RODD'S CHEMISTRY OF CARBON COMPOUNDS

A modern comprehensive treatise

SECOND EDITION

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MONOCARBONYL DERIVATIVES
OF ALIPHATIC HYDROCARBONS

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PREFACE TO VOLUME IC

THE reasons for this revised edition of *Rodd's* "Chemistry of Carbon Compounds", the general details with regard to Volume I, which deals with aliphatic (acyclic) compounds and the method adopted for splitting up the primary volume into a series of smaller sub-volumes for the greater convenience of the reader, are set out in the Prefaces to Volumes IA and IB.

The descriptive chapters in Volume IA dealt with aliphatic hydrocarbons and their halogen-substituted derivatives; those in Volume IB described the remaining singly-linked, mono-substituted aliphatic hydrocarbons.

The present book, Volume IC, contrives to describe a single broad class of compounds, namely, aliphatic monocarbonyl compounds, their analogues and derivatives, *i.e.* derivatives of aliphatic hydrocarbons in which one carbon atom carries a doubly-linked oxygen, sulphur or nitrogen atom, or two or more such atoms linked singly or by both modes of attachment. Aldehydes and ketones and their derivatives are discussed in Chapter 8, monocarboxylic acids and their analogues in Chapter 9, while Chapter 10 describes the chemistry of carbon monoxide, isocyanides and fulminic acid, compounds containing a single "bivalent" carbon atom, and Chapter 11, that of carbonic acid and its wide range of derivatives. Again, for obvious chemical reasons, halogeno- and nitro-aldehydes and -ketones are also described in Chapter 8 and halogeno-alkanemonocarboxylic acids are included in Chapter 9; nitroalkanemonocarboxylic acids will be described in Chapter 15 (Volume ID) along side aminoalkanecarboxylic acids.

S. COFFEY

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Chapter 8

Aldehydes and Ketones

J. G. BUCHANAN, N. A. HUGHES, F. J. McQUILLIN AND G. A. SWAN

1. Introduction

The close relationship which exists, on the one hand, between the primary alcohols, the aldehydes and the carboxylic acids, and, on the other hand, between the secondary alcohols and the ketones has already been pointed out.

Aldehydes and ketones resemble each other in containing the carbonyl group CO; in aldehydes this is combined with either two hydrogen atoms, in formaldehyde, or with one alkyl group and a hydrogen atom, in the higher members of the series; in ketones it is combined with two alkyl groups:

$R \cdot CO \cdot H$	$R \cdot CO \cdot R'$
Aldehyde	Ketone

Aldehydes and ketones can be regarded as the anhydrides of dihydroxy compounds in which both hydroxyl groups are attached to the same carbon atom. Where a reaction leads to a compound containing the group $C(OH)_2$, the corresponding compound containing the CO group is formed by loss of water, except in a few cases where the dihydroxy compound, the aldehyde or ketone hydrate, is stable. In aqueous solution there is an equilibrium between the two forms,

$$>C(OH)_2 \rightleftharpoons >CO + H_2O$$

The ethers of the two hydrated forms $R \cdot CH(OR')_2$ and $R \cdot C(OR')_2 \cdot R''$, known as acetals and ketals, respectively, are stable compounds.

A comprehensive account of the chemistry of aldehydes is to be found in "Die Methoden der Organischen Chemie", *J. Houben* and *T. Weyl*, 4th Edn., Ed. *E. Müller*, Thieme, Stuttgart, 1954, Vol. VII, Part 1.

Preparation. The following methods are common to aldehydes and ketones.

(1) Oxidation of the alcohols, whereby aldehydes are formed from the primary, and ketones from the secondary, alcohols:

$$\underset{\text{Primary alcohol}}{R\cdot CH_2OH} + O \longrightarrow \underset{\text{Aldehyde}}{R\cdot CHO} + H_2O$$

$$\underset{\text{Secondary alcohol}}{R\cdot CH(OH)\cdot R'} + O \longrightarrow \underset{\text{Ketone}}{R\cdot CO\cdot R'} + H_2O$$

These reactions involve dehydrogenation and *H. Wieland* showed that they can occur in the absence of free oxygen, in the presence of finely divided palladium and a suitable hydrogen-acceptor, such as a quinone (Ber., 1912, 45, 484; 1913, 46, 3327). Biological oxidations may be similar in mechanism (*Wieland, ibid.*, 1914, 47, 2085; *E. Baldwin*, "Dynamic Aspects of Biochemistry", 2nd Edn., Cambridge, 1953, Chap. 6). More recently, the oxidation of alcohols by chromic acid has been shown to involve chromate esters as intermediates (*F. H. Westheimer*, Chem. Reviews, 1949, 45, 419; *W. A. Waters*, Quart. Reviews, 1958, 12, 277).

