ALLYL ALCOHOL AND MONOALLYL DERIVATIVES

1. Introduction

Allyl alcohol, $CH_2{=}CH{-}CH_2OH$ (2-propen-1-ol) [107-18-6] is the simplest unsaturated alcohol. One hydrogen atom can easily be abstracted from the allylic methylene ($-CH_2-$) to form a radical. Since the radical is stabilized by resonance with the C=C double bond, it is very difficult to get high molecular weight polymers by radical polymerization. In spite of the fact that allyl alcohol has been produced commercially for some years (1), it has not found use as a monomer in large volumes as have other vinyl monomers.

More recently, however, the technology of introducing a new functional group to the double bond of allyl alcohol has been developed. Allyl alcohol is accordingly used as an intermediate compound for synthesizing raw materials such as epichlorohydrin and 1,4-butanediol, and this development is bringing about expansion of the range of uses of allyl alcohol.

2. Physical Properties

Allyl alcohol is a colorless liquid having a pungent odor; its vapor may cause severe irritation and injury to eyes, nose, throat, and lungs. It is also corrosive. Allyl alcohol is freely miscible with water and miscible with many polar organic solvents and aromatic hydrocarbons, but is not miscible with *n*-hexane. It forms an azeotropic mixture with water and a ternary azeotropic mixture with water and organic solvents (Table 1). Allyl alcohol has both bacterial and fungicidal effects. Properties of allyl alcohol are shown in Table 2.

3. Chemical Properties

3.1. Addition Reactions.

The C=C double bond of allyl alcohol undergoes addition reactions typical of olefinic double bonds. For example, when

Table 1. **Azeotropic Boiling Points of Allyl Alcohol–Water–Organic Solvent Systems**

		Component, wt %		
Organic solvent	Boiling point, °C	Allyl alcohol	Water	Solvent
none	88.9	72	28	
benzene	68.2	9.1	7.3	83.6
diallyl ether	77.8	8.7	12.4	78.9
allyl acetate	82.6	9	20	71
cyclohexane	66.2	10.9	8.1	81.0
toluene	80.6	31.4	15.2	53.4

Table 2. **Properties of Allyl Alcohol**[a]

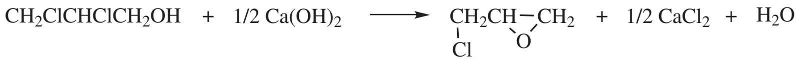
Property	Value
molecular formula	C_3H_6O
molecular weight	58.08
boiling point, °C	96.90
freezing point, °C	−129.00
density, d_4^{20}	0.8520
refractive index, n_D^{20}	1.413
viscosity at 20°C, mPa·s(=cP)	1.37
flash point[b], °C	25
solubility in water at 20°C, wt %	infinity

[a] Ref. 2.

[b] Closed cup.

bromine is added, a good yield of 2,3-dibromopropanol is obtained although 1,2,3-tribromopropane is obtained as a by-product. 1,2,3-tribromopropane is formed from substitution of the hydroxyl group of allyl alcohol by bromide and further addition of bromine to the C=C double bond. When this addition reaction is carried out in 2,3-dibromopropanol solvent, the substitution reaction is reduced and the yield of 2,3-dibromo adduct is increased (3). The addition of chlorine is different from that of bromine; the yield of 2,3-dichloro adduct is low (4), and much intermolecularly condensed ether by-product is formed. When hydrogen chloride dissolved in a solvent, such as a low boiling point ether, is used, the yield of 2,3-dichloro adduct can be increased (5). Furthermore, when an aqueous solution of hydrogen chloride above 45 wt % is used, the formation of ether by-product can be reduced, as can the formation of chlorohydrin which normally occurs in aqueous chlorine solution. Thus, a high yield of 2,3-dichloropropanol [616-23-9] can be obtained. For example, when chlorination is done continuously in a 50–60 wt % aqueous solution of hydrogen chloride at 0°C, allyl alcohol reacts completely with chlorine and 2,3-dichloropropanol is obtained in 95% yield (6). Ephichlorohydrin [106-89-8] is obtained by saponifying 2,3-dichloropropanol with calcium hydroxide.

$$CH_2{=}CHCH_2OH + Cl_2 \xrightarrow{HCl/H_2O} CH_2ClCHClCH_2OH$$



$$CH_2ClCHClCH_2OH \;+\; 1/2\,Ca(OH)_2 \longrightarrow \underset{Cl}{CH_2}CH{-}CH_2(O) \;+\; 1/2\,CaCl_2 \;+\; H_2O$$

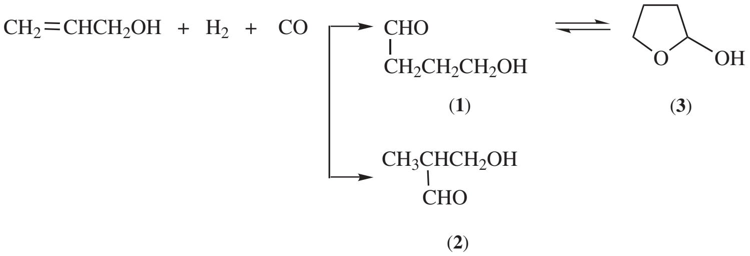
In fact, epichlorohydrin is being industrially manufactured by this method (7). The merit of this method is that it consumes only half the amount of chlorine and $Ca(OH)_2$ compared to that of the method via allyl chloride.

