MONOHYDRIC ALCOHOLS

Manufacture, Applications, and Chemistry

Edward J. Wickson, Editor

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Exxon Chemical Company

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FOREWORD

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PREFACE

Unsubstituted monohydric alcohols are the largest single class of oxygenated hydrocarbons made in the chemical industry. In fact, three of the alcohols—methanol, ethanol, and isopropyl alcohol—are in *Chemical and Engineering News* "Top 50 Chemicals" for 1979. These alcohols are used in a myriad of applications, some very large and others quite small. Solvents, fuels, antifreeze, germicides, frothers, antifoams, and inks are examples of where the alcohols are used as such. Derivatives cover an even wider range of applications, including resins, solvents, plasticizers, surfactants, lubricants, flavors, fragrances, capacitor fluids, and the fast growing gasoline additive MTBE, to name a few. In this sense, alcohols differ markedly from some of the very large volume organics such as ethylene, propylene, toluene, *p*-xylene, and urea, which are used in very large volumes but have relatively few end uses.

It is common practice to divide alcohols into lower alcohols (C_1–C_5) and higher alcohols (C_6 and higher). In turn, higher alcohols are generally subdivided into (polyvinyl chloride) plasticizer range (C_6–C_{11} or C_6–C_{12}) and detergent range (C_{11} or C_{12} and higher). Actually, the dividing line is not this clear cut, and one finds the lower alcohol *n*-butanol used in butyl benzyl phthalate and the detergent-range tridecyl alcohol used in ditridecyl phthalate. Both of these esters are important polyvinyl chloride plasticizers. Also, detergents based on mixed alcohols, including C_{11}, are produced commercially, and there are many surfactants, such as di-2-ethylhexyl sulfosuccinate, based on the so-called plasticizer-range alcohols.

In developing the symposium on which this book is based, our objective was not to cover all monohydric alcohols, but to cover representative lower and higher alcohols with special attention, when possible, to new developments and applications.

The book starts with a review of the chemistry of monohydric alcohols with references to many of the common reactions used in industry.

Much attention has been devoted in the professional journals and in the press to gasohol, and announcements of new ethanol plants and process improvements seem unending. A perspective on the problems and promise of gasohol is covered along with a status report on work in Brazil on (fuel) methanol from wood, not by destructive distillation used in the past, but by modern synthetic chemistry. Other promising new uses for

methanol are covered that together suggest enormous growth for this first member of the monohydric alcohol series.

A detailed discussion on surfactants from secondary alcohols which are relatively little known in the U.S. is included, together with a review of linear alcohol processes (Oxo and Ziegler) and detergent applications of the Ziegler alcohols. Also covered is a discussion of the revolutionary rhodium oxo process which has already resulted in a number of new plants—announced, under construction, or in operation, worldwide—for the manufacture of n-butanol and 2-ethylhexanol. Applications of these alcohols are also discussed.

The application of branched-chain alcohol diesters in part-synthetic lubricants is covered as one of the ways the petroleum industry is responding to the challenges brought on by the trend toward new smaller cars with more demanding lubricant requirements.

The history of monohydric alcohol–based ester-type plasticizers for polyvinyl chloride is reviewed, and a prediction of the future for these plasticizers in the eighties is made. Finally, although not in the large volume category compared to many monohydric alcohols, the rather sophisticated chemistry used to produce monohydric alcohols for the flavors and fragrance industry is covered.

EDWARD J. WICKSON
Exxon Chemical Company
P.O. Box 241
Baton Rouge, Louisiana 70821
April 3, 1981

CONTENTS

Chemistry of Monohydric Alcohols

F. M. BENITEZ

Exxon Chemical Company, Specialties Technology Division, P.O. Box 241,
Baton Rouge, LA 70821

Alcohols can be regarded as hydroxyl derivatives of hydro-carbons. They can be characterized by the number of hydroxyl groups (monohydric, dihydric, etc.), according to their structure (primary, secondary or tertiary), and by the structure of the hydrocarbon function to which the hydroxyl is attached (aliphatic, cyclic, saturated or unsaturated).

This chapter is concerned almost exclusively with the chemistry of saturated aliphatic monohydric alcohols with particular emphasis on the reactions used in the conversion of these alcohols to other useful compounds. Manufacture of many of the alcohols is covered in other chapters.

