ACETYLENE-DERIVED CHEMICALS

1. Introduction

Acetylene [74-86-2], C_2H_2, is an extremely reactive hydrocarbon, principally used as a chemical intermediate (see ACETYLENE). Because of its thermodynamic

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instability, it cannot easily or economically be transported for long distances. To avoid large free volumes or high pressures, acetylene cylinders contain a porous solid packing and an organic solvent. Acetylene pipelines are severely restricted in size and must be used at relatively low pressures. Hence, for large-scale operations, the acetylene consumer must be near the place of acetylene manufacture.

Historically, the use of acetylene as a raw material for chemical synthesis has depended strongly on the availability of alternative raw materials. The United States, which until recently appeared to have limitless stocks of hydrocarbon feeds, has never depended on acetylene to the same extent as Germany, which had more limited access to hydrocarbons (1). During World War I the first manufacture of a synthetic rubber was undertaken in Germany to replace imported natural rubber, which was no longer accessible. Acetylene derived from calcium carbide was used for preparation of 2,3-dimethyl-1,3-butadiene by the following steps:

$$\text{acetylene} \longrightarrow \text{acetaldehyde} \longrightarrow \text{acetic acid} \longrightarrow \text{acetone} \longrightarrow$$

$$2,3\text{-dimethyl-}2,3\text{-butanediol} \longrightarrow 2,3\text{-dimethyl-}1,3\text{-butadiene}$$

Methyl rubber, obtained by polymerization of this monomer, was expensive and had inferior properties, and its manufacture was discontinued at the end of World War I. By the time World War II again shut off access to natural rubber, Germany had developed better synthetic rubbers based upon butadiene [106-99-0] (see ELASTOMERS, SYNTHETIC SURVEY).

In the United States butadiene was prepared initially from ethanol and later by cracking four-carbon hydrocarbon streams (see BUTADIENE). In Germany, butadiene was prepared from acetylene via the following steps: acetylene ⟶ acetaldehyde ⟶ 3-hydroxybutyraldehyde ⟶ 1,3-butanediol ⟶ 1,3-butadiene.

Toward the end of the war, an alternative German route to butadiene was introduced, which required much less acetylene:

$$\underset{\text{acetylene}}{HC{\equiv}CH} + \underset{\text{formaldehyde}}{2\,CH_2O} \longrightarrow \underset{\text{1,4-butynediol}}{HOCH_2C{\equiv}CCH_2OH} \longrightarrow$$

$$\underset{\text{1,4-butanediol}}{HOCH_2CH_2CH_2CH_2OH} \longrightarrow \underset{\text{1,3-butadiene}}{CH_2{=}CHCH{=}CH_2}$$

Because of its relatively high price, there have been continuing efforts to replace acetylene in its major applications with cheaper raw materials. Such efforts have been successful, particularly in the United States, where ethylene has displaced acetylene as raw material for acetaldehyde, acetic acid, vinyl acetate, and chlorinated solvents. Only a few percent of U.S. vinyl chloride production is still based on acetylene. Propylene has replaced acetylene as feed for acrylates and acrylonitrile. Even some recent production of traditional Reppe acetylene chemicals, such as butanediol and butyrolactone, is based on new raw materials.

2. Reaction Products

2.1. Acetaldehyde. Acetaldehyde [75-07-0], C_2H_4O, (qv) was formerly manufactured principally by hydration of acetylene.

$$HC{\equiv}CH + H_2O \longrightarrow CH_3CHO$$

Many catalytic systems have been described; acidic solutions of mercuric salts are the most generally used. This process has long been superseded by more economical routes involving oxidation of ethylene or other hydrocarbons.

2.2. Acrylic Acid, Acrylates, and Acrylonitrile. Acrylic acid [79-10-7], $C_3H_4O_2$, and acrylates were once prepared by reaction of acetylene and carbon monoxide with water or an alcohol, using nickel carbonyl as catalyst. In recent years this process has been completely superseded in the United States by newer processes involving oxidation of propylene (2). In western Europe, however, acetylene is still important in acrylate manufacture (see ACRYLIC ACID AND DERIVATIVES; ACRYLIC ESTER POLYMERS).

In the presence of such catalysts as a solution of cuprous and ammonium chlorides, hydrogen cyanide adds to acetylene to give acrylonitrile [107-13-1], C_3H_3N (qv).

$$HC{\equiv}CH + HCN \longrightarrow CH_2{=}CHCN$$

Since the early 1970s this process has been completely replaced by processes involving ammoxidation of propylene (3).

2.3. Chlorinated Solvents. Originally, successive chlorination and dehydro-chlorination of acetylene was the route to trichloroethylene [79-01-6], C_2HCl_3, and perchloroethylene [127-18-4], C_2Cl_4.

$$HC{\equiv}CH + 2\,Cl_2 \longrightarrow CHCl_2CHCl_2 \longrightarrow CHCl{=}CCl_2 + HCl$$

$$CHCl{=}CCl_2 + Cl_2 \longrightarrow CHCl_2CCl_3 \longrightarrow CCl_2{=}CCl_2 + HCl$$

This route has been completely displaced, first by chlorination and dehydrochlorination of ethylene or vinyl chloride, and more recently by oxychlorination of two-carbon raw materials (2) (see CHLOROCARBONS AND CHLOROHYDROCARBONS SURVEY).

2.4. Cyclooctatetraene (COT). Tetramerization of acetylene to cyclooctatetraene [629-20-9], C_8H_8, although interesting, does not seem to have been used commercially. Nickel salts serve as catalysts. Other catalysts give benzene. The mechanism of this cyclotetramerization has been studied (4).

2.5. Ethylene. During World War II the Germans manufactured more than 60,000 t/year of ethylene [74-85-1], C_2H_4, by hydrogenation of acetylene, using palladium on silica gel as catalyst. Subsequently, cracking of hydrocarbons displaced this process. However, it is still utilized for purification of ethylene containing small amounts of acetylene as contaminant (5) (see ETHYLENE).

2.6. Vinyl Acetate.

Vinyl acetate [108-05-04], $C_4H_6O_2$, used to be manufactured by addition of acetic acid to acetylene.

$$HC{\equiv}CH + CH_3COOH \longrightarrow CH_2{=}CHOOCCH_3$$

Liquid- and vapor-phase processes have been described; the latter appear to be advantageous. Supported cadmium, zinc, or mercury salts are used as catalysts. In 1963 it was estimated that 85% of U.S. vinyl acetate capacity was based on acetylene, but it has been completely replaced since ~1982 by newer technology using oxidative addition of acetic acid to ethylene (2) (see VINYL POLYMERS). In western Europe production of vinyl acetate from acetylene still remains a significant commercial route.

2.7. Vinylacetylene and Chloroprene.

In the presence of cuprous salt solutions, acetylene dimerizes to vinylacetylene [689-97-4], C_4H_4. Yields of 87% monovinylacetylene, together with 10% of divinylacetylene, have been described (6).

$$2\ HC{\equiv}CH \longrightarrow HC{\equiv}CCH{=}CH_2$$

Using cuprous chloride as catalyst, hydrogen chloride adds to acetylene, giving 2-chloro-1,3-butadiene [126-99-8], chloroprene, C_4H_5Cl, the monomer for neoprene rubber.

$$HC{\equiv}CCH{=}CH_2 + HCl \longrightarrow CH_2{=}CClCH{=}CH_2$$

Manufacture via this process has been completely replaced by chlorination of butadiene (3) (see CHLOROPRENE; POLYCHLOROPRENE).

2.8. Vinyl Chloride and Vinylidene Chloride.

In the presence of mercuric salts, hydrogen chloride adds to acetylene giving vinyl chloride [75-01-4], C_2H_3Cl.

$$HC{\equiv}CH + HCl \longrightarrow CH_2{=}CHCl$$

Once the principal route to vinyl chloride, in all but a few percent of current U.S. capacity this has been replaced by dehydrochlorination of ethylene dichloride. A combined process in which hydrogen chloride cracked from ethylene dichloride was added to acetylene was advantageous but it is rarely used because processes to oxidize hydrogen chloride to chlorine with air or oxygen are cheaper (7) (see VINYL POLYMERS).

In similar fashion, vinylidene chloride [75-35-4], $C_2H_2Cl_2$, has been prepared by successive chlorination and dehydrochlorination of vinyl chloride (see VINYLIDENE CHLORIDE MONOMER AND POLYMERS).

$$CH_2{=}CHCl + Cl_2 \longrightarrow CH_2ClCHCl_2$$

$$CH_2ClCHCl_2 \longrightarrow CH_2{=}CCl_2 + HCl$$

2.9. Vinyl Fluoride. Vinyl fluoride [75-02-5], C_2H_3F, the monomer for poly(vinyl fluoride), is manufactured by addition of hydrogen fluoride to acetylene (see FLUORINE CONTAINING COMPOUNDS, POLY(VINYL FLUORIDE)).

$$HC{\equiv}CH + HF \longrightarrow CH_2{=}CHF$$

3. Ethynylation Reaction Products

The name ethynylation was coined by Reppe to describe the addition of acetylene to carbonyl compounds (8).

$$HC{\equiv}CH + RCOR' \longrightarrow HC{\equiv}CC(OH)RR'$$

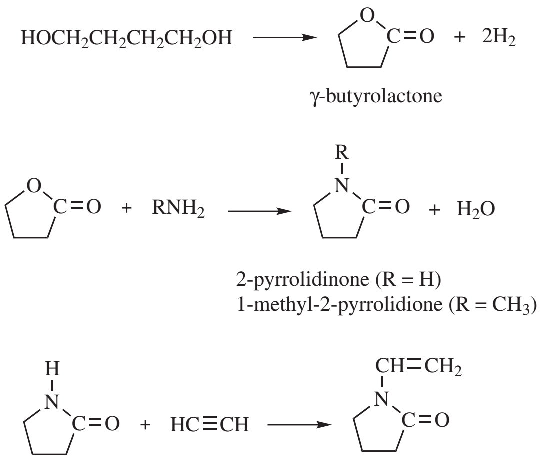
Although stoichiometric ethynylation of carbonyl compounds with metal acetylides was known as early as 1899 (9), Reppe's contribution was the development of catalytic ethynylation. Heavy metal acetylides, particularly cuprous acetylide, were found to catalyze the addition of acetylene to aldehydes. Although ethynylation of many aldehydes has been described (10), only formaldehyde has been catalytically ethynylated on a commercial scale. Copper acetylide is not effective as catalyst for ethynylation of ketones. For these, and for higher aldehydes, alkaline promoters have been used.