In the reaction of allyl alcohol with an aqueous chlorine solution, addition of hypochlorous acid to the double bond of allyl alcohol yields glycerol monochlorohydrin and as a by-product, glycerol dichlorohydrin. Thus, a poor yield of glycerol monochlorohydrin is obtained (8). To improve the yield of glycerol monochlorohydrin, addition of sodium carbonate in an amount equivalent to that of the hydrogen chloride in the aqueous chlorine solution, has been proposed (9).

When thiol is added to the double bond of allyl alcohol under radical forming conditions, Markovnikov reaction selectivity takes place. Mercury compounds, light, and oxygen accelerate the addition reaction. In the presence of $(CH_3S)_2Hg$, light, and oxygen, $CH_3S(CH_2)_3OH$ can be obtained in 93% yield. In the presence of light and oxygen only, the yield decreases to 61%; the reaction cannot occur in the presence of light only (10). On the other hand, under ionic reaction conditions, an anti-Markovnikov reaction takes place (11).

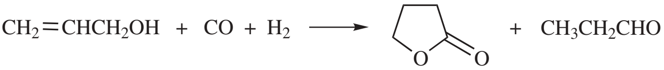
Under alkaline conditions, an amine addition reaction can occur. For example, in the reaction of $C_6H_5CH_2CH_2NH_2$ and allyl alcohol in the presence of sodium alcoholate at 108°C for 80 h, 43.4% *N*-(3-hydroxypropyl)phenylethylamine is formed (12).

3.2. Hydroformylation. Hydroformylation of allyl alcohol is a synthetic route for producing 1,4-butanediol [110-63-4], a raw material for poly(butylene terephthalate), an engineering plastic (qv); many studies on the process have been carried out.



After it was found that the rhodium carbonyl–triphenylphospine–complex, $HRh(CO)[P(C_6H_5)_3]_3$, is very effective in increasing the yield of hydroformylated product, many studies were done in greater detail with rhodium catalysts (13). The reactions are generally performed under the following conditions: 60–100°C, 0.69–3.4 MPa (7–35 kg/cm^2), H_2 to CO molar ratio more than one, and excess ligand phosphine. By-products are branched aldehyde **(2)**, 2-hydroxymethylpropionaldehyde [38433-80-6], propionaldehyde produced by isomerization of allyl alcohol and *n*-propanol produced by hydrogenation of allyl alcohol. The types of by-products and the yield are affected by the reaction temperature, the molar ratio between phosphine and rhodium, the kind of phosphine, and the molar ratio between H_2 and CO. The yield of linear aldehyde **(1)**, 4-hydroxybutyraldehyde [25714-71-0], depends on the kind of ligand. A yield of 60–70% is obtained even with excess triphenylphosphine, but a yield of more than 80% is obtained with 1-bis(diphenylphosphino)ferrocene (14). Addition of a great excess of triphenylphosphine causes a gradual decrease in catalytic activity. On the other hand, addition of excess triphenylphosphine and bidentate phosphine, especially, 1,4-bis(diphenylphosphino) butane to the rhodium complex in equimolar amounts enables the catalytic activity to be maintained, and the molar ratio of linear aldehyde to branched aldehyde is 9:1 and the selectivity to 2-hydroxytetrahydrofuran [5371-52-8] (**3**) is 80% (13). In the case of homogeneous reaction, separation and recovery of catalyst poses a problem. To solve this problem, gas-phase reaction was attempted and it was found that linear aldehyde is selectively produced in 99% yield, using silica containing a small amount of alumina as the catalyst carrier. From this experimental result, the gas-phase reaction was found to be regiospecific. Catalytic activity is maintained for at least 250 hours by using tris-*p*-tolylphosphine (15).

In the reaction of allyl alcohol with carbon monoxide using cobalt carbonyl, $Co(CO)_8$ as the catalyst, in the presence of a small amount of hydrogen and carbon monoxide under pressure, 9.8 MPa (1420 psi), at 100°C, intramolecular hydroesterification takes place, yielding γ-butyrolactone [96-48-0] (16).



With solvents having a nitrile group like acetonitrile, the selectivity of γ-butyrolactone is increased, resulting in a yield of 60%.

3.3. Substitution of Hydroxyl Group.

The substitution activity of the hydroxyl group of allyl alcohol is lower than that of the chloride group of allyl chloride and the acetate group of allyl acetate. However, allyl alcohol undergoes substitution reactions under conditions in which saturated alcohols do not react. Reactions proceed in catalytic systems in which a π-allyl complex is considered as an intermediate. It can thus be said that this substitution reaction is a specific reaction of allyl alcohol. The reaction of allyl alcohol with diethylamine, using palladium acetyl acetonate [14024-61-4] and triphenylphosphine [603-35-0] as the catalyst, at 50°C for 30 min yields 95% diethylallylamine (17). However, in this reaction, the catalyst is deactivated gradually during the reaction due to oxidation of phosphine by allyl alcohol. The reactivity of ammonia is lower than that of dialkylamine and even under the above-mentioned conditions, a substitution reaction cannot take place. Catalytic activity decreases markedly in the presence of ammonia; however, using diphosphine as the ligand, improves catalytic activity and stability (18). For instance, in the reaction of allyl alcohol and ammonia with palladium acetyl acetonate and 1,3-bis(diphenylphosphono)propane [6737-42-4] as the catalyst and propylene glycol as the solvent at 110°C for 4 h, a mixture of monoallylamine, diallylamine, and triallylamine is obtained with a 73.5% conversion of allyl alcohol and a selectivity of 98.9% to amines. In the conventional process for synthetizing allylamine from allyl chloride and amine, the reaction vessel becomes badly corroded (19). Moreover, it has the disadvantage of forming sodium chloride as a by-product. The new process is, therefore, economically attractive.

