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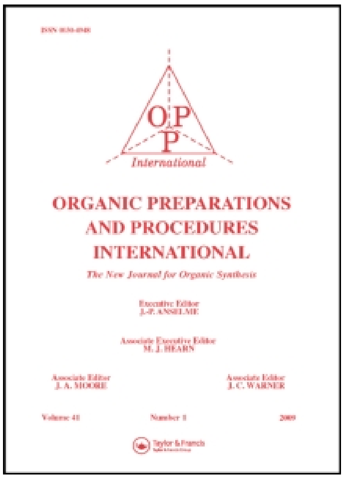

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SYNTHESIS OF α,ω-ALKANEDIOLS. A REVIEW

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SYNTHESIS OF α,ω-ALKANEDIOLS. A REVIEW

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SYNTHESIS OF α,ω-ALKANEDIOLS. A REVIEW

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INTRODUCTION

The study of insect pheromones has attracted a great deal attention because of their favorable perspective for the control of insects. A great number of these pheromones produced by moth species belonging to the order *Lepidoptera* and certain pheromonal compounds belonging to other orders are saturated straight-chain aliphatic alcohols, acetates or aldehydes.[1,2] Monoprotected derivatives of the symmetrical diols of the general structure, $HOCH_2(CH_2)_nCH_2OH$, constitute attractive intermediates in the synthesis of these sex pheromones. A variety of compounds containing two similar or different functional groups at the terminal positions on a straight-chain may be obtained from such α,ω-alkanediols.

General methods for the synthesis of alcohols can be applied to the preparation of diols. The synthesis of diols and their derivatives have been briefly summarized by Waight.[3] The present review covers general methods for the synthesis of α,ω-alkanediols from a variety of starting materials. Specific methods employed for the synthesis of diols (from 1,3-propanediol to 1,19-nonadecanediol) are covered under "Special Methods". 1,2-Ethanediol and 1,4-butanediol are, however, excluded from this section as both are commercially available on a large scale.

I. GENERAL METHODS

α,ω-Alkanediols can be obtained from a variety of starting compounds bearing functional groups at ends of the chain.

1. From α,ω-Diacids and their Esters

a) Catalytic Hydrogenation

Hydrogenation of α,ω-diacids and diesters in the presence of catalysts produces α,ω-alkanediols. A variety of catalysts can be used. Reduction of dicarboxylic esters by hydrogenation over copper-chromium oxide (Adkins' catalysts) is a very useful and general method for the preparation of diols;[4] the catalyst is effective in the temperature range of 125-150°.[5] Adipic ester in the presence of methanol and Cu-Al-Ni catalyst activated by sodium hydroxide, affords 1,6-hexanediol in 94% yield.

$$RO_2C(CH_2)_4CO_2R \xrightarrow[H_2]{\text{Cu–Al–Ni}} HO(CH_2)_6OH$$

In the absence of methanol the yield is reduced considerably.[6] Catalytic hydrogenation over the catalyst obtained by reduction of metal oxides derived from Cu, Fe, Co and Ni at higher temperatures and pressures yielded diols in good yields,[7] e.γ., glutaric acid yielded 1,5-pentanediol in 93% yield in the presence of a Ni catalyst obtained by hydrogenation of nickel oxide. 1,6-Hexane-, 1,8-octane-,

$$HO_2C(CH_2)_3CO_2H \xrightarrow[Ni]{H_2} HO(CH_2)_5OH$$

1,9-nonane- and 1,12-dodecanediols were obtained by hydrogenation of the corresponding diacids in the presence of a catalyst containing 71% Co, 20% Cu, 5% Mn and 4% polyphosphoric acid.[8]

High yields (>90%) of glycols can be obtained from diesters in which the ester groups are separated by three or more carbon atoms. In fact, with pure ester and a catalyst of good quality, the hydrogenation affords glycols in yields >95% at 250° at about 4000 psi.[9] Hydrogenations catalyzed by copper-chromium oxide ($CuO{:}CuCr_2O$) gave 1,5-pentane-, 1,6-hexane-, 1,10-decane-, and 1,14-tetradecanediols in nearly quantitative yields.[10,11] A mixture of dicarboxylic acid and the corresponding diol when reduced in the presence of a catalyst containing 89% Co and 2% Mo afforded α,ω-alkanediols in higher yields.[12]

$$\underset{n = 6,\ 10,\ 12}{HO_2C(CH_2)_{n-2}CO_2H \ + \ HO(CH_2)_nOH} \xrightarrow[H_2]{Co,Mo} HO(CH_2)_nOH$$

Several dicarboxylic acids and some of the corresponding anhydrides have been hydrogenated in the presence of homogeneous catalysts such as ruthenium carbonyl hydride clusters to the corresponding alkanediols or lactones. The highest activity is exhibited by the tributylphosphine-substituted derivative, $H_4Ru_4(CO)_8(PBu_3)_4$, at 100-200° under a pressure of 100-200 atm. of hydrogen. Anhydrides are reduced at lower temperature than acids; under these conditions esters are not reduced.[13]

b) *Alkali Metal and Alcohol*

Reduction of diesters to alkanediols with alkali metal and alcohol is an old method (Bouveault-Blanc reaction). In most instances, sodium metal and ethanol have been used.[14] α,ω-Hexamethylene-[15], heptamethylene-[16] and decamethylenediols[17] were thus obtained from the corresponding diesters. Decamethylene glycol has also been prepared from dimethyl sebacate by means of sodium in butanol and toluene.[18] More recently, this method has largely been supplanted by the more convenient lithium aluminum hydride reagent. Aluminum amalgam in alcohol has been found to be an efficient method; eg. diethyl succinate is converted into tetramethylene glycol.[19]

c) *Alkali Metal Hydrides*

Reduction of diesters with lithium aluminum hydride (LAH) is preferred to the catalytic hydrogenation method since it is more convenient and affords consistently good yields (>80-90%).[20-22] The reduction has been carried out in diethyl ether as well as in higher boiling ethers such as tetrahydrofuran, 1,2-dimethoxyethane, diglyme, etc. Reduction of the free carboxylic acids is reported to proceed less satisfactorily.[23] The conditions of reduction in this method are particularly mild and the reaction proceeds quite well at room temperature. LAH is often taken in large excess (2- to 4-fold excess). Decamethylenediol, a pheromone intermediate, has been prepared from diethyl sebacate by reduction with LAH-toluene containing 5-10% tetrahydrofuran, glyme or diglyme.[24] Bromoesters such as diethyl α-bromoglutarate or dimethyl α,α'-dibromopimelate are reduced with LAH to the corresponding diols.[25] Lithium borohydride is less effective than lithium aluminum hydride. Thus, ethyl sebacate is reduced to decamethylene diol in only 60% yield;[31] catalytic amounts of alkenes, however, markedly enhance the rate of ester reduction.[32] Metal alkoxyaluminum hydrides may also be employed to reduce carboxylic acids and esters to the corresponding diols.[26] Sodium *bis*(2-methoxy ethoxy)aluminum hydride, $NaAlH_2(OCH_2\ CH_2OCH_3)_2$, in benzene or toluene, reduced dimethyl adipate to 1,6-hexanediol[27] and diethyl sebacate to decamethylenediol in quantitative yields.[28] A powerful reducing system, KBH_4-$ZnCl_2$-THF-toluene, reduces carboxylic acids to alcohols at 93-95° in fair to good yields.[29] KBH_4-$AlCl_3$-THF is also an effective reducing system;[30] higher ratios of $AlCl_3$ enhance the reducing power of this system.