The following series of reactions illustrates the manufacture of the principal Reppe acetylene chemicals.

$$HC{\equiv}CH + 1 \text{ or } 2\ HCHO \longrightarrow \underset{\text{propargyl alcohol}}{HC{\equiv}CCH_2OH} + \underset{\text{2-butyne-1,4-diol}}{HOCH_2C{\equiv}CCH_2OH}$$

$$HOCH_2C{\equiv}CCH_2OH + H_2 \longrightarrow \underset{\text{2-butene-1,4-diol}}{HOCH_2CH{=}CHCH_2OH}$$

$$HOCH_2C{\equiv}CCH_2OH + 2\ H_2 \longrightarrow \underset{\text{1,4-butanediol}}{HOCH_2CH_2CH_2CH_2OH}$$



γ-butyrolactone

2-pyrrolidinone (R = H)
1-methyl-2-pyrrolidione (R = CH_3)

N-vinyl-2-pyrrolidinone

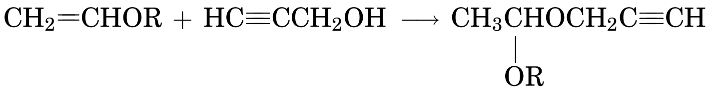
Except for the pyrrolidinones (see PYRROLE AND PYRROLE DERIVATIVES), these products are discussed in the following.

3.1. Propargyl Alcohol. Propargyl alcohol [107-19-7],2-propyn-1-ol, C_3H_4O, is the only commercially available acetylenic primary alcohol. A colorless, volatile liquid, with an unpleasant odor that has been described as “mild geranium,” it was first prepared in 1872 from β-bromoallyl alcohol (11). Propargyl alcohol is miscible with water and with many organic solvents. Physical properties are listed in Table 1.

Reactions. Propargyl alcohol has three reactive sites—a primary hydroxyl group, a triple bond, and an acetylenic hydrogen—making it an extremely versatile chemical intermediate.

The hydroxyl group can be esterified with acid chlorides, anhydrides, or carboxylic acids and it reacts with aldehydes (12) or vinyl ethers (13) in the presence of an acid catalyst to form acetals.

$$RCHO + 2\,HC{\equiv}CCH_2OH \longrightarrow RCH(OCH_2C{\equiv}CH)_2 + H_2O$$



$$CH_2{=}CHOR + HC{\equiv}CCH_2OH \longrightarrow CH_3\underset{\displaystyle OR}{\underset{|}{C}}HOCH_2C{\equiv}CH$$

At low temperatures, oxidation with chromic acid gives propynal [624-67-9], C_3H_2O (14), or propynoic acid [471-25-0], $C_3H_2O_2$ (15), which can also be prepared in high yields by anodic oxidation (16).

$$HC{\equiv}CCH_2OH \longrightarrow HC{\equiv}CCHO$$

$$HC{\equiv}CCH_2OH \longrightarrow HC{\equiv}CCOOH$$

Various halogenating agents have been used to replace hydroxyl with chlorine or bromine. Phosphorus trihalides, especially in the presence of pyridine, are particularly suitable (17,18). Propargyl iodide is easily prepared from propargyl bromide by halogen exchange (19).

Table 1. **Physical Properties of Propargyl Alcohol**

Property	Value
melting point, °C	−52
boiling point, °C	114
specific gravity, $d^{20}{}_4$	0.948
refractive index, $n^{20}{}_D$	1.4310
viscosity at 20°C, mPa s (= cP)	1.65
dielectric constant, ε	24.5
specific heat, $C^{20}{}_p$, J/(g K)[a]	2.577
heat of combustion at constant vol, kJ/mol[b]	1731
heat of vaporization at 112°C, kJ/mol[b]	42.09
flash point, Tagliabue open cup, °C	36

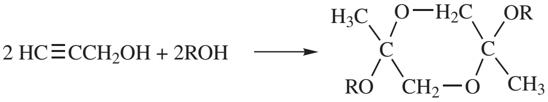
[a] To convert J/(g·K) to cal/(g·°C) divide by 4.184.

[b] To convert kJ/mol to kcal/mol divide by 4.184.

Hydrogenation gives allyl alcohol [107-18-6], C_3H_6O, its isomer propanal [123-38-6] (20), or propanol, C_3H_8O [71-23-8] (21). With acidic mercuric salt catalysts, water adds to give acetol, hydroxyacetone, $C_3H_6O_2$ [116-09-6] (22).

$$HC{\equiv}CCH_2OH + H_2O \longrightarrow CH_3COCH_2OH$$

Using alcohols instead of water under similar conditions gives cyclic ketals (23), which can be hydrolyzed to acetol.



Halogens add stepwise, giving almost exclusively dihaloallyl alcohols (24,25).

$$HC{\equiv}CCH_2OH + X_2 \longrightarrow CHX{=}CXCH_2OH$$

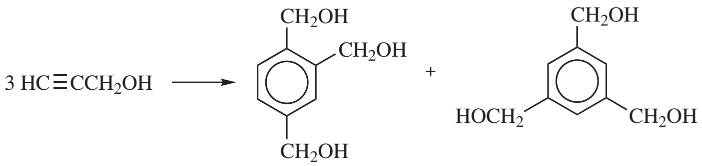
A second mole of halogen adds with greater difficulty; oxidative side reactions can be minimized by halogenating an ester instead of the free alcohol (26).

$$(HC{\equiv}CCH_2O)_3PO + 6\,Br_2 \longrightarrow (HCBr_2CBr_2CH_2O)_3PO$$

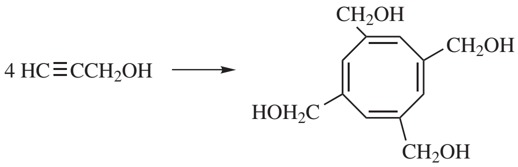
With mercuric salt catalysts, hydrogen chloride adds to give 2-chloroallyl alcohol, 2-chloroprop-2-en-1-ol [5976-47-6] (27).

$$HC{\equiv}CCH_2OH + HCl \longrightarrow CH_2{=}CClCH_2OH$$

In the presence of suitable nickel or cobalt complexes, propargyl alcohol trimerizes to a mixture of 1,3,5-benzenetrimethanol [4464-18-0] and 1,2,4-trimethanol [25147-76-6] benzene (28).



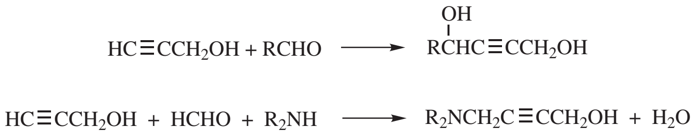
Cyclization with various nickel complex catalysts gives up to 97% selectivity to a mixture of cyclooctatetraene derivatives, with only 3% of benzene derivatives. The principal isomer is the symmetrical 1,3,5,7-cyclooctatetraene-1,3,5,7-tetramethanol (29).



Nickel halide complexes with amines give mixtures of linear polymer and cyclic trimers (30). Nickel chelates give up to 40% of linear polymer (31).

When heated with ammonia over cadmium calcium phosphate catalysts, propargyl alcohol gives a mixture of pyridines (32).

In the presence of copper acetylide catalysts, propargyl alcohol and aldehydes give acetylenic glycols (33). When dialkylamines are also present, dialkylaminobutynols are formed (34).



$$HC{\equiv}CCH_2OH + RCHO \longrightarrow R\overset{OH}{\overset{|}{C}}HC{\equiv}CCH_2OH$$

$$HC{\equiv}CCH_2OH + HCHO + R_2NH \longrightarrow R_2NCH_2C{\equiv}CCH_2OH + H_2O$$

With two equivalents of an organomagnesium halide, a Grignard reagent is formed, capable of use in further syntheses (35,36). Cuprous salts catalyze oxidative dimerization of propargyl alcohol to 2,4-hexadiyne-1,6-diol [3031-68-3] (37).

$$2\,HC{\equiv}CCH_2OH + \frac{1}{2}\,O_2 \longrightarrow HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OH + H_2O$$

Manufacture. Propargyl alcohol is a by-product of butynediol manufacture. The original high pressure butynediol processes gave ~5% of the by-product; newer lower pressure processes give much less. Processes have been described that give much higher proportions of propargyl alcohol (38,39).

BASF produces propargyl alcohol in its plants in New Jersey and Germany. Processes for producing propargyl alcohol using (*1*) 1,2,3-trichloropropane and (*2*) 2, 3-dichloro-1-propanol in an industrially advantageous manner have been described (40).

Shipment, Storage, and Price. Propargyl alcohol is available in tank cars, tank trailers, and drums. It is usually shipped in unlined steel containers and transferred through standard steel pipes or braided steel hoses; rubber is not recommended. Clean, rust-free steel is acceptable for short-term storage. For longer storage, stainless steel (types 304 and 316), glass lining, or phenolic linings (Lithcote LC-19 and LC-24, Unichrome B-124, and Heresite) are suitable. Aluminum, epoxies, and epoxy-phenolics should be avoided.

Specifications and Analytical Methods. The commercial material is specified as 97% minimum purity, determined by gas chromatography or acetylation. Moisture is specified at 0.05% maximum (Karl-Fischer titration). Formaldehyde content is determined by bisulfite titration.

Health and Safety Factors. Although propargyl alcohol is stable, violent reactions can occur in the presence of contaminants, particularly at elevated temperatures. Heating in undiluted form with bases or strong acids should be avoided. Weak acids have been used to stabilize propargyl alcohol prior to distillation. Since its flash point is low, the usual precautions against ignition of vapors should be observed.

Propargyl alcohol is a primary skin irritant and a severe eye irritant and is toxic by all means of ingestion; all necessary precautions must be taken to avoid contact with liquid or vapors. The LD_{50} is 0.07 mL/kg for white rats and 0.06 mL/kg for guinea pigs.

Uses. Propargyl alcohol is a component of oil-well acidizing compositions, inhibiting the attack of mineral acids on steel (see CORROSION AND CORROSION CONTROL). It is also employed in the pickling and plating of metals.

It is used as an intermediate in preparation of the miticide Omite [2312-35-8], 2-(4′-*tert*-butylphenoxy)cyclohexyl 2-propynyl sulfite (41); sulfadiazine [68-35-9] (42); and halogenated propargyl carbonate fungicides (43).

3.2. Butynediol. Butynediol, 2-butyne-1,4-diol, [110-65-6] was first synthesized in 1906 by reaction of acetylene bis(magnesium bromide) with paraformaldehyde (44). It is available commercially as a crystalline solid or a 35% aqueous solution manufactured by ethynylation of formaldehyde. Physical properties are listed in Table 2.