By further oxidation the aldehydes yield carboxylic acids having the same number of carbon atoms, whilst the ketones are broken down to smaller fragments.

Conversely, aldehydes and ketones are reconverted into primary and secondary alcohols by the addition of hydrogen:

$$\underset{\text{Acetaldehyde}}{CH_3\cdot CHO} + H_2 \longrightarrow \underset{\text{Ethanol}}{CH_3\cdot CH_2\cdot OH}$$

$$\underset{\text{Acetone}}{CH_3\cdot CO\cdot CH_3} + H_2 \longrightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2CH\cdot OH}$$

(2) The dry distillation of the calcium, barium or other heavy metal salts of monobasic fatty acids or of a mixture of salts of two different acids, gives in the first case symmetrical and in the second unsymmetrical ketones:

$$\underset{\text{Calcium acetate}}{(CH_3\cdot CO_2)_2Ca} \longrightarrow \underset{\text{Acetone}}{CH_3\cdot CO\cdot CH_3} + CaCO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3\cdot CO_2)_2Ca} + \underset{\text{Calcium propionate}}{(C_2H_5\cdot CO_2)_2Ca} \longrightarrow \underset{\text{Ethyl methyl ketone}}{C_2H_5\cdot CO\cdot CH_3} + 2CaCO_3$$

If one acid is formic acid, an aldehyde is produced:

$$\underset{\text{Calcium formate}}{(H\cdot CO_2)_2Ca} + \underset{\text{Calcium acetate}}{(CH_3\cdot CO_2)_2Ca} \longrightarrow 2\underset{\text{Acetaldehyde}}{CH_3CHO} + 2CaCO_3$$

When this reaction is applied to the calcium salts of dibasic acids such as adipic, pimelic and suberic acid, *cyclic* ketones are produced.

(3) Aldehydes and ketones are obtained by direct addition of water to acetylenic hydrocarbons in the presence of a mercury salt as catalyst (see Vol. 1A, p. 457).

(4) Alkyl hypochlorites, obtained from the alcohols by the action of chlorine and alkali, decompose under suitable conditions of light and temperature to yield aldehydes or ketones and hydrogen chloride. The hypochlorites of tertiary alcohols yield ketones and alkyl chlorides (*F. D. Chattaway* and *O. G. Backeberg*, J. chem. Soc., 1923, **123**, 2999):

$$R\cdot CH_2OCl \longrightarrow R\cdot CHO + HCl$$

$$R_2CHOCl \longrightarrow R\cdot CO\cdot R + HCl$$

$$R_3C\cdot OCl \longrightarrow R\cdot CO\cdot R + RCl$$

2. Saturated aldehydes

(a) Aldehydes, alkanals, $C_nH_{2n+1}\cdot CHO$

The homologous aldehydes show in their properties a gradation similar to that of the alcohols. The lower members are gaseous or volatile liquids, soluble in water, and have a characteristic odour, but the higher are solids, insoluble in water. In general, they are less soluble in water and more volatile than the alcohols. Chemically, they are neutral substances. Their reactivity places them amongst the most important synthetic reagents.

Nomenclature and isomerism. Empirically, the aldehydes are distinguished from the alcohols by possessing two atoms less of hydrogen—hence their name, suggested by Liebig (from *Alcohol dehydrogenatus*).

The common name of an aldehyde is derived from that of the acid of the same number of carbon atoms to which it gives rise on oxidation *e.g.* acetaldehyde from acetic acid. In the Geneva nomenclature, now adopted by the I.U.P.A.C., the names of the aldehydes are formed from the corresponding saturated hydrocarbons by substituting the final "e" by the suffix al; thus acetaldehyde, $CH_3\cdot CHO$ is ethanal. The systematic numbering starts from the CHO group; *e.g.* $(CH_3)_2CH\cdot CHO$ is 2-methylpropanal.