Acidity and Basicity

Alcohols are amphoteric and thus can function both as weak Brønsted acids and as bases:

$$R-OH + Z^{\ominus} \rightleftharpoons R-O^{\ominus} + ZH \quad (ROH \text{ acting as an acid})$$

$$R-OH + HA \rightleftharpoons ROH_2^{\oplus} + A^{\ominus} \quad (ROH \text{ acting as a base})$$
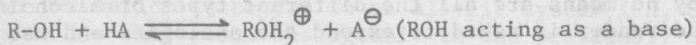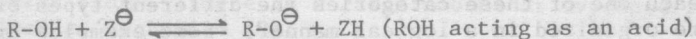
The acidity of the hydroxyl group can be seen in the rapid proton-deuteron exchange that can take place when alcohols are dissolved in D_2O (Reaction I), alkali metals (Reaction II) and organometallic reagents (Reaction III and IV).

$$CH_3CH_2OH + D_2O \rightleftharpoons CH_3CH_2OD + DOH \quad (I)$$

$$CH_3OH + Na \longrightarrow CH_3O^{\ominus}Na^{\oplus} + 1/2\ H_2 \quad (II)$$

$$CH_3CH_2CH_2OH + CH_3Li \longrightarrow CH_3CH_2CH_2O^{\ominus}Li^{\oplus} + CH_4 \quad (III)$$

$$CH_3CH_2CH_2OH + C_3H_7MgBr \longrightarrow CH_3CH_2CH_2O^{\ominus}MgBr^{\oplus} + C_3H_8 \quad (IV)$$
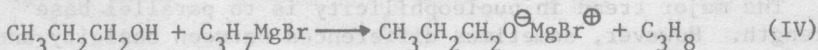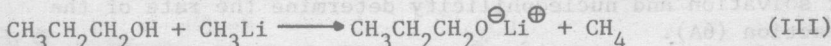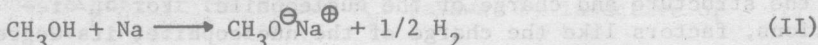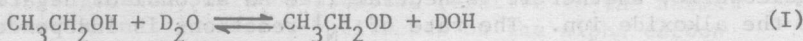
The most complete measurements of the acidity of alcohols in water were made some time ago by Long and Ballinger ([1],[2],[3]) using conductivity methods. The pKa values for substituted methanols (RCH$_2$OH) ([2]) are a linear function of the Taft σ* constants ([4],[5]) for the R substituents, allowing the prediction of the actual pKa by using the formula: pKa = 15.9 - 1.42 σ*.

In recent years the question of acidity and basicity has been reopened by the development of techniques to measure them in the gas phase([6]). The results available reemphasize the fact that solvation factors have a profound influence on the course of acid-base reactions.

Brauman and Blair have determined ([6]) that the acidity of some substituted alcohols increases as the size and number of substituents increase. This is exactly the opposite effect seen in solution measurements. The conclusion that must be deduced from this is that there are two kinds of acidity that must not be confused: a) an intrinsic acidity, which is best approximated by gas-phase measurements and which reflects the properties of the ions and the molecules in isolation, and (b) a practical liquid phase acidity in which solvation effects play a very important role. In the interpretation of structure-acidity relationships in solvents, the results will probably be misleading unless the structures being compared are very similar.

Categories of Chemical Reactions of Alcohols

The following sections on the chemical reactions of alcohols has been broken down into five categories: (A) Nucleophilic reactions of alcohols, (B) displacement of the hydroxyl group, (C) dehydration of alcohols, (D) oxidation of alcohols, and (E) analytical determination of the hydroxyl group.

Under each one of these categories the different types of reactions are organized in a logical manner. Some examples are given, but by no means are all the different types of alcohols covered. The reader is asked to extend the analogies and use the references given to pursue his areas of interest.

Nucleophilic Reactions

Any species having an unshared pair of electrons may act as a nucleophile, whether it is neutral like an alcohol or negative like the alkoxide ion. The rate of S$_N$1 reactions is independent of the structure and charge of the nucleophile. For S$_N$2 reactions, factors like the charge of the nucleophile, its degree of solvation and nucleophilicity determine the rate of the reaction (6A).

The major trend in nucleophilicity is to parallel base strength. However, sometimes differences between basicity and nucleophilicity of a species occur because the two are somewhat different. Basicity measures attack on hydrogen and it is

thermodynamically controlled. Nucleophilicity on the other hand measures attack on carbon and it is kinetically controlled.