Table 2. **Physical Properties of Butynediol, Butenediol, and Butanediol**

Property	Butynediol	Butenediol	Butanediol
molecular formula	$C_4H_6O_2$	$C_4H_8O_2$	$C_4H_{10}O_2$
CAS Registry Number	[110-65-6]	[110-64-5]	[110-63-4]
melting point, °C	58	11.8	20.2
boiling point, °C at kPa[a]			
0.133	101	84	86
1.33	141	122	123
13.3	194	176	171
101.3	248	234	228
specific gravity	$d_4^{20} = 1.114$	$d_{15}^{25} = 1.070$	$d_4^{20} = 1.017$
refractive index $n^{25}{}_{\mathrm{D}}$	$\alpha = 1.450 \pm 0.002$ $\beta = 1.528 \pm 0.002$	1.4770	1.4445
heat of combustion,[b] kJ/mol[c]	2204		
flash point, Tagliabue open cup, °C	152	128	121
viscosity at 20°C, mPa s (=cP)		22	84.9
at 38°C		10.8	
at 99°C		2.5	
surface tension at 20°C, mN/m (=dyn/cm)			44.6
dielectric constant at 20°C, ε			31.5
solubility, g/100 mL solvent at 25°C			
water (0°C)	2		
water	374		miscible
ethanol	83		miscible
acetone	70		miscible
ether	2.6		3.1
benzene	0.04		0.3
hexane			<0.1

[a] To convert kPa, to mm Hg, multiply by 7.5.

[b] At constant volume.

[c] To convert kJ to kcal, divide by 4.184.

Reactions. Butynediol undergoes the usual reactions of primary alcohols. Because of its rigid, linear structure, many reactions forming cyclic products from butanediol or *cis*-butenediol give only polymers with butynediol.

Both hydroxyl groups can be esterified normally (45). The monoesters are readily prepared as mixtures with diesters and unesterified butynediol, but care must be taken in separating them because the monoesters disproportionate easily (46).

The hydroxyl groups can be alkylated with the usual alkylating agents. To obtain aryl ethers a reverse treatment is used, such as treatment of butynediol toluenesulfonate or dibromobutyne with a phenol (45). Alkylene oxides give ether alcohols (47).

In the presence of acid catalysts, butynediol and aldehydes (48) or acetals (49) give polymeric acetals, useful intermediates for acetylenic polyurethanes suitable for high energy solid propellants.

$$HOCH_2C{\equiv}CCH_2OH + CH_2O \longrightarrow HO(CH_2C{\equiv}CCH_2OCH_2O)_nH$$

Electrolytic oxidation gives acetylene dicarboxylic acid [142-45-0] (2-butynedioic acid) in good yields (50); chromic acid oxidation gives poor yields (51). Oxidation with peroxyacetic acid gives malonic acid [141-82-2] (qv) (52).

Butynediol can be hydrogenated partway to butenediol or completely to butanediol.

$$HOCH_2C{\equiv}CCH_2OH \longrightarrow HOCH_2CH{=}CHCH_2OH \longrightarrow HOCH_2CH_2CH_2CH_2OH$$

Noble metal containing hydrogenation catalyst for selective hydrogenation of 1,4-butynediol to 1, 4-butanediol and a process for preparation has been described (53).

Dichlorobutyne [821-10-3] and dibromobutyne [2219-66-1] are readily prepared by treatment with thionyl or phosphorus halides. The less-stable diiodobutyne is prepared by treatment of dichloro- or dibromobutyne with an iodide salt (54).

Addition of halogens proceeds stepwise, sometimes accompanied by oxidation. Iodine forms 2,3-diiodo-2-butene-1,4-diol (55). Depending on conditions, bromine gives 2,3-dibromo-2-butene-1,4-diol, 2,2,3,3-tetrabromobutane-1,4-diol, mucobromic acid, or 2-hydroxy-3,3,4,4-tetrabromotetrahydrofuran (56). Addition of chlorine is attended by more oxidation (57–59), which can be lessened by esterification of the hydroxyl groups.

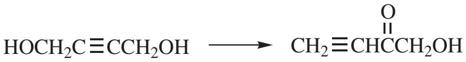
Uncatalyzed addition of hydrochloric acid is accompanied by replacement of one hydroxyl group, giving high yields of 2,4-dichloro-2-buten-1-ol (60); with mercuric or cupric salt catalysts, addition occurs without substitution (61, 62).

$$HOCH_2C{\equiv}CCH_2OH + 2\ HCl \longrightarrow ClCH_2CH{=}CClCH_2OH + H_2O$$

$$HOCH_2C{\equiv}CCH_2OH \xrightarrow[\text{catalyst}]{HCl} HOCH_2CCl{=}CHCH_2OH \xrightarrow[\text{catalyst}]{HCl} HOCH_2CCl_2CH_2CH_2OH$$

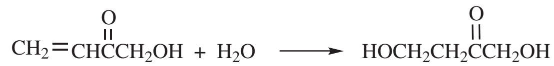
When aqueous solutions of sodium bisulfite are heated with butynediol, one or two moles add to the triple bond, forming sodium salts of sulfonic acids (63).

In the presence of mercuric salts, butynediol rapidly isomerizes to 1-hydroxy-3-buten-2-one (64).



$$HOCH_2C{\equiv}CCH_2OH \longrightarrow CH_2{\equiv}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH$$

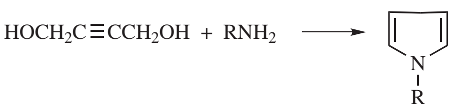
This adds compounds with active hydrogen such as water, alcohols, and carboxylic acids (65), to give 1,4-dihydroxy-2-butanone or its derivatives.



$$CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH + H_2O \longrightarrow HOCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH$$

Butynediol is more difficult to polymerize than propargyl alcohol, but it cyclotrimerizes to hexamethylolbenzene [2715-91-5] (benzenehexamethanol) with a nickel carbonyl–phosphine catalyst (66); with a rhodium chloride–arsine catalyst a yield of 70% is claimed (67).

When heated with acidic oxide catalysts, mixtures of butynediol with ammonia or amines give pyrroles (68) (see PYRROLE AND PYRROLE DERIVATIVES).



Manufacture. All manufacturers of butynediol use formaldehyde ethynylation processes. The earliest entrant was BASF, which, as successor to I. G. Farben, continued operations at Ludwigshafen, FRG, after World War II. Later BASF also set up a U.S. plant at Geismar, La. The first company to manufacture in the United States was GAF in 1956 at Calvert City, Ky., and later at Texas City, Tex., and Seadrift, Tex.

At the end of World War II, the butynediol plant and process at Ludwigshafen were studied extensively (69, 70). Variations of the original high pressure, fixed-bed process, which is described below, are still in use. However, all of the recent plants use low pressures and suspended catalysts (71–77).

The hazards of handling acetylene under pressure must be considered in plant design and construction. Although means of completely preventing acetylene decomposition have not been found, techniques have been developed that prevent acetylene decompositions from becoming explosive. The original German plant was designed for pressures up to 20.26 MPa (200 atm), considered adequate for deflagration (nonexplosive decomposition), which could increase pressures approximately 10-fold. It was not practical to design for control of a detonation (explosive decomposition), which could increase pressure nearly 200-fold (78).

The reactors were thick-walled stainless steel towers packed with a catalyst containing copper and bismuth oxides on a siliceous carrier. This was activated by formaldehyde and acetylene to give the copper acetylide complex that functioned as the true catalyst. Acetylene and an aqueous solution of formaldehyde were passed together through one or more reactors at ~90–100°C and an acetylene partial pressure of ~500–600 kPa (5–6 atm) with recycling as required. Yields of butynediol were over 90%, in addition to 4–5% propargyl alcohol.

Shipment, Storage, and Price. Butynediol, 35% solution, is available in tank cars, tank trailers, and drums. Stainless steel, nickel, aluminum, glass, and various plastic and epoxy or phenolic liners have all been found satisfactory. Rubber hose is suitable for transferring. The solution is nonflammable and freezes at about −5°C.

Butynediol solid flakes are packed in polyethylene bags inside drums. The product is hygroscopic and must be protected from moisture.

Specifications and Analytical Methods. The commercial aqueous solution is specified as 34% minimum butynediol, as determined by bromination or refractive index. Propargyl alcohol is limited to 0.2% and formaldehyde to 0.7%.

The commercial flake is specified as 96.0% minimum butynediol content, with a maximum of 2.0% moisture. Purity is calculated from the freezing point (at least 52°C).

Health and Safety Factors. Although butynediol is stable, violent reactions can take place in the presence of certain contaminants, particularly at elevated temperatures. In the presence of certain heavy metal salts, such as mercuric chloride, dry butynediol can decompose violently. Heating with strongly alkaline materials should be avoided.

Butynediol is a primary skin irritant and sensitizer, requiring appropriate precautions. Acute oral toxicity is relatively high: LD_{50} is 0.06 g/kg for white rats.

Uses. Most butynediol produced is consumed by the manufacturers in manufacture of butanediol and butenediol. Small amounts are converted to ethers with ethylene oxide.

Butynediol is principally used in pickling and plating baths. Small amounts are used in the manufacture of brominated derivatives, useful as flame retardants. It was formerly used in a wild oat herbicide, Carbyne (Barban), 4-chloro-2-butynyl-*N*-(3-chlorophenyl)carbamate [101-27-9], $C_{11}H_9Cl_2NO_2$ (79).

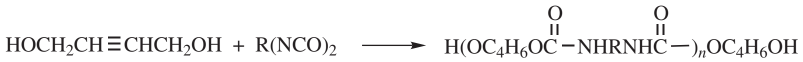
3.3. Butenediol. 2-Butene-1,4-diol [110-64-5] is the only commercially available olefinic diol with primary hydroxyl groups. The commercial product consists almost entirely of the cis isomer.

trans-2-Butene-1,4-diol diacetate was prepared from 1,4-dibromo-2-butene in 1893 (80) and hydrolyzed to the diol in 1926 (81). The original preparation of the cis diol utilized the present commercial route, partial hydrogenation of butynediol.

Physical properties are listed in Table 2. Butenediol is very soluble in water, lower alcohols, and acetone. It is nearly insoluble in aliphatic or aromatic hydrocarbons.

Reactions. In addition to the usual reactions of primary hydroxyl groups and of double bonds, *cis*-butenediol undergoes a number of cyclization reactions.

