the Phoenix, AZ area, and give some 1969 projected costs, somewhat obsolete unless corrected for inflation.

While the volumes of ethoxylated alcohols used today are still relatively small, increased usage is sure to develop, despite the fact that very small quantities of retardant are employed per pound of water saved. Those areas of the world with already critical water supplies – Israel, Egypt, North Africa, India, and to a lesser extent Arizona, New Mexico and southern California in the U.S. – are certain to benefit from this use of specially tailored film-forming fatty acid derivatives. Our children are sure to be the chief beneficiaries.

There are other applications, largely unexplored, for this kind of usefulness which may be very valuable in agriculture. Consider the control of water loss through transpiration from plants and fruits by a thin monomolecular film coating; also, even potentially greater, consider the possibility of the control of evaporation from the soil surface by thin monomolecular films for those rain deficient countries that suffer from late spring or summer droughts. Both of these have potentially the greatest significance.

REFERENCES

1. Anon., A Season to Burn Bright, Chem. Week, December 18, 1965, pp. 59-61.
2. Hercules Powder Co., Fine and Paper Chemicals Dept., "Aquapel," 1963; C.H. Chapman (to Hercules Powder Co.) U.S. Pat. 2,369,919, February 20, 1945.
3. Weaver, J.W., H.A. Schuyler, J.G. Frick, Jr., and J.D. Reid, J. Org. Chem. 16:1111 (1951); A.W. Baldwin and E.E. Walker (to ICI, Ltd.) U.S. Pat. 2,146,392, February 7, 1939.
4. Iler, R.K., (to E.I. duPont de Nemours & Co.) U.S. Pat. 2,273,040, Feb. 17, 1942.
5. Anon., Sales Spurt Puts New Zip into Fabric Softeners, Chem. Week, December 30, 1969, pp. 36-37.
6. Anon., New Way to Add Soft Touch to the Washing, Chem. Week, March 1, 1972, p. 22.
7. Anon., Open Road for Concrete Additives, Chem. Week, January 15, 1966, pp. 71-74.
8. Anon., Chem. Eng. News, Oct. 31, 1966, p. 48.
9. Anon., Chem. Eng. News, December 24, 1962, pp. 28-29.
10. Suzuki, M., K. Chigasaki, Y. Shimochara, Y. Mihara, M. Coka, and T. Tomioka, (to Nikken Chemicals Co., Ltd.) U.S. Pat. 3,146,059, August 25, 1964.
11. Great Lakes Biochemical Co., Inc. (Milwaukee, WI) Practical Uses of Newly Created Evaporation Retardants for Evaporation Control and Transpiration Control.
12. Reiser, C.O., Ind. Eng. Chem., Proc. Design Dev. 8(1):63 (1969).

Fatty Alcohols

J.A. MONICK, Colgate-Palmolive Co.,
909 River Road, Piscataway, NJ 08854.

ABSTRACT

"Fatty" or higher alcohols are mostly C_{11} to C_{20} monohydric compounds. In probably no other homologous aliphatic series is the current balance between natural and synthetic products so vividly evident. Natural sources, such as plant or animal esters (waxes), can be made to yield straight chain (normal) alcohols with a terminal (primary) hydroxyl, along with varying degrees of unsaturation. In the past, so-called fatty alcohols were prepared commercially by three general processes from fatty acids or methyl esters, occasionally triglycerides. Fatty acids add hydrogen in the carboxyl group to form fatty alcohols when treated with hydrogen under high pressure and suitable metal catalysts. By a similar reaction, fatty alcohols are prepared by the hydrogenation of glycerides or methyl esters. Fatty alcohols are also prepared by the sodium reduction of esters of fatty acids in a lower molecular weight alcohol. The sodium reduction method was ordinarily too expensive; it was displaced early by the other methods; finally most unsaturated alcohols made by this route were largely replaced. Methyl ester reduction continues to provide perhaps 20% of the saturated fatty alcohols, and selective hydrogenation with the use of special catalysts such as copper or cadmium oxides was developed for the production of oleyl alcohol. Synthetic or petroleum technology for long chain alcohols include the Ziegler process, useful for straight chain, even-numbered saturated products. A second is the carbonylation and reduction of olefins affording medium or highly branched chain alcohols. Paraffin oxidation affords mixed primary alcohols. Fatty alcohols undergo the usual reactions of alcohols. They may be reacted with ethylene oxide to yield a series of polymeric polyoxyethylene alcohols or with acetylene under pressure to yield vinyl ethers or with vinyl acetate to give vinyl ethers.

INTRODUCTION AND HISTORY

Background

The term "fatty alcohols" has become synonymous with "higher alcohols," which is that class of monohydric aliphatic alcohols containing six or more carbon atoms, and derived from either natural or synthetic sources. The common usage of "fatty alcohols" is for those higher alcohols derived from natural fats or petroleum feed stocks, independent of the method of synthesis or procurement. The two major natural groupings of alcohols are the "coconut alcohols" and "tallow alcohols" which, of course, reflect their origin. Alcohols from petrochemical origin are usually called "synthetic higher alcohols." Here again we have a subdivision that reflects on the chemical process for synthesis and we obtain "Oxo alcohols," "Ziegler alcohols," etc.

Alcohols are also classified according to their market usage. The principal market for primary alcohols between six and eleven carbon atoms is the plasticizer ester industry. The major use of higher alcohols with eleven or more carbon atoms is the detergent industry. Therefore, a logical subdivision of alcohols could be "plasticizer-range alcohols (C_6-C_{10})" and "detergent-range (C_{11} and up) alcohols." This division at C_{11} is arbitrary and crossover of alcohols does occur; C_{13} Oxo alcohol is used to make phthalate plasticizers, and a small amount of C_8-C_{10} alcohols is used to make nonionic surfactants for industrial cleaning.

History and Sources

The knowledge of fermentation to produce ethyl alcohol goes back about 6,000 years. This is long before any written records, and makes ethanol one of the oldest known organic chemicals. Alcohols have two parents: "mother nature" for many centuries and "father science" for less than two. During the last 200 years, nature and science produced alcohols with a wide variety of molecular configuration and character. Simple saturated aliphatic alcohols, such as methanol and ethanol, rarely are found as such in nature. Higher primary monohydric acyclic alcohols of 7, 8, 9, 10, and 12 carbon atoms occur to a limited extent in the oil of leaves, flowers, and fruit. Since they have a characteristic odor, they are valuable ingredients for compounded perfumes.

Natural Sources

Alcohols in combined form are many, many times more prevalent in nature than the free compounds. Esters of n-hexyl, and n-octyl alcohols are found in certain plant oils, and the caprylic ester of n-nonyl alcohol occurs in orange-flower oil. Esters of the higher, saturated, aliphatic monohydric alcohols are quite ubiquitous in nature; for example, cetyl palmitate is the chief ingredient of spermaceti; ceryl cerotate is found in Chinese wax; myricyl palmitate in beeswax; and montanyl and gossypyl alcohols in American cotton wax.

