CROTONALDEHYDE

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INTRODUCTION

In this review, an attempt has been made to cover exhaustively the literature found in *Chemical Abstracts* in the years 1946 through 1958. The emphasis is on reactions of crotonaldehyde rather than uses or syntheses. The nomenclature used is, as far as possible, that of *Chemical Abstracts*. Unless otherwise noted, all temperatures are in degrees centigrade.

Although crotonaldehyde has not found wide industrial importance, it has been the object of considerable investigation. This review may help to focus the diverse interests in this chemical.

I. PHYSICAL PROPERTIES OF *trans*-CROTONALDEHYDE

The physical properties of the *cis*-isomer have not been reported. The properties listed below are those of commercial crotonaldehyde which is the *trans*-isomer.

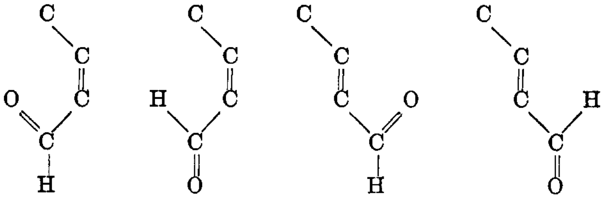
Molecular weight	70.09
$d^{20}{}_{20}$	0.853
Melting point	$-69°$ (-76.5)
Boiling point	102.2° (104.0)
$n^{17.8}{}_D$	1.4384
Heat of combustion, kcal./mole	542.1
Solubility, g. crotonaldehyde in 100 g. H_2O	18.1 g. at 20° 19.2 g. at 5°
g. H_2O in 100 g. crotonaldehyde	9.5 g. at 20° 8.0 g. at 5°
Flash point, open cup	55°F.
Weight per gallon	7.12 lb.
Appearance	Colorless liquid
Heat of vaporization	222 B.T.U./lb. or 123 cal./g.
Specific heat (liquid)	0.7
Vapor density (air = 1)	2.41
Explosive limits in air	2.95–15.5% (by vol.)
Azeotrope with water	84°, 24.8% H_2O
Azeotrope with water and ethanol	78°, 4.8% H_2O 87.9% ethanol
Dipole moment	3.67D (347)

The following references are on spectra of crotonaldehyde and derivatives: (16, 23, 33, 40, 93, 142, 143, 163, 235, 290). References are given also on dipole moments (25, 108), ultrasonic absorption (83, 84, 85), solubilities (120), inductive and resonance effects in acetals (210), complexes (218), polarography (276), and ionization potential (267, 361).

II. STRUCTURE

The bond angles and distances of crotonaldehyde in the vapor state have been measured by electron diffraction (219) and are listed for the four rotamers of crotonaldehyde.

Mackle and Sutton (219) state that the energy difference between the *s-cis* and *s-trans* rotamers is in the range 2.5 to 6 kcal./mole, with the *s-trans* possessing the lower potential energy. Such a small energy difference is in line with the fact that these species are not separable.



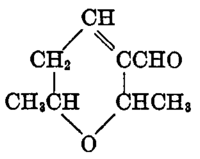
	s-cis *d-cis*	*s-trans* *d-cis*	*s-cis* *d-trans*	*s-trans* *d-trans*
C_1–O	1.21 Å.	1.21 Å.	1.21 Å.	1.21 Å.
C_1–C_2	1.46	1.46	1.46	1.46
C_2–C_3	1.36	1.36	1.36	1.36
C_3–O	2.90	3.59	2.90	3.59
C_3–C_4	1.52	1.52	1.52	1.52
C_4–O	2.50	4.05	4.35	4.90
H–C–H	109.5°	109.5°	109.5°	109.5°
Others	120°	120°	120°	120°

C═C (ethylene) 1.34 ± 0.02 Å.
C═O (formaldehyde) 1.21 ± 0.01 Å.
C—C (ethane) 1.55 ± 0.03 Å.

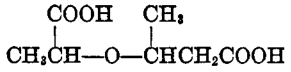
Comparison of the bond distances for crotonaldehyde with those for the pure bond types indicates a considerable contribution from an excited structure to the resonance hybrid. This partial double bond character of the C_1–C_2 bond accounts for the existence of *s-cis* and *s-trans* rotamers, and for the planarity of the carbon-oxygen skeleton.

A study of the influence of induced charge on the π-electron system of the configuration C═C—C═O indicates (275) that substituents that are less electronegative than hydrogen lower the total π-electron energy and thereby raise the resonance energy to make the molecule more stable. Substituents which are more electronegative than hydrogen have the opposite effect. With equal differences in electronegativity the former substituents have a greater effect than the latter. The resonance energy, however, depends on the position of the substituent: those that are less electronegative than hydrogen raise the resonance energy on C_1, while those that are more electronegative raise it on C_3. It is suggested that 1,2-addition occurs when the former groups are on C_3 or the latter groups are on C_1; 1,4-addition is favored when the former groups are on C_1, or the latter groups are on C_3. This is supported by the percentages of 1,4-addition products formed when ethylmagnesium bromide and phenylmagnesium bromide are made to react with various compounds of this type.

Dimeric crotonaldehyde can be separated into *cis* and *trans* isomers by fractional crystallization from petroleum ether at $-60°$. The structure of the *trans* dimer was proved to be



by permanganate oxidation to

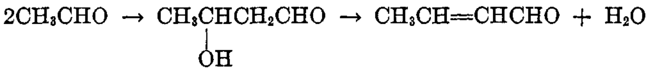


$$CH_3\overset{\text{COOH}}{\overset{|}{C}}H\text{—O—}\overset{CH_3}{\overset{|}{C}}HCH_2COOH$$

Structure is also considered in a number of references in relation to photochemistry (31), spectra (34, 358), polarography (73), derivatives (140), and reactions (321, 366).

III. SYNTHESIS AND MANUFACTURE

The most widely used commercial method for the synthesis of crotonaldehyde is the aldol condensation of acetaldehyde accompanied or followed by dehydration. Various catalysts and conditions are reported for this reaction (5, 15, 51, 74, 87, 90, 92, 111, 127, 138, 155, 158, 164, 179, 254, 304, 340)



$$2CH_3CHO \rightarrow CH_3\underset{\text{OH}}{\underset{|}{CH}}CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

Both acidic and basic ion exchange resins have been found to catalyze the aldol condensation and formation of crotonaldehyde from acetaldehyde (104, 105, 106, 224).

The equilibrium constant for this reaction

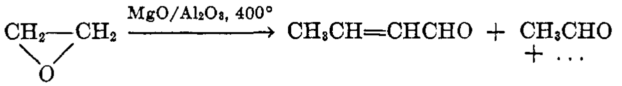
$$K = (\text{crotonaldehyde})/(\text{acetaldol})$$

has been found to be 0.61 or greater at 40–50° in dilute aqueous solution (214). Related reactions are

$CH_3CHO + CH_2{=}C(OCH_3)_2 \rightarrow CH_3CH{=}CHCHO + \ldots$ (229)

$$CH_3CHO \xrightarrow{300^\circ} CH_3CH{=}CHCHO \xrightarrow[ZnCrO_4]{355\text{–}390^\circ} CH_2{=}CHCH{=}CH_2$$

(191)



(221)

$$CH{\equiv}CH + H_2O \xrightarrow[330\text{–}350^\circ]{\text{Zn–W on }Al_2O_3} CH_3CH{=}CHCHO + CH_3CHO + CH_3COOH$$

(56)

Direct oxidation of hydrocarbons offers a possible synthesis of crotonaldehyde. In most cases only trace amounts are formed (166). Recently the oxidation of 1,3-butadiene has been reported to give conversions as high as 34% (72).

$$CH_2{=}CH_2 + N_2O \xrightarrow{300^\circ,\ 500\ \text{atm.}} CH_3CHO + CH_3CH{=}CHCHO$$

(44)

$$CH_3CH{=}CHCH_3 + O_2 \rightarrow CH_3CH{=}CHCHO + \ldots.$$

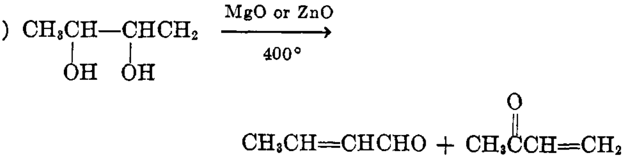
(64, 95, 96, 156, 294)

Activated alumina in phosphomolybdic acid catalyzes the air oxidation of propane, ethylene, acetaldehyde, acetic acid, propionic acid, or acetone to mixtures of maleic acid, acetic acid, crotonaldehyde, formaldehyde, and carbon dioxide (155).