$$EtO_2CCHBrCH_2CH_2CO_2Et \xrightarrow{\text{LAH}} HO(CH_2)_5OH$$

$$MeO_2CCHBr(CH_2)_3CHBrCO_2Me \xrightarrow{\text{LAH}} HO(CH_2)_7OH$$

Borane in the presence of lithium chloride (BH_3-LiCl) in THF reduces acid anhydrides rapidly at room temperature to alcohols or diols; the presence of LiCl accelerates the rate of reduction. Reduction of glutaric anhydride with BH_3 at room temperature yielded 80% 1,5-pentanediol in 8 hrs., whereas with LiCl present, the reaction was complete in 1 hr. and gave a quantitative yield of diol.[33]

Higher alkanediols are obtained by electrolysis of lower α,ω-acid esters in methanol containing sodium followed by LAH reduction of the higher acid thus obtained.[34b]

$$MeO_2C(CH_2)_7CO_2H \xrightarrow[\text{Na, e}^-]{\text{MeOH}} MeO_2C(CH_2)_{14}CO_2Me$$

$$\xrightarrow[\text{2. LAH}]{\text{1. KOH}} HO(CH_2)_{16}OH$$

2. From ω-Hydroxy- and ω-Chlorocarboxylic Acids

a) Destructive Hydrogenation

ω-Hydroxycarboxylic acids when heated to 200° *in vacuo* produce the corresponding polyesters which on destructive hydrogenation over Cu-Cr catalyst at 250-260° and 200 atm. are converted in 70-80% to α,ω-diols.[34a,35] Polyesters have also been treated directly with skeletal Ni (Ni sponge) in toluene at 180-210° in a hydrogen atmosphere followed by destructive hydrogenation.[36] α,ω-Diols are

$$H[O(CH_2)_nCO]_xOH \xrightarrow[\text{Cu–Cr}]{H_2} HO(CH_2)_{n+1}OH$$

also obtained from ω-chloroalkanoic acids. The chloro acid is first converted into a polyester by condensation of its potassium salt which is then subjected to destructive hydrogenation over Cu-Cr.[37]

b) Electrolysis

Electrolysis of ω-chloroalkanoic acids on a platinum mesh anode and stainless steel cathode in methanol in the presence of Na_2CO_3 or metallic sodium gives α,ω-dichloroalkanes. These are then hydrolyzed in 10% NaOH at high temperature in an autoclave to afford higher α,ω-alkanediols. Thus, 1,8-Octamethylenediol can be obtained from ω-chloroadipic acid.[38]

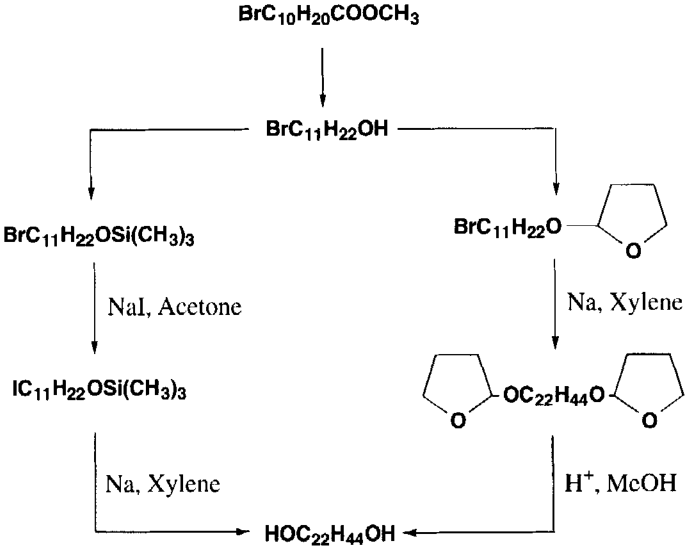
$$Cl(CH_2)_4COOH \longrightarrow Cl(CH_2)_8Cl \longrightarrow HO(CH_2)_8OH$$

ω-Chloroalkanoic acids, prepared by hydrolysis of the corresponding α,α,α,ω-tetrachloroalkane with fuming nitric acid, were converted in 70-90% yield to ω-hydroxyalkanoic acids by heating with alkali. Kolbe electrolysis of the resulting ω-hydroxy acids over titanium electrodes plated with platinum produced the higher α,ω-alkanediols[38] as shown.

$$Cl(CH_2)_nCCl_3 \xrightarrow{HNO_3} Cl(CH_2)_nCOOH \xrightarrow{NaOH} HO(CH_2)_nCOOH \xrightarrow[\text{electrolysis}]{\text{kolbe}} HO(CH_2)_{2n}OH$$

c) *Miscellaneous*

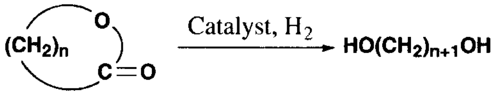
An interesting method starts with an ω-bromoalkanoic ester which is reduced with LAH to the corresponding ω-bromoalkanol. Protection of the alcohol function with trimethylsilyl or tetrahydrofuranyl groups followed by the Wurtz reaction in anhydrous ether or xylene[39] affords a long chain α,ω-alkanediol. For example, 1,22-docosanediol was prepared by this method as shown.