The most important combined alcohol is glycerol, which is an essential ingredient of animal and vegetable fats. These triglycerides contain C_{12} to C_{18} fatty acids which can be released as such, or converted to methyl esters prior to conversion to fatty alcohols.

Hydrolysis of Organic Esters. In past decades, the wax esters in sperm oil from whales have been a commercial source of higher monohydric fatty alcohols. Sperm whale oil has from 66-74% esters of higher alcohols and acids, which includes 10% spermaceti (essentially cetyl palmitate) which can be removed by chilling. The remainder is mostly triglycerides, and wax esters. Treating this fraction with hot concentrated caustic solution will saponify the esters to form soaps of the fatty acids and the free alcohol.

When this reaction mixture is distilled at reduced pressures, fatty alcohols go into the overhead, leaving soap as bottoms. The fatty alcohol fraction is mostly cetyl, oleyl, and arachidyl, and comprises ca. 30% of the original oil. This process was employed in Europe and Japan, and produced alcohols which were exported to the United States. However, the U.S. Department of the Interior in 1970 placed eight species of whale (including Sperm whale) on the "endangered species" list and banned importation of oil, meat or other products derived from them.

Wool grease is refined and saponified to yield a complex mixture of alcohols, diols and sterols. This mixture is valuable for use in cosmetics and is sold as such under the composite name of lanolin. Further modification such as ethoxylation produces a mixture that is easier to handle and blend with other components.

Reduction of esters. Since the early 1900s, starting with Bouvealt and Blanc, a specific chemistry and technology has been developed for the reduction of natural and synthetic esters to the corresponding alcohols. Common starting materials with industrial value are tallow, lard, coconut oil, sperm oil, palm kernel oil, castor oil, and fish oils. While the fatty acid portion of esters is usually a random mixture of varying carbon chain lengths and degrees of unsaturation, nevertheless fairly uniform blends of fatty alcohols from tallow and coconut are commercially produced.

Natural fatty alcohols are predominantly straight chain primary alcohols that consist almost entirely of an even number of carbon atoms. Most synthetic processes that do not start with natural materials produce higher alcohols which have some branched chains and substantial amounts of odd-carbon chain length. An important exception to this statement, however, is the fairly recent "Alfol" process which produces straight chain, even-carbon alcohols via Ziegler chemistry with alkylaluminum catalysts. Two reduction processes, based on natural starting materials, have attained commercial importance in the United States.

Sodium reduction process. Reduction of esters with metallic sodium (in the presence of a reducing alcohol) was discovered by Bouvealt and Blanc in 1903, and further improved by Hausley and Peddicord. While DuPont originated a working process in the United States, it was Proctor and Gamble who first produced fatty alcohols commercially by sodium reduction in 1942. This process maintains original unsaturated bonds, and produces unsaturated alcohols.

High pressure hydrogenolysis process. Since the mid 1950s, catalytic hydrogenation has replaced sodium reduction as a better economic route to fatty alcohols. Again, alkali refining and drying are needed to remove fatty acids and moisture. Since the use of glycerides causes contamination problems, process trends have been towards the use of fatty acids, as starting materials, and in the last two decades to methyl esters.

Synthetic Sources

Alcohols from natural sources tend to be variable in composition and expensive and difficult to purify; therefore, considerable incentive existed to develop synthetic methods for special alcohols.

Aldol condensation. Aldehydes or ketones with a hydrogen atom on the carbon adjacent to the carbonyl group can be condensed to β-hydroxy aldehydes or ketones, respectively. Dehydration, followed by catalytic hydrogenation, then forms the alcohol.

Oxo (hydroformylation) reaction. In general, an olefin is reacted with carbon monoxide and hydrogen in the presence of a catalyst and under high pressure. The aldehyde mixture produced is reduced with hydrogen to the corresponding alcohols. Commercially, each manufacturing process uses unique technology in terms of catalyst, process conditions, byproduct formation and purification.

The Ziegler Process. Here we produce straight chain normal alcohols by addition of ethylene to triethylaluminum. In various steps, trialkylaluminum is formed, which is converted to the corresponding aluminum alkoxide by air oxidation. Hydrolysis then leads to a mixture of linear primary alcohols.

CHEMICAL AND PHYSICAL PROPERTIES

Chemical Reactions

Chemical reactions of alcohols are essentially related to the hydroxyl group and its position in the molecule. Additional influence is exerted by the presence of other functional groups, and also by the nature of the hydrocarbon backbone. Alcohols are neutral compounds and do not ionize in water. However, they can act as acids by reacting with alkali metals. They also function as bases by reacting with strong acids. The most basic alcohols are the tertiary ones because the alkyl groups donate electrons to the carbon where oxygen is attached. This electron transfer increases electron density at the oxygen atom and makes it more attractive toward a proton, thereby making it more basic. Characteristic chemical reactions are alphabetically presented.

Alkylation. A unit process whereby an alkyl or aralkyl group is introduced into a compound by addition or substitution. Primary alcohols alkylate most readily; secondary alsochols require more drastic operating conditions; and tertiary alcohols are not considered to be practical alkylating agents. Alcohols are alkylated by alkyl sulfates in the presence of a base to form ethers. One alkyl group is usually added, but both groups can react if concentration and temperature are increased:

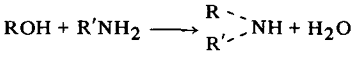
$$ROH + (CH_3)_2SO_4 + NaOH \longrightarrow ROCH_3 + NaCH_3SO_4 + H_2O$$

$$2ROH + (CH_3)_2SO_4 + 2NaOH \longrightarrow 2ROCH_3 + Na_2SO_4 + 2H_2O$$

Ammonolysis and aminolysis. Alcohols generally react with ammonia to give amines and with amines to give further alkylation products:

$$ROH + NH_3 \longrightarrow RNH_2 + H_2O$$

alkylamine



$$ROH + R'NH_2 \longrightarrow \begin{matrix}R\\R'\end{matrix}\!>NH + H_2O$$

dialkylamine

Dehydration. Dehydration of alcohols may proceed in two directions: an intramolecular step to produce alkenes (olefins)–

$$RCH_2CH_2OH \longrightarrow RCH = CH_2 + H_2O$$

alkene

or an intermolecular route to form ethers–

$$2ROH \longrightarrow ROR + H_2O$$

ether

While both products tend to be formed in the course of a reaction, conditions can be varied to favor one route over the other. The most important factor is temperature, with higher temperatures favoring alkene formation. Distillation of monohydric alcohols with dehydrating agents such as phosphorus pentoxide, sulfuric acid, zinc chloride, boron trioxide, or oxalic acid will remove one molecule of water and form the correspondence olefin. Secondary alcohols dehydrate more readily than primary ones, while tertiary alcohols dehydrate more than secondary ones. The Saytzeff rule indicates that in dehydration of alcohols, hydrogen is eliminated preferentially from the adjacent carbon atom that is poorer in hydrogen. Dehydration of alcohols is suitable for industrial preparation of alkenes; some dihydric alcohols can also be converted to diolefins. Hydrobromic acid of 48% concentration is useful for laboratory dehydration.