Crotonaldehyde can be made by the reaction of formic and crotonic acids over Mn, Th, and Fe oxides at 300–400° (91). This reaction probably involves decarboxylation followed by formylation.

Pyrolysis of various hydroxy compounds can lead to crotonaldehyde. Some examples are

(a)

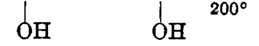


$$\underset{\text{OH}}{\underset{|}{CH_3CH}}{-}\underset{\text{OH}}{\underset{|}{CHCH_2}} \xrightarrow[400^\circ]{\text{MgO or ZnO}} CH_3CH{=}CHCHO + CH_3\overset{\text{O}}{\overset{\|}{C}}CH{=}CH_2$$

(216, 11)

(b) Erythrol + HCl (aq.) $\xrightarrow{\text{reflux}}$ $CH_3CH{=}CHCHO$ (30)

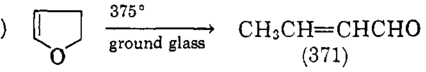
(c)



$$\underset{\text{OH}}{\underset{|}{CH_2}}CH{=}CH\underset{\text{OH}}{\underset{|}{CH_2}} \xrightarrow[200^\circ]{Al_2O_3} CH_3CH{=}CHCHO$$

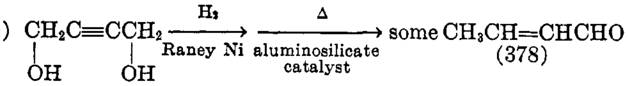
(37, 277, 349)

(d)



(371)

(e)

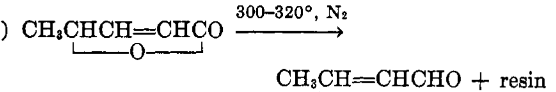


$$\underset{\text{OH}}{\underset{|}{CH_2}}C{\equiv}C\underset{\text{OH}}{\underset{|}{CH_2}} \xrightarrow[\text{Raney Ni}]{H_2} \xrightarrow[\text{aluminosilicate catalyst}]{\Delta} \text{some } CH_3CH{=}CHCHO$$

(378)

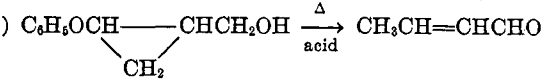
(f) $CH_3CH_2CH_2CH(OBu)_2 \xrightarrow{\text{distil}}$
$C_3H_7CHO + CH_3CH{=}CHCHO + C_4H_9OH + (C_3H_7CO)_2O + C_4H_9OCH_2CH{=}CHCH_3$ (292)

(g)



(302)

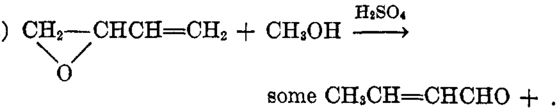
(h)



(190)

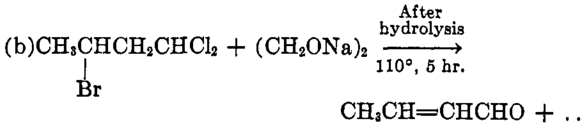
Other reactions which produce crotonaldehyde are

(a)



(19)

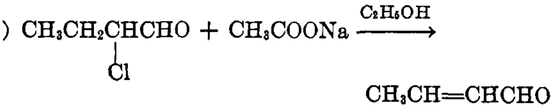
(b)



$$CH_3\underset{\text{Br}}{\underset{|}{C}}HCH_2CHCl_2 + (CH_2ONa)_2 \xrightarrow[110^\circ,\ 5\ \text{hr.}]{\text{After hydrolysis}} CH_3CH{=}CHCHO + \ldots$$

(196)

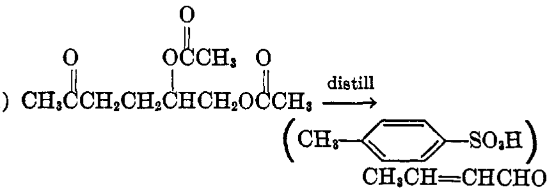
(c)



$$CH_3CH_2\underset{\text{Cl}}{\underset{|}{C}}HCHO + CH_3COONa \xrightarrow{C_2H_5OH} CH_3CH{=}CHCHO$$

(208)

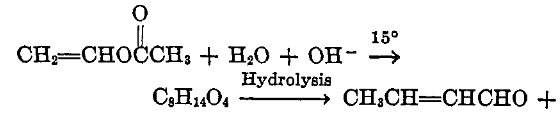
(d)



(265)

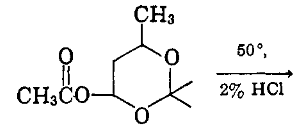
(e) $CH_3C{\equiv}CCH(OC_2H_5)_2 + H_2 \xrightarrow{Pd}$ $cis\text{-}CH_3CH{=}CHCH(OC_2H_5)_2$ (285)

(f)



$$CH_2{=}CHO\overset{\text{O}}{\overset{\|}{C}}CH_3 + H_2O + OH^- \xrightarrow{15^\circ} C_8H_{14}O_4 \xrightarrow{\text{Hydrolysis}} CH_3CH{=}CHCHO +$$

(167)

(g) 

HCHO + $CH_3CH{=}CHCHO$ (319)

The above dioxane is prepared by the reaction of HCHO and acetaldol in ether solution followed by acetylation.

Besides the above reactions which produce crotonaldehyde, this chemical exists if only in trace quantities in many natural products (256, 257, 266, 357).

IV. REACTIONS

As a result of its structure crotonaldehyde may react in a great variety of ways involving either or both of its functional groups. It undergoes 1,2- and 1,4-addition as well as various substitution reactions.

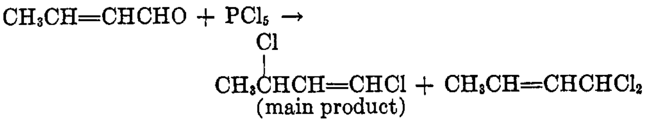
A. HALOGENATION

Direct chlorination of crotonaldehyde at room temperature results first in the addition of two chlorine atoms, then, on warming to 50° in the presence of water, the third chlorine atom is attached to yield 2,2,3-trichlorobutanal monohydrate (272).

Bromination of cooled crotonaldehyde and boiling with an excess of 1% HCl in absolute ethanol gives a 42% yield of 2-bromo-1,1,3-triethoxybutane. This compound is dehydrobrominated on refluxing with sodium ethoxide (162) to yield 1,1,3-triethoxybutene-2.

The kinetics of the acid-catalyzed addition of Cl_2 and Br_2 to crotonaldehyde in acetic acid solution indicates a nucleophilic mechanism (86). Addition of water, however, reduces the nucleophilic rate, and with sufficient water the electrophilic reaction is established and further dilution increases the rate.