  Reactions of the Alkoxide Ion. The nucleophilic reactions of the alkoxide ion (RO^-) are very similar to those of the hydroxide ion (OH^-) with the exception that the latter has an extra ionizable proton which can lead to further reaction after the initial nucleophilic attack.

  The displacement of the bromide ion from an alkyl bromide (Reaction V) by an alkoxide has been found to be a first order reaction in both the reactant and substrate (7). It is implicit

$$RO^{\ominus} + R'-Br \longrightarrow ROR' + Br^{\ominus} \qquad (V)$$
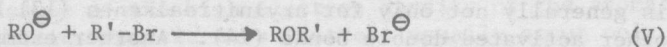
in the reaction above that inversion of configuration will take place at the alkyl halide. The nucleophilic displacement of a halide by an alkoxide is commonly known as the Williamson ether synthesis and is still the best general method for the preparation of symmetrical and unsymmetrical ethers (7A).

  The transformation of chlorohydrins into the corresponding epoxides (Reaction VI) may be regarded as a special case of the Williamson reaction. Many epoxides have been made this way
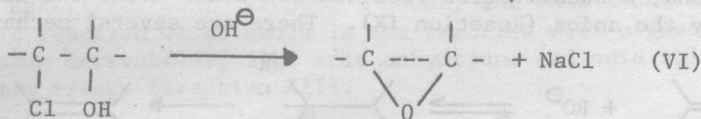

$$(VI)$$

and the method is generally useful for the synthesis of five and six-membered rings. There is a large amount of evidence for an intramolecular mechanism (8).

  When the halide is bonded to an allylic system ($CH_2=CH-CH_2-X$) an alkoxide ion will react analogously to the previously described S_N2 displacement on an alkyl halide. The most significant difference is the rate enhancing effect of the alkene moiety which has been attributed to a decrease in the activation energy of the reaction (9). A second possible mode of reaction is available with allylic halides. This mode of displacement is usually called S_N2' and, in general, will be promoted relative to the normal displacement when there are substituents on the alpha carbon which tend to inhibit the normal S_N2 pathway by inductive or steric effects (Reaction VII).

$$(VII)$$
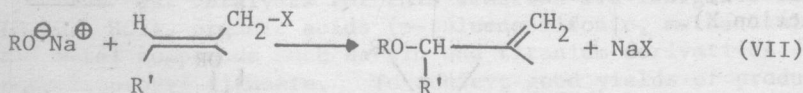
  Thus, while alpha-methylallyl chloride yields only a small amount of "abnormal" product with ethoxide ion in ethanol (10),

tert-butylallyl chloride forms substantial amounts of "abnormal"
product derived through the S_N2' pathway (11).

The high electron density in the double bond system of
ethylenes makes nucleophilic attack unfavorable unless the
system is substituted with one or more electron withdrawing
groups such as $-NO_2$, $-CN$, $-COR$. When these substituents are
present, attack by alcohols or alkoxide ions occurs at the
beta-carbon predominantly. For example, researchers have
found (12) that sodium methoxide or sodium ethoxide added
rapidly at room temperature to beta-nitrostyrene leads to the
alkoxide formation of the derivative (Reaction VIII). This
reaction is generally not only for arylnitroalkenes (13) but
also for other activated double bonds (14). Another example
of alcohol addition to an activated double bond includes the
reaction of alcohols with acrylonitrile to produce a cyano-
ethylated ether (14A).

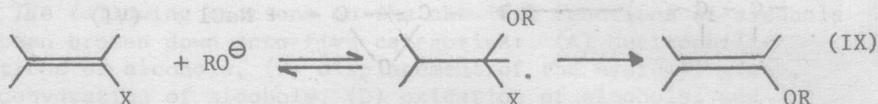$$C_6H_5CH=CHNO_2 + RO^{\ominus} \longrightarrow C_6H_5\underset{\underset{OR}{|}}{C}H-CH_2-NO_2 \qquad (VIII)$$
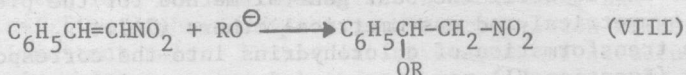
If there is a labile substituent directly attached to the
double bond, a substitution reaction can occur after the initial
attack by the anion (Reaction IX). There are several mechanisms

$$ \qquad (IX)$$

which can account for the product formed, the most important of
these is the "elimination-addition" mechanism in which an inter-
mediate acetylene is initially formed which then adds an alcohol.