3. From Lactones

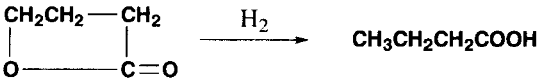
a) Catalytic Hydrogenation

Lactones are hydrogenated in the presence of Cu chromite at 240-270° under 130-200 atm to give diols.[40] ε-Caprolactone gives a 97% yield of 1,6-hexanediol by this method. Increased yields are obtained by use of Raney Cu or $CuCr_4O_7$ catalysts activated by barium oxide.[41]

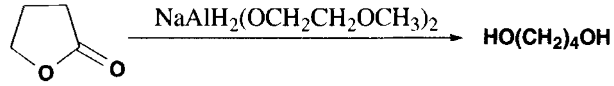


b) Metal Alkoxy Aluminum Hydride

Dialkyl aluminum hydride or triisoalkylaluminum or a complex of these with alkali metal hydride are used to reduce lactones to the corresponding diols.[26] Pentadecanolide is reduced to 1,5-pentadecanediol in 83% yield.[42] A competing reaction leading to an acid may occur as shown below for γ-butyrolactone. However, higher percentages of the diol hydrogenation products can be obtained



if higher ratios of catalyst to lactone are used.[9] Metal alkoxyaluminum hydrides reduce lactones to diols.[26] Sodium *bis*-(2-methoxyethoxy)aluminum hydride reduces γ-butyrolactone to butanediol in 78% yield.[27] Reduction of lactones goes to completion rapidly with AlH_3.[43]



4. From Aldehydes and Ketones

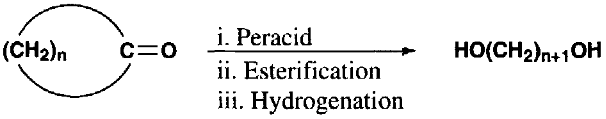
a) Catalytic Hydrogenation

Several rhodium and iridium complexes have been used in the homogeneous hydrogenation of aldehydes and ketones to alcohols.[44] Dialdehydes are reduced over Ni- or Ru-type catalyst to α,ω-diols. 1,9-Nonanediol is thus obtained from the corresponding dialdehyde[45] using Raney nickel in *n*-octanol at 100° under 20 atm. of hydrogen. Diols are readily obtained in good yields from dialdehydes in the presence of catalytic amounts of $Rh_6(CO)_6$ or $Fe(CO)_5$ in water and ethanol or in methoxyethanol in an atmosphere of carbon monoxide.[46] α-Hydroxyaldehydes are also reduced with Ni catalyst and hydrogen to diols. Pentamethylene glycol is produced in 96% yield from 5-hydroxy

$$OHC(CH_2)_7CHO \xrightarrow{\text{R-Ni, } H_2} HO(CH_2)_9OH$$

$$HO(CH_2)_4CHO \xrightarrow{\text{R-Ni, } H_2} HO(CH_2)_5OH$$

pentanal by catalytic reduction with Raney Ni.[47] Cyclic ketones of 4-10 carbon atoms are oxidized by aliphatic peracids at 70-80° in the presence of cationic ion exchange resin to give a mixture of ω-acyloxyalkyl acids, ω-hydroxyalkyl acids, and dibasic acids, all having the same number of carbon



atoms as that of the starting ketones. The product may be esterified with an alcohol and the resulting mixture of ω-hydroxy ester and diesters can be hydrogenated to alkanediols.[48]

b) Lithium Aluminum Hydride

Alcohols are invariably obtained in uniformly good yields from the reduction of aldehydes and ketones with LAH.[23]

5. From Halides

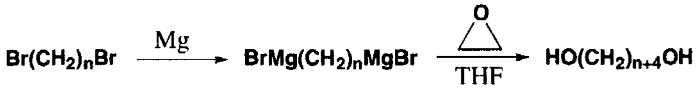
a) Hydrolysis

Hydrolysis of dihalides with aqueous potassium carbonate gives α,ω-alkanediols in good yields.[49a] For example, 1,3-propanediol is obtained in 89% yield from the corresponding dihalide. Aqueous potassium acetate reacts with dibromoalkanes in an autoclave at elevated temperature to yields alkanediols.[49b] Halohydrins or dihalides may also be hydrolyzed using hydriodic acid.[50] α,ω-Dichloroalkane, when allowed to react with two equivalents of solid sodium formate in the presence of tetrabutylammonium bromide (TBAB) are converted to the formate ester, which can in turn be hydrolyzed without isolation by aqueous NaOH to α,ω-alkanediol in quantitative yield.[51]

$$Cl(CH_2)_nCl + HCOONa \xrightarrow{TBAB} CHO{-}O(CH_2)_nOCHO \xrightarrow{NaOH} HO(CH_2)_nOH$$

b) Grignard Reagent

Grignard reagents prepared from α,ω-dibromoalkanes react with ethylene oxide in tetrahydrofuran to yield higher alkandiols.[52]



Reaction of Grignard reagents with acrolein produces an intermediate which can be converted to a dibromo derivative as shown. Treatment of the bromo derivative with diacetate affords an unsaturated diol. Catalytic hydrogenation of the latter gives a saturated diol.[53,54]

$$BrMg(CH_2)_nMgBr \xrightarrow{CH_2=CHCHO} (CH_2)_n(CH_2OHCH=CH_2)_2 \xrightarrow{PBr_3}$$

$$(CH_2)_n(CH_2=CHCH_2Br)_2 \xrightarrow{2\ steps} HO(CH_2)_{n+6}OH$$

c) Electrolysis

Halohydrins can be electrolytically coupled in a divided cell over a Cu cathode in an aqueous system containing Cu ions and a ligand. For example, 1,4-butanediol was obtained by electrochemical coupling of 2-iodoethanol using such an apparatus where the cathode chamber was charged with NH_4NO_3, 2-iodoethanol, CuCl, NH_4OH and water, and the anode chamber contained NH_4NO_3 and NH_4I.[55]

$$ICH_2CH_2OH \longrightarrow HO(CH_2)_4OH$$

6. From Ethers

a) Hydrobromic Acid-Silver Acetate

α,ω-Dialkoxyalkane reacts with gaseous hydrobromic acid to give dibromo derivatives which on treatment with silver acetate in the presence of acetic acid yield the corresponding diacetates. Hydrolysis of the diacetates affords the corresponding diols.[56]

$$MeO(CH_2)_{12}OMe \xrightarrow{\text{HBr}} Br(CH_2)_{12}Br \xrightarrow{\text{AgOAc,AcOH}} AcO(CH_2)_{12}OAc \xrightarrow{\text{Hydrol}} HO(CH_2)_{12}OH$$

b) Hydriodic Acid-Base

Refluxing an α,ω-diakoxyalkane with hydriodic acid followed by treatment with base gave the α,ω-alkanediol.[57]

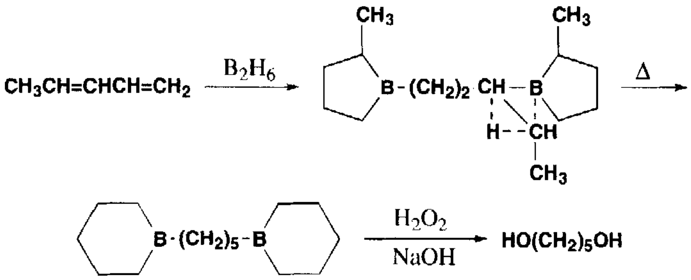
7. From Olefins

a) Hydroformylation-Reduction

α,ω-Diolefins are hydroformylated by an equimolar mixture of CO and H_2 in the presence of cobalt carbonyl complexes at higher pressure and temperatures of 100-120° to produce dialdehydes which may then be hydrogenated to the corresponding α,ω-diols.[58] Hydroformylation of dienes can be conducted at lower pressure with catalysts derived from Rh complexes containing specific ligands.[59]

b) Hydroboration-Oxidation

Hydroboration of dienes followed by oxidation of the resulting organoborane affords diols.[60] Various reagents have been used for the preparation of organoboranes. Treatment of 1,3-butadiene with diborane generated from sodium borohydride and boron trifluoride etherate in glyme,