The reaction of crotonaldehyde with phosphorus pentachloride proceeds as shown (7)

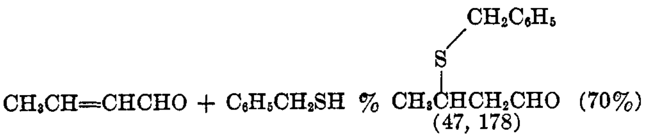


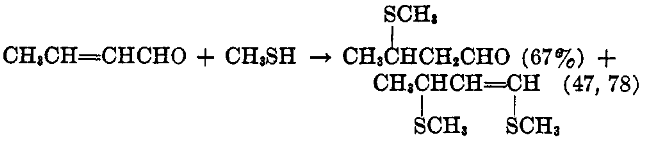
$$CH_3CH{=}CHCHO + PCl_5 \rightarrow \underset{\text{(main product)}}{CH_3\overset{Cl}{C}HCH{=}CHCl} + CH_3CH{=}CHCHCl_2$$

B. ADDITION TO THE CARBON–CARBON DOUBLE BOND

1. *Sulfur Compounds*

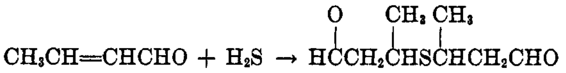
Generally mercaptan addition to crotonaldehyde is 1,4-addition (159) as shown in the examples





$$CH_3CH{=}CHCHO + CH_3SH \rightarrow CH_3\overset{SCH_3}{C}HCH_2CHO\ (67\%) + CH_3\underset{SCH_3}{C}HCH{=}\underset{SCH_3}{C}H\ (47, 78)$$

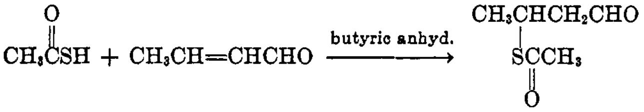
The reaction with H_2S gives predominantly the thioether (133)



$$CH_3CH{=}CHCHO + H_2S \rightarrow H\overset{O}{C}CH_2\overset{CH_3}{C}HS\overset{CH_3}{C}HCH_2CHO$$

This product does not revert to crotonaldehyde on treatment with mineral acid.

Thiolacetic acid (46) adds similarly



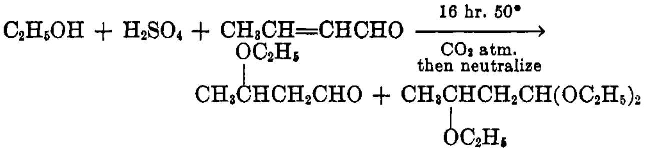
$$CH_3\overset{O}{\overset{\|}{C}}SH + CH_3CH{=}CHCHO \xrightarrow{\text{butyric anhyd.}} \begin{array}{l}CH_3CHCH_2CHO\\ \quad S\underset{\overset{\|}{O}}{C}CH_3\end{array}$$

Sulfathiazole reacts with crotonaldehyde (100) to give a compound of unestablished structure $C_{13}H_{13}O_2N_3S_2$ which is insoluble in cold dilute aqueous NaOH.

Crotonaldehyde reacts with SO_3 in dioxane solution (97) to give a sulfonic acid $CH_3\underset{SO_3H}{C}{=}CHCHO$ which is unstable even in solution.

2. *Alcohols*

In addition to forming the acetal, ethanol adds to the carbon–carbon double bond of crotonaldehyde (118)



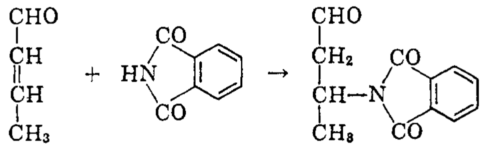
$$C_2H_5OH + H_2SO_4 + CH_3CH{=}CHCHO \xrightarrow[\text{CO}_2\text{ atm. then neutralize}]{16\text{ hr. }50°} CH_3\overset{OC_2H_5}{C}HCH_2CHO + CH_3\underset{OC_2H_5}{C}HCH_2CH(OC_2H_5)_2$$

With fused sodium sulfate in absolute ethanol saturated with dry HCl crotonaldehyde yields 1,1-diethoxy-3-chlorobutane which on refluxing with potassium hydroxide is dehydrochlorinated to crotonaldehyde diethyl acetal in 80% yield.

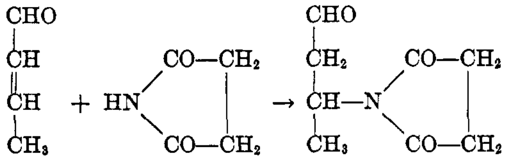
Allyl alcohol reacts in the presence of aqueous sodium hydroxide to form 3-allyloxybutyraldehyde (160). This compound can be hydrogenated over palladium to 3-propoxybutanal.

3. *Amides*

Phthalimide under the influence of sodium ethoxide reacts with crotonaldehyde to form the N-substituted imide (237)

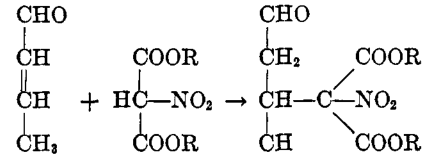


Similarly

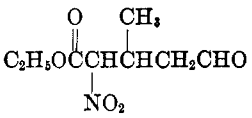


4. Nitro Compounds

Nitromalonic ester (359) and nitro acetic ester (238), in the presence of a basic catalyst, add to crotonaldehyde.

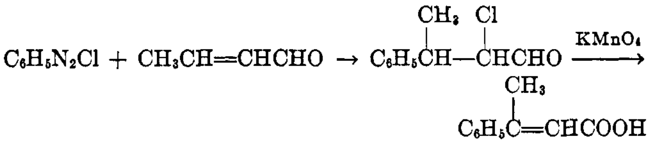


$CH_3CH{=}CHCHO + NO_2CH_2COOC_2H_5 \rightarrow$



$C_2H_5O\overset{\overset{O}{\|}}{C}\underset{\underset{NO_2}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_2CHO$

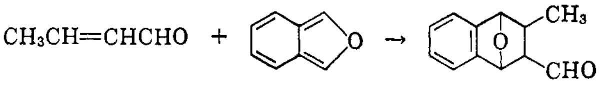
An aromatic substituent may be added to the molecule by reaction of crotonaldehyde with the appropriate diazonium salt (98)



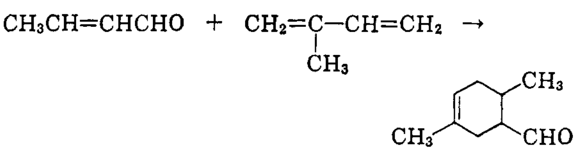
$C_6H_5N_2Cl + CH_3CH{=}CHCHO \rightarrow C_6H_5\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{Cl}{|}}{C}HCHO \xrightarrow{KMnO_4} C_6H_5\overset{\overset{CH_3}{|}}{C}{=}CHCOOH$

C. DIELS–ALDER REACTION

Crotonaldehyde enters into a wide variety of Diels–Alder reactions in which it may play the role of dienophile by undergoing 1,2-addition to its carbon–carbon double bond, or of diene by undergoing 1,4-addition. Some of the dienes with which it reacts are shown along with the corresponding products.



(109, 110)



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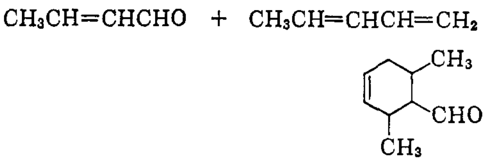
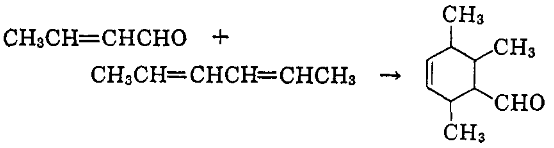


(152, 212, 289)



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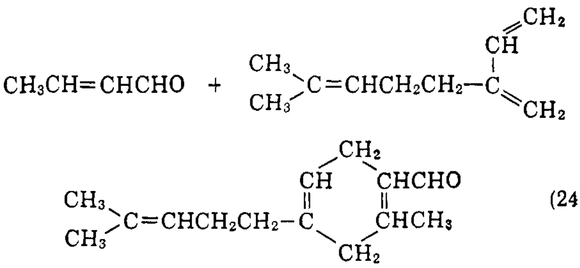

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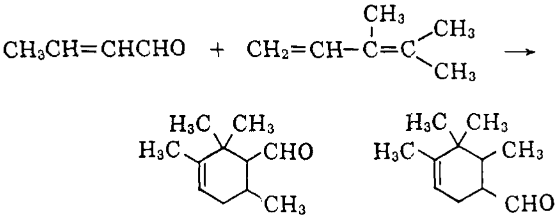