In general, the "addition-elimination" mechanism will be
favored for compounds with low electron density on the beta-carbon,
while the "elimination-addition" pathway will be favored by cis-
isomers where there is a good chance of eliminating the elements
of HX from a trans-position.

Addition to Acetylenes. Since triple bonds are more suscep-
tible to nucleophilic attack than double bonds, it might be
expected that bases would catalyze additions particularly well.
This is the case, and vinyl ethers as well as acetals may be
produced by the reaction of acetylenes with alcohols (15,15A)
(Reaction X).

$$R-C\equiv C-R + ROH \longrightarrow C=C \longrightarrow -\underset{\underset{|}{|}}{C}-\underset{\underset{|}{|}}{C}-OR \qquad (X)$$
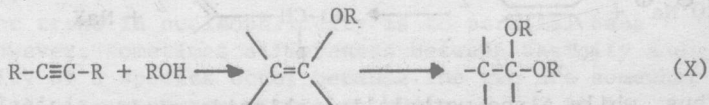
As with alkenes, the addition of alcohols to acetylenes is
facilitated by the presence of electron-withdrawing substituents

and is believed to proceed by a trans-mechanism(16). Thus, addition of alcohols to an acetylene dicarboxylate gives mainly the trans-compound (Reaction XI); some exceptions occur at high temperatures and with dicyanoacetylenes where the cis-isomer is sometimes produced.

$$ROOC-C\equiv C-COOR + R'OH \longrightarrow \begin{array}{c} ROOC \quad\quad H \\ \diagdown \quad\quad \diagup \\ C=C \\ \diagup \quad\quad \diagdown \\ R'O \quad\quad COOR \end{array} \quad\quad (XI)$$
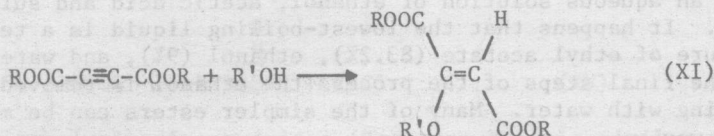
Because of the high electron density of the aromatic systems, nucleophilic aromatic substitutions usually occur only where the ring is substituted with one or more electron-withdrawing groups ortho and/or para to the position of substitution.

In general, the reactions are second-order, first-order with respect to both nucleophile and substrate (17). The relative activating effects of various substituents have been determined (18) to be in the order:

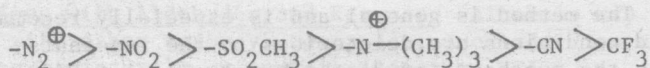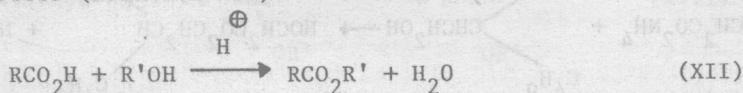$$-N_2^{\oplus} > -NO_2 > -SO_2CH_3 > -N^{\oplus}-(CH_3)_3 > -CN > CF_3$$

Esterification. Without a doubt, the best known nucleophilic reaction of alcohols is the reaction with organic acids and some derivatives, like acid anhydrides and acid chlorides, to form esters (Reaction XII).

$$RCO_2H + R'OH \xrightarrow{\overset{\oplus}{H}} RCO_2R' + H_2O \quad\quad (XII)$$

Esterification is an acid catalyzed reversible reaction which is known to proceed according to the following mechanism:

$$\underset{\overset{\|}{RC-OH}}{\overset{O}{}} + H^{\oplus} \rightleftharpoons \underset{\overset{\|}{R-C-OH}}{\overset{\overset{\oplus}{OH}}{}} \overset{R'OH}{\rightleftharpoons} \underset{\overset{\overset{|}{H}}{R-C-O^{\oplus}R'}}{\overset{\overset{|}{OH}}{}} \rightleftharpoons \underset{\overset{|}{R-C-OR'}}{\overset{\overset{\oplus}{OH_2}}{}} \longrightarrow$$