The hydroxyl groups can be esterified normally: the interesting diacrylate monomer (82) and the biologically active haloacetates (83) have been prepared in this manner. Reactions with dibasic acids have given polymers capable of being cross-linked (84) or suitable for use as soft segments in polyurethanes (85). Polycarbamic esters are obtained by treatment with a diisocyanate (86) or via the bischloroformate (87).



$$HOCH_2CH{\equiv}CHCH_2OH + R(NCO)_2 \longrightarrow H(OC_4H_6O\overset{O}{\overset{\|}{C}}-NHRNH\overset{O}{\overset{\|}{C}}-)_nOC_4H_6OH$$

$$HOCH_2CH{=}CHCH_2OH + COCl_2 \longrightarrow ClOCH_2CH{=}CHCH_2OCCl + \xrightarrow{R(NH_2)_2} H_2NRNH(\overset{O}{\overset{\|}{C}}OC_4H_6O\overset{O}{\overset{\|}{C}}NHRNH)_nH$$

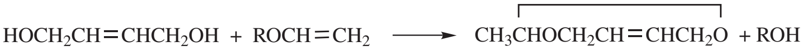
The hydroxyl groups can be alkylated in the usual manner. Hydroxyalkyl ethers may be prepared with alkylene oxides and chloromethyl ethers by reaction with formaldehyde and hydrogen chloride (88). The terminal chlorides can be easily converted to additional ether groups.

$$HOCH_2CH{=}CHCH_2OH + HCHO + HCl \longrightarrow$$

$$ClCH_2OCH_2CH{=}CHCH_2OCH_2Cl \xrightarrow{NaOR} ROCH_2OCH_2CH{=}CHCH_2OCH_2OR$$

cis-Butenediol reacts readily with aldehydes (89), vinyl ethers (90), or dialkoxyalkanes (91) in the presence of acidic catalysts to give seven-membered cyclic acetals (4,7-dihydro-1,3-dioxepins).

$$HOCH_2CH{=}CHCH_2OH + RCHO \longrightarrow RCHOCH_2CH{=}CHCH_2O + H_2O$$



$$HOCH_2CH{=}CHCH_2OH + ROCH{=}CH_2 \longrightarrow CH_3CHOCH_2CH{=}CHCH_2O + ROH$$

$$HOCH_2CH{=}CHCH_2OH + RR'C(OR'')_2 \longrightarrow RR'COCH_2CH{=}CHCH_2O + R''OH$$

The hydroxyl groups of butenediol are replaced by halogens by treatment with thionyl chloride or phosphorus tribromide (92, 93); by stopping short of total halogenation, mixtures can be obtained containing 4-halobutanols as the major constituent (94). The hydroxyl groups undergo typical allylic reactions such as being replaced by cyanide with cuprous cyanide as catalyst (95).

With a palladium chloride catalyst, butenediol is carbonylated by carbon monoxide, giving 3-hexenedioic acid [4436-74-2], $C_6H_8O_4$ (96).

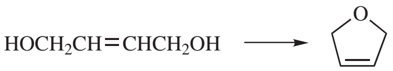
$$HOCH_2CH{=}CHCH_2OH + 2\,CO \longrightarrow HOOCCH_2CH{=}CHCH_2COOH$$

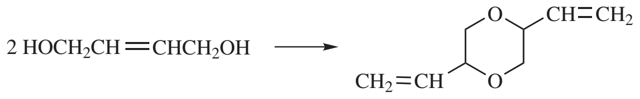
An early attempt to hydroformylate butenediol using a cobalt carbonyl catalyst gave tetrahydro-2-furanmethanol (97), presumably by allylic rearrangement to 3-butene-1,2-diol before hydroformylation. Later, hydroformylation of butenediol diacetate with a rhodium complex as catalyst gave the acetate of 3-formyl-3-buten-1-ol (98). Hydrogenation in such a system gave 2-methyl-1,4-butanediol (99).

Heating with cuprous chloride in aqueous hydrochloric acid isomerizes 2-butene-1,4-diol to 3-butene-1,2-diol (100)] Various hydrogen-transfer catalysts isomerize it to 4-hydroxybutyraldehyde [25714-71-0], $C_4H_8O_2$ (101), acetals of which are found as impurities in commercial butanediol and butenediol.

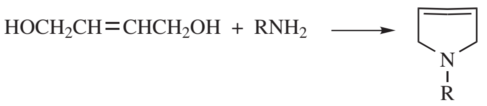
$$HOCH_2CH{=}CHCH_2OH \longrightarrow HOCH_2CH_2CH_2CHO$$

Treatment with acidic catalysts dehydrates *cis*-butenediol to 2,5-dihydrofuran [1708-29-8], C_4H_6O (102). Cupric (103) or mercuric (104) salts give 2,5-divinyl-1,4-dioxane [21485-51-8], presumably via 3-butene-1,2-diol.





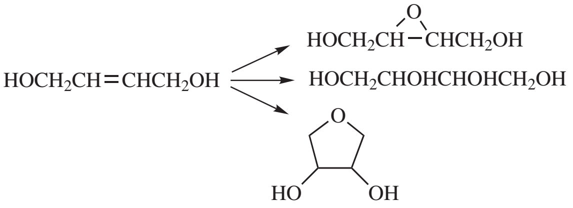
Mixtures of butenediol and ammonia or amines cyclize to pyrrolines when heated with acidic catalysts (68).



Halogens add to butenediol, giving 2,3-dihalo-1,4-butanediol (92, 93). In a reaction typical of allylic alcohols, hydrogen halides cause substitution of halogen for hydroxyl (105).

When butenediol is treated with acidic dichromate solution, dehydration and oxidation combine to give a high yield of furan [110-00-9], $C_4H_4O_2$ (106) (see FURAN DERIVATIVES).

Treatment with hydrogen peroxide converts butenediol to 2,3-epoxy-1,4-butanediol (107) or gives hydroxylation to erythritol [149-32-6], $C_4H_{10}O_4$ (108). Under strongly acidic conditions, tetrahydro-3,4-furanediol is the principal product (109).



Butenediol is a weak dienophile in Diels-Alder reactions. Adducts have been described with anthracene (110) and with hexachlorocyclopentadiene (111).

Butenediol does not undergo free-radical polymerization. A copolymer with vinyl acetate can be prepared with a low proportion of butenediol (112).

Manufacture. Butenediol is manufactured by partial hydrogenation of butynediol. Although suitable conditions can lead to either cis or trans isomers (113), the commercial product contains almost exclusively *cis*-2-butene-1,4-diol. Trans isomer, available at one time by hydrolysis of 1,4-dichloro-2-butene, is unsuitable for the major uses of butenediol involving Diels-Alder reactions. The liquid-phase heat of hydrogenation of butynediol to butenediol is 156 kJ/mol (37.28 kcal/mol) (114).

The original German process used either carbonyl iron or electrolytic iron as hydrogenation catalyst (115). The fixed-bed reactor was maintained at 50–100°C and 20.26 MPa (200 atm) of hydrogen pressure, giving a product containing substantial amounts of both butynediol and butanediol. Newer, more selective processes use more active catalysts at lower pressures. In particular, supported palladium, alone (50) or with promoters (116, 117), has been found useful.

Shipment, Storage, and Price. Butenediol is available in unlined steel tank cars, tank trailers, and various sized drums. Because of its relatively high freezing point, tank cars are fitted with heating coils.

Specifications and Analytical Methods. Purity is determined by gas chromatography (gc). Technical grade butenediol, specified at 95% minimum, is typically 96–98% butenediol. The cis isomer is the predominant constituent; 2–4% is trans.

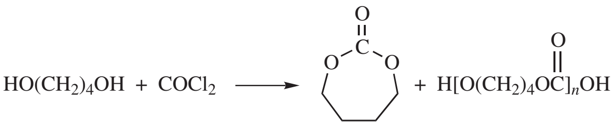
Principal impurities are butynediol (specified as 2.0% maximum, typically <1%), butanediol, and the 4-hydroxybutyraldehyde acetal of butenediol. Moisture is specified at 0.75% maximum (Karl-Fischer titration). Typical technical grade butenediol freezes at ~8°C.

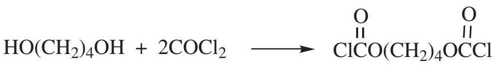
Health and Safety Factors. Butenediol is noncorrosive and stable under normal handling conditions. It is a primary skin irritant but not a sensitizer; contact with skin and eyes should be avoided. It is much less toxic than butynediol. The LD_{50} is 1.25 mL/kg for white rats and 1.25–1.5 mL/kg for guinea pigs.

Uses. Butanediol is used to manufacture the insecticide Endosulfan, other agricultural chemicals, and pyridoxine (vitamin B_6) (see VITAMINS) (118). Small amounts are consumed as a diol by the polymer industry.

3.4. Butanediol. 1,4-Butanediol [110-63-4], tetramethylene glycol, 1,4-butylene glycol, was first prepared in 1890 by acid hydrolysis of *N,N′*-dinitro-1,4-butanediamine (119). Other early preparations were by reduction of succinaldehyde (120) or succinic esters (121) and by saponification of the diacetate prepared from 1,4-dihalobutanes (122). Catalytic hydrogenation of butynediol, now the principal commercial route, was first described in 1910 (123). Other processes used for commercial manufacture are described in the section on Manufacture. Physical properties of butanediol are listed in Table 2.

Reactions. The chemistry of butanediol is determined by the two primary hydroxyls. Esterification is normal. It is advisable to use nonacidic catalysts for esterification and transesterification (124) to avoid cyclic dehydration. When carbonate esters are prepared at high dilutions, some cyclic ester is formed; more concentrated solutions give a polymeric product (125). With excess phosgene the useful bischloroformate can be prepared (126).



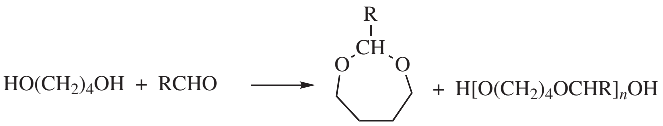


$$HO(CH_2)_4OH + 2COCl_2 \longrightarrow Cl\overset{O}{\overset{\|}{C}}O(CH_2)_4O\overset{O}{\overset{\|}{C}}Cl$$

Ethers are formed in the usual way (127). The bis(chloromethyl) ether is obtained using formaldehyde and hydrogen chloride (88).

$$HO(CH_2)_4OH + 2\,HCHO + 2\,HCl \longrightarrow ClCH_2O(CH_2)_4OCH_2Cl + 2\,H_2O$$

With aldehydes or their derivatives, butanediol forms acetals, either seven-membered rings (1,3-dioxepanes) or linear polyacetals; the rings and chains are easily intraconverted (128, 129).



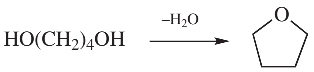
Heating butanediol with acetylene in the presence of an acidic mercuric salt gives the cyclic acetal expected from butanediol and acetaldehyde (130).

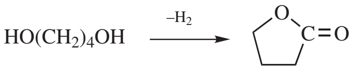
A commercially important reaction is with diisocyanates to form polyurethanes (131) (see Urethane polymers).

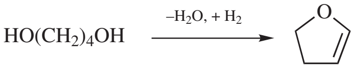
$$HO(CH_2)_4OH + R(NCO)_2 \longrightarrow H[O(CH_2)_4O\overset{O}{\overset{\|}{C}}NHRNH\overset{O}{\overset{\|}{C}}]_nO(CH_2)_4OH$$

Thionyl chloride readily converts butanediol to 1,4-dichlorobutane [110-56-5] (132) and hydrogen bromide gives 1,4-dibromobutane [110-52-1] (133). A procedure using 48% HBr with a Dean-Stark water trap gives good yields of 4-bromobutanol [33036-62-3], free of diol and dibromo compound (134).

With various catalysts, butanediol adds carbon monoxide to form adipic acid. Heating with acidic catalysts dehydrates butanediol to tetrahydrofuran [109-99-9], C_4H_8O (see Furan derivatives). With dehydrogenation catalysts, such as copper chromite, butanediol forms butyrolactone (135). With certain cobalt catalysts both dehydration and dehydrogenation occur, giving 2,3-dihydrofuran (136).