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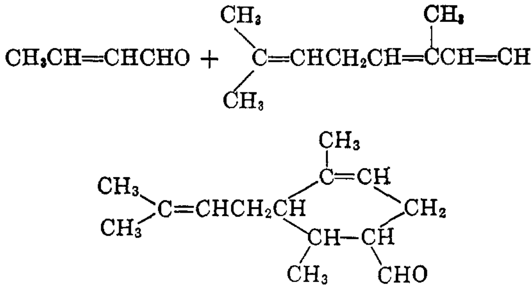
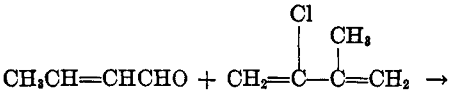
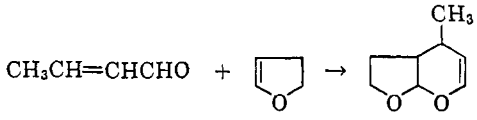


(293)



$CH_3CH{=}CHCHO + CH_2{=}\overset{\overset{Cl}{|}}{C}-\overset{\overset{CH_3}{|}}{C}{=}CH_2 \rightarrow$ no reaction (26)

In the role of diene crotonaldehyde reacts with a variety of unsaturated compounds as exemplified by the reactions



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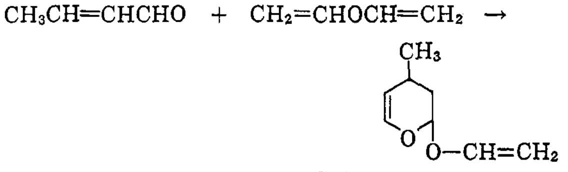

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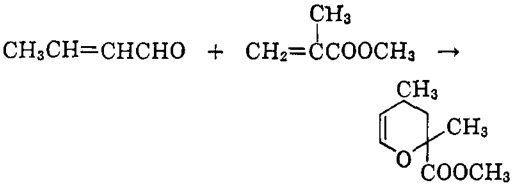
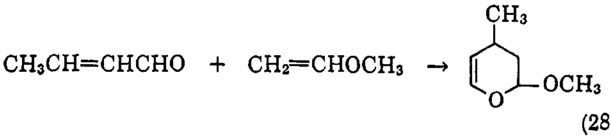
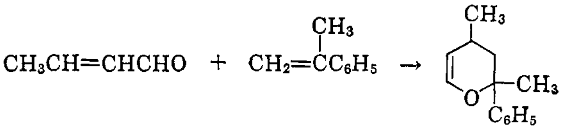


(316, 286)



(286)



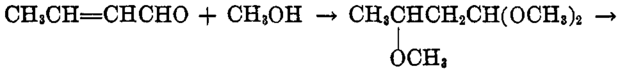
(286)

An unidentified aromatic product has been obtained (250) from the reaction with maleic anhydride.

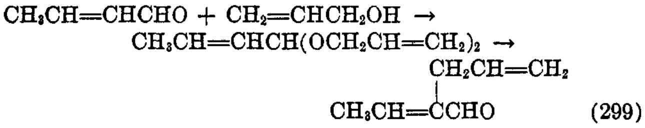
Flaig (117) has written an excellent review of the reactions of enolized crotonaldehyde with dienophiles.

D. ACETAL FORMATION

Crotonaldehyde forms many acetals, usually under relatively mild conditions and with acid catalysts. Some examples are

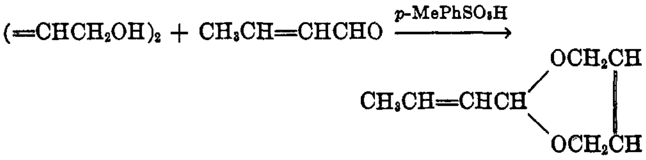


$$CH_3CH{=}CHCHO + CH_3OH \rightarrow CH_3\underset{OCH_3}{\underset{|}{C}}HCH_2CH(OCH_3)_2 \rightarrow CH_2{=}CHCH{=}CHOCH_3 \quad (67)$$



$$CH_3CH{=}CHCHO + CH_2{=}CHCH_2OH \rightarrow CH_3CH{=}CHCH(OCH_2CH{=}CH_2)_2 \rightarrow CH_3CH{=}\overset{CH_2CH{=}CH_2}{\overset{|}{C}}CHO \quad (299)$$

A similar reaction using the unsaturated glycol yields the dioxepene (38)



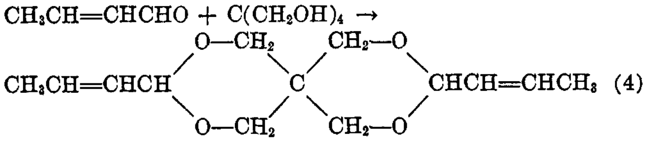
Other unsaturated alcohols react similarly to form α-alkenyl-crotonaldehydes. The reaction can be carried out in one step by heating a 5:1 mole ratio of alcohol-aldehyde to 150–300° and distilling the product. Polyvinyl alcohol (243) forms unsaturated acetals with crotonaldehyde.

Orthoformic esters react to form acetals (338)

$$CH_3CH{=}CHCHO + HC(OC_2H_5)_3 \xrightarrow{NH_4NO_3} CH_3CH{=}CHCH(OC_2H_5)_2$$

Butanediol-1,3 (154) reacts with crotonaldehyde at temperatures below 35° in alcoholic HCl to form an acetal which boils at 55–58° (7 mm.). This acetal reacts with water gas to give an unidentified dialdehyde fraction which boils at 136° at 5 mm.

With pentaerythritol the reaction is



Acetal formation is used to protect crotonaldehyde in the oxo synthesis. In this case (154) ethylene glycol is used. Some acetals of crotonaldehyde (butyl, isopropyl, hexyl) can be pyrolyzed at 260–300° to form the corresponding alkoxybutadiene (300).

Butadienyl ethers and alcohols react to form crotonaldehyde acetals (69) according to the reaction

$$CH_2{=}CHCH{=}CHOC_2H_5 + C_2H_5OH \xrightarrow[300°]{acid} CH_3CH{=}CHCH(OC_2H_5)_2$$

Many other acetals may be made by this method which lends itself especially to the synthesis of acetals containing dissimilar alcohol radicals. The butadienyl ethers can be regenerated by refluxing the corresponding acetal to 1,1,3-trialkoxybutane for several hours (68).

Crotonaldehyde also forms mercaptals by reaction with mercaptans (375)

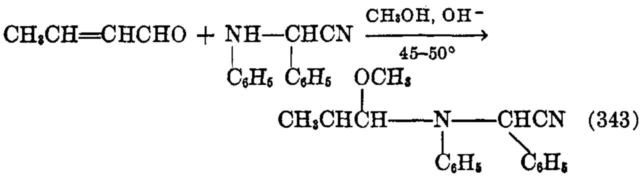
$$CH_3CH{=}CHCHO + CH_3SH \rightarrow CH_3CH{=}CHCH(SCH_3)_2$$

E. ADDITION TO THE CARBONYL GROUP

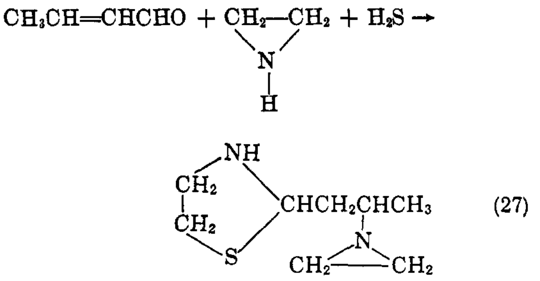
1. Amines

Crotonaldehyde undergoes the characteristic reactions of aldehydes with amines. Some examples are

$$CH_3CH{=}CHCHO + C_6H_5NH_2 \rightarrow CH_3CH{=}CHCH{=}NC_6H_5 \quad (8)$$



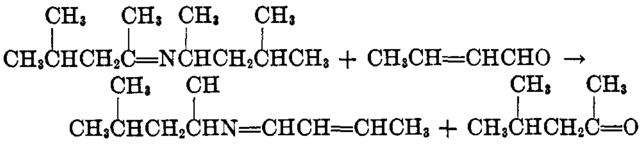
$$CH_3CH{=}CHCHO + \underset{C_6H_5}{\underset{|}{N}}H{-}\underset{C_6H_5}{\underset{|}{C}}HCN \xrightarrow[45\text{–}50°]{CH_3OH,\ OH^-} CH_3CH\overset{OCH_3}{\overset{|}{C}}H{-}\underset{C_6H_5}{\underset{|}{N}}{-}\underset{C_6H_5}{\underset{\diagdown}{C}}HCN \quad (343)$$