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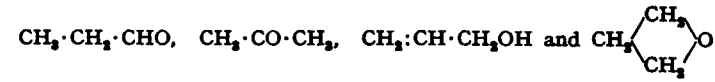
The number of isomeric aldehydes of definite carbon content equals the number of possible primary alcohols having the same carbon content. The aldehydes are isomeric with the ketones, the ethylenic alcohols and the anhydrides of the ethylene glycol series, containing an equal number of carbon atoms; thus the following are isomeric:



Propionaldehyde Acetone Allyl alcohol Trimethylene oxide (1,3-epoxypropane)

(i) Formation and preparation

(1) *By the oxidation of primary alcohols*, whereby the $CH_2 \cdot OH$ is converted into the CHO group, *e.g.* by potassium dichromate and dilute sulphuric acid or by atmospheric oxygen in the presence of a catalyst (*R. R. Davies* and *H. H. Hodgson*, J. chem. Soc., 1943, 282).

When chlorine is used as an oxidising agent, the aldehyde is first formed, but chlorination of the alkyl group follows.

The main by-products in the oxidation of primary alcohols to aldehydes are carboxylic acids which may become esterified during the reaction. Volatile aldehydes should therefore be removed by distillation as formed (Org. Synth., 1932, 12, 64).

Aldehydes may be prepared by a modification of the Oppenauer method of oxidation (Vol. IB, p. 14) (*A. Lauchenauer* and *H. Schinz*, Helv., 1949, 32, 1265).

tert-Butyl chromate is a fairly specific reagent for the oxidation of primary alcohols to aldehydes (*R. V. Oppenauer* and *H. Oberrauch*, Anales Asoc. quím. argentina, 1949, 37, 246).

(2) *By direct decomposition (dehydrogenation) of a primary alcohol* by passing alcohol vapours through a red-hot tube or better over finely divided copper at 200–250° (*W. Ipatiew*, Ber., 1903, 36, 1990; *P. Sabatier* and *J. B. Senderens*, Compt. rend., 1903, 136, 738; *L. Bouveault*, Bull. Soc. chim. Fr., 1908, [iv], 4, 119; *H. Adkins et al.*, J. Amer. chem. Soc., 1933, 55, 2992; *R. E. Dunbar* and *M. R. Arnold*, J. org. Chem., 1945, 10, 501).

Dehydrogenation can also be effected by heating with Raney nickel. In the case of optically active alcohols, such as 2-methylbutan-1-ol, this can occur without loss of optical activity (*E. J. Badin* and *E. Pacsu*, J. Amer. chem. Soc., 1944, 66, 1963).

(3) *By heating the calcium salts of fatty acids with calcium formate* (*F. Krafft*, Ber., 1880, 13, 1413).

(4) *By the reduction of acid chlorides* by sodium in moist ether (*W. H. Perkin* jun. and *J. J. Sudborough*, Proc. chem. Soc., 1894, 10, 216) or prefer-

ably by hydrogenation in the presence of a poisoned palladium-barium sulphate catalyst (*K. W. Rosenmund*, Ber., 1918, 51, 585; *E. Mosettig* and *R. Mozingo*, Org. Reactions, 1948, 4, 362),

$$CH_3COCl + 2H \longrightarrow CH_3CHO + HCl$$

or by lithium tri-*tert*-butoxyaluminohydride at —70°; at 0° the aldehydes, are themselves reduced further (*H. C. Brown* and *R. F. McFarlin*, J. Amer. chem. Soc., 1958, 80, 5372).

(5) *By the reduction of carboxylic acids with sodium amalgam* (*Davies* and *Hodgson*, J. Soc. chem. Ind., 1943, 62, 128).

(6) *From alkyl cyanides.* (a) By way of their iminochlorides.

The cyanide is added to a solution of stannous chloride in ether saturated with hydrogen chloride. The product is hydrolysed by warm water to the aldehyde, which is extracted with a solvent or steam-distilled. The yields are very good with the higher cyanides (*H. Stephen*, J. chem. Soc., 1925, 127, 1874; *Mosettig*, Org. Reactions, 1954, 8, 246):

$$RCN + HCl \longrightarrow RCCl{:}NH$$

$$RCCl{:}NH + SnCl_2 + 2HCl \longrightarrow RCH{:}NH,HCl + SnCl_4$$

$$RCH{:}NH + H_2O \longrightarrow RCHO + NH_3$$

(b) By catalytic hydrogenation in the presence of semicarbazide (*H. Plieninger* and *G. Werst*, Ber., 1955, 88, 1956).