Dehydrogenation. Primary saturated alcohols are dehydrogenated to aldehydes by passing alcoholic vapors over heated catalysts such as finely divided copper, nickel, zinc, or aluminum:

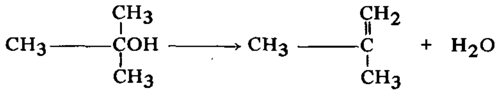
$$CH_3CH_2OH \xrightarrow{200\ C} CH_3CHO + H_2$$

acetaldehyde

In a similar manner, secondary alcohols form ketones, while tertiary alcohols become olefins:

$$CH_3CHOHCH_3 \xrightarrow{250\ C} CH_3COCH_3 + H_2$$

2-propanol acetone



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OH \longrightarrow CH_3-\overset{\displaystyle CH_2}{\underset{\displaystyle CH_3}{\overset{\|}{\underset{|}{C}}}} + H_2O$$

tert-butyl alcohol isobutylene

In general, the dehydrogenation reaction is endothermic, and requires high temperatures for a favorable equilibrium.

Ester formation. Esters, in the simplest sense, are nonionic organic compounds formed by the elimination of water from an acid and alcohol:

$$ROH + R'\ COOH \rightleftharpoons R'\ COOR + H_2O$$

Esterification is an equilibrium reaction except for the production of a monoester from an acid anhydride. Since equilibrium is reached slowly, an acid catalyst such as sulfuric acid, toluenesulfonic acid, boron trifluoride, or dry hydrochloric acid is normally used. The reaction can be driven to completion by upsetting the equilibrium in the following ways: (a.) large excess of alcohol, (b.) large excess of acid, or (c.) removal of water as an azeotrope.

The rate of esterification is influenced by the position of hydroxyl groups along the chain. For example, primary and secondary alcohols will react with acetic acid at 155 C to form esters. Under similar conditions, a tertiary alcohol will lose water and form an olefin. Esterification of alcohols with acid derivatives (such as acid chlorides, acid anhydrides, and simple alkyl esters of acids) is similar to the reaction with organic acids. Reaction with an acid halide is rapid and normally requires no catalyst:

$$ROH + R'COCl \rightleftharpoons R'COOR + HCl$$

acid halide ester

$$ROH + R'COOCH_3 \rightleftharpoons R'COOR + CH_3OH$$

alkyl ester ester

Acid anhydrides react irreversibly with alcohols to form esters:

$$ROH + (R'CO)_2O \longrightarrow R'COOR + R'COOH$$

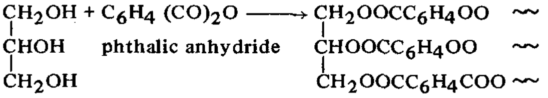
anhydride ester acid

Esterification of an alcohol with acids, or acid derivatives, is the principal type of reaction involved in resin formation. In the synthesis of acrylic esters, the "R" group may vary from methyl through lauryl (C_{12}):

$$ROH + CH_2 = CHCOOH \longrightarrow CH_2 = CHCOOR + H_2O$$

acrylic acid acrylic ester

Production of alkyl resins is based on the esterification reaction:



$$\begin{array}{lcl} CH_2OH + C_6H_4\ (CO)_2O & \longrightarrow & CH_2OOCC_6H_4OO \sim \\ | & & | \\ CHOH \quad \text{phthalic anhydride} & & CHOOCC_6H_4OO \sim \\ | & & | \\ CH_2OH & & CH_2OOCC_6H_4COO \sim \end{array}$$

Polyester formation starts with the resin esterification step:

$$HOCH_2CH_2OH + HOOC\ (CH_2)_4\ COOH$$

ethylene glycol adipic acid

$$\longrightarrow -CH_2CH_2OOC\ (CH_2)_4\ COO- \ + 2H_2O$$

polyester

Alcohol reacts with acetylketene by an addition mechanism to produce an acetoacetate:

$$ROH + CH_3COCH = C = O \longrightarrow CH_3COCH_2COOR$$

acetylketene acetoacetate derivative

The urethane series of derivatives are esters which are useful for the identification of alcohols by means of the formation of phenyl-α-naphthyl-, carbamyl-, and *p*-nitrophenyl-urethanes.

$$ROH + ArN = C = O \longrightarrow ArNHCOOR$$

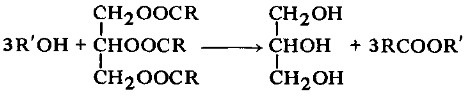
substituted carbamate

Tertiary alcohols are usually dehydrated to olefins by isocyanates, in contrast to primary and secondary alcohols which undergo the above reaction.

Ester interchange. Exchange of alkoxy groups between esters and alcohols (also known as alcoholysis, transesterification, or reesterification) is used in preparing both low molecular weight esters and glycerol from naturally occurring fats and oils by treatment with lower alcohols. The general reaction is:

$$ROH + R'COOR'' \longrightarrow R''OH + R'COOR$$

Alcoholysis of a glyceride can be represented as:



$$3R'OH + \begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOR'$$

ester glycerol new ester

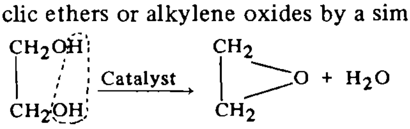
Acid or basic catalysts are used to speed the alcoholysis reaction, which also proceeds more readily with lower alcohols (C_1 - C_4).

Ether formation. As mentioned under dehydration, the intermolecular dehydration of alcohols will lead to ethers:

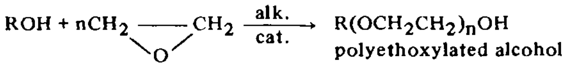
$$2ROH \longrightarrow ROR + H_2O$$

ether

In contrast to intramolecular dehydration, ether formation is favored by lower temperatures. Typical catalysts are sulfuric acid, phosphoric acid, boron trioxide, methionic acid, or benzenesulfonic acid, and they are usually employed in a liquid phase environment. A vapor phase operation can be employed over alumina, thoria, titania, or promoted copper. Di- and polyhydric alcohols form cyclic ethers or alkylene oxides by a similar route:

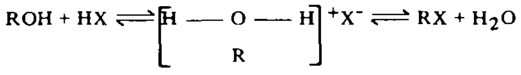


Ethoxylation. The reaction of alcohols with ethylene oxide gives polymeric products in which many units of the ethoxy group ($-CH_2CH_2O-$) are incorporated:



Ethylene oxide adducts of linear alcohols are made commercially where the molar quantity of EO varies from n=1 to n=40. Propylene oxide gives a similar product mix. Commercial products are mostly based on mixed alcohols. A large end use is as feed stock for ethoxy sulfates.