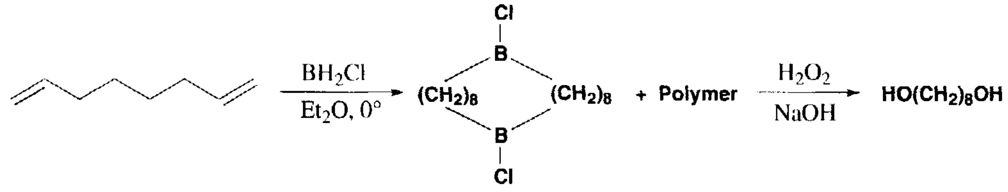
yielded an organoborane which was converted predominantly to 1,4-butandiol by oxidation with alkaline hydrogen peroxide.[61] 1,3-Pentadiene when similarly treated produced an intermediate which isomerized on heating. The isomerized intermediate afforded 1,5-pentanediol on oxidation.[62]

Disiamylborane[*bis*(3-methyl-2-butyl)borane] possesses a significantly greater selectivity over diborane for the terminal carbon atom of the double bond. This reagent is more advantageous for the hydroboration of simple terminal dienes when undesired side products are to be avoided.

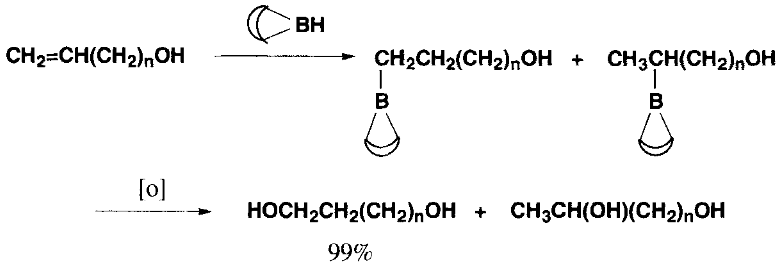
$$H_2C{=}CH(CH_2)_2CH{=}CH_2 \xrightarrow{[(CH_3)_2CHCHCH_3]_2BH} HO(CH_2)_6OH$$

1,5-Hexadiene on treatment with disiamylborane followed by oxidation of the resulting intermediate yielded 1,6-hexanediol in 93% yield.[63]

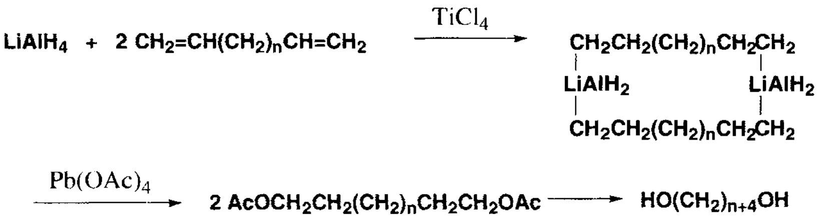
The boron heterocycle and polymer intermediates, produced during the hydroboration of α,ω-dienes with monochloroborane etherate, gave quantitative yields of α,ω-alkanediols on oxidation with alkaline hydrogen peroxide. For example, 1,7-Octadiene on treatment with monochloroborane etherate, (obtained by reaction of $LiBH_4$ with boron trichloride at 0° in ether) gave an 18-membered boron heterocycle which are oxidized quantitatively to 1,8-octanediol.[64]



Terminal alkenes containing a remote functional group are hydroborated with a remarkable regioselectivity (> 98% terminal) with 9-borobicyclo[3.3.1]nonane (9-BBN). 10-Undecenyl alcohol and 4-pentene-1-ol are hydroborated with 9-BBN; oxidation of the resulting intermediate afforded dihydroxy compounds[65,66] as shown.



Alkadienes were converted to alkanediols when hydroborated with $NaBH_4$ in the presence of $ZrCl_4$ or $TiCl_3$ and 18-crown-6 followed by oxidation of the inter-mediates.[67] Hydroalumination of α,ω-diolefins with $LiAlH_4$ in THF in the presence of $TiCl_4$ as catalyst produced dihydroaluminates as intermediate products.[68] Since reaction of the intermediates with oxygen was slow due to insolubility in THF, this was not a practical route to α,ω-diols. In contrast, treatment of the intermediates with lead (IV) acetate provided α,ω-diacetates which were successfully hydrolyzed to the corresponding diols.

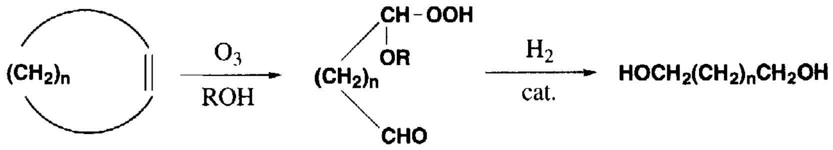


c) Reductive Cleavage of Ozonides

Compounds with ethylenic groups have been ozonized and treatment of the resulting ozonides without isolation, with $NaBH_4$ or $LiAlH_4$ give alcohols. The ozonolysis product of cyclohexene on treatment with $NaBH_4$ underwent reductive cleavage to 1,6-hexanediol and similar treatment of the ozonide from oleic acid with $LiAlH_4$ produced 1,9-nonanediol.[69]

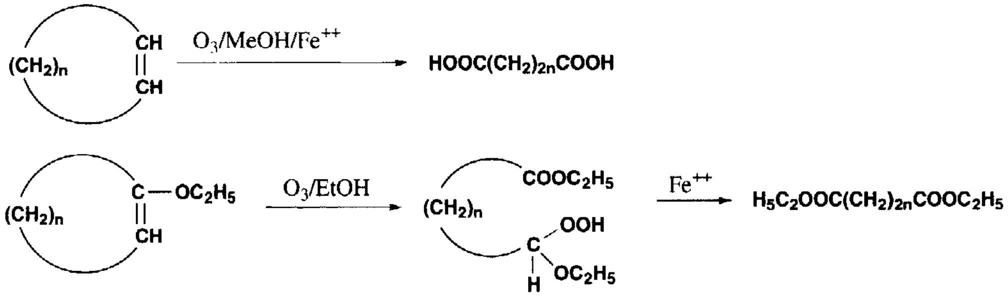
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[\text{2. LAH}]{\text{1. } O_3} CH_3(CH_2)_7CH_2OH + HO(CH_2)_9OH$$