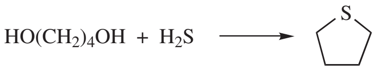




Heating butanediol or tetrahydrofuran with ammonia or an amine in the presence of an acidic heterogeneous catalyst gives pyrrolidines (137,138). With a dehydrogenation catalyst, one or both of the hydroxyl groups are replaced by amino groups (139).

$$HO(CH_2)_4OH + R_2NH \longrightarrow \text{mixture of } R_2N(CH_2)_4OH \text{ and } R_2N(CH_2)_4NR_2$$

With an acidic catalyst, butanediol and hydrogen sulfide give tetrahydrothiophene [110-01-0], C_4H_8S (140).



Vapor-phase oxidation over a promoted vanadium pentoxide catalyst gives a 90% yield of maleic anhydride [108-31-6] (141). Liquid-phase oxidation with a supported palladium catalyst gives 55% of succinic acid [110-15-6] (142).

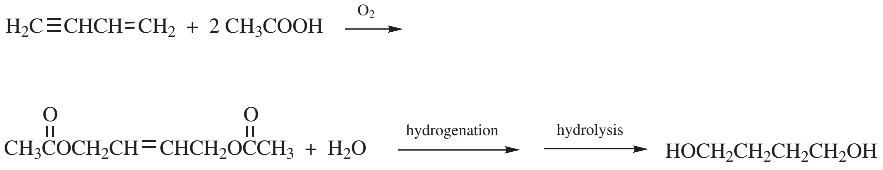
Manufacture. Most butanediol is manufactured in Reppe plants via hydrogenation of butynediol. Recently, an alternative route involving acetoxylation of butadiene has come on stream and, more recently, a route based upon hydroformylation of allyl alcohol.

Another process, involving chlorination of butadiene, hydrolysis of the dichlorobutene, and hydrogenation of the resulting butenediol, was practiced by Toyo Soda in Japan until the mid-1980s (143).

Reppe Process

$$HC{\equiv}CH + 2\ HCHO \longrightarrow HOCH_2C{\equiv}CCH_2OH \xrightarrow{H_2} HOCH_2CH_2CH_2CH_2OH$$

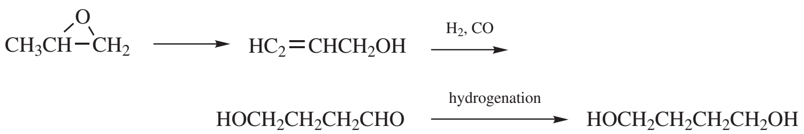
Acetoxylation Process



$$H_2C{\equiv}CHCH{=}CH_2 + 2\ CH_3COOH \xrightarrow{O_2}$$

$$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH{=}CHCH_2O\overset{O}{\overset{\|}{C}}CH_3 + H_2O \xrightarrow{\text{hydrogenation}} \xrightarrow{\text{hydrolysis}} HOCH_2CH_2CH_2CH_2OH$$

Hydroformylation Process



Economic Aspects. Table 3 lists the U.S. producers of 1,4-butanediol and their capacities. All current production except for Lyondell and BP Amoco is

Table 3. **U.S. Producers of 1,4-Butanediol and their Capacities**[a]

Producer	Capacity, $\times 10^6$ kg ($\times 10^6$ lb)
BASF, Geismar, La.	127 (280)
BP Amoco, Lima, Ohio	64 (140)
DuPont, LaPorte, Tex.	102 (225)
ISP, Texas City, Tex.	29 (65)
Lyondel, Channelview, Tex.	54 (120)
Total	*376* (*830*)

[a] From Ref. 144.

based on the traditional method of reacting acetylene and formaldehyde (Reppe process). Lyondell uses propylene oxide. BPAmoco's process is based in butane oxidation.

BASF is planning a plan to produce 90×10^6 kg (200×10^6 lb) per year. It would use butane/maleic anhydride as feed.

Demand for butanediol in 1998 was 293×10^6 kg (645×10^6 lb). The projected demand for 2003 is 363×10^6 kg (800×10^6 lb). Growth rate is expected at the rate of 4.5% through 2003 (144).

Current high price is \$0.90/lb tank, fob, frt, equald. Current low price is \$0.65/lb same basis. Current spot pricing is \$0.50–0.60/lb, same basis.

Shipment and Storage. Tank cars and tank trailers, selected to prevent color formation, are of aluminum or stainless steel, or lined with epoxy or phenolic resins; drums are lined with phenolic resins. Flexible stainless steel hose is used for transfer. Because of butanediol's high freezing point (~20°C) tank car coil heaters are provided.

Specifications and Analytical Methods. Butanediol is specified as 99.5% minimum pure, determined by gc, solidifying at 19.6°C minimum. Moisture is 0.04% maximum, determined by Karl-Fischer analysis (directly or of a toluene azeotrope). The color is APHA 5 maximum, and the Hardy color (polyester test) is APHA 200 maximum. The carbonyl number is 0.5 mg KOH/g maximum; the acetal content can also be measured directly by gc.

Health and Safety Factors. Butanediol is much less toxic than its unsaturated analogous. It is neither a primary skin irritant nor a sensitizer. Because of its low vapor pressure, there is ordinarily no inhalation problem. As with all chemicals, unnecessary exposure should be avoided. The LD_{50} for white rats is 1.55 g/kg.

Uses. The largest uses of butanediol are internal consumption in manufacture of tetrahydrofuran (45%) and butyrolactone (22%). The largest merchant uses are for poly(butylene terephthalate) resins 24% (see POLYESTERS, THERMOPLASTIC) and in polyurethanes 5%, both as a chain extender and as an ingredient in a hydroxyl-terminated polyester used as a macroglycol. miscellaneous uses account for 4% of consumption and include uses as a solvent, as a coating resin raw material, and as an intermediate in the manufacture of other chemicals and pharmaceuticals.

3.5. Butyrolactone. γ-Butyrolactone [96-48-0], dihydro-2(3*H*)-furanone, was first synthesized in 1884 via internal esterification of 4-hydroxybutyric acid

Table 4. **Physical Properties of Butyrolactone**

Property	Value
freezing point, °C	−44
boiling point, °C at kPa[a]	
0.133	35
1.33	77
13.3	134
101.3	204
specific gravity, $d^{20}{}_4$	1.129
$d^{25}{}_4$	1.125
refractive index, $n^{20}{}_D$	1.4362
$n^{25}{}_D$	1.4348
viscosity at 25°C, mPa s (= cP)	1.75
dielectric constant at 20°C, ε	39.1
heat capacity at 20°C, J/(g K)[b]	1.60
critical temperature, °C	436
critical pressure, MPa[c]	3.43
flash point, Tagliabue open cup, °C	98

[a] To convert kPa to mm Hg multiply by 7.5.

[b] To convert J to cal divide by 4.184.

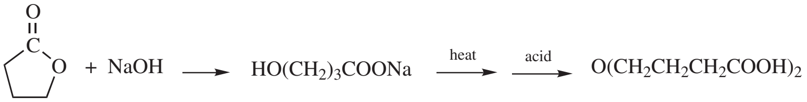
[c] To convert MPa to atm divide by 0.1013.

(145). In 1991 the principal commercial source of this material is dehydrogenation of butanediol. Manufacture by hydrogenation of maleic anhydride (146) was discontinued in the early 1980s and resumed in the late 1980s. Physical properties are listed in Table 4.

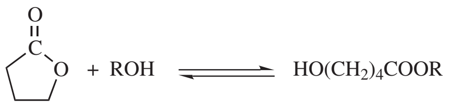
Butyrolactone is completely miscible with water and most organic solvents. It is only slightly soluble in aliphatic hydrocarbons. It is a good solvent for many gases, for most organic compounds, and for a wide variety of polymers.

Reactions. Butyrolactone undergoes the reactions typical of γ-lactones. Particularly characteristic are ring openings and reactions in which ring oxygen is replaced by another heteroatom. There is also marked reactivity of the hydrogen atoms alpha to the carbonyl group.

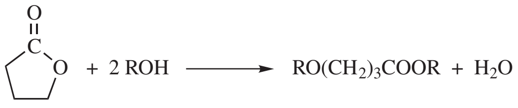
Hydrolysis in neutral aqueous solutions proceeds slowly at room temperature and more rapidly at acidic conditions and elevated temperatures. The hydrolysis–esterification reaction is reversible. Under alkaline conditions hydrolysis is rapid and irreversible. Heating the alkaline hydrolysis product at 200–250°C gives 4,4′-oxydibutyric acid [7423-25-8] after acidification (147).

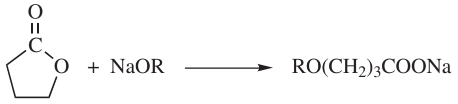


With acid catalysts, butyrolactone reacts with alcohols rapidly even at room temperature, giving equilibrium mixtures consisting of esters of 4-hydroxybutyric acid [591-81-1] with unchanged butyrolactone as the main component. Attempts to distill such mixtures ordinarily result in complete reversal to butyrolactone and alcohol. The esters can be separated by a quick flash distillation at high vacuum (148).

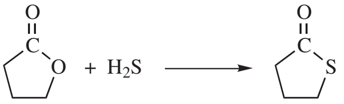


When butyrolactone and alcohols are heated for long times and at high temperatures in the presence of acidic catalysts, 4-alkoxybutyric esters are formed. With sodium alkoxides, sodium 4-alkoxybutyrates are formed (149).

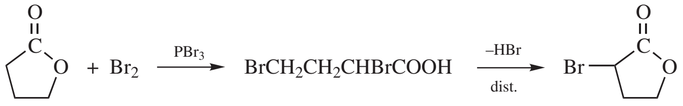




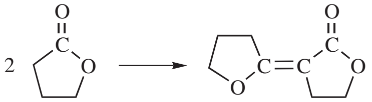
Butyrolactone and hydrogen sulfide heated over an alumina catalyst result in replacement of ring oxygen by sulfur (150).

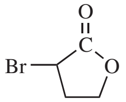


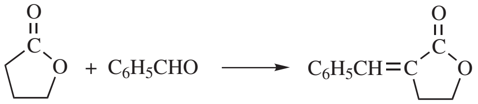
Heating butyrolactone with bromine at 160–170°C gives a 70% yield of α-bromobutyrolactone (151). With phosphorus tribromide as catalyst, bromination is accelerated, giving 2,4-dibromobutyric acid, which dehydrobrominates to α-bromobutyrolactone when distilled (152). Chlorination gives α-position monochlorination at 110–130°C and α-dichlorination at 190–200°C (153).

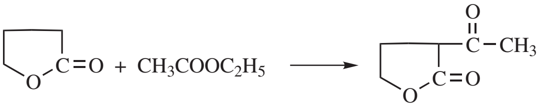


The α-methylene group of butyrolactone condenses easily with a number of different types of carbonyl compounds; eg, sodium alkoxides catalyze self-condensation to α-dibutyrolactone (154), benzaldehyde gives α-benzylidenebutyrolactone (155), and ethyl acetate gives α-acetobutyrolactone (156).