Halogenation. Replacement of hydroxy group by halogens forms halide derivatives. Several reagents can affect this change, the most useful being halogen acids, thionyl chloride, and phosphorus tri- and pentahalides. Reaction of an alcohol with a halogen acid is believed to proceed via the formation and decomposition of an oxonium salt:



$$ROH + HX \rightleftharpoons \left[H - \underset{R}{O} - H\right]^+ X^- \rightleftharpoons RX + H_2O$$

Position of the hydroxyl group affects the ease of replacement; the order of decreasing activity is tertiary, secondary, primary. The particular halogen used in the reaction also influences the reaction rate; the sequence of decreasing activity is iodide, bromide, chloride. An important application of this reaction is preparation of high molecular weight halides.

Phosphorus tri- and pentahalides will generally form a halide derivative:

$$3ROH + PCl_3 \longrightarrow 3\ RCl + P(OH)_3$$

However, conditions can be established in which alkyl phosphites are formed:

$$3ROH + PCl_3 \longrightarrow 3HCl + P(OR)_3$$

Tertiary alcohols invariably form alkyl halides; secondary alcohols react to form alkyl halides and phosphites; and primary alcohols form phosphites with PCl_3, and an alkyl halide with PBr_3. Thionyl chloride gives analogous reactions to those obtained with tri- and pentahalides:

$$ROH + SOCl_2 \longrightarrow RCl + HCl + SO_2$$

Oxidation. Oxidation is the process whereby oxygen is introduced into, or hydrogen removed from an organic compound by means of an oxidizing agent. Partial oxidation of alcohols may result in valuable compounds, but this requires close control of operating conditions and of the oxidation catalyst.

Primary alcohols may be oxidized to aldehydes, and the reaction may further proceed to the acid:

$$\underset{\text{primary alcohol}}{RCH_2OH} \xrightarrow{+O} \underset{\text{aldehyde}}{RCHO} + H_2O \xrightarrow{+O} \underset{\text{acid}}{RCOOH} + H_2O$$

Secondary alcohols are oxidized to ketones:

$$\underset{\text{secondary alcohol}}{RCHOHR'} \xrightarrow{+O} \underset{\text{ketone}}{RCOR'} + H_2O$$

Tertiary alcohols are quite stable in the presence of oxidizing agents in alkaline or neutral solution, but dehydrate to alkenes in acid solution. The alkenes can be further oxidized with a consequent breaking of the carbon chain:

$$RR'R''COH \longrightarrow \text{Dehydration, or no reaction}$$

Reaction with metals. Alkali metals (sodium, potassium, or calcium) replace hydrogen on hydroxyl groups to form a metal alkoxide (alcoholate) and hydrogen gas:

$$2ROH + 2Na \longrightarrow \underset{\text{sodium alkoxide}}{2RONa} + H_2\uparrow$$

Aluminum and magnesium may also be made to form alkoxides, but they require a catalytic action via amalgamation and traces of carbon tetrachloride. Dissolving sodium or potassium hydroxide in strong alcohol forms an alkoxide, but an excess of water will reverse the reaction:

$$ROH + NaOH \rightleftharpoons RONa + H_2O$$

Sodium peroxide reacts with alcohol to form an alkoxide and sodium hydroperoxide:

$$ROH + Na_2O_2 \longrightarrow \underset{\text{sodium alkoxide}}{RONa} + \underset{\text{sodium hydroperoxide}}{NaOOH}$$

The hydroxyl hydrogen is most reactive on a primary alcohol, then decreases in activity as it occurs on secondary and tertiary alcohols. Consequently, the reaction with tertiary alcohols requires increased temperature and longer reaction time.

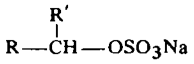
Sulfation and sulfonation. The preparation of straight chain sulfated alcohols requires the action of sulfuric acid, sulfur trioxide, or chlorosulfonic acid on higher alcohols:

$$ROH + H_2SO_4 + SO_3 \longrightarrow ROSO_3H + H_2SO_4$$

$$ROH + \underset{\text{chlorosulfonic acid}}{ClSO_3H} \longrightarrow \underset{\text{alkyl sulfate}}{ROSO_3H} + HCl$$

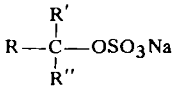
Clark and Malkemus have reported on sulfonation of alcohols by the use of sulfamic acid to form $R\text{-}SO_3$ Na. Gilbert and Jones give examples of sulfonation agents for a variety of starting alcohols. Unsaturated alcohols require special sulfating agents and conditions such as pyridine plus SO_3.

Since many alcohols have branched chains with an-OH group in secondary or tertiary position, secondary alkyl sulfates have been widely studied in Europe. Following are structural representations of several important variations:



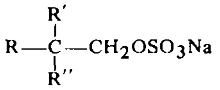
$$R-\overset{R'}{CH}-OSO_3Na$$

Secondary aliphatic sulphate, in which R is a long aliphatic chain, usually containing not less than eight carbon atoms.



$$R-\overset{R'}{\underset{R''}{C}}-OSO_3Na$$

Tertiary aliphatic sulphate, in which R, R', and R″ are all methyl or larger aliphatic groups, the total number of carbon atoms usually being at least twelve.



$$R-\overset{R'}{\underset{R''}{C}}-CH_2OSO_3Na$$

Branched chain primary aliphatic sulphate, normally saturated, in which R, R', and R″ may themselves be branched.

Secondary and branched chain aliphatic sulfates have good wetting-out properties, good water solubility, and reduce surface tension of water. However, they are inferior to primary sulfates in detergency.

