketone	187	19	10[373]	159/743, 1.4193
	1-Methoxyethyl *n*-propyl ketone	187	33	10[375]	155/746, 1.4091, 169Se
		187	73	10[382]	93/100, 170Se
	1-Methoxyethyl isopropyl ketone	187	13	10[375]	58/31, 1.4092, 146Se
	1-Methoxypropyl ethyl ketone	187	79	10[378]	63/40, 1.4080[25], 145Se
	α-Methoxypinacolone	124	59	6[173]	83/4, 189Dn
	n-Propoxymethyl ethyl ketone	187	46	10[376]	56/4, 1.4122
	Isopropoxymethyl ethyl ketone	187	41	10[376]	47/11, 1.4082, 103Dn
	sym-Diethoxyacetone	187	67	10[208]	105/35, 1.4202, 91Se
	2-Methoxycyclohexanone	179	46	10[210]	59/8, 1.4519[25]
	4-Methoxycyclohexanone	179	65	10[207]	85/14, 1.4560, 178Se, 150Dn
C_8	Methoxymethyl *n*-amyl ketone	187	46	10[373]	191/753, 1.4220
	Methoxymethyl isoamyl ketone	187	71	10[373]	186/752, 1.4210
	1-Methoxyethyl *n*-butyl ketone	187	63	10[375]	82/36, 1.4160, 154Se
	1-Methoxyethyl isobutyl ketone	187	21	10[375]	52/9, 1.4128, 145Se
	1-Methoxyethyl *s*-butyl ketone	187	43	10[375]	77/36, 1.4158, 127Se
	1-Methoxyethyl *t*-butyl ketone	187	14	10[375]	64/34, 1.4130, 121Se
	1-Methoxypropyl *n*-propyl ketone	187	69	10[378]	86/42, 1.4131[25], 157Se
	1-Methoxypropyl isopropyl ketone	187	44	10[378]	66/23, 1.4159, 136Se
	6-Ethoxy-2-hexanone	184	60†	10[291]	92/13, 64Dn
	Ethoxymethyl *s*-butyl ketone	187	29	10[377]	173/743, 1.4158

For explanations and symbols see pp. xi–xii.

TABLE 38 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aliphatic and Alicyclic Keto Ethers *(continued)*				
C_8	1-Isopropoxy-3-methyl-2-butanone	187	17	10[374]	160, 88Dn
	Methyl α-(*s*-butoxy)-ethyl ketone	187	69	10[383]	163/750, 1.4080, 118Se
	Methoxymethyl cyclopentyl ketone	187	22	10[384]	87/14, 1.4486[25], 129Dn
C_9	3-Methyl-6-ethoxy-2-hexanone	184	69†	10[293]	99/17
	Methoxymethyl cyclohexyl ketone	187	33	10[384]	111/21, 1.4552[25], 102Se
	Aromatic Keto Ethers				
C_9	Phenoxyacetone	115	93	6[51]	120/19
		187	16	10[380]	112/12, 1.5228, 176Se
	α-Methoxyacetophenone	124	79	6[173]	126/19, 129Se
	p-Methoxyacetophenone	178	66	10[26]	125/5, 198Se
		178	96	10[6]	139/15, (37), 87-Ox*
C_{10}	Phenoxymethyl ethyl ketone	187	62	10[380]	100/5, 1.5201, 102Se
	α-Methoxypropiophenone	124	60	6[173]	89–95/4, 160Dn
	β-Methoxyethyl phenyl ketone	189	90	10[404]	1.5250, 176Dn
	α-Ethoxyacetophenone	124	81	6[173]	127/11, 128Se
		187	68	10[377]	122/15, 1.5250
	p-Methoxypropiophenone	116	88	6[96]	152/19
		178	87	10[6]	125/4
	p-Ethoxyacetophenone	178	77	10[29]	147/16, 1.5429[25]
	2,5-Dimethoxyacetophenone	178	71	10[134]	160/15
	3,5-Dimethoxyacetophenone	190	57	10[436]	(43)
C_{11}	γ-Phenoxypropyl methyl ketone	189	78	10[292]	121/2, (50), 110Dn
	Phenoxymethyl *n*-propyl ketone	187	64	10[380]	112/4, 1.5148, 108Se
	β-Ethoxyethyl phenyl ketone	189	82	10[404]	1.5190, 161Dn
	n-Propoxymethyl phenyl ketone	187	37	10[376]	118/6, 1.5150
C_{12}	δ-Phenoxybutyl methyl ketone	184	61†	10[292]	130/2, 1.5071[25], 101Dn
	β-*n*-Propoxyethyl phenyl ketone	189	82	10[404]	1.5193, 158Dn