(27)

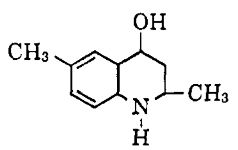
$$CH_3CH{=}CHCHO + NH_2OH \rightarrow CH_3CH{=}CHCH{=}NOH \quad (252)$$

Crotonaldehyde undergoes an interesting reaction (317)



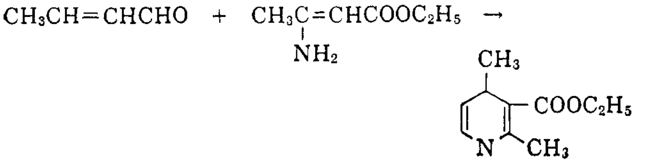
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}{=}N\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_3 + CH_3CH{=}CHCHO \rightarrow$$
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH}{\overset{|}{C}}HN{=}CHCH{=}CHCH_3 + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}{=}O$$

After standing for some time in sulfuric acid a quinoline derivative was obtained (332) from the reaction of crotonaldehyde with *p*-toluidine



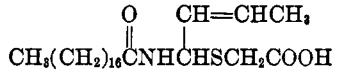
Refluxing crotonaldehyde with morpholine and methanol using an acetic acid catalyst yields a mixture of long chain polyene aldehydes. Hydrogenation of this product with Raney nickel produced a variety of polyhydroxy alcohols (305).

An interesting condensation reaction occurs with ethyl 3-aminocrotonate (354)



2. Amides

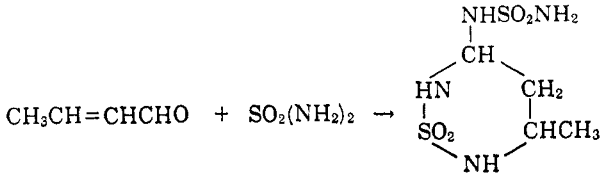
Reaction with stearic acid amide and thioglycolic acid at 60–100° yields



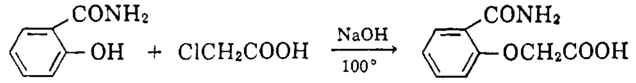
$$CH_3(CH_2)_{16}\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH=CHCH_3}{|}}{C}HSCH_2COOH$$

(296)

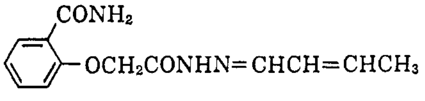
The Leuckart–Wallach reaction (244) with dimethylformamide gives a poor yield of dimethylbutylamine. Urea reacts with crotonaldehyde to form tetrahydro-6-methyl-4-ureido-2(1H)-pyrimidone. A similar reaction (244) is



The hydrazide of the acid formed by the reaction of salicylamide with chloroacetic acid

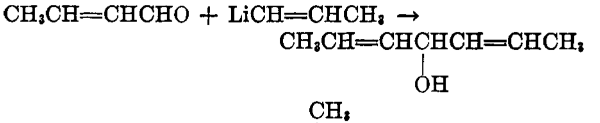


reacts with crotonaldehyde to yield the hydrazone (203)



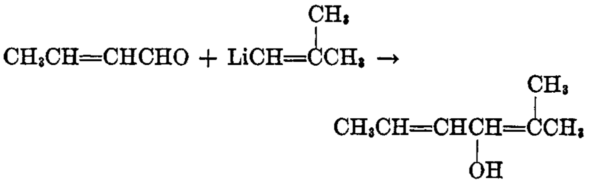
3. Metallo-organic Compounds

Metal alkyls react with the carbonyl group of crotonaldehyde to produce 40 to 60% yields of the secondary alcohol after hydrolysis.



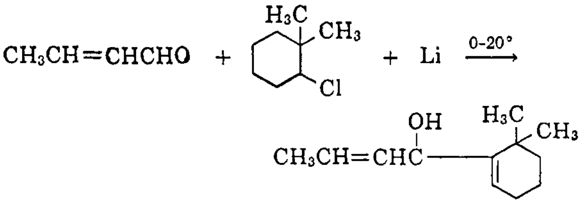
$$CH_3CH=CHCHO + LiCH=CHCH_3 \rightarrow CH_3CH=CH\underset{\underset{OH}{|}}{C}HCH=CHCH_3$$

(39)

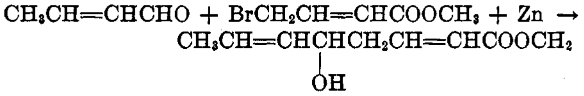


$$CH_3CH=CHCHO + LiCH=\overset{\overset{CH_3}{|}}{C}CH_3 \rightarrow CH_3CH=CH\underset{\underset{OH}{|}}{C}H=\overset{\overset{CH_3}{|}}{C}CH_3$$

(10)



(42)



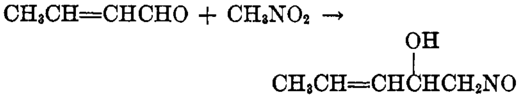
$$CH_3CH=CHCHO + BrCH_2CH=CHCOOCH_3 + Zn \rightarrow CH_3CH=CH\underset{\underset{OH}{|}}{C}HCH_2CH=CHCOOCH_2$$

(188)

Attempts to prepare α,β-unsaturated thiol ethers by the Reformatzky reaction of $Br\text{–}S\text{–}CH_2COSCH_3$ were unsatisfactory. Sorbic acid and a crystalline thio ether of sorbic acid were recovered; however, the main product was not determined (9).

4. Nitroalkanes

Reactions of crotonaldehyde with nitroalkanes usually result in the secondary alcohols. These reactions generally are catalyzed by bases. An example is the reaction with nitromethane

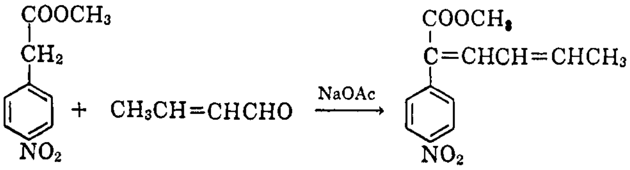


$$CH_3CH=CHCHO + CH_3NO_2 \rightarrow CH_3CH=CH\overset{\overset{OH}{|}}{C}HCH_2NO_2$$

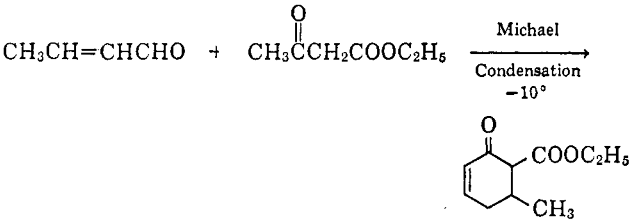
(119, 353)

5. Other Reactive Methylene Compounds

Crotonaldehyde undergoes most of the Claisen-type condensations typical of aldehydes. Acetaldehyde, for example, yields sorbaldehyde (57, 71). Other examples are the reaction with *p*-nitrophenylacetic ester (152)



and acetoacetic ester (246)

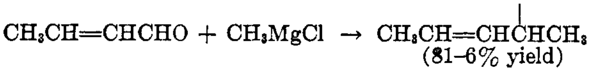


The Knoevenagel condensation of acetone with crotonaldehyde (3) leads to trimers instead of the 1:1 condensation product. Reppe (287) also discusses this reaction. The Knoevenagel condensation of crotonaldehyde diethyl acetal with malonic ester gives the expected product without the intermediate formation of free aldehyde.

Crotonaldehyde reacts with crystal violet base methyl ether to form a 52% yield of 5,5,5-tris-(*p*-dimethylaminophenyl)-2-pentanal (253).