Borane-dimethyl sulfide $[(CH_3)_2S{:}BH_3]$ is a milder but efficient reagent for the direct reduction of ozonides to alcohols in methylene chloride.[70] Treatment of the ozonide of methyl 10-undecenoate with 5 equivalents of $(CH_3)_2S{:}BH_3$ was led to 1,10-decanediol in 65% yield and, in similar fashion, cyclohexene ozonide with 4 equivalents of this reagent afforded 1,6-hexanediol in 95% yield. Hydroperoxides obtained from the ozonolysis of cyclic monoolefins can be catalytically hydrogenated at elevated temperature and pressure to α,ω-diols.[71] A two-stage hydrogenation of the ozonolysis product, first at low temperature (0-15°) and then at elevated temperature (35-100°) over platinum or Raney nickel catalysts, gave excellent yields of diols.[73]



d) Dimerization of Hydroperoxides

Higher α,ω-alkanediols may be obtained from alkoxyhydroperoxides by reaction with metal salts.[72] Alkoxyhydroperoxides, produced in the ozonolysis of olefins in alcoholic solution, are treated with ferrous sulfate. Radicals formed in the C-C bond scission undergo dimerization. Ozonides also react in the same manner. The alkoxyhydroperoxides produced by ozonolysis of olefinic monoesters afford, on treatment with ferrous sulfate, higher α,ω-dialkyl esters by dimerization of the radicals. Application of radical coupling reaction to cycloalkenes and cyclic enol ethers also affords higher α,ω-diesters. Reduction of these acids and esters by the methods described earlier in this review affords the higher diols.



8. From Alkynes

Hydrogenation of diacetylene glycols in the presence of iron group metals gives alkanediols in high yields. For example, 2,4-hexadiyne-1,6-diol was hydrogenated in methanol in the presence of Raney nickel to afford 1,6-hexanediol in 90% yield.[74]

II. SPECIAL METHODS

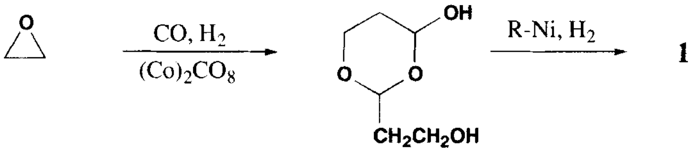
It is possible to prepare specific diols from a variety of precursors. The following examples illustrate the range of such possibilities in the context of the target diol. The suitability of a reaction sequence is based on several factors, such as availability of starting material, scale of preparation, experimental facility and expertise pertinent to specialized reactions involving high-pressure, bio-catalysts, etc.

1. 1,3-Propanediol [$HO(CH_2)_3OH$ (1)], bp. 210-211°.[3]

The aldehyde obtained by hydration of acrolein was hydrogenated over Raney nickel catalyst to produce **1**.[75]

$$CH_2{=}CHCHO \xrightarrow{\text{hydration}} HOCH_2CH_2CHO \xrightarrow{\text{R-Ni, H}_2} \mathbf{1}$$

Ethylene oxide was hydroformylated with CO and H_2 in the presence of dicobalt octacarbonyl to yield 2-(2-hydroxyethyl)-4-hydroxy-1,3-dioxane which was then hydrogenated over Raney nickel to **1**.[76] Ethylene oxide was also carbonylated to **1** with synthesis gas by heating in an autoclave in tetraglyme in the presence of a catalyst containing Rh and phosphine ligand, hydriodic acid, and hydroquinone.[77]



It has been observed that certain strains of *Lactobacillus brevis* and *L. buchneri* grow well in a mixture of glucose and glycerol. The glycerol is dehydrated to 3-hydroxypropanal which is subsequently anaerobically reduced to **1**.[78]

$$HOCH_2CHOHCH_2OH \longrightarrow CHOCH_2CH_2OH \longrightarrow \mathbf{1}$$

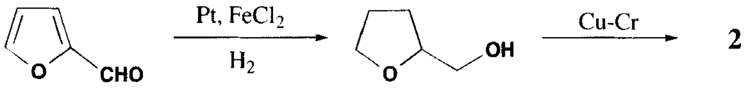
Ethyl glycidate is reduced with $LiAlH_4$ in ether to afford **1** along with the isomeric 1,2-glycol.[79]

The aldol product from the condensation of formaldehyde and acetaldehyde was hydrogenated over Raney nickel to 1,3-propanediol.[80]

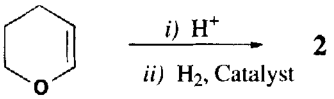
$$CH_3CHO + CH_2O \xrightarrow{K_2CO_3} OHCH_2CH_2CHO \xrightarrow{\text{R-Ni, H}_2} \mathbf{1}$$

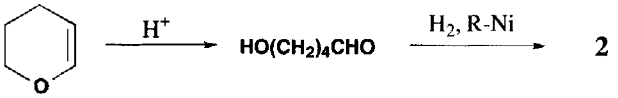
2. 1,5-Pentanediol [HO(CH_2)$_5$OH (2)], bp. 239.4°.[3]

Furfural was hydrogenated in 95% ethanol over Pt black and $FeCl_2$ to give 1,5-pentanediol in low yield; the tetrahydrofurfuryl alcohol, obtained as a major product, could be hydrogenated further in the presence of Cu-Cr catalyst to **2** in good yield.[81,82] When Na_2SiO_3 was used in this reaction as a chromite binder, tetrahydrofuran formation was suppressed and **2** is obtained in 90% yield.[83]

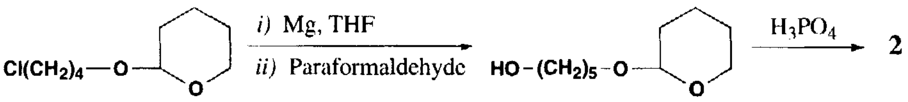


Hydrolysis of dihydropyran with dilute hydrochloric acid followed by hydrogenation over Ni on Kieselguhr at elevated temperature and pressure gave **2**[84] in 93% yield. Dihydropyran may also be hydrogenated in water over various other catalysts.[85] 5-Hydroxyvaleraldehyde, obtained by hydrolysis of 2,3-dihydropyran with Amberlite IR-120, was hydrogenated over Raney nickel to afford 86% of **2**.[86]

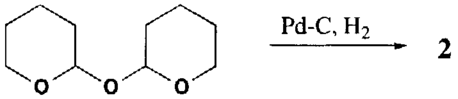




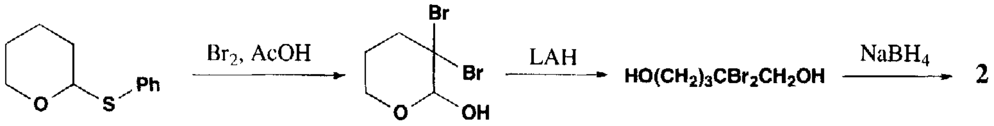
Reduction of 5-hydroxyvaleraldehyde by KBH_4-Al_2O_3 gave **2** in 93% yield.[87] The tetrahydropyranyl ether of ω-chlorobutanol on refluxing in THF with Mg followed by the addition of paraformaldehyde afforded an 80% yield of 5-hydroxypentyl tetrahydropyranyl ether, which on heating with H_3PO_4 gave **2**[88] in 90% yield.