PHYSICAL PROPERTIES

The common higher alcohols are colorless liquids or solids, depending on the number of carbon atoms. Hydrogen bonding, which are secondary attractive forces between hydroxyl groups in adjacent molecules, are the main reason alcohols have higher melting and boiling points than the corresponding hydrocarbons. Hence, physical properties of the homologous series of primary higher alcohols exhibit a correlation with increasing molecular weight: (a.) water solubility decreases to nil above C_8; (b.) oil solubility increases; (c.) boiling points increase ca. 20 C. for each CH_2 unit added to a normal primary monohydric alcohol; (d.) specific gravity (d^{20}_{20}) increases ca. 0.003 units per CH_2 unit; (e.) below C_{12} the physical form is a colorless, mobile oily liquid; (f.) above C_{12} the alcohols are solid

TABLE I

Physical Properties of Higher Saturated Acrylic (Aliphatic) Alcohols

IUPAC Name	Other common name	Formula	F_p.°C	Bp. °C 760 mm	Specific gravity 20/4°C	Refractive index n_d^{20}
1-Undecanol	n-Undecyl alcohol	$C_{11}H_{23}OH$	19	243	0.8298	1.4404
5-Ethyl-2-nonamol	Methyl (3-ethyl-n-heptyl) carbinol	$C_{11}H_{23}OH$	-70	225.4	0.8348	1.4393
1-Dodecanol	n-Dodecyl alcohol, lauryl alcohol	$C_{12}H_{25}OH$	23.9	259	0.8309^{24}	1.4282^{60}
1-Tridecanol	n-Tridecyl alcohol	$C_{13}H_{27}OH$	30.6	155^{15}	0.8223^{31}	---
1-Tetradecanol	n-Tetradecyl alcohol, myristyl alcohol	$C_{14}H_{29}OH$	38.3	286^{750}	0.8236^{38}	1.4347^{50}
7-Ethyl-2-methyl-4-hendecanol	Isobutyl (3-ethyl-n-heptyl) carbinol	$C_{14}H_{29}OH$	-65	264.1	0.8340	1.4443
1-Pentadecanol	n-Pentadecyl alcohol	$C_{15}H_{31}OH$	43.8	---		
1-Hexadecanol	Cetyl alcohol palmityl alcohol	$C_{16}H_{33}OH$	49.6	344	0.8176^{50}	$1.4394^{51.5}$
1-Heptadecanol	Margaryl alcohol	$C_{17}H_{35}OH$	53	308	0.8475	
1-Octadecanol	Stearyl alcohol, n-octadecyl alcohol	$C_{18}H_{37}OH$	58.1	332	0.8124^{59}	1.4390^{60}
1-Nonadecanol	n-Nonadecyl alcohol	$C_{19}H_{39}OH$	62-3	166-7	0.8090^{64}	1.4328^{75}
1-Eicosanol	Arachidyl alcohol	$C_{20}H_{41}OH$	66.5	369	0.8405	1.4550
1-Docosanol	Behenyl alcohol	$C_{22}H_{45}OH$	70.6	$180^{0.22}$		
1-Tetracosanol	Lignoceryl alcohol	$C_{24}H_{49}OH$	76.5-77.5	$210^{0.40}$	0.7950^{77}	
1-Hexacosanol	Ceryl alcohol cerotin,n-hexacosyl alcohol	$C_{26}H_{53}OH$	79.5	305^{20}	0.7890^{62}	
1-Octacosanol	Montanyl alcohol	$C_{28}H_{57}OH$	83.3		0.7830^{85}	
1-Triacontanol	Myricyl alcohol	$C_{30}H_{61}OH$	88			
1-Hentriacontanol	Melissyl alcohol	$C_{31}H_{63}OH$	87.1	$244^{0.50a}$	0.7770^{88}	
1-Dotriacontanol	Lacceryl alcohol	$C_{32}H_{65}OH$	89.4	$257^{0.50}$		
1-Tetratriacontanol	Geddyl alcohol	$C_{34}H_{69}OH$	91.9			

[a] 0.50 Means at 0.50 mm Hg.

at room temperature and progress from soft, crystalline platelets to crystalline waxes; (g.) viscosity increases with molecular weight at the same temperature; (h.) vapor enthalpy and liquid enthalpy decrease.

Selected physical properties are shown for the more important higher saturated alcohols in Table I. The tabulation is arranged according to number of carbon atoms, and shows the variation of physical properties with molecular weight, and indicates that a secondary>CHOH structure and branching of the carbon chain lowers melting and boiling points, as compared to primary (——CH_2OH) characterization and straight carbon chain structure, respectively.

SATURATED HIGHER ALIPHATIC ALCOHOLS

The following section presents a short discussion of only four saturated higher aliphatic alcohols that contain 11 or more carbon atoms. Table I presents some physical data for the more common or important alcohols. They are listed in terms of increasing number of carbon atoms.

Lauryl Alcohol

1-Dodecanol, $CH_3(CH_2)_{10}CH_2OH$, (n-dodecyl alcohol, lauryl alcohol) is a primary, straight chain, 12-carbon or dodecyl alcohol with a fatty, perfumed odor. It has a molecular weight of 186.34. This compound is a low melting solid which is insoluble in water, but completely soluble in ethyl alcohol and ether at room temperature. The n-dodecyl alcohol may be crystallized from ethanol by cooling. 1-Dodecanol has been produced commercially for many years by a process that proceeds with the preparation of ethyl esters of coconut oil, purification to ethyl laurate by distillation, followed by reduction with sodium and absolute alcohol to the 12-carbon alcohol. A high quality lauryl alcohol is currently produced by catalytic reduction of coconut oil, coconut oil fatty acids, or their esters, under high pressure. The C_{12} content of commercial lauryl alcohol made by this process is ca. 96%. Process improvements in the past decade have emphasized the value of starting with fatty esters in order to improve yield and especially product purity. Mixed alcohols with 71% or 65% C_{12} alcohol contents, respectively, can be obtained more economically. These products of lower purity are commercially significant when the mixture is suitable for the end-use, and the carbon chain length is only a minor factor in the intended application. As was the case with n-decyl alcohol, 1-dodecanol can now be produced by the trialkylaluminum process, but is only available commercially in the form of mixed normal, even-carbon alcohols. Of the two most important grades, one contains 55% lauryl alcohol and 43% myristyl alcohol (C_{14}), and the other grade consists of 63% lauryl alcohol, 24% myristyl alcohol, and 10% cetyl alcohol (C_{16}). The Shell Chemical Company has recently offered a blend of linear C_{12} and C_{13} primary alcohols named "Neodols" which originated from a petroleum feed stock.

Lauryl alcohol is insoluble in water, but it is completely miscible above 30 C. with methanol, 95% ethanol, ethyl ether, and benzene.

The chemical properties of 1-dodecanol are typical of the higher primary alcohols, and involve the characteristic reactions of the hydroxyl group. Lauryl alcohol can be esterified with acids in the presence of a catalyst, oxidized to aldehydes and acids, sulfated with chlorosulfonic or sulfuric acids, and dehydrated over aluminum oxide catalyst to the corresponding olefin.