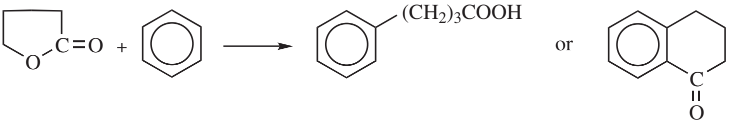




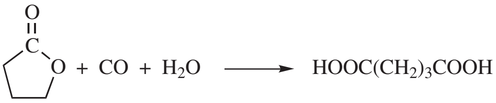
The α-acetobutyrolactone, with or without isolation, can be used in the preparation of various 5-substituted 2-butanone derivatives, presumably by decarboxylation of the acetoacetic acid obtained by ring hydrolysis. Simple hydrolysis gives 5-hydroxybutan-2-one (157) and acidolysis with hydrochloric acid gives 5-chlorobutan-2-one in good yields (158).

The α-methylene groups also add to double bonds; eg, 1-decene at 160°C gives up to 80% of α-decylbutyrolactone (159). With photochemical initiation similar additions take place at room temperature (160).

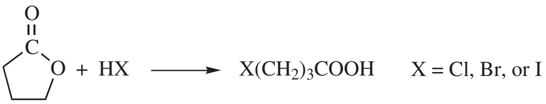
With Friedel-Crafts catalysts, butyrolactone reacts with aromatic hydrocarbons. With benzene, depending on experimental conditions, either phenylbutyric acid or 1-tetralone can be prepared (161).



Carbonylation of butyrolactone using nickel or cobalt catalysts gives high yields of glutaric acid [110-94-1] (162).

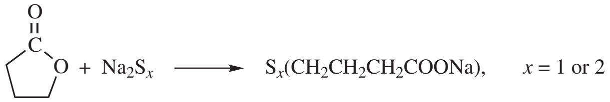


A series of ring-opening reactions are frequently unique and synthetically useful. Butyrolactone and anhydrous hydrogen halides give high yields of 4-halobutyric acids (163).In the presence of alcohols, esters are formed.

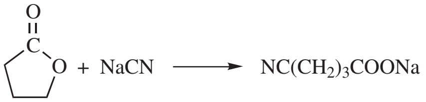


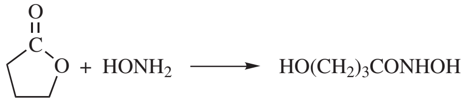
Phosgene (164) or thionyl chloride in the presence of an acid catalyst (165) gives good yields of 4-chlorobutyryl chloride. Heating butyrolactone and thionyl chloride in an alcohol gives good yields of 4-chlorobutyric esters (166).

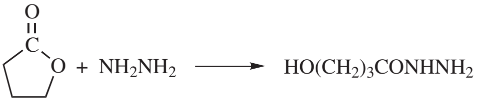
Butyrolactone with sodium sulfide or hydrosulfide forms 4,4′-thiodibutyric acid (167); with sodium disulfide, the product is 4,4′-dithiodibutyric acid (168).



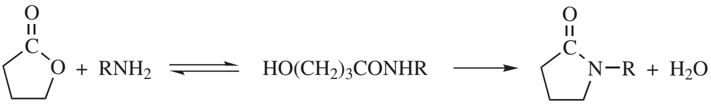
Salts of thiols (169) or of sulfinic acids (170) react like the alkoxides, giving 4-alkylthio- or 4-alkylsulfono-substituted butyrates. Alkali cyanides give 4-cyanobutyrates (171), hydroxylamine gives a hydroxamic acid (172), and hydrazine a hydrazide (173).







Butyrolactone reacts rapidly and reversibly with ammonia or an amine forming 4-hydroxybutyramides (174), which dissociate to the starting materials when heated. At high temperatures and pressures the hydroxybutyramides slowly and irreversibly dehydrate to pyrrolidinones (175). A copper-exchanged Y-zeolite (176) or magnesium silicate (177) is said to accelerate this dehydration.



Manufacture. Butyrolactone is manufactured by dehydrogenation of butanediol. The butyrolactone plant and process in Germany, as described after World War II (178), approximates the processes presently used. The dehydrogenation was carried out with preheated butanediol vapor in a hydrogen carrier over a supported copper catalyst at 230−250°C. The yield of butyrolactone after purification by distillation was ∼90%. Preparation of γ-butyrolactone by catalytic hydrogenation of maleic anhydride has been described (179).

Shipment and Storage. Butyrolactone is shipped in unlined steel tank cars and plain steel drums. Plain steel, stainless steel, aluminum, and nickel are suitable for storage and handling; rubber, phenolics, and epoxy resins are not suitable. Butyrolactone is hygroscopic and should be protected from moisture. Because of its low freezing point (−44°C), no provision for heating storage vessels is needed.

γ-Butyrolactone is produced by BASF, Alfa Resan, The chemical Co., Penta Manufacturing Co., Quaked City Chemicals, and Vopak U.S.A.

Specifications and Analytical Methods. Purity is specified as 99.5% minimum, by gc area percentage, with a maximum of 0.1% moisture by Karl-Fischer titration. Color, as delivered, is 40 APHA maximum; samples may darken on long storage.

Health and Safety Factors. Butyrolactone is neither a skin irritant nor a sensitizer; however, it is judged to be a severe eye irritant in white rabbits. The acute oral LD_{50} is 1.5 mL/kg for white rats or guinea pigs. Subacute oral feeding studies were carried out with rats and with dogs. At levels up to 0.8% of butyrolactone in the diet there were no toxicologic or pathologic effects in the three months of the test.

Because of its high boiling point (204°C), it does not ordinarily represent a vapor hazard.

Uses. Butyrolactone is principally consumed by the manufacturers by reaction with methylamine or ammonia to produce *N*-methyl-2-pyrrolidinone [872-50-4] and 2-pyrrolidinone [616-45-5], C_4H_7NO, respectively. Considerable amounts are used as a solvent for agricultural chemicals and polymers, in dyeing and printing, and as an intermediate for various chemical syntheses.

4. Other Alcohols and Diols

Secondary acetylenic alcohols are prepared by ethynylation of aldehydes higher than formaldehyde. Although copper acetylide complexes will catalyze this reaction, the rates are slow and the equilibria unfavorable. The commercial products are prepared with alkaline catalysts, usually used in stoichiometric amounts.

Ethynylation of ketones is not catalyzed by copper acetylide, but potassium hydroxide has been found to be effective (180). In general, alcohols are obtained at lower temperatures and glycols at higher temperatures. Most processes use stoichiometric amounts of alkali, but true catalytic processes for manufacture

Table 5. **Commercial Secondary and Tertiary Acetylenic Alcohols and Glycols**

Alcohol or glycol	Molecular formula	CAS Registry No.	Starting material
1-hexyn-3-ol	$C_6H_{10}O$	[105-31-7]	butyraldehyde
4-ethyl-1-octyn-3-ol	$C_{10}H_{18}O$	[5877-42-9]	2-ethylhexanal
2-methyl-3-butyn-2-ol	C_5H_8O	[115-19-5]	acetone
3-methyl-1-pentyn-3-ol	$C_6H_{10}O$	[77-75-8]	methyl ethyl ketone
2,5-dimethyl-3-hexyne-2,5-diol	$C_8H_{14}O_2$	[142-30-3]	acetone
3,6-dimethyl-4-octyne-3,6-diol[a]	$C_{10}H_{18}O_2$	[78-66-0]	methyl ethyl ketone
2,4,7,9-tetramethyl-5-decyne-4,7-diol[a]	$C_{14}H_{26}O_2$	[126-86-3]	methyl isobutyl ketone

[a] These glycols are commercially available as mixtures of diastereoisomers.

Table 6. **Physical Properties of Acetylenic Alcohols**

Property	Hexynol	Ethyl-octynol	Methyl-butynol	Methyl-pentynol
molecular weight	98	154	84	98
freezing point, °C	−80	−45	2.6	−30.6
boiling point, °C	142	197.2	103.6	121.4
specific gravity, d^{20}_{20}	0.882	0.873	0.8672	0.8721
refractive index, n^{20}_{D}	1.4350	1.4502	1.4211	1.4318
viscosity at 20°C, mPa s (= cP)			3.79	2.65[a]
flash point, Tagliabue open cup, °C		83	25	38
water solubility (20°C), wt %	3.8	<0.1	miscible	9.9

[a] At 31°C.

of the alcohols have been described; the glycols appear to be products of stoichiometric ethynylation only.

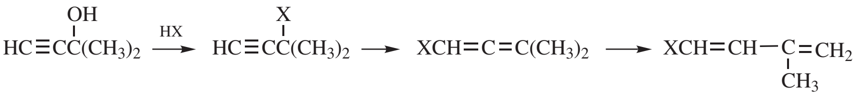
Table 5 lists the principal commercially available acetylenic alcohols and glycols; Tables 6 and 7 list the physical properties of acetylenic alcohols and glycols, respectively.

4.1. Methylbutynol.

2-Methyl-3-butyn-2-ol [115-19-5], prepared by ethynylation of acetone, is the simplest of the tertiary ethynols, and serves as a prototype to illustrate their versatile reactions. There are three reactive sites, ie, hydroxyl group, triple bond, and acetylenic hydrogen. Although the triple bonds and acetylenic hydrogens behave similarly in methylbutynol and in propargyl alcohol, the reactivity of the hydroxyl groups is very different.

Reactions. As with other tertiary alcohols, esterification with carboxylic acids is difficult and esters are prepared with anhydrides (181), acid chlorides (182), or ketene (183). Carbamic esters may be prepared by treatment with an isocyanate (184) or with phosgene followed by ammonia or an amine (185).

The labile hydroxyl group is easily replaced by treatment with thionyl chloride, phosphorous chlorides, or even aqueous hydrogen halides. At low temperatures aqueous hydrochloric (186) or hydrobromic (187) acids give good yields of 3-halo-3-methyl-1-butynes. At higher temperatures these rearrange, first to 1-halo-3-methyl-1,2-butadienes, then to the corresponding 1,3-butadienes (188,189).

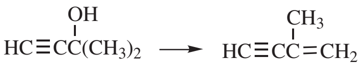


$$HC{\equiv}C\overset{OH}{C}(CH_3)_2 \xrightarrow{HX} HC{\equiv}C\overset{X}{C}(CH_3)_2 \longrightarrow XCH{=}C{=}C(CH_3)_2 \longrightarrow XCH{=}CH{-}\underset{CH_3}{C}{=}CH_2$$

Table 7. **Physical Properties of Acetylenic Glycols**

Property	Dimethyl-hexynediol	Dimethyl-octynediol	Tetramethyl-decynediol
molecular weight	142	170	226
melting point, °C	96–97	49–51	37–38
boiling point, °C	206	222	260
surface tension, mN/m (= dyn/cm) 0.1% in water at 25°C	60.9	55.3	31.6
water solubility (20°C), wt %	27.0	10.5	0.12

With acid catalysts in the liquid (190) or vapor (191) phase, methylbutynol is dehydrated to isopropenylacetylene.