Hydrogenation of *bis*(Tetrahydro-2-pyranyl)ether in water over palladized charcoal gave **2**[84] in 90% yield.

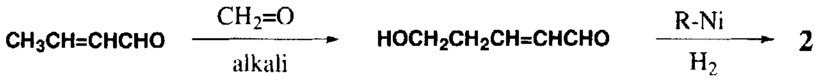


The action of bromine in acetic acid on phenyl 2-tetrahydropyranyl sulfide resulted in the formation of a crystalline dibromide along with a disulfide. Reduction of the dibromide with $LiAlH_4$ yielded 2,2-dibromo-1,5-pentanediol, which could be further reduced with $NaBH_4$ to **2**.[89]



The dye-sensitized photooxygenation of cyclopentadiene followed by hydrogenolysis of the resulting 4,5-epoxy-*cis*-2-pentanal over Raney nickel afforded **2** in moderate yield.[90]

Condensation of 2-butene-1-al with formaldehyde in the presence of an alkaline condensing agent followed by hydrogenation of the product over Raney nickel gave 1,5-pentanediol.[91]



$$CH_3CH{=}CHCHO \xrightarrow[\text{alkali}]{CH_2{=}O} HOCH_2CH_2CH{=}CHCHO \xrightarrow[H_2]{\text{R-Ni}} \mathbf{2}$$

3. 1,6-Hexanediol [$HO(CH_2)_6OH$ (3)], mp. 43°, bp. 243°.[3]

Reaction of acetylene with paraformaldehyde in the presence of cupric oxide in methanol provided propargyl alcohol. Further oxidative coupling of propargyl alcohol using cuprous chloride and ammonium chloride at 50-60° yielded 93% 1,6-hexa-2,4-diynediol, which was smoothly hydrogenated in presence of Raney nickel in methanol to **3** in quantitative yield.[92]

$$HC{\equiv}CH + (CH_2O)_3 \xrightarrow{CuO} HC{\equiv}CCH_2OH \xrightarrow[O_2,\ H_2O]{CuCl,\ NH_4Cl}$$

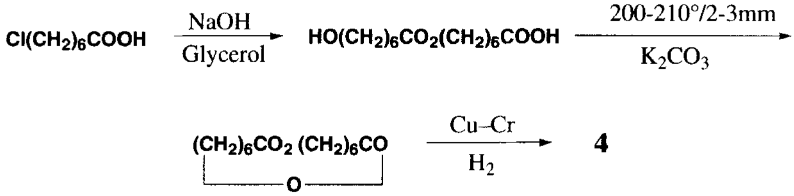
$$HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OH \xrightarrow{Ni,\ MeOH,\ H_2} \mathbf{3}$$

1,6-Hexanediol is obtained in moderate yield from different starting materials such as nitromethyltetrahydropyran,[93] hexamethylenediamine,[94] byproducts in liquid-phase oxidation of cyclohexane,[95] and 5-hydroxymethylfurfural.[96]

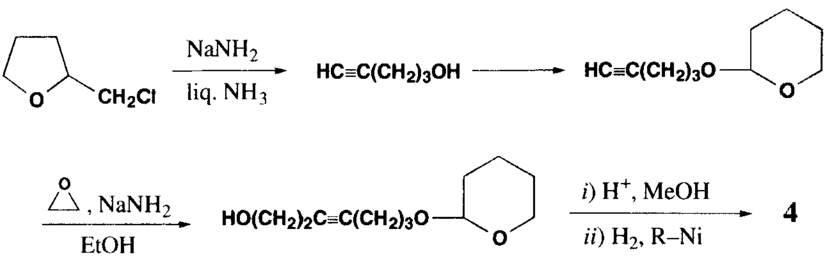
Biomass, a renewable resource[7] was hydrolyzed to provide 5-hydroxymethylfurfural which was hydrogenated in the presence of a catalyst to give 2,5-*bis*(hydroxymethyl)tetrahydrofuran, which on further hydrogenation afforded 1,6-hexanediol.[97]

4. 1, 7 - Heptanediol [HO(CH$_2$)$_7$OH(4)], mp. 20.2°, bp. 151°/14mm.[3]

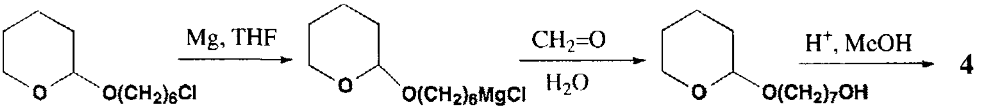
The half ester obtained from 7-chloroheptanoic acid was heated with potassium carbonate to give the lactone as one of the main products which, on hydrogenation over Cu-Cr catalyst at high temperature and pressure, yielded **4**.[98]



Treatment of tetrahydrofurfuryl chloride with sodamide in liquid ammonia provided pent-4-yn-1-ol, which was converted into tetrahydropyranyl ether. The chain was extended by treating the tetrahydropyranyl ether with ethylene oxide in the presence of sodamide to give 7-(2'-tetrahydropyranyloxy)hept-3-yn-1-ol. Removal of the tetrahydropyranyl group followed by hydrogenation with Raney nickel gave 1,7-heptanediol.[99]



The tetrahydropyranyl ether of 6-chlorohexanol was converted into a Grignard reagent which on treatment with formaldehyde afforded 7-tetrahydropyranyloxyheptane-1-ol, hydrolysis of the latter yielded **4**.[100]



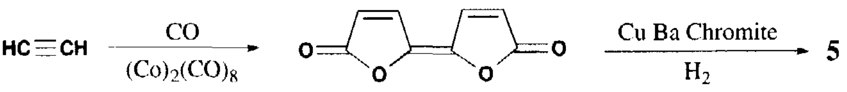
5. 1,8-Octanediol[$HO(CH_2)_8OH$(5)], mp. 62°, bp. 154-156°/12 mm.[3]