Myristyl Alcohol

1-Tetradecanol, $CH_3(CH_2)_{12}CH_2OH$ (n-tetradecy alcohol, myristyl alcohol), a primary, straight chain, 14-carbon alcohol of molecular weight 214.40, exists as a low melting white solid at room temperature. The alcohol is almost insoluble in water, completely miscible with ether, and only partially soluble in ethyl alcohol, from which it can be crystallized in the form of aque leaflets. 1-Tetradecanol has been produced commercially for many years by the sodium reduction process, which simultaneously yields 1-decanol and 1-dodecanol. Ethyl esters of coconut oil are purified by distillation to form ethyl myristate. Subsequent reduction with sodium and absolute alcohol forms the corresponding 14-carbon primary alcohol. High quality 1-tetradecanol has also been manufactured during the past two decades by the catalytic reduction of coconut oil, or coconut oil fatty acids, or methyl esters under high pressure.

Table II shows a typical distribution of fatty acids in the triglycerides of coconut oil in terms of percent by weight, and hence the distribution of the corresponding alcohols that can be expected from coconut oil as a raw material. By appropriate fractional distillation, a commercial product

TABLE II

Fatty Acid Distribution in Coconut Oil

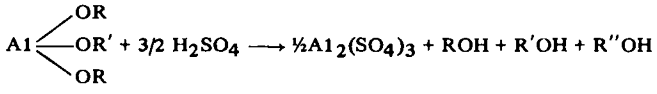
Number of carbon atoms in saturated acids	% by Wt.
C_6	0.5
C_8	8
C_{10}	7
C_{12}	48
C_{14}	17
C_{16}	9
C_{18}	2
C_{16} = (unsaturated)	0.2
C_{18} = (unsaturated)	6

with 95% of the primary C_{14} alcohol is obtained for sale. Again, mixed normal alcohols with lower contents of C_{14} alcohols are produced more economically when the commercial application allows for the utilization of mixtures. The Ziegler or trialkylaluminum process synthetically produces a mixture of even-carbon, straight chain alcohols from ethylene. A pure grade containing 97% of C_{14} straight chain alcohol is produced, as well as a mixture of 43% C_{14} and 55% C_{12}, and another mixture of 24% C_{14}, 63% C_{12} and 10% C_{16} primary alcohols. Small amounts of myristyl alcohol are obtained from spermaceti wax by saponification. Shell Chemical Company recently offered a mixture of C_{14} and C_{15} linear primary alcohols derived from a petroleum feedstock. Chemical properties of 1-tetradecanol are typical of the higher primary alcohols and involve the characteristic reactions of the hydroxyl group. Myristyl alcohol can be esterified with acids in the presence of a catalyst, oxidized to aldehydes and acids, sulfated with chlorosulfonic or sulfuric acids, and dehydrated over aluminum oxide catalyst to the corresponding olefin.

Cetyl Alcohol

1-Hexadecanol, $CH_3(CH_2)_{14}CH_2OH$, (cetyl alcohol, n-hexadecyl alcohol, palmityl alcohol, ethal, ethol) is a white, crystalline, waxlike solid with a rose odor, and a molecular weight of 242.45. It was prepared in 1818 by Chevreul from the cetyl ester of palmitic acid by saponification with alcoholic potassium hydroxide. The ester comes from sperm oil which is found in the head and vertebrae of the sperm whale. Hence, the name cetyl is derived from the Greek word "ketos" which means whale. The alcohol is prepared commercially by the catalytic reduction of fats which contain palmitic acid, as well as by the saponification of spermaceti wax. Beef and mutton tallow fatty acids provide a source of starting material for conversion to the 16-carbon straight chain alcohol.

The major commercial method of preparation in the early twentieth century involved the sodium reduction of ethyl esters in the presence of a reducing alcohol. For the past two decades, American industry has practiced the catalytic hydrogenation of tallow, tallow acids, or tallow esters. Most recently, the Ziegler or trialkylaluminum process has been put into full scale production with plants that have annual capacities of ca. 150 million lb./yr of assorted higher alcohols:



$$Al(OR)(OR')(OR'') + 3/2\ H_2SO_4 \longrightarrow \tfrac{1}{2}Al_2(SO_4)_3 + ROH + R'OH + R''OH$$

This process yields a purity of 95% after suitable distillation, or a commercial mixture such as 63% C_{16} and 30% C_{18} normal alcohols. These synthetic compounds are linear, primary alcohols with an even number of carbon atoms in the chain. The C_{16} straight chain alcohol is insoluble in water, but partly soluble in common organic solvents.

Chemical properties of cetyl alcohol are typical of the higher, normal, primary alcohols, and involve the characteristic reactions of the hydroxyl group. Cetyl alcohol can be dehydrated to form hexadecene, esterified with acids in the presence of a catalyst to form corresponding esters, and oxidized to cetyl aldehyde and subsequently to hexadecanoic acid.

Stearyl Alcohol

1-Octadecanol, $CH_3(CH_2)_{16}CH_2OH$, (stearyl alcohol, n-octadecyl alcohol), is a white crystalline and waxlike solid with a faint, fatty odor. The molecular weight is 270.50. Stearyl alcohol occurs naturally as an ester in montan and cotton waxes, and the sperm and blubber oils of the whale, porpoise, and dolphin. It has also been found in the oil of herring, and in the caudal glands of the goose. As discussed under 1-hexadecanol, beef and mutton tallow provide a mixture of triglycerides which are rich in 16- and 18-carbon fatty acids. Hydrogenation of tallow is a conventional commercial operation which converts a sizeable portion of the unsaturated compounds in tallow into the more stable saturated derivatives. The saturated 18-carbon fatty acid (stearic) occurs abundantly in natural fats and oils. In the early part of the twentieth century, stearyl alcohol was produced by sodium reduction of the ethyl ester of C_{18} acids. Catalytic hydrogenation of tallow, tallow acids, or tallow esters has supplanted this procedure, and in turn this process now faces competition from the trialkylaluminum ethylene route.

The ethylene synthesis method produces an octadecanol of 91% purity (after suitable purification), as well as commercial mixtures with 30 or 63% of 1-octadecanol. Stearyl alcohol is insoluble in water at room temperature, but partly soluble in several organic solvents. Stearyl alcohol crystallizes from ethanol in the form of shining leaflets. Chemical properties of 1-octadecanol are typical of the higher primary alcohols, and involve the characteristic reactions of the hydroxyl group. Stearyl alcohol can be esterified with acids in the presence of a catalyst, oxidized to stearyl aldehyde and subsequently to octadecanoic acid, sulfated with chlorosulfonic or sulfuric acids, and dehydrated over aluminum oxide catalyst to the corresponding olefin. The detergent industry requires stearyl alcohol for many applications which are similar to those fulfilled by cetyl alcohol. Heavy duty detergents contain sodium stearyl sulfate of the corresponding sulfate.