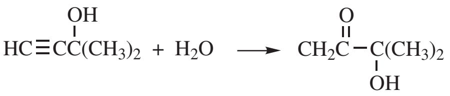


$$HC\equiv C\overset{OH}{C}(CH_3)_2 \longrightarrow HC\equiv C\overset{CH_3}{C}=CH_2$$

Hydrogenation of methylbutynol gives 2-methyl-3-buten-2-ol and then 2-methylbutan-2-ol in stepwise fashion (192).

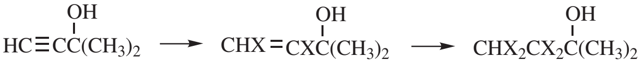
$$HC\equiv CC(OH)(CH_3)_2 \longrightarrow CH_2=CHC(OH)(CH_3)_2 \longrightarrow CH_3CH_2C(OH)(CH_3)_2$$

Acidic mercury salts catalyze hydration to form a ketone (193).



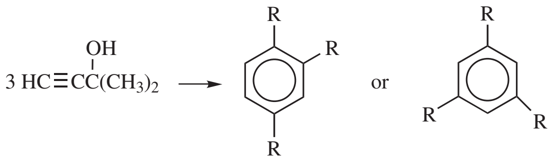
$$HC\equiv C\overset{OH}{C}(CH_3)_2 + H_2O \longrightarrow CH_2\overset{O}{\overset{\|}{C}}-\underset{OH}{C}(CH_3)_2$$

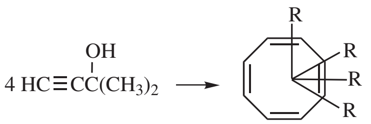
Bromination in polar solvents usually gives *trans*-3,4-dibromo-2-methyl-3-buten-2-ol; in nonpolar solvents, with incandescent light, the cis isomer is the principal product (194). Chlorine adds readily up to the tetrachloro stage, but yields are low because of side reactions (195).



$$HC\equiv C\overset{OH}{C}(CH_3)_2 \longrightarrow CHX=CX\overset{OH}{C}(CH_3)_2 \longrightarrow CHX_2CX_2\overset{OH}{C}(CH_3)_2$$

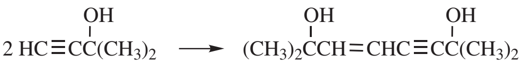
Upon treatment with suitable cobalt complexes, methylbutynol cyclizes to a 1,2,4-substituted benzene. Nickel complexes give the 1,3,5-isomer (196), sometimes accompanied by linear polymer (25) or a mixture of tetrasubstituted cyclooctatetraenes (26).





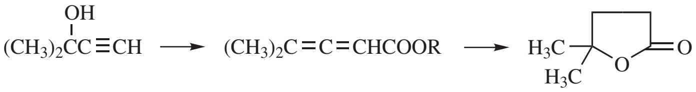
R = α-hydroxyisopropyl

When bis(π-allyl)nickel is used, only small amounts of cyclic product are obtained and the principal product is formed by addition of one triple bond to another (197).



$$2\ HC\equiv C\overset{OH}{C}(CH_3)_2 \longrightarrow (CH_3)_2\overset{OH}{C}CH=CHC\equiv C\overset{OH}{C}(CH_3)_2$$

With a nickel carbonyl catalyst, hydrochloric acid, and an alcohol the initially formed allenic ester cyclizes on distillation (198).



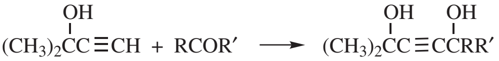
With palladium chloride catalyst, carbon monoxide, and an alcohol the labile hydroxyl is alkylated during carbonylation (199).

$$(CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CH \longrightarrow (CH_3)_2\overset{OR}{\overset{|}{C}}CH{=}CHCOOR$$

Copper salts catalyze oxidative dimerization to conjugated diynediols in high yields (200).

$$2\,(CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CH \longrightarrow (CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CC\equiv C\overset{OH}{\overset{|}{C}}(CH_3)_2$$

Glycols are obtained by treatment with a ketone using alkali as catalyst or with an aldehyde using alkali or copper acetylide as catalyst (201,202).

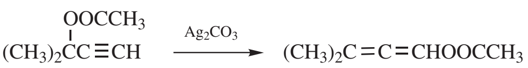


$$(CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CH + RCOR' \longrightarrow (CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv C\overset{OH}{\overset{|}{C}}RR'$$

Hypohalites replace the acetylenic hydrogen with chlorine, bromine, or iodine (203).

$$(CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CH + NaOX \longrightarrow (CH_3)_2\overset{OH}{\overset{|}{C}}C\equiv CX$$

Ethynyl carbinols rearrange to conjugated unsaturated aldehydes. Copper or silver salts catalyze isomerization of the acetate to an allenic acetate, which can be hydrolyzed to an unsaturated aldehyde (204).



$$(CH_3)_2\overset{OOCCH_3}{\overset{|}{C}}C\equiv CH \xrightarrow{Ag_2CO_3} (CH_3)_2C{=}C{=}CHOOCCH_3$$

Manufacture. In general, manufacture is carried out in batch reactors at close to atmospheric pressure. A moderate excess of finely divided potassium hydroxide is suspended in a solvent such as 1,2-dimethoxyethane. The carbonyl compound is added, followed by acetylene. The reaction is rapid and exothermic. At temperatures < 5°C the product is almost exclusively the alcohol. At 25–30°C the glycol predominates. Such synthesis also proceeds well with non-complexing solvents such as aromatic hydrocarbons, although the conversion is usually lower (205).

Continuous processes have been developed for the alcohols, operating under pressure with liquid ammonia as solvent. Potassium hydroxide (206) or anion exchange resins (207) are suitable catalysts. However, the relatively small manufacturing volumes militate against continuous production. For a while a continuous catalytic plant operated in Ravenna, Italy, designed to produce about 40,000 t/year of methylbutynol for conversion to isoprene (208,209).

A number of secondary and tertiary acetylenic alcohols and glycols are manufactured by Air Products and Chemicals Co.

Health and Safety Factors. Under normal conditions acetylenic alcohols are stable and free of decomposition hazard. The more volatile alcohols present a fire hazard.

The alcohols are toxic orally, through skin absorption, and through inhalation. The secondary alcohols are more toxic than the tertiary. The glycols are relatively low in toxicity.

Compound	LD_{50}, mL/kg (mice)
hexynol	0.175
ethyloctynol	2.1
methylbutynol	2.2
methylpentynol	0.7
tetramethyldecynediol	4.6

Uses. The secondary acetylenic alcohols hexynol and ethyloctynol are used as corrosion inhibitors in oil-well acidizing compositions (see CORROSION AND CORROSION CONTROL). The tertiary alcohols methylbutynol and methylpentynol are used as chemical intermediates, for manufacture of Vitamin A and other products, and in metal plating and pickling operations. Dimethylhexynediol can be used in manufacture of fragrance chemicals and peroxide catalysts. Higher acetylenic glycols and ethoxylated acetylene glycols are useful as surfactants and electroplating additives.

5. Vinylation Reaction Products

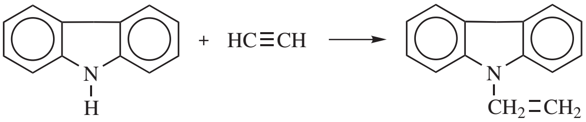
Unlike ethynylation, in which acetylene adds across a carbonyl group and the triple bond is retained, in vinylation a labile hydrogen compound adds to acetylene, forming a double bond.

In early work, vinyl chloride had been heated with stoichiometric amounts of alkali alkoxides in excess alcohol as solvent, giving vinyl ethers as products (210). Supposedly, this involved a Williamson ether synthesis, where alkali alkoxide and organic halide gave an ether and alkali halide. However, it was observed that small amounts of acetylene were formed by dehydrohalogenation of vinyl chloride, and that this acetylene was consumed as the reaction proceeded. Hence, acetylene was substituted for vinyl chloride and only catalytic amounts of alkali were used. Vinylation proceeded readily with high yields (211).

Catalytic vinylation has been applied to a wide range of alcohols, phenols, thiols, carboxylic acids, and certain amines and amides. Vinyl acetate is no longer prepared this way in the United States, although some minor vinyl esters such as stearates may still be prepared this way. However, the manufacture of vinyl-pyrrolidinone and vinyl ethers still depends on acetylene.

5.1. *N*-Vinylcarbazole.

Vinylation of carbazole proceeds in high yields with alkaline catalysts (212,213). The product, 9-ethenylcarbazole, $C_{14}H_{11}N$ [1484-13-5], forms rigid high melting polymers with outstanding electrical properties.



5.2. Neurine.

Neurine is trimethylvinylammonium hydroxide, $C_5H_{13}NO$ [463-88-7]. Tertiary amines and their salts vinylate readily at low temperatures with catalysis by free tertiary amines.

$$(CH_3)_3N + HC{\equiv}CH + H_2O \longrightarrow [(CH_3)_3NCH{=}CH_2]^+[OH]^-$$

Above ~50°C tetramethylammonium hydroxide is formed as a by-product; it is the sole product above 100°C (214).

5.3. *N*-Vinyl-2-pyrrolidinone.

1-Ethenyl-2-pyrrolidinone [88-12-0], C_6H_9NO, *N*-vinylpyrrolidinone, was developed by Reppe's laboratory in Germany at the beginning of World War II and patented in 1940 (215).

The major use of vinylpyrrolidinone is as a monomer in manufacture of poly(vinylpyrrolidinone) (PVP) homopolymer and in various copolymers, where it frequently imparts hydrophilic properties. When PVP was first produced, its principal use was as a blood plasma substitute and extender, a use no longer sanctioned. These polymers are used in pharmaceutical and cosmetic applications, soft contact lenses, and viscosity index improvers. The monomer serves as a component in radiation-cured polymer compositions, serving as a reactive diluent that reduces viscosity and increases cross-linking rates (see VINYL POLYMERS, *N*-VINYLAMIDE POLYMERS).

5.4. Vinyl Ethers.

The principal commercial vinyl ethers are methyl vinyl ether (methoxyethene, C_3H_6O) [107-25-5]; ethyl vinyl ether (ethoxyethene, C_4H_8O) [104-92-2]; and butyl vinyl ether (1-ethenyloxybutane, $C_6H_{12}O$) [111-34-2]. (See Table 8 for physical properties.) Others such as the isopropyl, isobutyl, hydroxybutyl, decyl, hexadecyl, and octadecyl ethers, as well as the divinyl ethers of butanediol and of triethylene glycol, have been offered as development chemicals (see ETHERS).