6. Grignard Reaction

This reaction gives the expected product (66, 204, 251) as illustrated by the reaction of methylmagnesium chloride

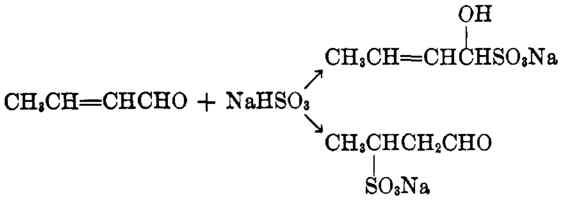


$$CH_3CH=CHCHO + CH_3MgCl \rightarrow CH_3CH=CH\overset{\overset{OH}{|}}{C}HCH_3$$

(81–6% yield)

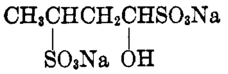
7. *Sodium Bisulfite*

The reaction of crotonaldehyde with sodium bisulfite can lead to addition to the carbonyl group, to the carbon–carbon double bond, or to both (172). The first step is the addition of one bisulfite molecule



$$CH_3CH{=}CHCHO + NaHSO_3 \begin{array}{l} \nearrow CH_3CH{=}CH\overset{\overset{OH}{|}}{C}HSO_3Na \\ \searrow CH_3\underset{\underset{SO_3Na}{|}}{C}HCH_2CHO \end{array}$$

Both of these compounds can react further to form

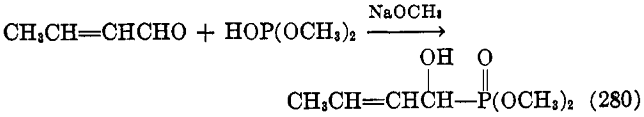


$$CH_3\underset{\underset{SO_3Na}{|}}{C}HCH_2\underset{\underset{OH}{|}}{C}HSO_3Na$$

The carbonyl bisulfite group is removed easily by treatment with alkali. The other bisulfite group is removed only with difficulty. References (209) and (22) discuss some reactions of the crotonaldehyde–bisulfite adducts.

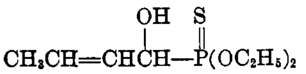
8. *Phosphorus Compounds*

Dialkyl phosphites undergo 1,2-addition to crotonaldehyde



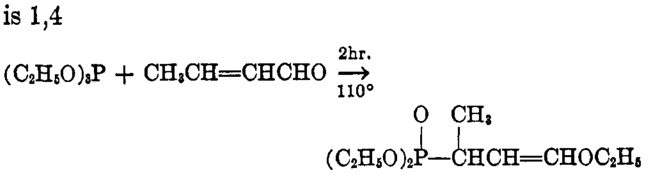
$$CH_3CH{=}CHCHO + HOP(OCH_3)_2 \xrightarrow{NaOCH_3} CH_3CH{=}CH\overset{\overset{OH}{|}}{C}H{-}\overset{\overset{O}{\|}}{P}(OCH_3)_2 \quad (280)$$

A similar reaction occurs with $HSP(OC_2H_5)_2$ (281) to form in 44% yield



$$CH_3CH{=}CH\overset{\overset{OH}{|}}{C}H{-}\overset{\overset{S}{\|}}{P}(OC_2H_5)_2$$

Addition of trialkyl phosphites (192) to crotonaldehyde is 1,4

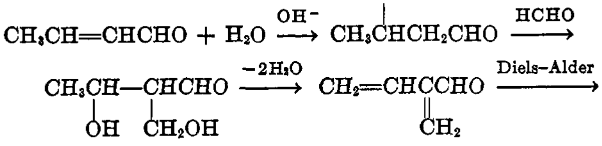


$$(C_2H_5O)_3P + CH_3CH{=}CHCHO \xrightarrow[110°]{2hr.} (C_2H_5O)_2\overset{\overset{O}{|}}{P}{-}\overset{\overset{CH_3}{|}}{C}HCH{=}CHOC_2H_5$$

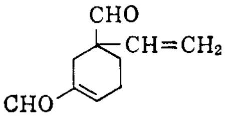
This addition is believed to proceed through a dipolar ion which cyclizes to an intermediate. Thus, trialkyl phosphites are capable of adding to π-π and σ-π conjugated systems.

9. *Formaldehyde*

Formaldehyde reacts with crotonaldehyde or acetaldol to form the methylol derivative which can react further (282, 283, 284)

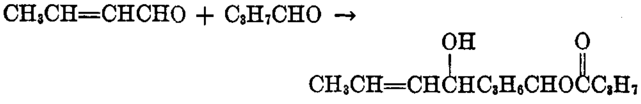


$$CH_3CH{=}CHCHO + H_2O \xrightarrow{OH^-} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO \xrightarrow{HCHO}$$
$$CH_3\underset{\underset{OH}{|}}{C}H{-}\underset{\underset{CH_2OH}{|}}{C}HCHO \xrightarrow{-2H_2O} CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CHO \xrightarrow{Diels\text{–}Alder}$$



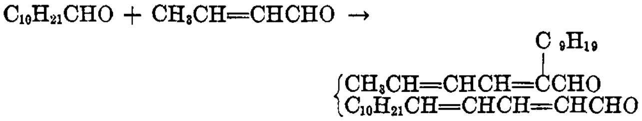
10. *Other Aldehydes*

Acetaldehyde reacts with crotonaldehyde to form, after hydrogenation, hexanol, octanol, and decanol (227). Glycol esters are produced at room temperature by treating aliphatic aldehydes or their mixtures with magnesium aluminum alkoxides which effect a condensation of three molecules of the aldehydes into a molecule of glycol ester (258)



$$CH_3CH{=}CHCHO + C_3H_7CHO \rightarrow CH_3CH{=}CH\overset{\overset{OH}{|}}{C}HC_3H_6CHO\overset{\overset{O}{\|}}{C}C_3H_7$$

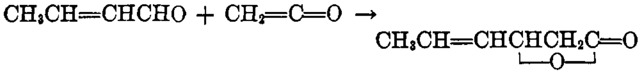
The condensation of crotonaldehyde with $C_{10}H_{21}CHO$ using piperidine acetate catalyst results in two products which can be separated by chromatography (325)



$$C_{10}H_{21}CHO + CH_3CH{=}CHCHO \rightarrow \left\{\begin{array}{l} CH_3CH{=}CHCH{=}\overset{\overset{C_9H_{19}}{|}}{C}CHO \\ C_{10}H_{21}CH{=}CHCH{=}CHCHO \end{array}\right.$$

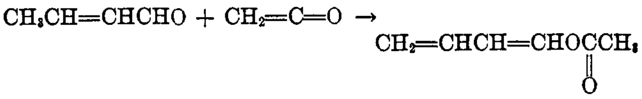
11. *Ketene*

Crotonaldehyde reacts with ketene in at least two ways depending upon the catalyst used. In the presence of boric acid (157), boron trifluoride (161), or zinc salts (50), the β-lactone is formed



$$CH_3CH{=}CHCHO + CH_2{=}C{=}O \rightarrow CH_3CH{=}CH\underbrace{CHCH_2C}_{O}{=}O$$

This lactone can be pyrolyzed to piperylene (157) or to sorbic acid (50, 161). With strong acids the acetoxy compound is formed (1)

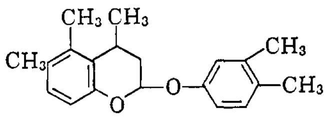


$$CH_3CH{=}CHCHO + CH_2{=}C{=}O \rightarrow CH_2{=}CHCH{=}CHO\underset{\underset{O}{\|}}{C}CH_3$$

The catalysts were X–SO_3H where X is F, Br, Cl, OH, CH_3O.

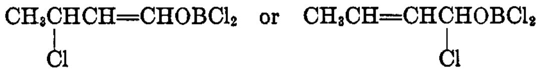
12. *Phenols*

Two molecules of 3,4-dimethylphenol react with crotonaldehyde in acetic acid solution to produce 2-(3,4-dimethylphenoxy)-4,6,5(or 7)-trimethylchromane (65)



13. *Boron Trichloride*

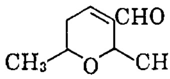
A 1:1 addition compound has been isolated in the reaction of crotonaldehyde with boron trichloride (121). The evidence presented favors the formulation of this compound as a dichloroboronite and not as a coördination compound. This compound may then be regarded as the 1,4- or the 1,2-addition product


$$\underset{\displaystyle Cl}{CH_3CH}CH{=}CHOBCl_2 \quad \text{or} \quad CH_3CH{=}CH\underset{\displaystyle Cl}{CH}OBCl_2$$

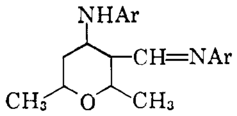
Pyrolysis of this compound gives 1,3-dichlorobutene-1.