TABLE 38 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
	Aromatic Keto Ethers *(continued)*				
C_{12}	β-Isopropoxyethyl phenyl ketone	189	89	10[404]	1.5083, 175Dn
C_{13}	β-Naphthoxyacetone	115	85	6[51]	(77)
C_{14}	Phenoxymethyl phenyl ketone	187	45	10[380]	187/8, (74), 187Se
	m-Methoxybenzophenone	179	25†	10[211]	(38)
		187	77	10[385]	185/4, (40)
	p-Methoxybenzophenone	178	89	10[26]	(62.5), 180Dn
	p-Phenoxyacetophenone	178	68	10[107]	154/2, (49)
C_{15}	*p*-Methoxyphenyl benzyl ketone	190	74	10[429]	(77), 118-Ox
	2-Methoxybenzil	179	60†	10[212]	(72)
	4-Methoxybenzil	179	90	10[198]	(63), 124-Ox
C_{16}	2-Ethoxybenzil	179	60†	10[212]	(102)
	4-Ethoxybenzil	179	60†	10[212]	(71)
	Desoxyanisoin	221	98	10[346]	(112)
	2,2′-Dimethoxybenzil	179	40†	10[212]	(129)
	3,3′-Dimethoxybenzil	179	60†	10[212]	(83)
	4,4′-Dimethoxybenzil (anisil)	179	52†	10[212]	(133)
		179	97	10[194]	(132), 255Se*

For explanations and symbols see pp. xi-xii.

TABLE 39. KETO ALDEHYDES

C_n	Compound	Method	Yield (%)	Chapter[ref.]	B.p./mm., n_D^t, (M.p.), Deriv.
C_3	Methylglyoxal	157	50	9[181]	52/12, 148Ph, 254Se
C_5	3-Formyl-2-butanone	146	75	9[173]	
C_6	*t*-Butylglyoxal	157	52	9[180]	115, 172Dn, 101-Ox
C_7	Pivaloylacetaldehyde	146	50	9[171]	45/13, 126Cu
	Hydroxymethylene-methyl isobutyl ketone	146	80	9[173]	
	α-Formylcyclohexanone	146	60	9[174]	88/14, 1.5130
C_8	Cyclohexylglyoxal	157	59	9[182]	72/17
	1-Methyl-3-hydroxy-methylene-2-cyclo-hexanone	146	45	9[263]	87/12
	Phenylglyoxal	152	87†	9[189]	(73)
		157	72	9[177]	97/25
C_9	*p*-Acetylbenzaldehyde	162	43	9[234]	190Ph, 181-Ox

For explanations and symbols see pp. xi-xii.

TABLE 39 *(continued)*

C_n	Compound	Method	Yield (%)	Chapter ref.	B.p./mm., n_D^t, (M.p.), Deriv.
C_{11}	Mesitylglyoxal	157	83	9[179]	106/4, 1.5520[19]
	2-Hydroxymethylene-1-tetralone	146	94	9[259]	180/28
C_{12}	β-Naphthylglyoxal	152	30	9[189]	(109)
C_{14}	*p*-Xenylglyoxal	152	90	9[189]	(121)

For explanations and symbols see pp. xi–xii.

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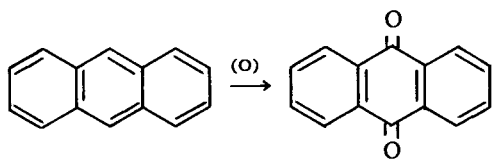
11

Quinones

CONTENTS

236. Oxidation of Aromatic Hydrocarbons



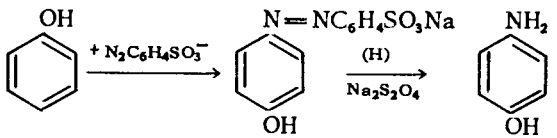
Polycyclic quinones are prepared by careful oxidation of the corresponding hydrocarbons with chromic-sulfuric acid mixture in acetic acid solution or as an agitated aqueous suspension, e.g., 2,3-dimethyl-1,4-naphthoquinone (80%),[1] 9,10-phenanthroquinone (80%),[2] and acenaphthenequinone (60%).[4] A laboratory reactor has been described in which an acetic acid solution of chromic acid and another solution of hydrocarbon are mixed as a film at 90°. The reaction mixture is then fed into water to prevent further oxidation. By this procedure, the yield of 2-methyl-1,4-naphthoquinone has been raised from 29% by the usual process to 45%.[5,6]

Other oxidizing agents have been used. Sodium chlorate with vanadium pentoxide catalyst attacks anthracene readily but is not powerful enough for the conversion of hydrocarbons of the naphthalene and phenanthrene series.[7,8] An acetic acid solution of 30% hydrogen peroxide has also been used.[9,10]