$$\underset{\overset{\|}{R-C-OR'}}{\overset{O}{}} + H_2O + H^{\oplus}$$
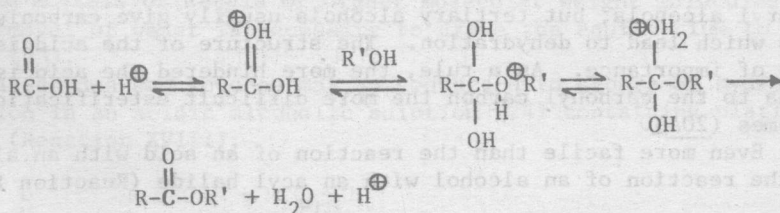
The best catalysts for this reaction are inorganic acids (H_2SO_4, HCl), organic acids (p-toluenesulfonic, methanesulfonic) and metal compounds such as tin and titanium derivatives - e.g. tetraisopropyl titanate. To achieve good yields of products, not only is a catalyst generally necessary but also the means to drive the equilibrium to the right as written in the reactions above.

There are many ways of changing the equilibrium, among which are: (a) The addition of an excess of a reactant, (b) the removal of the ester or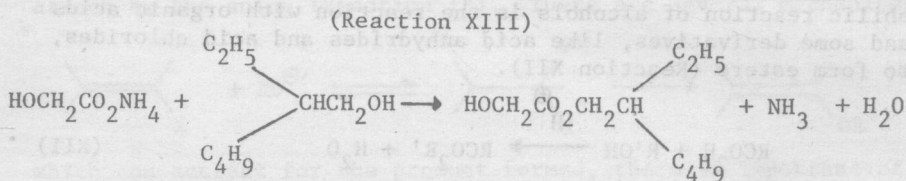 more commonly the water by distillation using an azeotroping agent, and (c) the removal of water by a dehydrating agent. An example is the commercial preparation of ethyl acetate from an aqueous solution of ethanol, acetic acid and sulfuric acid. It happens that the lowest-boiling liquid is a ternary mixture of ethyl acetate (83.2%), ethanol (9%), and water (7.8%). In the final steps of the process the ethanol is removed by washing with water. Many of the simpler esters can be made in this way.

The necessity for the continuous removal of water can be avoided by operating in a system composed of an aqueous and a non-aqueous layer. When a mixture of adipic acid, methanol, sulfuric acid, and ethylene chloride is heated, dimethyl adipate passes into the ethylene chloride layer; the lower layer contains the water (19).

Esters can also be made in satisfactory yields by heating an alcohol with the ammonium salt of an acid under conditions permitting removal of both ammonia and water from the reaction mixture. The method is general and is especially recommended where acid conditions are deleterious to the reactants. An example is the synthesis of 2-ethylhexyl glycolate (20) (Reaction XIII).

<div align="center">(Reaction XIII)</div>

$$HOCH_2CO_2NH_4 + \begin{matrix} C_2H_5 \\ | \\ CHCH_2OH \\ | \\ C_4H_9 \end{matrix} \longrightarrow HOCH_2CO_2CH_2CH\begin{matrix} C_2H_5 \\ | \\ \\ | \\ C_4H_9 \end{matrix} + NH_3 + H_2O$$

In general, the acid catalyzed esterification of organic acids can be accomplished easily with primary or secondary alkyl or aryl alcohols, but tertiary alcohols usually give carbonium ions which lead to dehydration. The structure of the acid is also of importance. As a rule, the more hindered the acid is alpha to the carbonyl carbon the more difficult esterification becomes (20A).

Even more facile than the reaction of an acid with an alcohol is the reaction of an alcohol with an acyl halide (Reaction XIV).

$$\overset{O}{\overset{\|}{RC}}-X + R'OH \longrightarrow RCOOR' + HX \qquad (XIV)$$
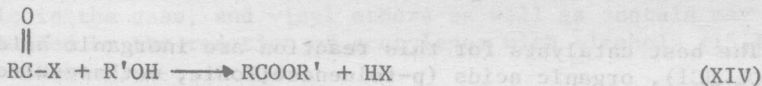
The reaction is of very wide scope (21), and many functional groups do not interfere. A base such as pyridine is frequently added to combine with the HX formed. The alcohol may be primary,

secondary, or tertiary alkyl, or aryl. Enolic esters can also be prepared by this method, although C-acylation can be a side reaction.
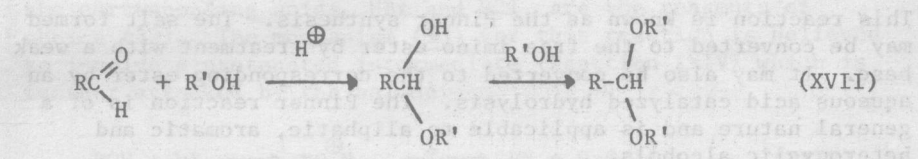
When phosgene is the acyl halide, haloformic esters (22) or carbonates may be obtained (Reaction XV).