The polyethoxylated stearyl alcohols, and alcohol ether sulfates, are generally found in light-duty detergents. The three classes of surfactants are biodegradable by current definition and are used as "soft" detergents. An increasing amount of quaternary salts containing tallow-derived alkyls are used as textile softeners. Miscellaneous applications are as an ingredient in ink compositions, a softener for leather, an ingredient in polishing compositions, and an intermediate for insecticides. Stearyl alcohol resembles cetyl alcohol in its ability to form compressed films on the surface of water. Hence, 1-octadecanol also finds use as a suppressor of water evaporation on ponds and reservoirs.

UNSATURATED ACYCLIC (ALIPHATIC) ALCOHOLS

Introduction

Higher unsaturated monohydric alcohols have been produced for many years in the United States and Europe by the "sodium reduction process." This method starts with the preparation of ethyl esters from a suitable triglyceride which contains unsaturated fatty chains. The esters are reduced to the corresponding alcohol with only a minor reduction of unsaturation. Catalytic hydrogenation, in general, saturates more double bonds than sodium reduction. Common starting materials are tallow, unsaturated vegetable oils, and fish oils. Oleyl alcohol (9-octadecen-1-ol) is perhaps the best known of the unsaturated fatty alcohols.

TABLE III

Physical Properties of Higher Unsaturated Acyclic Alcohols

IUPAC name	Common name	Formula	Melting point, °C	Boiling point, °C	d_4^{20}	n_D^{20}
1-Hexen-3-ol	---	$CH_2{=}CHCHOHCH_2CH_2CH_3$	---	140-1	0.834^{23}	1.4329
3-Hexen-1-ol (cis)	Leaf alcohol	$CH_3CH_2CH{\equiv}CHCH_2CH_2OH$	---	156	0.8495	1.4380
1-Hexyn-3-ol	Hexynol	$CH{\equiv}CCHOHCH_2CH_2CH_3$	-80^a	142	0.880	1.4350
3-Methyl-1-pentyn-3-ol	Methyl pentynol	$CH{\equiv}CC(CH_3)OHCH_2CH_3$	-30.6^a	121-2	0.8706	1.4318
4-Methyl-1-pentyn-3-ol	---	$CH{\equiv}CCHOHCH(CH_3)CH_3$	-43^a	131-2	0.876	1.4357
1-Octen-3-ol	1-n-Amylvinyl-carbinol	$CH_3(CH_2)_4CHOHCH{=}CH_2$	---	173.5^{742}	0.8395^{13}	1.4391^{12}
2-Octyn-1-ol	Pentyl propargyl alcohol	$CH_3(CH_2)_4C{\equiv}CCH_2OH$	-20	$98\text{-}9^{15}$	0.884^{17}	1.4550
4-Ethyl-1-octyn-3-ol	Ethyl octynol	$CH{\equiv}CCHOHCH(Et)(CH_2)_3CH_3$	-45^a	197.2	0.871	1.4502
Octadecen-1-ol (cis)	Oleyl alcohol	$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH$	-7.5	333-5	0.8489	1.4607

[a] Freezing point.

The manufacturing process begins with the purification of ethyl esters by distillation or fractionation prior to reduction of the ester.

Physical and chemical properties of the unsaturated alcohols and glycols are more complex than for the saturated homologs due to the presence of acetylenic and olefinic linkages. In the case of 1-hexyn-3-ol, three reactive centers* are present in its structure $C^*H{\equiv}^*CCHOH^*CH_2CH_2CH_3$. The hydroxyl group (—OH) undergoes the characteristic reactions of the primary alcohols with additional activation from the unsaturated linkage. The triple bond (≡) gives the addition reactions of unsaturated compounds. The methine (H—) hydrogen is also activated by the triple bond and becomes another reaction center.

Reactions of the hydroxyl group include oxidation to aldehyde and acids, addition to methyl vinyl ether to form acetals, and replacement of the OH group to form halogen compounds, esters and ethers. Reactions of the double and triple bond include reduction of acetylenic linkage to olefinic, and saturated compounds, classic addition of hydrogen, water, halogen, halogen acids, alcohols, sodium bisulfite, and addition to alcohols to form cyclic acetals. Reactions of the Methine Hydrogen include reactions with aldehydes, oxidative coupling with air or oxygen, reaction with halogen, Grignard reagent, dialkylamine, and formaldehyde, dimerization and trimerization.

Table III presents physical constants for selected olefinic and acetylenic alcohols.

Oleyl Alcohol

cis-9-Octadecen-1-ol, $CH_3(CH_2)_7CH{=}CH(CH_2)_8OH$ (oleyl alcohol), and 18-carbon primary ethylenic alcohol of molecular weight 268.47 exists as a colorless viscous liquid. In nature, oleyl alcohol is the most abundant of the unsaturated alcohols and occurs widely in fish and marine mammal oils. Oleyl alcohol is thought to constitute 66-70% of the alcohols of sperm body oil.

The most important commercial method of producing oleyl alcohol is by the reduction of corresponding esters with metallic sodium and a lower alcohol. The unsaturated bond of oleyl ester is not affected by hydrogen in this reaction. Hence, unsaturated oleyl alcohol is obtained in crude form. Oleyl alcohol may also be prepared from oleates by catalytic hydrogenation with specific catalysts.

The trans isomer, elaidyl alcohol, is a solid at room temperature with a melting point of 36-37 C.

MANUFACTURING METHODS AND PRODUCTION CAPACITY

Natural Sources

One of the two general manufacturing categories is the conversion of natural fats and oils, with appropriate purification steps.

Hydrolysis of natural esters. Crude sperm oil from whales was used until the ban in 1970, to make fatty alcohols. Until 1971 the Dyes and Chemical Division of E.I. DuPont de Nemours operated a facility for saponification of sperm oil. The plant produced a technical grade of oleyl alcohol. Wool-grease may be refined and saponified to yield a complex mixture of alcohols, diols, and sterols. Due to the high cost of purification, this mixture is called "lanolin" and used for cosmetics and synthesis of emulsifiers. Additional modification such as ethoxylation produces a mixture which is easier to handle and blend with other components.

Reduction of natural esters. Starting with Bouvealt and Blanc in the early 1900s, a specific chemistry and technology has been developed for the reduction of natural and synthetic esters to the corresponding alcohols. Common starting materials are tallow, lard, coconut oil, palm kernel oil, castor oil, sperm oil, and fish oil. While the fatty acid portion of esters is usually a random mixture of carbon chain length and degree of unsaturation, nevertheless fairly uniform blends of fatty alcohols are produced from tallow and coconut oil.

Sodium reduction. This process is a variation of hydrogenolysis where hydrogen is obtained from the reaction of sodium on alcohol. This process has been completely replaced in the U.S. by a catalytic hydrogenation, which is cheaper and makes a purer product. The benefit of making unsaturated alcohols by sodium reduction is partially negated by specific hydrogenation catalysts that are able to leave double bonds to a large extent.