237. Oxidation of Phenols, Aminophenols, and Aryl Diamines

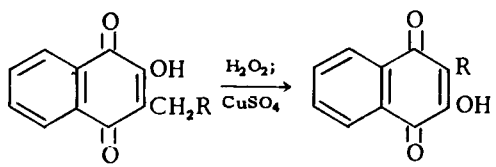
Derivatives of phenol or aniline can be oxidized to quinones, the yield and ease of oxidation depending on the substituents. If an amino or hydroxyl group is in the *para* position, the reaction proceeds readily, as illustrated by the synthesis of quinone from hydroquinone by oxidation with a sodium chlorate-vanadium pentoxide mixture (96%)[7] or with chromic-sulfuric acid mixture (92%).[13] A *para* halogen atom usually has a favorable effect. Any group in the *para* position is eliminated or oxidized. *o*-Quinones are usually prepared from the corresponding catechols. A survey of procedures for the synthesis of benzoquinones by oxidation has been made.[35]

Polymethylquinones and certain polycyclic quinones are prepared by the oxidation of aminophenols and their polycyclic analogs. The latter substances are readily obtained by coupling the corresponding phenolic compound with diazotized sulfanilic acid followed by a reductive cleavage of the azo compound.



Oxidation of the crude aminophenol is carried out with chromic acid[14,15] or manganese dioxide.[17] The over-all yields are good (50–90%). For the preparation of 1,2-naphthoquinone, ferric chloride is a milder and a better oxidant than chromic acid (94%).[21] Similarly, diamines are oxidized with ferric chloride, as in the synthesis of duroquinone (90%).[20]

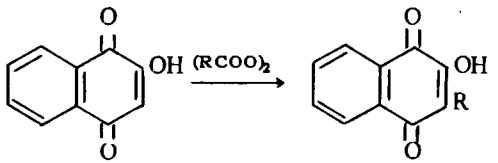
238. Oxidation of 2-Hydroxy-1,4-naphthoquinones



The conversion of 2-hydroxy-3-alkyl-1,4-naphthoquinones by the action of alkaline permanganate into the next lower homolog has been extensively studied.[33] A modified procedure involves the treatment of the naphthoquinone with hydrogen peroxide in dioxane-soda solution followed

by the action of copper sulfate and alkali on an intermediate acid (93% over-all). It has been established that the hydroxyl and alkyl groups change places in the course of the oxidation. The method has been found valuable in the synthesis of certain homologs difficult to obtain by direct alkylation (method 239).[32]

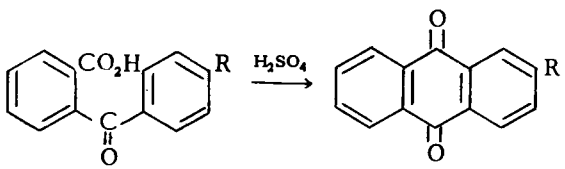
239. Alkylation of Quinones



Diacyl peroxides are good agents for the alkylation of *p*-benzo- and 1,4-naphthoquinones having a free position in the quinoid ring, particularly when the normal- or iso-alkyl chains are desired (30–60%).[11,32] The method has been widely applied in the synthesis of 2-hydroxy-1,4-naphthoquinones substituted in the 3-position. The procedure consists in adding slowly a solution of the diacyl peroxide in ether to a solution of the quinone in acetic acid at 90–95°.

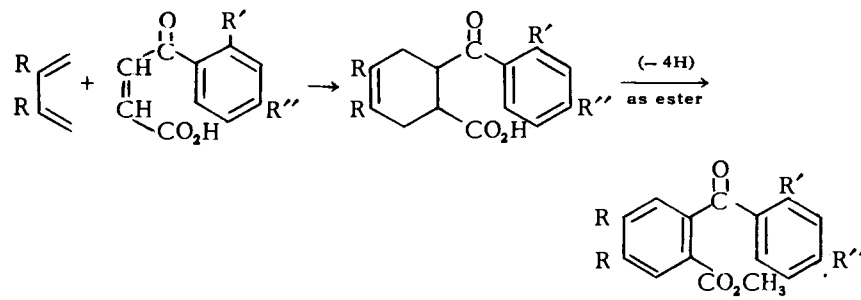
Alkyl groups in the low-molecular-weight range are also introduced by heating the quinone with the corresponding acid, excess red lead, and a promoter, which is a compound containing an active hydrogen, such as malonic ester or acetoacetic ester.[12]