Reaction of 1-chloro-4-acetoxy-2-butene with powdered Fe in acetonitrile gave 1,8-diacetoxy-2,6-octadiene, which on refluxing with methanol containing a catalytic amount of hydrochloric acid, afforded 1,8-dihydroxy-2,6-octadiene. Hydrogenation of the latter furnished **5**.[101]

$$AcOCH_2CH{=}CHCH_2Cl \xrightarrow{Fe,\ CH_3CN} AcOCH_2CH{=}CH(CH_2)_2CH{=}CHCH_2OAc$$

$$\xrightarrow{MeOH,\ H^+} HOCH_2CH{=}CH(CH_2)_2CH{=}CHCH_2OH \xrightarrow{H_2} \mathbf{5}$$

Treatment of 1,3-butadiene with dimethyl benzylhydroperoxide in the presence of ferrous sulfate heptahydrate in acetone provided 1,8-*bis*(dimethylbenzyloxy)-2,6-octadiene, which was hydrogenated over Raney nickel. Acid-catalyzed decomposition of the hydrogenation products afforded **5**.[102] Treatment of acetylene with CO in presence of cobalt carbonyl resulted in the formation of dilactone, which was hydrogenated over CuBa chromite catalyst in dioxane to **5**.[103]



1,8-Octanediol was obtained from 1,8-*bis*(trifluorosilyl) octane by oxidation with *m*-chloroperbenzoic acid in DMF[104]

$$F_3Si(CH_2)_8SiF_3 \xrightarrow{McPBA,\ DMF} \mathbf{5}$$

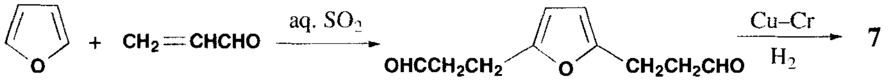
1,8-Octanediol can also be obtained by electrolysis of α-chloroadipic acid.[38]

6. 1,9-Nonanediol [$HO(CH_2)_9OH$ (6)], mp. 43°, bp. 173°/14 mm.[3]

Reductive cleavage of the ozonolysis product of oleic acid with $LiAlH_4$ gave **6**.[67] 1,9-Nonanediol has also been prepared by hydrogenation of 1,9-nonanedial using Ni- or Ru-type catalysts.[45]

7. 1,10-Decanediol [$HO(CH_2)_{10}OH$ (7)], mp. 72-74°, bp. 179°/15 mm.[3]

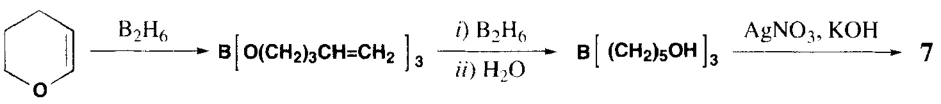
2,5-Furanodipropionaldehyde, obtained by reaction of acrolein with furan in aqueous SO_2, afforded 1,10-decanediol (**7**) by hydrogenation over Cu-Cr.[105]



Propargyl alcohol reacted with 1,4-dichloro-1,3-butadiene in the presence of NaCl-CuCl yielding decan-5-ene-2,8-diyne-1,10-diol, which was hydrogenated to yield **7**.[106]

$$HCC{\equiv}CH_2OH + ClCH{=}CHCH{=}CHCl \xrightarrow{NaCl\text{–}CuCl} HOCH_2C{\equiv}CCH_2CH{=}CHCH_2C{\equiv}CCH_2OH \xrightarrow{H_2} \mathbf{7}$$

Heating the hydroboration product of 2,3-dihydropyran in a sealed tube at 200° followed by treatment with diborane, then by water gave the hydroxy product which afforded **7** on treatment with $AgNO_3$ and 10% KOH.[107]



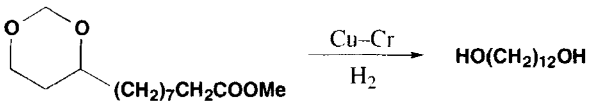
Diol **7** was formed when ricinoleyl alcohol, obtained by $LiAlH_4$ reduction of methyl ricinoleate was subjected to alkaline cleavage with aqueous NaOH in 2-octanol.[108]

8. 1,11-Undecanediol [$HO(CH_2)_{11}OH$ (8)], mp. 63°.[3]

Reduction of undecylenic acid ester $CH_2{=}CH(CH_2)_8CO_2Et$, with diisobutylaluminum hydride and followed by oxidation of the intermediate product in the stream of nitrogen and oxygen gave 1,11-undecanediol (**8**).[109]

9. 1,12-Dodecanediol[$HO(CH_2)_{12}OH$ (9)], mp. 79-89.5°, bp. 175-180°/3mm.[111]

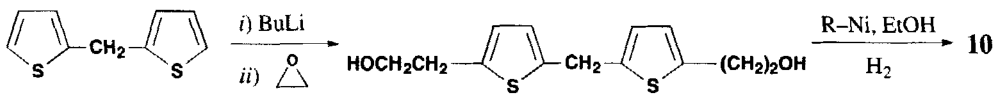
The acid products obtained in the condensation of undecylenic acid with formaldehyde in the presence of sulfuric acid were esterified with methanol to give 4-(8-carbomethoxyoctyl)-1,3-dioxane as a major product. Hydrogenation of this compound over Cu-Cr catalyst afforded **9**.[111]



Electrolysis of a mixture of monoesters of malonic and sebacic acids in methanol containing a catalytic amount of sodium methoxide gave dodecanedioic acid which on reduction with $LiAlH_4$ gave **9**. In the same electrolysis, octadecamethylene glycol also was obtained.[112] Additive trimerization of 1,3-butadiene in ethanol followed by hydrogenation gave **9** in low yield.[110]

10. 1,13-Tridecanediol [$HO(CH_2)_{13}OH$ (10)], mp. 75-77°.[3]

Di-2-thienylmethane when treated with two equivalents of *n*-butyllithium in ether, followed by treatment with ethylene oxide, gave *bis*[5-(2-hydroxyethyl)-2-thienyl] methane. The latter on hydrogenolysis by refluxing with Raney nickel in ethanol afforded **10** in good yield.[113]

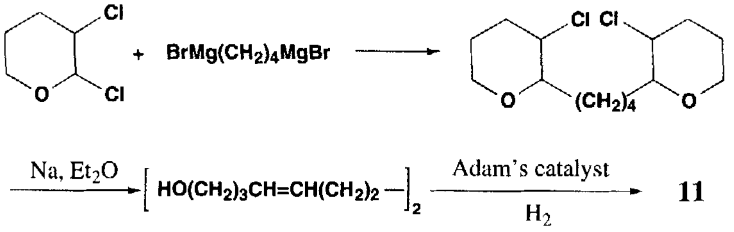


11. 1,14-Tetradecanediol [HO$(CH_2)_{14}$OH (11)], mp. 84-85°.[3]

Treatment of ustilic acid with commercial sodium bismuthate in acetic acid and subsequent hydrogenation of the resulting oily product over Raney nickel yielded **11.**[114]