F. AUTOCONDENSATION AND REACTIONS OF CONDENSATION PRODUCTS

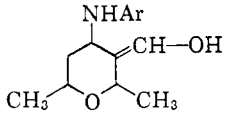
The autocondensation of crotonaldehyde can be made to yield a variety of products by varying catalyst and conditions. In acid solution crotonaldehyde dimerizes



This compound reacts readily with primary amines in the cold to form the Schiff bases (183, 184). This reaction is immediately reversed by the action of aqueous mineral acid. The reaction of the crotonaldehyde dimer and an excess of an aromatic amine produces compounds of the general formula

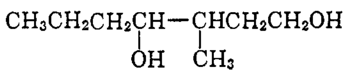


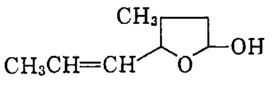
which on hydrolysis produce

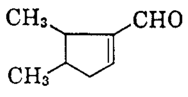


Condensation in the presence of secondary amines produces 4,6-dihydro-*o*-tolualdehyde along with linear polyene aldehydes (151). Barium oxide or calcium oxide at 300° converts crotonaldehyde directly to *o*-tolualdehyde (369). Aldol-type condensations are brought about by various catalysts including amines and Friedel–Crafts type catalysts (45, 113, 151, 217, 269, 309). It has been shown (309) that a molar proportion of the amine catalyst is required along with an acid of p*K* between 3 and 5.

Reductive dimerization using sodium amalgam at 0° yields several products (247) apparently by an aldol-type reaction


$$CH_3CH_2CH_2\underset{\displaystyle OH}{CH}{-}\underset{\displaystyle CH_3}{CH}CH_2CH_2OH$$





and an unidentifiable aldehyde.

G. PYROLYTIC AND PHOTOLYTIC REACTIONS

The photochemically induced reaction of an aldehyde with 1-alkenes normally produces a ketone, carbon monoxide, and an alkene derived from the alkyl radical of the aldehyde. The corresponding reaction of crotonaldehyde, however, produces mainly polymeric compounds (195, 339). When photolyzed with acetone at 2654 Å. and 120–350°, butene is formed. Butene is also produced by pyrolyzing a mixture of di-*tert*-butyl peroxide with crotonaldehyde at 170° (273).

In the reaction of ethanol with acetaldehyde to produce butadiene, crotonaldehyde appears to be an intermediate and may be substituted for acetaldehyde (341). The reaction temperature is 300–400°, and oxides of Zr, Ta, and Cb are used as catalyst.

H. REDUCTION

Crotonaldehyde can be reduced selectively at the carbonyl group, at the carbon–carbon double bond, or at both groups. Reductive cyclization reactions also can be made to occur. A tabulation is given of the various agents which can be used to reduce crotonaldehyde along with other pertinent data

1. Reduction of Carbonyl Group

Agent	Catalyst	Conditions	Yield, %	Product	References
$LiBH_4$	—	—	70	Crotyl alc.	(262)
$NaBH_4$	—	—	85	Crotyl alc.	(55)
KBH_4	—	—	55	Crotyl alc.	(174)
$LiAlH_4$	—	—	70	Crotyl alc.	(363)
H_2	Colloidal Pt or Pd-on-boneblack	—	—	2-Butene	(76, 198)
H_2	$Co(CO)_4$ (if C=C is not β,γ, a new carbonyl is formed at β-position)	150–300°	—	Crotyl alc.	(364)
H_2	Cd	200 atm. 275°	—	Crotyl alc.	(43)
Raney Zn		—	—	Crotyl alc.	(122)
Zn + CH_3COOH	None	—	Quant.	3-Methyl-3,4-dihydroxy-heptene-1,5	(240)
H_2	Lebedev catalyst	—	—	1,3-Butadiene	(354, 355)

Continued on next page

2. *Reducton of Carbon–Carbon Double Bond*

Agent	Catalyst	Conditions	Yield, %	Product	References
H_2	Pd (amt. and type of redn. depends on amt. of catalyst)	—	—	Butyraldehyde	(75)
H_2	Raney Ni	40–70°	70–90	Butyraldehyde	(28, 94, 225, 268)
BuOH	Cu, atm. P	300°	70	Butyraldehyde	(297, 298)
H_2, BuOH	Cu	165°	91	Butyraldehyde	(89)
H_2	Ni–Cr–Mg or Ni–Cr–Al on pumice	112°	84	Butyraldehyde	(125, 126)

See also (21, 104, 110, 168).

3. *Reduction of Both Groups*

Agent	Catalyst	Conditions	Yield, %	Product	References
H_2	Raney Ni	140–50°	—	Butanol	(225)
H_2	Raney Cu	—	—	Butanol	(185)
Mg in HAc	—	—	—	Hydroxytetrahydrofurans	(135)
H_2	Cu or Cu-Ni on Kieselguhr	180–200°	95	Butanol	(107, 220, 241, 242)
H_2	Vapor phase	—	—	Butanol	(10, 18, 360)
H_2	CuO on inert support	150°	100	Butanol	(88)
H_2CO	—	—	31	Butanol	(363)

See also ref. 186, 197, and 367.

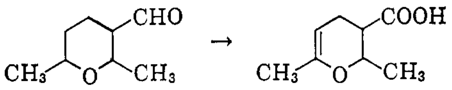
I. OXIDATION

1. *Autoxidation*

The air oxidation of crotonaldehyde has been widely studied (123, 168, 194, 306, 307, 344). Using an organic solvent and acetates or crotonates of Mn, Co, and Cu (preferably 15% Co + 85% Cu salts), crotonic anhydride and crotonic acid are formed. Yields are in the vicinity of 70% (194). At 5–10° in acetic acid and using Mn catalyst (306), free oxygen converts crotonaldehyde to crotonic acid in yields of 40–80%. The presence of water does not hinder the reaction (307). Another author (344) states that this oxidation is improved by using finely dispersed silver or silver compounds. Still another (168) claims that pyridine improves the air oxidation of crotonaldehyde.

One-half to one equivalent of hydrogen peroxide converts crotonaldehyde to crotonic acid. In this reaction (314) a heteropoly acid catalyst is used.

A by-product of crotonaldehyde production is the dimer 2,6-dimethyl-5,6-dihydro-3-formylpyran. Air oxidation of this compound using $Mn(OOCCH_3)_2$ yields the corresponding carboxylic acid (123)



β-Dicarbonyl formation in the preflame reaction of several compounds including crotonaldehyde has been studied (20).

2. *Ozone*

The ozonolysis of crotonaldehyde results in a simultaneous attack on the carbonyl group and the carbon-carbon double bond (79). Abnormal products have been isolated from the ozonolysis of allylic isomers of the types RCH=CHCHRX and RCHXCH=CHR. The abnormalities are often such as to make the starting materials appear to be mixtures of isomers. Carbon monoxide is liberated spontaneously or on gentle warming of these ozonides. For a series of compounds of the type —C=C—CX—, the extent of abnormal reaction appears to be related to the basicity of the unshared electron pairs on group X.

$$CH_3CH{=}CHCHO + O_3 \rightarrow 90\%\ CH_3COOH_2 + 10\%\ HCOOH$$

3. *Bromine*

Oxidation of crotonaldehyde by bromine can be made to proceed almost exclusively at the carbonyl group at 200–600° (335)

$$CH_3CH{=}CHCHO + Br_2 \rightarrow CH_3CH{=}CHCOBr$$

The reaction is exothermic and may be applied to compounds of the general structure RCH=CHCHO.

4. *Miscellaneous*

Studies (213) on the oxidation rate of acrolein and its homologs by $Mn_4(P_2O_7)_3$ indicate that the initial rate-determining step is formation of the enol form of 3-hydroxypropanal. In the case of acrolein the first oxidation product appears to be $HOCH_2CHOHCHO$ and later a chelate manganite complex of glyceric acid is suggested.