With active methylene compounds, the carbanion substitutes for the hydroxyl group of allyl alcohol (17,20). Reaction of allyl alcohol with acetylacetone at 85°C for 3 h yields 70% monoallyl compound and 26% diallyl compound. Malonic acid ester in which the hydrogen atom of its active methylene is substituted by *N*-acetyl, undergoes the same substitution reaction with allyl alcohol and subsequently yields α-amino acid by decarboxylation (21).

In the reaction of allyl alcohol and Grignard reagent with $[P(C_6H_5)_3]_2\text{-}NiCl_2$ as the catalyst, formation of the carbon–carbon bond proceeds at a high yield (22).

$$CH_2{=}CHCH_2OH + RMgBr \longrightarrow CH_2{=}CHCH_2R + MgBrOH$$

For reaction with hydrogen halides, the substitution reaction with halide ion easily occurs when a cuprous or cupric compound is used as the catalyst

(23) and yields a halogenated allyl compound. With a cuprous compound as the catalyst at 18°C, the reaction is completed in 6 h. Zinc chloride is also a good catalyst (24), but a by-product, diallyl ether, is formed.

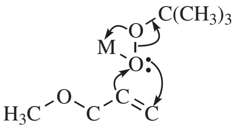
$$CH_2{=}CHCH_2OH + HCl \longrightarrow CH_2{=}CHCH_2Cl + H_2O$$

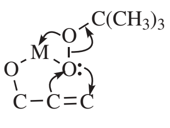
3.4. Oxidation.

The C=C double bond of allyl alcohol undergoes epoxidation by peroxide, yielding glycidol [556-52-5]. This epoxidation reaction is applied in manufacturing glycidol as an intermediate for industrial production of glycerol [56-8-5], using a typical epoxidation agent such as peracetic acid.

$$CH_2{=}CHCH_2OH + CH_3COOOH \longrightarrow \underset{\diagdown O \diagup}{CH_2{-}CH}CH_2OH + CH_3COOH$$

In the past, FMC Corporation industrially produced glycerol in two steps: production of glycidol from allyl alcohol in high boiling point ketone solvent, followed by hydrolysis of glycidol to glycerol. Daicel Chemical Industries produces glycerol with a reaction–distillation system to prevent a decrease in yield caused by intermolecular reaction of glycidol, by feeding water to the distillation column and converting the main part of the glycidol to glycerol *in situ* and not isolating glycidol as an intermediate (25). Shell Chemical Company produced glycerol, using hydrogen peroxide as the oxidant (25). The reaction, which is carried out with tungstic acid, H_2WO_4, as the catalyst, enables glycerol to be obtained in one step. When the pH (4–6), concentration and other conditions are controlled and the reaction temperature is at 45°C, yield of glycidol can reach 82–87% (26). Degussa A.G. produced glycidol by using sodium tungstate, $NaHWO_4$, as the catalyst. It is necessary to use a catalyst in the epoxidation reaction of olefinic double bonds (such as hydrogen peroxide or alkyl hydroperoxide). However, epoxidation of allyl alcohol is different from that of typical olefins in reactivity considerations such as the reaction rate and selectivity, because of interaction between the hydroxyl group of allyl alcohol and the catalyst. When tungstenic acid is used as the catalyst, the reaction rate of epoxidation of allyl alcohol by hydroperoxide as the oxidation reagent is 30 times faster than that of allyl chloride (27). Further, in the case of epoxidation by $(CH_3)_3COOH$ with a vanadium catalyst, the epoxidation rate of allyl alcohol is 1000 times faster than that of methyl allyl ether. It is postulated that a covalent alkoxide intermediate is formed between the metal and the hydroxyl group (28).





This chemical bond between the metal and the hydroxyl group of allyl alcohol has an important effect on stereoselectivity. Asymmetric epoxidation is well-known.

The most stereoselective catalyst is $Ti(OR)_4$, which is one of the early transition metal compounds and has no oxo group (28). Epoxidation of isopropylvinylcarbinol [4798-45-2] (1-isopropylallyl alcohol) using a combined chiral catalyst of $Ti(OR)_4$ and L-(+)-diethyl tartrate and $(CH_3)_3COOH$ as the oxidant, stops at 50% conversion, and the erythro:threo ratio of the product is 97:3. The reason for the reaction stopping at 50% conversion is that only one enantiomer can react and the unreacted enantiomer is recovered in optically pure form (28).