$$Cl-\overset{\overset{\text{O}}{\|}}{C}-Cl + 2ROH \longrightarrow ROCOR + 2HCl \qquad (XV)$$
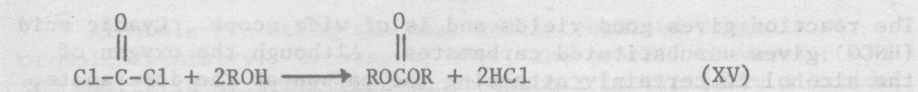
The alcoholysis of anhydrides (Reaction XVI) is similar in scope to the reaction of alcohols with acyl halides. The reaction is catalyzed by general esterification catalysts, but usually they are not needed unless the anhydride is unreactive or the di-ester (such as a phthalate) is the product sought.

$$R-\overset{\overset{\text{O}}{\|}}{C}-O-\overset{\overset{\text{O}}{\|}}{C}-R + R'OH \longrightarrow RCOOR' + RCOOH \qquad (XVI)$$
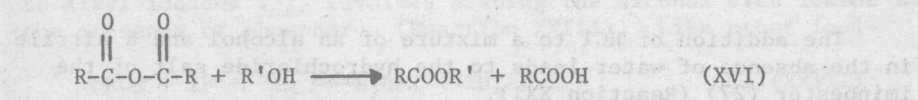
<u>Reactions with Aldehydes and Ketones</u>. Alcohols may combine additively with other carbonyl compounds; such addition compounds are known as hemiacetals or acetals (Reaction XVII).

$$RC\overset{\text{O}}{\underset{\text{H}}{\diagup}} + R'OH \overset{H^{\oplus}}{\longrightarrow} RCH\overset{OH}{\underset{OR'}{\diagdown}} \overset{R'OH}{\longrightarrow} R-CH\overset{OR'}{\underset{OR'}{\diagdown}} \qquad (XVII)$$

When the reaction is carried out with a ketone the product is known as a ketal. With low molecular weight unbranched aldehydes and ketones the equilibrium lies to the right. If it is desired to make acetals or ketals of higher molecular weight molecules, the removal of water is necessary to drive the equilibrium to the right (23).

Aldehydes and ketones may be converted to ethers by hydrogenation in an acidic alcoholic solution (24) containing platinum oxide (Reaction XVIII).

$$R-\overset{\overset{\text{O}}{\|}}{C}-R' + R''OH + H_2 \xrightarrow[H^{\oplus}]{PtO_2} R-\overset{}{\underset{OR''}{C}}H-R' + H_2O \qquad (XVIII)$$
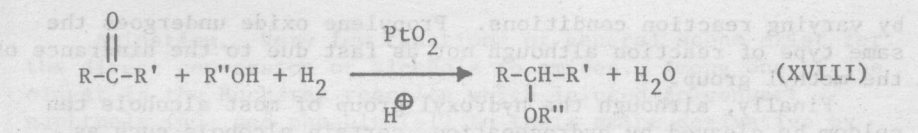
Addition to Other Unsaturated Molecules. When isocyanates
are treated with alcohols, substituted methanes or carbamates
are prepared (Reaction XIX).

$$R-N=C=O + R'OH \longrightarrow R-NHCOOR' \qquad (XIX)$$

The reaction gives good yields and is of wide scope. Cyanic acid
(HNCO) gives unsubstituted carbamates. Although the oxygen of
the alcohol is certainly attacking the carbon of the isocyanate,
hydrogen bonding complicates the details of the mechanism and the
kinetic picture (25).

In a very similar fashion, alcohols react with ketenes to
give esters (26) (Reaction XX).

$$\diagdown C=C=O + R'OH \longrightarrow \diagdown CH-COOR' \qquad (XX)$$
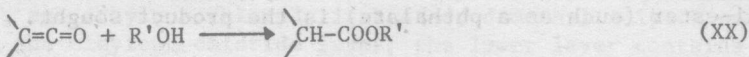
The addition of HCl to a mixture of an alcohol and a nitrile
in the absence of water leads to the hydrochloride salt of the
iminoester (27) (Reaction XXI).