J. POLYMERS AND POLYMERIZATION

The polymerization of crotonaldehyde has been studied extensively. It undergoes condensation polymerization and addition polymerization as well as reacting with numerous polymers. A detailed examination of the information covered in the literature would be excessively cumbersome. Therefore, the various reactions will only be mentioned briefly.

Crotonaldehyde forms condensation polymers with ethylamine (53) and ethyleneimine (99) as well as with ammonium thiocyanate (102) and guanazoles (12). It also reacts with such hydroxy compounds as resorcinol (215), phenol (112), sulfonated polyhydric phenols (6), alkyl phenols (58, 223), polyhydric alcohols (301, 308), and polyvinyl alcohol (115).

Crotonaldehyde is polymerized by triethylamine to form a resin with film-forming properties (82). Other amines also catalyze this polymerization (177). Brittle, high-melting polymers are formed when crotonaldehyde is polymerized at pressures up to 10^4 atmospheres (199).

Other compounds with which crotonaldehyde has reacted to form polymers are rosin and rosin oil (180), 5-(2-furyl)-2,4-pentadienal and formaldehyde (103), thiophene (17), ketene (116), 2-alkenyl esters (333), acetone (165) and acetone cyanohydrin (348), bis-(acetoacetic acid)-thiodiethylene glycol ester (14), aminosulfonic acids to yield ion-exchange resins (279), derivatives of urea, thiourea, and guanidine (206, 207, 255), vinyl esters (29), and aromatic vinyl compounds (170).

V. DERIVATIVES AND ANALYSIS

A. DERIVATIVES

The derivatives tabulated can be used for the identification of crotonaldehyde.

Derivative	M. p., °C.	References
Oxime	119–120	(139)
Semicarbazone	198–199	(101, 141)
4-Phenylsemicarbazone	179	(144)
Thiosemicarbazone	167	(145)
Phenylhydrazone B. p.	169–171 (25mm.)	(146)
Methone	193–194	(173)
2,4-Dinitrophenylhydrazone	190	(228, 233)
2,4-Dinitrophenylsemicarbazone	230 dec.	(134, 232)
Hexahydrobenzhydrazide	151	(264)
2-Diphenylacetyl-1,3-indandione-1-hydrazone	184.5–185.5	(44)
α-Methylaminobenzoylhydrazone	185	(147)
p-Methylaminobenzoylhydrazone	218	(147)
Selenosemicarbazone	166–167	(175)
3-Methyl-4-chloro-2,6-dinitrophenylhydrazone	175	(189)
Cyanoacetic acid hydrazone	159	(201)
Salicylic acid hydrazone	190–192	(202)
(*p*-Azophenyl-phenyl)-4-semicarbazone	211–212	(372)

The aldehyde may be regenerated from the 2,4-dinitrophenylhydrazone by heating for a few minutes with levulinic acid solution containing hydrochloric acid (193) or by reversed-phase paper chromatography (234).

B. SEPARATION

Crotonaldehyde and other aldehydes are retained quantitatively by ion-exchange resins in their bisulfite form (128). These authors observed a high reaction velocity with Amberlite IRA-400. In this way crotonaldehyde can be separated from non-aldehydic compounds. The aldehyde is regenerated by washing with bicarbonate or carbonate solutions. Anion exchange resins in the CN^- form appear to be unsuitable for quantitative adsorption or separation of the free carbonyl compounds (129).

Another method (222) involves vaporizing the volatile aldehyde or ketone onto a surface containing an acetic acid solution of *p*-nitrophenylhydrazine. Paper chromatography of crotonaldehyde in mixtures with other carbonyl compounds is also described (278) along with paper chromatography of various derivatives (130, 372).

C. DETECTION

Crotonaldehyde can be detected as its 2,4-dinitrophenylhydrazone (239, 291). *m*-Phenylenediamine dihydrochloride is a specific reagent for α,β-unsaturated aldehydes and ketones and a few other reactive aldehydes (362).

D. DETERMINATION

Several methods have been developed for the quantitative analysis of crotonaldehyde. Among these are: (a) determination of crotonaldehyde and acetaldehyde in vinyl acetate (52, 376). (b) Potentiometric titration with bromine in methanol; methanol reacts to form the acetal of the aldehyde to prevent interference with bromine (211). In this way unsaturated aldehydes are determined in the presence of saturated aldehydes. (c) Acetaldehyde is determined in the presence of crotonaldehyde (311) by heating the mixture with sodium bisulfite and then distilling off acetaldehyde in the presence of sodium bicarbonate. (d) Iodometric method (351). Other methods are discussed in (236, 370, 373).

E. SPECTRA

The ultraviolet spectrum of crotonaldehyde is given in ref. (148). This compound may be determined in the presence of acetaldehyde, acetic acid, acetone, and acetylene using the band at 365 mμ. At this wave length the Bouguer–Beer law is followed at 0.1–12.8% by volume in aqueous solution (327). The determination may also be performed in organic solvents.

The effect of structure of various derivatives of crotonaldehyde on their spectra has been extensively studied (81, 176, 249, 337).

VI. MISCELLANEOUS PROPERTIES AND USES

A. TOXICOLOGY

Crotonaldehyde is more toxic than the saturated analog. Its most pronounced feature is its irritating effect on the nose, pharynx, and larynx. It has been found to cause damage to the lungs of mice (310, 312). The biochemical properties of crotonaldehyde and its derivatives have been the subject of considerable study. It has, for example, been used to treat certain plant virus diseases (136, 260). It has been assayed for fungistatic activity against various organisms (230). The reaction of 2-sulfanilamide-4-methylpyrimidine (21) with crotonaldehyde and sodium bisulfite yields solutions which are useful as chemotherapeuticals. The 2-methyl-4-pyridylcarbazone is said to be effective against tuberculosis (182). Crotonaldehyde is a volatile active principal in tuberculin (2).

A study of the toxicity of α,β-unsaturated compounds to microörganisms has produced the following generalizations (323): (a) toxicity of carbonyl compounds is in the order aldehydes > ketones > esters > acids; (b) toxicity thresholds in one biochemical system can be applied qualitatively to other systems; (c) toxicity is related to the reactivity of the α,β-conjugated carbonyl group. Activity of crotonaldehyde has been shown against Newcastle disease virus (NJKD strain) and influenza virus (PR-8 strain) (236).

B. USES

The applications of crotonaldehyde are so widespread that they will only be enumerated here without any attempt to discuss them in detail.

1. Polymers or Polymerization

Crotonaldehyde reacts with wool to give a product which is less soluble in alkali (231) and with cotton fibers to yield insoluble modified fibers (124); it is a solvent for polyvinyl chloride (318); it reacts with palm oil to form crayon (181), the polymer with ketones on heating to high temperatures forms resins which can be added to ordinary rubber to increase its strength (205); it acts as a shortstopper in vinyl chloride polymerization (80); it increases the yield of polymer formed in castor oil–olefin reactions (34); it reacts with water-soluble fusible hydroxylated vinyl resins to render them insoluble (54); forms resins which act as pickling inhibitors by condensing with amine thiocyanates (169); and forms anion-exchange resins with tetrazines (13); addition to vinyl acetate polymerization decreases the degree of polymerization but improves the distribution of degree of polymerization (226, 329); it forms plasticizers with terpene resins (356); it forms an adhesive resin with resorcinol (24, 331) and other alkyl phenols (274); and forms tanning materials with sulfonated phenols (324).

Crotonaldehyde has a marked inhibiting effect on the polymerization of vinyl acetate, even at a concentration of 2×10^{-4} mole per 100 gram of monomer.

2. Miscellaneous Applications

Briefly listed these are: as flavors produced from it and L-cystine (263); absorption on hide (36, 259, 365); hardening agent for gelatine (374); stabilizer for tetraethylead (49) in the preparation of surface active agents (59, 60, 61, 62, 63, 131, 132); in the preparation of textile and paper sizes (32, 295); in the preparation of insecticidal compounds (342, 187); and for improving the strength of viscose threads and films (352). The reaction with melamine or sulfonamide produces compounds suitable as fertilizers (288). Flotation agents are produced by the reaction with saturated aliphatic alcohols (350).

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