Allyl alcohol can be easily oxidized to yield acrolein [107-02-8] and acrylic acid [79-10-7]. In an aqueous potassium hydroxide solution of $RuCl_3$, allyl alcohol is oxidized by a persulfate such as $K_2S_2O_8$ at room temperature, yielding acrylic acid in 45% yield (29). There are also examples of gas-phase oxidation reactions of allyl alcohol, such as that with Pd–Cu or Pd–Ag as the catalyst at 150–200°C, in which allyl alcohol is converted by 80% and acrolein and acrylic acid are selectively produced in 83% yield (30).

3.5. Miscellaneous Reactions.

Allyl alcohol can be isomerized to propionaldehyde [123-38-6] in the presence of solid acid catalyst at 200–300°C. When copper or alumina is used as the catalyst, only propionaldehyde is obtained, because of intramolecular hydrogen transfer. On the other hand, acrolein and hydrogen are produced by a zinc oxide catalyst. In this case, it is considered that propionaldehyde is obtained mainly by intermolecular hydrogen transfer between allyl alcohol and acrolein (31).

$$CH_2{=}CHCH_2OH \longrightarrow CH_2{=}CHCHO + H_2$$

$$CH_2{=}CHCH_2OH + CH_2{=}CHCHO \longrightarrow CH_2{=}CHCHO + CH_3CH_2CHO$$

Friedel-Crafts reaction of allyl alcohol with benzene or alkylbenzene yields many kinds of products, in which the reaction species and the product ratio depend on the type of catalyst. Zinc chloride is the most effective catalyst for producing allyl compounds by this reaction (32).

Allyl alcohol undergoes reactions typical of saturated, aliphatic alcohols. Allyl compounds derived from allyl alcohol and used industrially, are widely manufactured by these reactions. For example, reactions of allyl alcohol with acid anhydrides, esters, and acid chlorides yield allyl esters, such as diallyl phthalates and allyl methacrylate; reaction with chloroformate yields carbonates, such as diethylene glycol bis(allyl carbonate); addition of allyl alcohol to epoxy groups yields products used to produce allyl glycidyl ether (33,34).

4. Industrial Manufacturing Processes for Allyl Alcohol

There are four processes for industrial production of allyl alcohol. One is alkaline hydrolysis of allyl chloride (1). In this process, the amount of allyl chloride, 20 wt % aqueous NaOH solution, water, and steam are controlled as they are added to the reactor and the hydrolysis is carried out at 150°C, 1.4 MPa (203 psi) and pH 10–12. Under these conditions, conversion of allyl chloride is 97–98%, and allyl alcohol is selectively produced in 92–93% yield. The main by-products are diallyl ether and a small amount of high boiling point substance. The alkali concentration and pH value are important factors. At high alkali concentrations, the amount of by-product, diallyl ether, increases and at low concentrations, conversion of allyl chloride does not increase.

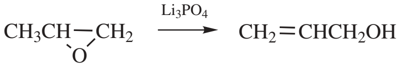
A second process has two steps. The first step is oxidation of propylene [115-07-1] to acrolein and the second step is reduction of acrolein to allyl alcohol by a hydrogen transfer reaction, using isopropyl alcohol (25).

$$CH_2{=}CHCH_3 + O_2 \longrightarrow CH_2{=}CHCHO + H_2O$$

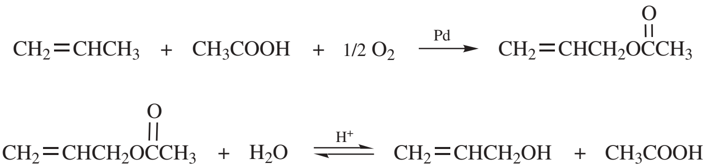
$$CH_2{=}CHCHO + (CH_3)_2CHOH \longrightarrow CH_2{=}CHCH_2OH + CH_3COCH_3$$

This process has defects such as co-production of acetone and a low yield of allyl alcohol.

At present, neither of these two processes are being used industrially. Another process is isomerization of propylene oxide [75-56-9].



In this process, the fine powder of lithium phosphate used as catalyst is dispersed, and propylene oxide is fed at 300°C to the reactor, and the product, allyl alcohol, together with unreacted propylene oxide is removed by distillation (25). By-products such as acetone and propionaldehyde, which are isomers of propylene oxide, are formed, but the conversion of propylene oxide is 40% and the selectivity to allyl alcohol reaches more than 90% (25). However, allyl alcohol obtained by this process contains approximately 0.6% of propanol. Until 1984, all allyl alcohol manufacturers were using this process. Since 1985 Showa Denko K.K. has produced allyl alcohol industrially by a new process which they developed (6,7). This process, which was developed partly for the purpose of producing epichlorohydrin via allyl alcohol as the intermediate, has the potential to be the main process for production of allyl alcohol. The reaction scheme is as follows:



$$CH_2{=}CHCH_3 + CH_3COOH + 1/2\,O_2 \xrightarrow{Pd} CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C}CH_3$$

$$CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C}CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_2{=}CHCH_2OH + CH_3COOH$$

In the first step of the reaction, the acetoxylation of propylene is carried out in the gas phase, using solid catalyst containing palladium as the main catalyst at 160–180°C and 0.49–0.98 MPa (70–140 psi). Components from the reactor are separated into liquid components and gas components. The liquid components containing the product, allyl acetate, are sent to the hydrolysis process. The gas components contain unreacted gases and CO_2. After removal of CO_2, the unreacted gases, are recycled to the reactor. In the second step, the hydrolysis, which is an equilibrium reaction of allyl acetate, an acid catalyst is used. To simplify the process, a solid acid catalyst such as ion-exchange resin is used, and the