$$RC{\equiv}N + R'OH + HCl \longrightarrow R-C{=}NH_2^{\oplus} \ Cl^{\ominus} \qquad (XXI)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad OR'$$
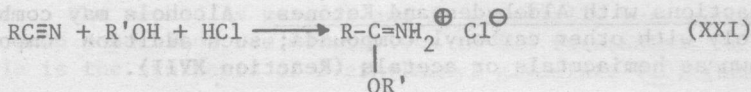
This reaction is known as the Pinner synthesis. The salt formed
may be converted to the free imino ester by treatment with a weak
base. It may also be converted to the corresponding ester by an
aqueous acid catalyzed hydrolysis. The Pinner reaction is of a
general nature and is applicable to aliphatic, aromatic and
heterocyclic alcohols.

Alkoxylation. The reaction of alcohols with ethylene oxide
gives polymeric products in which many units of the ethoxy group
are incorporated (Reaction XXII). The reaction can be controlled

$$ROH + n \ CH_2{-}CH_2 \xrightarrow{\ OH^{\ominus}\ } R(OCH_2CH_2)_n OH \qquad (XXII)$$
$$\qquad\qquad \diagdown O \diagup$$
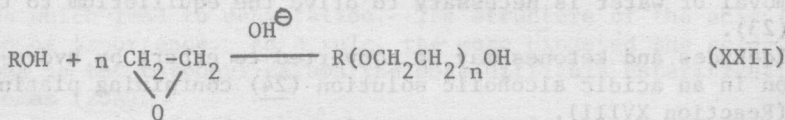
by varying reaction conditions. Propylene oxide undergoes the
same type of reaction although not as fast due to the hindrance of
the methyl group.

Finally, although the hydroxyl group of most alcohols can
seldom be cleaved by hydrogenation, certain alcohols such as
benzyl are susceptible and often readily undergo reduction (28).
The most common catalysts are copper chromite and palladium-on-
charcoal. Mixtures of $AlCl_3$ and $LiAlH_4$ have also been used for

this purpose (29). Though the mechanism of alcohol hydro-
genolysis is obscure, in some cases nucleophilic substitution
has been demonstrated (30).

Displacement of the Hydroxyl Group

Alcohols are among the most easily obtained reagents of
organic chemistry. Because of this, the overall conversion of
ROH ⟶ RX is of great importance where X is typically a halide,
hydride, azide, alkyl or an amine.

This section will provide a survey of the importance in
syntheses of replacing a hydroxyl group by other functional
groups.

Alkyl Halides. The classical method for converting alcohols
to alkyl iodides (31) involves heating the alcohol with iodine in
the presence of phosphorus (Reaction XXIII). Like other iodi-

$$6ROH + 2P + 3I_2 \longrightarrow 6RI + 2H_3PO_3 \qquad\qquad (XXIII)$$
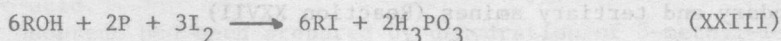
nations using these reagents, the reaction proceeds through an
intermediate ester which is decomposed by the *in situ* generated
hydriodic acid.

For the preparation of bromides and chlorides from alcohols,
the corresponding acids, HBr and HCl, are the reagents of
choice (32). The mechanism (33) for this reaction is believed
to involve a protonated intermediate (Reaction XXIV) which is
further attacked by the halide.

$$ROH + HX \longrightarrow RO\overset{\oplus}{H}_2 \overset{X^{\ominus}}{\longrightarrow} RX + H_2O \qquad\qquad (XXIV)$$
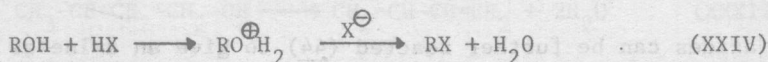
The observed reactivity gradation for this type of reaction
is for the acid: HI > HBr > HCl > HF, and for the alcohols
tertiary > secondary > primary.

Other halogenating agents include Ph_2PCl_3 (34), PBr_5 (35),
AlI_3 (36), and many sulfur containing reagents (37) of which
only thionyl bromide and thionyl chloride have attained wide
application. The ultimate choice of the halogenating agent to
be used will depend on the stereochemistry desired of the final
product (38,39).

Amination. Very few reactions of general scope exist for
the direct conversion of alcohols to amines. Among one of the
oldest is the Bucherer reaction which is used to convert
naphthols (40) and phenols (41) to their amine derivative by
reaction with aqueous sodium bisulphite and ammonia (Reaction
XXV).