Ethyl vinyl ether was the first to be prepared, in 1878, by treatment of diethyl chloroacetal with sodium (216). Methyl vinyl ether was first listed in Reppe patents on vinylation in 1929 and 1930 (210,211).

Reactions. Vinyl ethers undergo all of the expected reactions of olefinic compounds plus a number of reactions that are both useful and unusual.

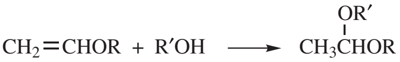
With a suitable catalyst, usually a Lewis acid, many labile hydrogen compounds add across the vinyl ether double bond in the Markovnikov direction.

Table 8. **Physical Properties of Vinyl Ethers**[a]

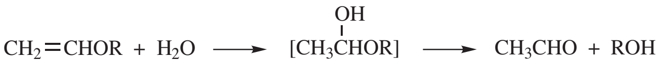
Property	Methyl	Ethyl	Butyl
molecular weight	58	72	100
freezing point, °C	−122.8	−115.4	−91.9
boiling point, °C	5.5	35.7	93.5
vapor pressure at 20°C, kPa[b]	156.7	57	5.6
specific gravity, $d^{20}{}_4$	0.7511	0.7541	0.7792
refractive index, $n^{20}{}_D$	1.3730 (0°C)	1.3767	1.4020
flash point, °C	−56	<−18	−1
water solubility at 20°C, wt %	1.5	0.9	0.2

[a] Lower vinyl ethers are miscible with nearly all organic solvents.
[b] To convert kPa to mm Hg, multiply by 7.5.

Alcohols give acetals. This reaction has been frequently used to provide blocking groups in organic synthesis. The acetals are stable under neutral or alkaline conditions and are easily hydrolyzed with dilute acid after other desired reactions have occurred (217,218). Water gives acetaldehyde and the corresponding alcohol, presumably via disproportionation of the hemiacetal (219). Carboxylic acids give 1-alkoxyethyl esters (220). Thiols give thioacetals (221).



$$CH_2{=}CHOR + R'OH \longrightarrow CH_3\overset{OR'}{\overset{|}{C}}HOR$$



$$CH_2{=}CHOR + H_2O \longrightarrow [CH_3\overset{OH}{\overset{|}{C}}HOR] \longrightarrow CH_3CHO + ROH$$

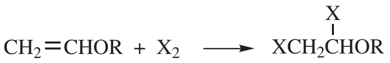
$$CH_2{=}CHOR + R'COOH \longrightarrow CH_3\overset{OOCR'}{\overset{|}{C}}HOR$$

Hydrogen halides react vigorously to give 1-haloethyl ethers, which are reactive intermediates for further synthesis (222). Conditions must be carefully selected to avoid polymerization of the vinyl ether. Hydrogen cyanide adds at high temperature to give a 2-alkoxypropionitrile (223).

$$CH_2{=}CHOR + HX \longrightarrow CH_3\overset{X}{\overset{|}{C}}HOR \quad (X = Cl \text{ or } Br)$$

$$CH_2{=}CHOR + HCN \longrightarrow CH_3\overset{CN}{\overset{|}{C}}HOR$$

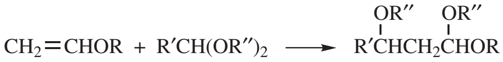
Chlorine and bromine add vigorously, giving, with proper control, high yields of 1,2-dihaloethyl ethers (224). In the presence of an alcohol, halogens add as hypohalites, which give 2-haloacetals (225,226). With methanol and iodine this is used as a method of quantitative analysis, titrating unconsumed iodine with standard thiosulfate solution (227).



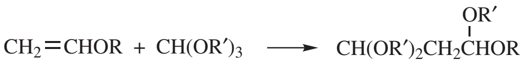
$$CH_2{=}CHOR + X_2 \longrightarrow XCH_2\overset{X}{C}HOR$$

$$CH_2{=}CHOR + X_2 + R'OH \longrightarrow XCH_2\underset{OR'}{C}HOR$$

With Lewis acids as catalysts, compounds containing more than one alkoxy group on a carbon atom add across vinyl ether double bonds. Acetals give 3-alkoxyacetals; since the products are also acetals, they can react further with excess vinyl ether to give oligomers (228–230). Orthoformic esters give diacetals of malonaldehyde (231). With Lewis acids and mercuric salts as catalysts, vinyl ethers add in similar fashion to give acetals of 3-butenal (232,233).



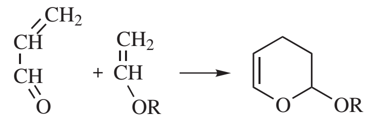
$$CH_2{=}CHOR + R'CH(OR'')_2 \longrightarrow R'\overset{OR''}{C}HCH_2\overset{OR''}{C}HOR$$

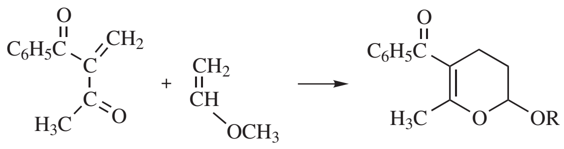


$$CH_2{=}CHOR + CH(OR')_3 \longrightarrow CH(OR')_2CH_2\overset{OR'}{C}HOR$$

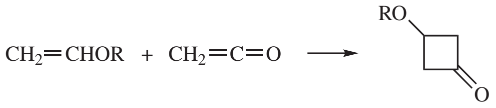
$$2\,CH_2{=}CHOR \longrightarrow CH_2{=}CHCH_2CH(OR)_2$$

Vinyl ethers and α,β-unsaturated carbonyl compounds cyclize in a hetero-Diels-Alder reaction when heated together in an autoclave with small amounts of hydroquinone added to inhibit polymerization. Acrolein gives 3,4-dihydro-2-methoxy-2*H*-pyran (234,235), which can easily be hydrolyzed to glutaraldehyde (236) or hydrogenated to 1,5-pentanediol (237). With 2-methylene-1,3-dicarbonyl compounds the reaction is nearly quantitative (238).





Vinyl ethers cyclize with ketenes to cyclobutanones (239).



Vinyl ethers serve as a source of vinyl groups for transvinylation of such compounds as 2-pyrrolidinone or caprolactam (240,241).

Compounds such as carbon tetrachloride (242) or trinitromethane (243) can add across the double bond.

$$CH_2{=}CHOR + CCl_4 \longrightarrow ROCHClCH_2CCl_3$$

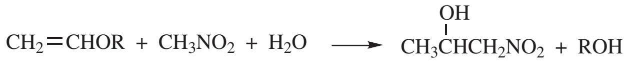
$$CH_2{=}CHOR + CH(NO_2)_3 \longrightarrow ROCH_2CH_2C(NO_2)_3$$

With thionyl chloride as catalyst, hydrogen peroxide adds to vinyl ethers in anti-Markovnikov fashion, as do monothioglycols with amine catalysts (244).

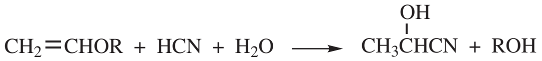
$$2\ CH_2{=}CHOR + HOOH \longrightarrow ROCH_2CH_2OOCH_2CH_2OR$$

$$CH_2{=}CHOR + HSCH_2CH_2OH \longrightarrow ROCH_2CH_2SCH_2CH_2OH$$

Substances that form carbanions, such as nitro compounds, hydrocyanic acid, malonic acid, or acetylacetone, react with vinyl ethers in the presence of water, replacing the alkyl group under mild conditions (245).

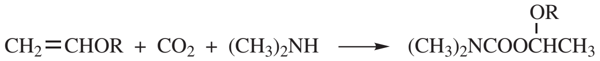


$$CH_2{=}CHOR + CH_3NO_2 + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_2NO_2 + ROH$$



$$CH_2{=}CHOR + HCN + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCN + ROH$$

The reaction of a vinyl ether with carbon dioxide and a secondary amine gives a carbamic ester (246).



$$CH_2{=}CHOR + CO_2 + (CH_3)_2NH \longrightarrow (CH_3)_2NCOO\overset{OR}{\overset{|}{C}}HCH_3$$

Manufacture. The principal manufacturers of vinyl ethers are BASF, Kowa American Corp. and Monomer Payment Dafoe Labs, Inc.

German vinyl ether plants were described in detail at the end of World War II and variations of these processes are still in use. Vinylation of alcohols from methyl to butyl was carried out under pressure: typically 2–2.3 MPa (20–22 atm) and 160–165°C for methyl, and 0.4–0.5 MPa (4–5 atm) and 150–155°C for isobutyl. An unpacked tower, operating continuously, produced about 300 t/month, with yields of 90–95% (247).

High boiling alcohols were vinylated at atmospheric pressure. The Germans used a tower packed with Raschig rings and filled with an alcohol containing 1–5% of KOH at 160–180°C. Acetylene was recycled continuously up through the tower. The heat of reaction, ~125 kJ/mol (30 kcal/mol), was removed by cooling coils. Fresh alcohol and catalyst were added continuously at the top and withdrawn at the bottom. Yields of purified, distilled product were described as quantitative (248).

Shipment, Storage, and Prices. Methyl vinyl ether is available in tank cars or cylinders, while the other vinyl ethers are available in tank cars, tank wagons, or drums. Mild steel, stainless steel, and phenolic-coated steel are suitable for shipment and storage. If protected from air, moisture, and acidic contamination, vinyl ethers are stable for years.

Specifications and Analytical Methods. Vinyl ethers are usually specified as 98% minimum purity, as determined by gas chromatography. The principal impurities are the parent alcohols, limited to 1.0% maximum for methyl vinyl ether and 0.5% maximum for ethyl vinyl ether. Water (by Karl-Fischer titration) ranges from 0.1% maximum for methyl vinyl ether to 0.5% maximum for ethyl vinyl ether. Acetaldehyde ranges from 0.1% maximum in ethyl vinyl ether to 0.5% maximum in butyl vinyl ether.

Health and Safety Factors. Because of their high vapor pressures (methyl vinyl ether is a gas at ambient conditions), the lower vinyl ethers represent a severe fire hazard and must be handled accordingly. Contact with acids can initiate violent polymerization and must be avoided. Although vinyl ethers form peroxides more slowly than saturated ethers, distillation residues must be handled with caution.

Inhalation should be avoided. A group of six rats that were exposed to 64,000 ppm of methyl vinyl ether in air for 4 h were anesthetized. All recovered and appeared normal after 72 h. One died after 96 h. The others survived the 2-week observation period without noticeable effect.

The lower vinyl ethers do not appear to be skin irritants or sensitizers. Oral toxicity is very low: Isobutyl vinyl ether has LD_{50} of 17 mL/kg for white rats.

Uses. Union Carbide consumes its vinyl ether production in the manufacture of glutaraldehyde [111-30-8]. BASF and GAF consume most of their production as monomers (see VINYL POLYMERS). In addition to the homopolymers, the copolymer of methyl vinyl ether with maleic anhydride is of particular interest.

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