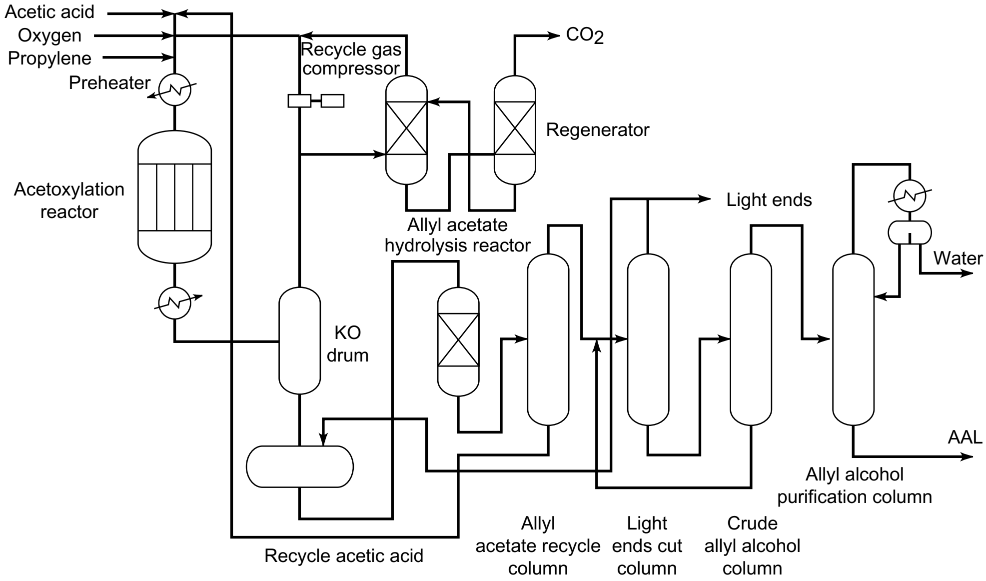


Fig. 1. The process for allyl alcohol (AAL) production via allyl acetate.

reaction is carried out at the fixed-bed liquid phase. The reaction takes place under the mild condition of 60–80°C and allyl alcohol is selectively produced in almost 100% yield. Acetic acid recovered from the hydrolysis process, is reused in the first step. As a result, it can be said that allyl alcohol is produced from oxidation of propylene by oxygen. Allyl alcohol forms an azeotropic mixture with water, and the mixture is a homogeneous liquid. Therefore, to obtain dry allyl alcohol, ternary azeotropic distillation and dehydration are required. This process for allyl alcohol production is shown in Figure 1.

The world's manufacturers of allyl alcohol are ARCO Chemical Company, Showa Denko K.K., Daicel Chemical Industries, and Rhône-Poulenc Chimie; total production is approximately 70,000 tons per year.

5. Uses of Allyl Alcohol

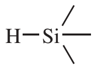
Recently, the uses of allyl alcohol have been greatly changing and increasing. Before 1985, the two principal uses of allyl alcohol were as a raw material for glycerol, which is industrially produced by the Daicel Chemical Company, and a monomer, diethylene glycol bis(allyl carbonate), for plastic optical lens (see ALLYL MONOMERS AND POLYMERS). It is estimated that each use is consuming several thousand tons of allyl alcohol per year. In 1985, Showa Denko K.K. started producing about 12,000 tons per year of epichlorohydrin using allyl alcohol as the raw material (7). Further in 1990, its production of epichlorohydrin increased to 24,000 tons per year, consuming 17,000–18,000 tons per year of allyl alcohol. Some epichlorohydrin manufacturers are planning to switch their production process to the allyl alcohol process. The consumption of allyl alcohol may therefore be expected to expand. In 1990, ARCO Chemical Company put on stream the world's largest allyl alcohol production plant, using the propylene oxide isomerization process, and at the same time, started producing 1,4-butanediol, consuming most of the allyl alcohol they produced, as the raw material. Since their production of 1,4-butanediol is said to be 35,000 tons per year, approximately 30,000 tons per year of allyl alcohol are needed. This is the first example of industrially producing 1,4-butanediol using allyl alcohol as the raw material (see ACETYLENE-DERIVED CHEMICALS). With ARCO Chemical Company starting up the allyl alcohol production plant, FMC Corporation stopped their allyl alcohol production plant. In addition to these applications, allyl alcohol is used as the raw material for producing allyl esters (diallyl phthalates and allyl methacrylate), allyl ether (allyl glycidyl ether), and a styrene–allyl alcohol copolymer. The styrene–allyl alcohol copolymer is produced by Monsanto Chemical Company (35) and is used in water-soluble paints, alkyd resins (qv), and urethanes as polyols.

6. Monoallyl Derivatives

In this article, mainly monoallyl compounds are described. Diallyl and triallyl compounds used as monomers are covered in the article entitled ALLYL MONOMERS AND POLYMERS and also in the literature (36,37).