(c) By reduction with lithium triethoxyaluminohydride (*Brown, C. J. Shoaf* and *C. P. Garg*, Tetrahedron Letters, 1959, 3, 9), lithium trimethylborohydride (*A. Khuri*, Diss. Abs., 1960, 21, 55) or lithium aluminium hydride (*Mosettig, loc. cit.* p. 252).

(7) *By reduction of a* N,N-*disubstituted amide* derived from *N*-methylaniline (*F. Weygand et al.*, Angew. Chem., 1953, 65, 525; *S. S. Nigam* and *B. C. L. Weedon*, J. chem. Soc., 1957, 3320), ethyleneimine (*Brown* and *A. Tsukamoto*, J. Amer. chem. Soc., 1961, 83, 2016) or a pyrazole (*W. Ried* and *F. J. Königstein*, Angew. Chem., 1958, 70, 165), with lithium aluminium hydride. Alternatively, the *N,N*-dimethylamide may be reduced with lithium diethoxyaluminohydride (*Brown* and *A. Tsukamoto*, J. Amer. chem. Soc., 1959, 81, 502). Reduction of substituted amides to aldehydes by alkali metals in liquid ammonia is also possible (*A. J. Birch, J. Cymerman-Craig* and *M. Slaytor*, Chem. and Ind., 1954, 1559; Australian J. Chem., 1955, 8, 512).

(8) *By the hydrolysis of Reissert's compounds* (1-acyl-1,2-dihydroquinaldonitriles); this provides an indirect method for the conversion of carboxylic

acids into aldehydes (*J. M. Grosheintz* and *H. C. L. Fischer*, J. Amer. chem. Soc., 1941, 63, 2021; *Mosettig, loc. cit.* p. 220).

(9) *By the alkaline decomposition of benzenesulphonacylhydrazides* (*M. Sprecher, M. Feldkimel* and *M. Wilchek*, J. org. Chem., 1961, 26, 3664).

(10) *By hydrolysis of some of their derivatives*; this method is of practical importance.

(a) From aldehyde-ammonia and aldehyde-bisulphite compounds (see pp. 40, 31); from oximes and hydrazones (pp. 45, 47).

(b) From alkylidene dihalides, *e.g.* $CH_3 \cdot CHCl_2$ by heating them with water and a base such as lead oxide.

(c) From acetals and alkylidene diacetates, by dilute acids or (in the latter case) alkalis:

$$CH_3 \cdot CH(OR)_2 \longrightarrow CH_3 \cdot CH(OH)_2 \longrightarrow CH_3 \cdot CHO$$

(11) *From αβ-glycols or their ethers*, containing at least one primary alcoholic group, by loss of water or alcohol, or from the corresponding ethylene oxide, by molecular rearrangement.

(a) Ethylene glycol yields acetaldehyde when heated with dilute sulphuric acid (*K. Krassusky*, J. Soc. phys.-chem. russe, 1902, 34, 537, 556).

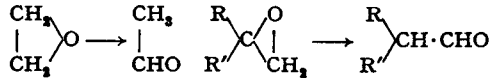
(b) Primary-secondary glycols under the same conditions yield a mixture of aldehyde and ketone:

$$R \cdot CHOH \cdot CH_2OH \begin{cases} \nearrow R \cdot CH_2 \cdot CHO \\ \searrow R \cdot CO \cdot CH_3 \end{cases}$$

(c) Primary-tertiary ethylene glycols yield aldehydes when heated with anhydrous formic or oxalic acid (*A. Béhal* and *M. Sommelet*, Compt. rend., 1904, 138, 89); the ethers $R_2C(OH) \cdot CH_2OR$ react particularly easily (*R. A. Barnes* and *W. M. Budde*, J. Amer. chem. Soc., 1946, 68, 2339):

$$R_2C(OH) \cdot CH_2OC_2H_5 \longrightarrow R_2CH \cdot CHO + C_2H_5OH$$

(d) Ethylene oxide and its homologues, especially the primary-tertiary compounds, undergo rearrangement when heated with alumina (*W. Ipatiew* and *W. Leontowitsch*, Ber., 1903, 36, 2016) or on boiling with dilute acid (*J. von Braun, ibid.*, 1923, 56, 2178; *Barnes and Budde, loc. cit.*):



(12) *From sodium salts of primary nitroparaffins*, which yield aldehydes and

nitrous oxide when treated with acids (*J. U. Nef*, Ann., 1894., **280**, 263; *K. Johnson* and *E. F. Degering*, J. org. Chem., 1943, **8**, 10). Nitro-olefins, $R_2C{:}CHNO_2$, on reduction yield aldoximes (*L. Bouveault* and *A. Wahl*, Compt. rend., 1902, **134**, 1145, 1226):

$$(CH_3)_2C{:}CHNO_2 \xrightarrow{Al/Hg} (CH_3)_2CH{\cdot}CH{:}NOH \longrightarrow (CH_3)_2CH{\cdot}CHO$$

(13) *By the action of alkalis on the dialkyl-chloroamines*, R_2NCl (see Vol. IB, p. 137) *and nitroamines* $R_2N{\cdot}NO_2$ (see Vol. IB, p. 148).