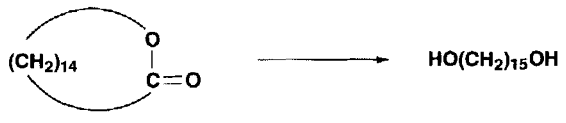
$$HO_2CCHOH(CH_2)_{12}CHOHCH_2OH \xrightarrow[ii)\ \text{Raney-Ni, EtOH, } H_2]{i)\ NaBiO_3,\ AcOH} HO(CH_2)_{14}OH$$

2,3-Dichlorotetrahydropyran was treated with an excess of the double Grignard reagent from 1,4-dibromobutane to give a mixture of stereoisomeric 1,4-*bis*-(3-chlorotetrahydropyran-2-yl) butanes as the major product. Treatment of this mixture with sodium in ether led to ring scission to give tetradeca-4,10,-diene-1,14-diol, which on hydrogenation in the presence of Adams' catalyst yielded **11.**[115]



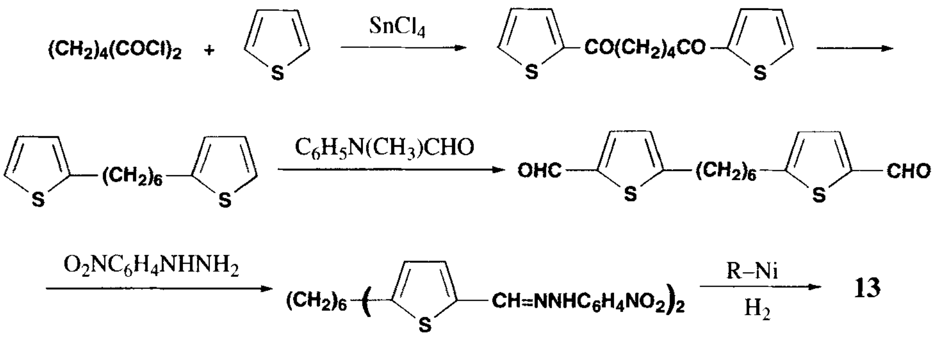
12. 1,15-Pentadecanediol [HO$(CH_2)_{15}$OH (12)], mp. 87-88°.[42]

Pentadecanolide is reduced with triisobutyl aluminumhydride to **12** in 83% yield.[42]



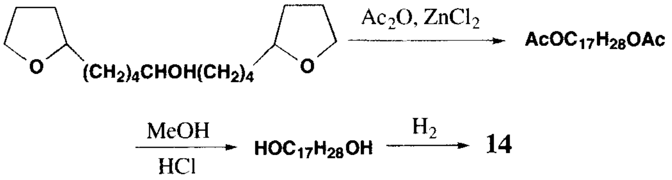
13. 1,16-Hexadecanediol [HO$(CH_2)_{16}$ (13)], mp. 91.5-92.7°.[116b]

Electrolysis of a mixture of 9-acetoxynonanoic acid and monoethyl azeleate in a steel vessel serving as the cathode and provided with a Pt anode in water containing K_2CO_3 followed by saponification with alcoholic KOH gave **13.**[116a] The saponified product also contains 1,16-hexadecanedioic acid, its potassium salt and 16-hydroxyhexadecanoic acid which may be further utilized to prepare **13.** Adipoyl chloride and thiophene in the presence of stannic chloride gave 1,4-*bis*(2-thenoyl)butane which by Wolff-Kishner reduction afforded 1,6-*bis*(2-thienyl)hexane. Subsequent formylation with N-methylformanilide produces 1,6-*bis*(2-formyl-5-thienyl)hexane. The *bis*(p-nitrophenylhydrazone) derivative of the latter on treatment with Raney nickel yielded 1,16-hexadecanediol.[116b]



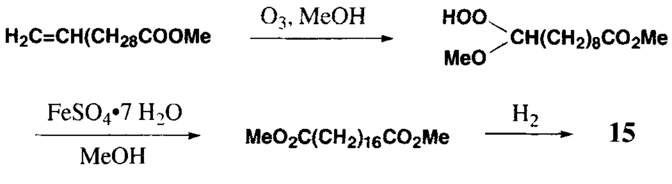
14. 1,17-Heptadecanediol[HO(CH$_2$)$_{17}$OH(14)], mp. 96.5°, bp. 215-220°/10mm.[117]

1,9-*bis*(Tetrahydro-2-furyl)-5-hydroxynonane when heated with acetic anhydride in the presence of zinc chloride gave heptadecatriene-1,17-diol diacetate. The diacetate was refluxed with alcoholic HCl to afford the corresponding diol, which was further hydrogenated to **14**.[117]



15. 1,18-Octadecanediol [HOCH$_2$)$_{18}$OH (15)], mp. 97-98°.[3]

Methyl undecylenate was subjected to ozonolysis in methanol and the intermediate methoxy hydroperoxide was treated with ferrous sulfate heptahydrate in methanol to give dimethyl hexadecanedicarboxylate,[118] which may be further reduced to give **15**.



Oleyl alcohol was hydroborated in *bis*(2-ethoxyethyl) ether with diborane generated externally from NaBH$_4$ and BF$_3$ etherate. The reaction product was then heated to 160° and then oxidized with alkaline hydrogen peroxide to give 1,8-octadecanediol.[119]

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH \xrightarrow[ii)\ BF_3{\bullet}Et_2O]{i)\ (EtOCH_2CH_2)_2O,\ B_2H_6} \mathbf{15}$$

$$iii)\ aq.\ NaOH,\ H_2O_2$$

16. 1,19-Nonadecanediol [$HO(CH_2)_{19}OH$ (16)], mp. 95-96.°[120]

The Grignard reagent from 1,9-dibromononane was treated with N-methylglutaramide and the product thus obtained was hydrolyzed to the corresponding diketo diacid which was then

$$\mathrm{BrMg(CH_2)_9MgBr} \xrightarrow{\mathrm{MeNHCO(CH_2)_3CONHMe}} \mathrm{MeNHCO(CH_2)_3CO(CH_2)_9CO(CH_2)_3CONHMe}$$

$$\xrightarrow{5\%\ \mathrm{H_2SO_4}} \mathrm{HO_2C(CH_2)_3CO(CH_2)_9CO(CH_2)_3CO_2H}$$

$$\xrightarrow[\mathrm{H_2NNH_2H_2O}]{\mathrm{Na,\ (CH_2OH)_2}} \mathrm{HO_2C(CH_2)_{17}CO_2H} \xrightarrow[ii)\ \mathrm{LAH}]{i)\ \mathrm{EtOH,\ H^+}} \mathrm{HO(CH_2)_{19}OH}$$

subjected to Wolff-Kishner reduction. The resulting heptadecamethylene diacid was esterified and the new diester was reduced with $LiAlH_4$ to **16.**[120]

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