6.1. Reactivity of Allyl Compounds.

Hydrosilylation. The addition reaction of silane



to the C=C double bond of allyl compounds is applied in the industrial synthesis of silane coupling agents.

$$CH_2{=}CHCH_2Y + HSiX_3 \longrightarrow X_3SiCH_2CH_2CH_2Y$$

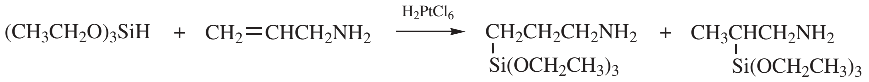
Usually, trichlorosilane, trialkoxysilane, methyl dichlorosilane, and methyl dialkoxysilane are used. For example, the reaction of trichlorosilane with allyl methacrylate is as follows:

$$CH_2{=}C(CH_3)COOCH_2CH{=}CH_2 + HSiCl_3 \longrightarrow CH_2{=}C(CH_3)COO(CH_2)_3SiCl_3 \qquad (4)$$

$$CH_2{=}C(CH_3)COO(CH_2)_3SiCl_3 + CH_3OH \longrightarrow CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3 \qquad (5)$$

Platinum compounds are the most active catalysts for hydrosilylation. Compounds such as H_2PtCl_6 and $PtCl_2(CH_3CHCOCH_3)_2$ are effective. In the reaction with allyl methacrylate, which has two C=C double bonds, the allylic double bond selectively reacts. For example, while refluxing 10.5 moles (1422 g) of $HSiCl_3$ with 1 mL of 0.01 *M* $PtCl_2(CH^3COCHCOCH_3)$ in an acetone solution, as the catalyst, allyl methacrylate is added dropwise over 2 h and the reaction solution is agitated for 2 h at room temperature, whereupon 9.94 moles (2600 g) of product (4) is obtained after removal of excess $HSiCl_3$ (38). Also, in the case of allyl glycidyl ether, the allylic double bond is more reactive than the glycidyl group to silane. In the presence of mesityl oxide dichloro platinum complex as the catalyst, trimethoxysilane reacts with allyl glycidyl ether of equivalent moles at 130–140°C yielding 91.5% (3-glycidoxypropyl)-trimethoxysilane [2530-83-8] (39).

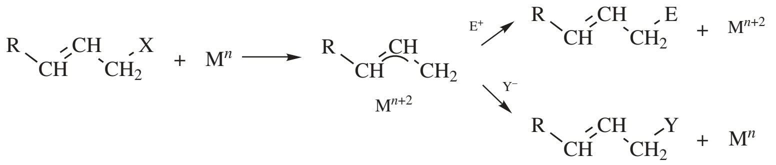
These examples show that silane reacts selectively with the γ-position of allyl compounds. However, in its reaction with allyl amine, a side reaction in which silane binds to the β-position takes place (40).



$$(CH_3CH_2O)_3SiH + CH_2{=}CHCH_2NH_2 \xrightarrow{H_2PtCl_6} \underset{\displaystyle Si(OCH_2CH_3)_3}{\underset{|}{C}}H_2CH_2CH_2NH_2 + CH_3\underset{\displaystyle Si(OCH_2CH_3)_3}{\underset{|}{C}}HCH_2NH_2$$

Use of $HRh(CO)[P(C_6H_5)_3]_3$ as the catalyst and an excess of triphenylphosphine improves the γ:β ratio. For example, reaction of triethoxysilane with allylamine of equivalent moles at 150°C for 10 h, yields the γ-form product in more than 70% and the γ:β ratio is 26. Compared with this, when H_2PtCl_6 is used as the catalyst, the γ:β ratio is 4 (41). Furthermore, when $Rh[(\mu\text{-}P(C_6H_5)_2\text{-}(cyclooctadiene)]_2$ is used as the catalyst, the yield of γ-form product is selectively increased to 92% and that of β-form product is decreased to 1.1% (42).

π-Allyl Complex Formation. Allyl halide, allyl ester, and other allyl compounds undergo oxidative addition reactions with low atomic valent metal complexes to form π-allyl complexes. This is a specific reaction of allyl compounds.



This π-allyl complex does not react with electrophilic reagent, E^+, in a catalytic way because the central metal remains in an oxidized state even after reaction. On the other hand, in the reaction with nucleophilic reagent, Y^-; the central metal is easily reduced to M^n, and the oxidative addition of allyl compound with M^n again takes place. Thus, this reaction continues in a catalytic way. Allyl compounds that carry out oxidative addition have as their functional group, X, halogen, RCOO, ROCOO, $(RO)_2COO$, RO, RNH, R_3N, NO_2, RSO_2, R_2S, and others. Metals that are effective as catalysts for the reaction of allyl compounds with nucleophilic reagents are Pd, Pt, Rh, Ru, Ni, Fe, Co, W, Mo, and others (43). Of these metals, Pd catalysts are the ones most studied. In the presence of nucleophilic reagent and carbon monoxide, a CO insertion can be done (44).