(14) *By the action of alkyl magnesium halides containing one carbon atom less than the required aldehyde on an excess of various formic acid derivatives* (*L. Gattermann* and *F. Maffezzoli*, Ber., 1903, **36**, 4152, *A. E. Tschitschibabin*, *ibid.*, 1904, **37**, 186; *F. Bodroux*, Compt. rend., 1904, **138**, 700; *Bouveault*, Bull. Soc. chim. Fr., 1904 [iii], **31**, 1322):

$$\underset{}{RMgX} + \underset{\text{Ester}}{H{\cdot}CO_2Et} \longrightarrow \underset{\text{Aldehyde}}{R{\cdot}CHO} + X{\cdot}MgOEt$$

$$\underset{}{RMgX} + \underset{\text{Dialkyl formamide}}{H{\cdot}CO{\cdot}NR'_2} \longrightarrow \underset{\text{Aldehyde}}{R{\cdot}CHO} + X{\cdot}MgNR'_2$$

$$\underset{}{RMgX} + \underset{\text{Orthoformic ester}}{HC(OEt)_3} \longrightarrow \underset{\text{Acetal}}{RCH(OEt)_2} + X{\cdot}MgOEt$$

$$\underset{}{RMgX} + \underset{\text{Imidoether}}{C_6H_5N{:}CHOEt} \longrightarrow \underset{\text{Aldimine}}{RCH{:}NC_6H_5} + X{\cdot}MgOEt$$

Alternatively, the Grignard reagent may be treated with 6-methyl-3-*p*-tolyl-3,4-dihydroquinazoline methiodide and the product hydrolysed by acid (*H. M. Fales*, J. Amer. chem. Soc., 1955, **77**, 5118), or with *p*-dimethylaminobenzaldehyde and the product treated with diazotised sulphanilic acid to yield an aldehyde (*M. Stiles* and *A. S. Sisti*, J. org. Chem., 1960, **25**, 1691). Related to these methods is the synthesis of aldehydes by the action of alkyllithiums on substituted formamides (*E. A. Evans*, J. chem. Soc., 1956, 4691):

$$RLi + Me_2N{\cdot}CHO \longrightarrow Me_2N{\cdot}CHR{\cdot}OLi \longrightarrow Me_2NH + R{\cdot}CHO\,.$$

(15) *By the Oxo Synthesis*, in which an olefin is heated with a mixture of carbon monoxide and hydrogen in the presence of a cobalt salt under

pressure (*H. Adkins* and *G. Krsek*, J. Amer. chem. Soc., 1949, **71**, 3051; *C. Schuster*, Fortschr. chem. Forsch., 1951, **2**, 311):

$$R_2C{:}CR_2 + CO + H_2 \longrightarrow R_2CH{\cdot}CR_2{\cdot}CHO$$

(16) *Reduction of αβ-unsaturated aldehydes, or better their acetals*, with sodium and alcohol or iron and acetic acid or by catalytic hydrogenation (*A. Skita*, Ber., 1912, **45**, 3312; *H. Fournier*, Bull. Soc. chim. Fr., 1910, [iv], **7**, 23) gives saturated aldehydes. Since αβ-unsaturated aldehydes result from aldol-type condensations of the lower saturated aldehydes (p. 49) this constitutes a method of passing synthetically up the aldehyde series.

(17) *By the hydrogenolysis of thiol esters* (*M. L. Wolfrom* and *J. V. Karabinos*, J. Amer. chem. Soc., 1946, **68**, 1455; *Mosettig*, Org. Reactions, 1954, **8**, 229; *P. Brandt*, Acta. chem. Scand., 1949, **3**, 1050).

The thiol-esters, obtained from acid chlorides and ethanethiol in pyridine, are heated with Raney nickel in aqueous ethanol under reflux; or with lithium hydride in toluene or xylene; the method is an alternative to the Rosenmund reduction of acid chlorides; p. 4).