240. Quinones by Ring Closure



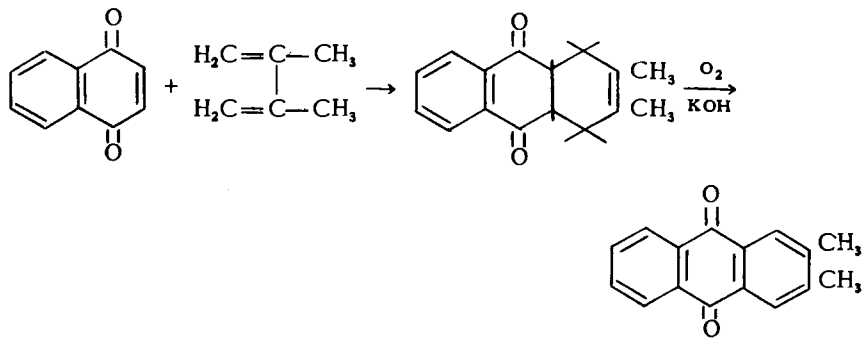
The intramolecular condensation of *o*-aroylbenzoic acids in the presence of concentrated sulfuric acid gives substituted anthraquinones. The acid strength, reaction temperature, and period of heating are carefully controlled to insure optimum yields and to avoid sulfonation products.[22,23] Boric acid has been added as a sulfonation inhibitor.[22] Substitution in the *para* position of the aroyl group leads to 2-alkyl-,[23] 2-chloro-,[25] and 2-bromo-anthraquinones.[26]

A number of anthraquinones have been synthesized by adding dienes to aroylacrylic acids, dehydrogenating the adducts in the form of the esters, and cyclizing as before.[27]



R = H, CH_3, C_6H_5; R′ = H, CH_3; R″ = H, CH_3, OCH_3

The diene synthesis[28,30] with quinones is valuable in providing hydroaromatic systems which are readily dehydrogenated, as illustrated by the synthesis of 2,3-dimethylanthraquinone (90% over-all).[29]



The synthesis has been adapted to the preparation of 1,2-naphthoquinone and its derivatives by an improved procedure.[30]

TABLE 40. QUINONES

C_n	Compound	Method	Yield (%)	Chapter ref.	(M.p.)
C_6	Benzoquinone	237	96	11[7]	(112)
		237	92	11[13]	
	Chlorobenzoquinone	237	92	11[8]	(54–64)
	Bromobenzoquinone	237	94	11[8]	(56)
C_7	Methylbenzoquinone	237	90	11[8]	(69)
C_8	*o*-Xyloquinone	237	62	11[17]	(57.5)
	m-Xyloquinone	237	75 †	11[14]	(75)
	p-Xyloquinone	237	81 †	11[19]	(124)
		237	40	11[18]	(125)
C_9	Trimethylbenzoquinone	237	95 †	11[14]	(26)
	4,7-Hydrindenequinone	237	93	11[17]	(205)
C_{10}	Duroquinone	237	90	11[20]	(110)
		237	60 †	11[14]	(112)
	1,2-Naphthoquinone	237	94	11[21]	(147)
	1,4-Naphthoquinone	237	81	11[16]	(125)
		240	88	11[30]	(124)
	1,2,3,4-Tetrahydro-5,8-naphthoquinone	237	60 †	11[17]	(56)
	2-Chloro-1,4-naphthoquinone	66	75 †	11[30]	(118)
	2-Hydroxy-1,4-naphthoquinone	97	46 †	11[31]	(192)
		240	95	11[30]	(196)
C_{11}	2-Methyl-1,4-naphthoquinone	236	29	11[5]	(106)
		236	45	11[6]	(105)
C_{12}	2-Ethyl-1,4-naphthoquinone	236	39	11[5]	(87)
	2,3-Dimethyl-1,4-naphthoquinone	236	78	11[9]	(127)
		236	80	11[1]	(127)
	Acenaphthenequinone	236	60	11[4]	(245)
C_{13}	2-Methyl-3-ethyl-1,4-naphthoquinone	239	41	11[12]	(73)
C_{14}	1,2-Phenanthraquinone	237	96 †	11[15]	(222)
	9,10-Phenanthraquinone	236	80	11[2]	(207)
	9,10-Anthraquinone	236	91	11[8]	(275)
	α-Chloroanthraquinone	....	98	11[34]	(160)
	β-Chloroanthraquinone	240	99	11[26]	(209)
	β-Bromoanthraquinone	240	95	11[25]	(209)
	β-Aminoanthraquinone	240	96	11[25]	(306) *
		435	97	11[36]	
C_{15}	β-Methylanthraquinone	240	90	11[23]	(174)
C_{16}	2,3-Dimethylanthraquinone	240	96	11[29]	(210)
C_{18}	β-*t*-butylanthraquinone	240	75	11[24]	(104)
C_{22}	2,3-Diphenyl-1,4-naphthoquinone	236	50	11[3]	(139)

For explanations and symbols see pp. xi–xii.

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