Table 3. **Properties of Important Allyl Compounds**

Property	Allylchloride	Allylacetate	Allylmethacrylate	AGE[a]	Allylamine	DMAA[b]
molecular formula	C_3H_5Cl	${}_5H_8O_2$	$C_7H_{10}O_2$	$C_6H_{10}O_2$	C_3H_7N	$C_5H_{11}N$
CAS Registry Number	[107-05-1]	[591-87-7]	[96-05-9]	[106-92-3]	[107-11-9]	[2155-94-4]
molecular weight	76.53	100.12	126.16	114.14	57.10	85.15
boiling point, °C	44.69	104	150	153.9	52.9	64.5
freezing point, °C	−134.5	−96	−60	−100	−88.2	
density, d_4^{20}	0.9382	0.9276	0.934	0.9698	0.7627	0.72
refractive index, n_D^{20}	1.416	1.404	1.436	1.435	1.420	
viscosity at 20°C, mPa·s(=cP)	3.36	0.52	13	1.20		0.44
flash point, °C	−31.7	6	33	57.2	−29	−23
solubility in water at 20°C, %	0.36	2.8			infinity	
limits of inflammability, %	2.9	2.1			2.2	
	11.30	13.0			22	

[a] Allyl glycidyl ether.

[b] Dimethylallylamine.

6.2. Physical Properties of Derivatives. The physical properties of some important monoallyl compounds are summarized in Table 3.

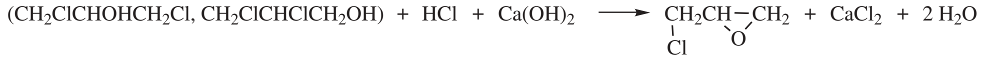
6.3. Allyl Chloride. This derivative, abbreviated AC, is a transparent, mobile, and irritative liquid. It can be easily synthesized from allyl alcohol and hydrogen chloride (23). However, it is industrially produced by chlorination of propylene at high temperature.

$$\mathrm{CH_2{=}CHCH_3 + Cl_2 \longrightarrow CH_2{=}CHCH_2Cl + HCl}$$

The process involving allyl alcohol has not been industrially adopted because of the high production cost of this alcohol. However, if the allyl alcohol production cost can be markedly reduced, and also if the evaluated cost of hydrogen chloride, which is obtained as a by-product from the substitutive chlorination reaction, is cheap, then this process would have commercial potential. The high temperature propylene–chlorination process was started by Shell Chemical Corporation in 1945 as an industrial process (1). The reaction conditions are a temperature of 500°C, residence time 2–3 s, pressure 1.5 MPa (218 psi), and an excess of propylene to chlorine. The yield of allyl chloride is 75–80% and the main by-product is dichloropropane, which is obtained as a result of addition of chlorine. Other by-products include monochloropropenes, dichloropropenes, 1,5-hexadiene. At low temperatures, the amount of by-product dichloropropane increases and above 550°C, the amount of by-product benzene increases. Excess propylene is recovered and recycled to the reactor after washing and dehydration treatment, and hydrogen chloride, the by-product is recovered as concentrated hydrochloric acid (1). The purity of allyl chloride in the market is 99–99.5%; the main impurities are 1,5-hexadiene and monochlorinated compounds.

Uses. Allyl chloride is industrially the most important allyl compound among all the allyl compounds (see CHLOROCARBONS AND CHLOROHYDROCARBONS, ALLYL CHLORIDE). It is used mostly as an intermediate compound for producing epichlorohydrin, which is consumed as a raw material for epoxy resins (qv). World production of AC is approximately 700,000 tons per year, the same as that of epichlorohydrin. Epichlorohydrin is produced in two steps: reaction of AC with an aqueous chlorine solution to yield dichloropropanol (mixture of 1,3-dichloropropanol and 2,3-dichloropropanol) by chlorohydrination, and then saponification with a calcium hydroxide slurry to yield epichlorohydrin.

$$\mathrm{CH_2{=}CHCH_2Cl + Cl_2 + H_2O \longrightarrow (CH_2ClCHOHCH_2Cl,\ CH_2ClCHClCH_2OH) + HCl}$$



$$\mathrm{(CH_2ClCHOHCH_2Cl,\ CH_2ClCHClCH_2OH) + HCl + Ca(OH)_2 \longrightarrow \underset{\displaystyle Cl}{\underset{|}{CH_2}}CH\underset{\displaystyle \diagdown O \diagup}{-}CH_2 + CaCl_2 + 2\,H_2O}$$

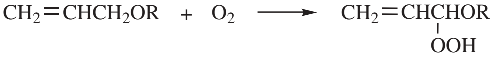
In the second step, a distillation-reaction system is applied to prevent hydrolysis of epichlorohydrin, by removing epichlorohydrin and water as an azeotropic mixture from the top of the distillation column. This operation is known as steam-stripping. In addition to being used in the synthesis of epichlorohydrin, AC is also used as a raw material for synthesizing other allyl compounds such as allyl esters, allyl ethers, and allylamines by nucleophilic substitution, utilizing the easily substituting property of its chloride group.

6.4. Allyl Esters. *Allyl Acetate.* Industrial production of allyl acetate started only rather recently. Nevertheless, among the allyl compounds, its production is second to that of allyl chloride. It is produced mostly for manufacturing allyl alcohol and its manufacture by acetoxylation of propylene has been described previously. The allyl acetate obtained may be separated and purified by distillation.

Allyl Methacrylate. At present, allyl methacrylate, AMA, is used mostly as a raw material for silane coupling agents. Utilizing the difference in the polymerizing ability of the allyl double bond and that of the methacrylate double bond, polymerization at the methacrylate double bond only is done by an anionic initiated reaction (45), yielding linear and soluble polymers with an allylic group attached to the pendant side chain. There are various methods for synthesizing AMA. For example, transesterification between allyl acetate and methyl methacrylate (46), esterification of methacrylic acid [79-41-4] with an excess of allyl alcohol (47), transesterification between methyl methacrylate [80-62-6] and allyl alcohol (48). This last method gives the highest yield of AMA. With an excess of methyl methacrylate and a combined catalyst of CaO and LiCl, allyl alcohol is converted by 97.7% and AMA is selectively produced in 95% yield (see also METHACRYLIC ACID AND DERIVATIVES).