(18) *By the oxidation of alkyl p-toluenesulphonates* (prepared from alkyl halides and silver *p*-toluenesulphonate), with dimethyl sulphoxide in sodium hydrogen carbonate solution (*N. Kornblum, W. J. Jones* and *G. J. Anderson*, J. Amer. chem. Soc., 1959, **81**, 4113). The action of alkyl halides or *p*-toluenesulphonates on excess of trimethylamine-*N*-oxide in chloroform also yields aldehydes (*V. Franze* and *S. Otto*, Ber., 1961, **94**, 1360).

(19) *From alkyl halides and hexamethylenetetramine by the Sommelet reaction* (*p.* 42; *S. J. Angyal*, Org. Reactions, 1954, **8**, 197).

(20) *By hydroboronation of a terminal acetylene, followed by treatment with hydrogen peroxide* (*H. C. Brown* and *G. Zweifel*, J. Amer. chem. Soc., 1959, **81**, 1512):

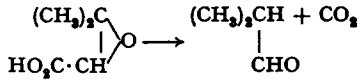
$$R_2BH + R'{\cdot}C{:}H \longrightarrow R'{\cdot}CH{:}CHBR_2 \xrightarrow{H_2O_2} R'{\cdot}CH_2{\cdot}CHO$$

The following *degradation reactions* produce aldehydes.

(21) *From α-hydroxycarboxylic acids*, $RCH(OH)CO_2H$, which yield aldehydes RCHO and formic acid (or $CO + H_2O$) by treatment with sulphuric acid, although the same result can often be better achieved by simply heating (*Davies* and *Hodgson*, J. Soc. chem. Ind., 1943, 128) or by treatment with lead tetracetate (*W. M. Lauer, W. J. Gensler* and *E. Miller*, J. Amer. chem. Soc., 1941, **63**, 1153).

Aldehydes are also formed by heating αβ-epoxy-carboxylic acids, or

glycidic acids (*G. Darzens*, G.P., 174,239/1906; *M. S. Newman* and *B. J. Magerlein*, Org. Reactions, 1949, 5, 413):

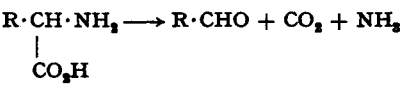


Similarly, α-ketonic acids when heated with dilute sulphuric acid yield aldehydes and carbon dioxide.

(22) *From α-amino-acids*, which give *N*-chloro-compounds when treated with sodium hypochlorite, the alkali salts of which break down with formation of aldehydes when heated in aqueous solution (*K. Langheld*, Ber., 1909, 42, 2360):

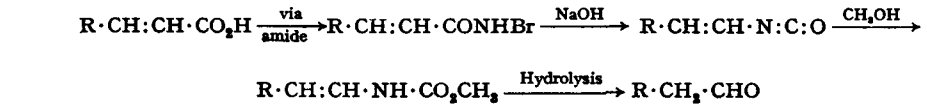
$$R\cdot CH(NH_2)\cdot CO_2H \longrightarrow R\cdot CH(NHCl)\cdot CO_2Na \longrightarrow R\cdot CHO$$

α-Amino-acids are also degraded to aldehyde by heating with certain carbonyl compounds (*R. M. Herbst*, Adv. in Enzymology, 1946, 4, 77; *A. Schönberg* and *R. Moubasher*, Chem. Reviews, 1952, 50, 261):



The amino group is not necessarily liberated as free ammonia.

(23) *From αβ-unsaturated acids* by the following series of reactions (*I. J. Rinkes*, Rec. Trav. chim., 1926, 45, 819):



(24) *By direct oxidation of a compound containing a double bond* to give a mixture of aldehydes, *e.g.* with hydrogen peroxide in ether in the presence of osmium tetroxide (*R. Criegee*, Ann., 1936, 522, 75).

Ozonides, formed by the action of ozone on olefins, may be decomposed to aldehydes by water (*C. Harries*, *ibid.*, 1905, 343, 311), zinc dust and acetic acid (*A. L. Henne* and *P. Hill*, J. Amer. chem. Soc., 1943, 65, 752) or by hydrogenolysis (*N. C. Cook* and *F. C. Whitmore*, *ibid.*, 1941, 63, 3540; *Henne* and *W. L. Perilstein*, *ibid.*, 1943, 65, 2183; *P. S. Bailey*, Chem. Reviews, 1958, 58, 925).

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