High pressure hydrogenolysis. The two companies that practice high pressure hydrogenolysis are Ashland Chemical Company and The Procter and Gamble Company. Ashland uses natural oil feed stocks such as tallow and rapeseed oil, yielding saturated C_{16} and C_{18} alcohols, and unsaturated oleyl alcohol. In fact, Ashland is the only remaining producer of oleyl alcohol in the United States. Their plant capacity is estimated at 20,000,000 lb. of a C_{14}-C_{22} range of products. The Procter and Gamble Company has three hydrogenolysis plants that start with methyl esters derived from coconut oil and tallow. The Ivorydale and Sacramento plants use coconut oil and have a capacity of 25 and 100 million lb./yr, respectively, of coconut alcohols. However, the output in 1976 was only 25,000,000, or a 21% operation rate. Their Kansas City plant produced 65,000,000 lb. tallow alcohol in 1970, (plant capacity 100,000,000). Formation of methyl esters from triglycerides is shown below:

$$\underset{\text{triglyceride}}{C_3H_5(OOCR)_3} + \underset{\text{methanol}}{CH_3OH} \xrightarrow{CH_3ONa} \underset{\text{ester}}{3RCOOCH_3} + \underset{\text{glycerol}}{C_3H_5(OH)_3}$$

Hydrogenation processes use catalysts such as copper chromite, nickel or copper carbonates, or copper and chromium oxides. General operating conditions are 200-

300 atm. pressure and 200-300 C. The overall reaction is quite simple, although pure reactants are necessary for good yields. Yields of purified alcohols from both processes are ca. 90-95%, based on starting triglyceride. Catalytic hydrogenation is favored commercially over sodium reduction in that it produces a more saturated alcohol, and at lower operating cost.

Synthetic Sources

Since the 1950s, the chemical industry in the United States has taken a major turn in the direction of synthetic or petroleum sources for manufacture of higher alcohols. These processes are described in the following section.

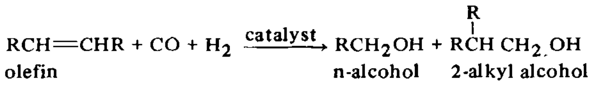
Aldol condensation. Aldehydes or ketones with a hydrogen atom on the carbon adjacent to the carbonyl group can be condensed to β-hydroxy aldehydes or ketones, respectively. Dehydration, followed by catalytic hydrogenation, then forms the alcohol. For example, acetone is condensed to β-hydroxy ketone, which is then dehydrated to mesityl oxide, and hydrogenated to methyl isobutyl carbinol. Union Carbide Corporation has plant capacity for 5-10 million lb./yr, and produces secondary alcohols with 12, 14, and 17 carbons.

Oxo (hydroformylation) reaction. In general, an olefin is reacted with carbon monoxide and hydrogen in the presence of a catalyst and under high pressure:

$$2RCH = CH_2 + 2CO + 2H_2 \xrightarrow[\text{catalyst}]{\text{high pressure}} RCH_2CH_2COH + RCH(CHO)CH_3$$

The aldehyde mixture produced previously is reduced with hydrogen to the corresponding alcohols. Commercially, each manufacturing process uses unique technology in terms of catalyst, process conditions, byproduct formation and purification.

Single state process. A special process from Shell Development Company converts olefins to alcohols in one step. This is possible by means of a modified oxo catalyst is which one carbonyl ligand is replaced by a trialkylphosphine ligand; namely, $HCO(CO)_3\,PR_3$.



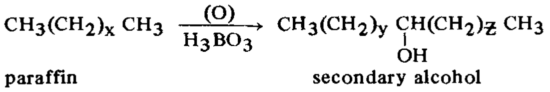
$$\underset{\text{olefin}}{RCH{=}CHR} + CO + H_2 \xrightarrow{\text{catalyst}} \underset{\text{n-alcohol}}{RCH_2OH} + \underset{\text{2-alkyl alcohol}}{R\overset{R}{\overset{|}{C}}H\,CH_2OH}$$

With linear olefins as starting material, the normal to iso ratio can be as high as 90:10 for plasticizer range products, and higher weight olefins yield a 75:25 ratio in detergent alcohols.

Two state process. Most oxo plants worldwide produce an intermediate aldehyde which is isolated, purified, and then hydrogenated. Catalyst is usually a cobalt hydrocarbonyl which is not modified by other ligands as in the case of the one-step process described above. Reduction to practice in the United States has been the production of isotridecyl alcohol from dodecene (propylene tetramer). The n-to iso-ratio of alcohols produced is lower than with the one-step procedure.

The Ziegler Process. Here we produce straight chain normal alcohols by addition of *ethylene* to *triethylaluminum*. In various steps, trialkylaluminum is formed, which is converted to the corresponding aluminum alkoxide by air oxidation. Hydrolysis then leads to a mixture of linear primary alcohols. Ziegler technology has led to two commercial processes. Continental Oil Company supplies "Alfol" alcohols with a wide spectrum of carbons. Their estimated plant capacity in 1978 is 220,000,000 lb./yr. Ethyl Corporation has a similar plant capacity of 225,000,000 lb. but is able to maximize production of lauryl and myristyl alcohols. Ethyl sells their alcohols under the "EPAL" trade name.

Paraffin oxidation. Liquid phase oxidation of paraffins was studied by German chemists in 1928 and manufacturing improvements made by Russian chemists in the late 1950s.



$$\underset{\text{paraffin}}{CH_3(CH_2)_x\,CH_3} \xrightarrow[H_3BO_3]{(O)} \underset{\text{secondary alcohol}}{CH_3(CH_2)_y\,\underset{OH}{\underset{|}{C}}H(CH_2)_z\,CH_3}$$

Union Carbide Corporation has a plant capacity of 54,000,000 lb. for linear C_{11} - C_{15} secondary alcohols which are sold under the "TERGITOL" name. They use very pure normal paraffins, and thereby virtually eliminate branched chains. Hydroxyl groups are located in a random manner on all except terminal carbon atoms.

Uses of higher alcohols. Higher alcohols are utilized in several hundreds of applications in the free form or as derivatives. The following table presents data on U.S. Consumption of Detergent-Range Alcohols in 1970.

TABLE IV

U.S. Consumption of Detergent-Range Alcohols – 1970[a]

Free alcohol	Carbon no. range	Consumption mm lb./yr
Alcohol derivatives	C_{12}-C_{22}	44
Sulfuric acid esters	C_{12}-C_{18}	115
Carboxylic acid esters	C_{12}-C_{20}	80
Phosphorus acid esters	C_{12}-C_{18}	4
Alkyl ethers	C_{11}-C_{20}	185
Alkyl halides	C_{12}-C_{18}	10
Nitrogen derivatives	C_{12}-C_{18}	4
		442

[a] Taken from Chemical Economics Handbook, Revision of 1973.