Other monoallyl esters are esters of caproic acid and amyl glycolic acid, which are used as perfumes.

6.5. Allyl Ethers. The C—H bond of the allyl position easily undergoes radical fission, especially in the case of allyl ethers, reacting with the oxygen in the air to form peroxide compounds.



$$CH_2{=}CHCH_2OR + O_2 \longrightarrow CH_2{=}CH\underset{\displaystyle OOH}{\underset{|}{C}}HOR$$

Therefore, in order to keep allyl ether for a long time, it must be stored in an air-tight container under nitrogen. Utilizing the peroxidation property, allyl glycidyl ether, glycerol monoallyl ether [25136-53-2], ethylene glycol monoallyl ether [111-45-45], and others are employed in unsaturated polyesters for "air-drying" coatings, but in this application, usually polyfunctional allyl ethers are used (36).

Allyl Glycidyl Ether. This ether is used mainly as a raw material for silane coupling agents and epichlorohydrin rubber. Epichlorohydrin rubber is synthesized by polymerizing the epoxy group of epichlorohydrin, ethylene oxide, propylene oxide, and allyl glycidyl ether, AGE, with an aluminum alkyl catalyst (36). This rubber has high cold-resistance.

In the synthesis of AGE with an acid as the catalyst, allyl alcohol is added to the epoxy group of epichlorohydrin, yielding 3-allyloxy-1-chloro-2-propanol [4638-03-3], which then undergoes cyclization with alkali to yield AGE. Catalysts such as H_2SO_4, $SnCl_4$, BF_4^-; $(C_2H_5)_2O$ (33), heteropolyacids, $HClO_4$, and *p*-$CH_3C_6H_4SO_3H$ (34) are used.

6.6. Allyl Amines. *Allylamine.* This amine can be synthesized by reaction of allyl chloride with ammonia at the comparatively high temperature of 50–100°C (49), or at lower temperatures using $CuCl_2$ (50) or CuCl (51) as the catalyst. In all such methods, a mixture of monoallyl, diallyl, and triallyl amines is obtained. For selectively obtaining monoallylamine, AAm, hydrolysis of by hydrochloric acid is used (52). The degree of polymerization of monoAAm is low. However, its hydrogen chloride salt is polymerized readily (53) and an industrial process for manufacturing polyAAm has been developed (54). AAm polymers are used as fixing agents for reactive dyes on fibers. If the production of silane coupling agents from monoAAm is established, industrial consumption of monoAAm may increase.

Organotin compounds derived from diallylamine and alkylthiophosphine, have low phytotoxicity and are useful as relatively stable insecticides (55).

Dimethylallylamine. When 1-dimethylamino-2,3-dichloropropane [5443-48-1], which is obtained by addition of chlorine to dimethylallylamine, DMAA, reacts with NaSCN, the dimethylamino group is transferred, yielding 1,3-dithiocyano-2-dimethylaminopropane, which is used to synthesize the carbamothioic ester, $(CH_3)_2NCH(CH_2SCONH_2)_2$ [15263-53-3] for pesticide use (56). Similarly, when 1-dimethylamino-2,3-dichloropropane reacts with Na_2S_x, 1,3-trithia-2-dimethylaminocyclopropane [31895-21-3], which is used as an insecticide (57), is produced. Furthermore, diallyldimethylammonium chloride (DADMAC) [7398-69-8], which is used as a monomer for synthesizing water-soluble polymers, is obtained from the reaction between DMAA and allyl chloride. DMAA is obtained in 95% yield by reaction of allyl chloride with two equivalent moles of dimethylamine at 23°C (58).

7. Health and Safety Factors

Most allyl compounds are toxic and many are irritants. Those with a low boiling point are lachrymators. Precautions should be taken at all times to ensure safe handling (59). Allyl compounds are harmful and may be fatal if inhaled, swallowed, or absorbed through skin. They are destructive to the tissues of the mucous membranes and upper respiratory tract, eyes, and skin (Table 4).

7.1. Handling and Storage.

Workers should be provided with appropriate respirators (NIOSH/MSHA approved), chemical resistant gloves, safety goggles, and other protective equipment. Work areas should be well-ventilated and be equipped with a safety shower and an eye bath. Care must be taken not to inhale any vapor and prevent it from getting into eyes, on skin, or on clothing. Prolonged or repeated exposure should be avoided. Thorough washing is

Table 4. **Toxicity of Important Monoallyl Compounds**[a]

Compound	LD_{50} rat, mg/kg
allyl alcohol	64
allyl chloride	64
allyl acetate	130
allyl methacrylate	430
allyl glycidyl ether	922
allylamine	102

[a] Ref. 59.

required after handling. The compounds should be kept in a tightly closed container away from heat, sparks, and open flames and be stored in a cool dry place. Allyl ethers must be stored under nitrogen, but allyl (meth)acrylate must not be stored under an inert atmosphere in order to inhibit polymerization.

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