of pyridine at room temperature for two hours, then removing all of the solvent under vacuum. The crude acid chloride was taken up in 100 ml. of benzene and added to 300 ml. of stirred ether suspension containing 0.2 mole of diphenylcadmium.[13] After stirring for five hours at room temperature the ether–benzene solution was washed and steam-distilled. The residue was hydrolyzed with 400 ml. of 5% methanolic potassium hydroxide and the solution poured into 3 liters of water, giving 32 g. of crystalline product, m. p. 200–203°. For analysis, 1 g. was recrystallized from acetone, giving stout needles, m. p. 203–204°.

Anal. Calcd. for $C_{30}H_{44}O_3$: C, 79.64: H, 9.73. Found: C, 79.69; H, 9.37.

The bulk of the hydroxy-ketone was treated with acetic anhydride and converted into 3,12-diacetoxy-norcholanyl phenyl ketone, which crystallized from acetic acid in prisms, m. p. 136–137°.

Anal. Calcd. for $C_{34}H_{48}O_5$: C, 76.12; H, 8.95. Found: C, 76.19; H, 9.22.

3,12-Diacetoxy-23-bromonorcholanyl Phenyl Ketone.—A solution of 1.6 g. of the diacetate in 35 ml. of acetic acid containing 1 drop of hydrobromic acid was treated with 0.5 g. of bromine. Decolorization occurred during thirty minutes. The product was separated with water and ether, washed, then crystallized from a small volume of acetone, giving 0.8 g. of white crystals; m. p. 106–108°; $[\alpha]^{29}\text{D} + 91°$ (57.8 mg. made up to 5 ml. with chloroform gave $\alpha + 1.05°$; $l = 1$ dm.). Recrystallization from acetone did not change the melting point. This is the labile form of the bromo-ketone.

Anal. Calcd. for $C_{34}H_{47}O_5Br$: C, 66.34; H, 7.92; Br, 13.0. Found: C, 66.58; H, 7.96; Br, 12.4.

The mother liquor sirup from the above bromination refused to crystallize until it was boiled in alcohol then cooled, whereupon 1 g. of white plates of a second bromo-ketone crystallized; m. p. 165–175°. In another preparation the whole product from 16 g. of the diacetate was boiled in ethanol then crystallized, giving 15 g. of the higher-melting bromo-ketone; $[\alpha]^{28}\text{D} + 105°$ (3% solution in chloroform).

Anal. Calcd. for $C_{34}H_{47}O_5Br$: C, 66.34; H, 7.92; Br, 13.0. Found: C, 66.05; H, 7.96; Br, 13.2.

When the 106–108° form is boiled in ethanol solution then cooled, plates of the 175°-bromo-ketone separate. The lower-melting form seems to be the primary bromination product, but it could be obtained in good yield only when small quantities of the diacetate were brominated and the product crystallized promptly.

In order to show that the 175°-bromo-ketone did not represent a rearrangement product, a sample was reconverted to the parent ketone. Two grams of the bromide in 200 ml. of acetone was covered with carbon dioxide, then treated with 25 ml. of 1 *N* chromous chloride solution at room temperature for three hours. Extraction and crystallization gave 1.4 g. of 3,12-diacetoxynorcholanyl phenyl ketone, m. p. 133–136°.

Debromination of Benzalacetophenone Dibromide.—A solution of 9.2 g. of benzalacetophenone dibromide[14] in 150 ml. of acetone was treated, under carbon dioxide, with 75 ml. of 1 molar chromous chloride solution. Heat developed and the color turned green immediately. After standing for one and one-half hours, the solution was diluted with water and extracted with ether. The halogen-free oily residue from the washed and dried ether solution gave 0.6 g. of white solid crystallizing from ethanol, m. p. 168–178°. This material which may be one of the dimerides of benzalacetophenone was not studied further. The remainder of the reaction product was distilled *in vacuo*. The fraction distilling at 160–170° air-bath temperature, 1 mm., weighed 2.9 g. (55%). The benzalacetophenone solidified upon moistening with methanol and scratching, and showed m. p. 54.5–57.5°.

Summary

A method for the dehalogenation of steroids by means of chromous chloride is described. By this method 5,6-dibromo-3-keto-steroids are converted into the corresponding Δ^4-3-keto-steroids, 5,6-dibromo-sterols give the Δ^5-sterols, and α-bromo-ketones are reduced to the parent ketone. The method may be useful in other fields.

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[13] *Cf.* Cole and Julian, THIS JOURNAL, **67**, 1369 (1945).

[14] "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 205.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. I. Catalytic Hydrolysis of Allyl Chloride

BY LEWIS F. HATCH AND REEDUS RAY ESTES[1]

Only recently has brief mention been made in the literature[2,3] of the catalytic hydrolysis of allyl chloride by a hydrochloric acid solution of cuprous chloride, although the preparation of the chloride from the alcohol using hydrochloric acid and cuprous chloride has been known for some time.[4] This method of acid hydrolysis was reported to give yields of both allyl alcohol and diallyl ether comparable to those obtained by hydrolysis using a basic medium. Because the reaction is of unusual interest from a theoretical standpoint and is potentially of wide application to the hydrolysis of other allylic chlorides as well, a series of investigations has been made on the catalytic hydrolysis of allyl chloride and various substituted allyl chlorides.

Experimental

Allyl Chloride.—Commercial grade allyl chloride was furnished us for this work by the Shell Development Company. It was fractionated through a 4-ft. helix-packed column and the material boiling constantly at 44.9° (751 mm.) was used.

Cuprous Chloride.—Merck "Reagent Grade" cuprous chloride was purified by the usual method.[5] Electrodeposition analysis indicated a cuprous chloride content of 99.8% assuming the impurity to be cupric chloride.

Continuous Hydrolysis of Allyl Chloride.—A diagram of the apparatus used in all the hydrolysis runs except those involving added sodium chloride is given in Fig. 1. The hydrolysis column *N* was made of three concentric Pyrex tubes 48 in. long and having outside diameters of 20 mm.,

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[1] Present address: The Armour Laboratories, Chicago, Illinois.

[2] Williams, *Trans. Am. Inst. Chem. Engrs.*, **37**, 157 (1941); *Chem. Met. Eng.*, **47**, 834 (1940).

[3] British Patent 549,001 to Shell Development Co. (1942).

[4] (a) Dewael, *Bull. soc. chim. Belg.*, **39**, 40 (1930); (b) Breckpot, *ibid.*, **39**, 462 (1930).

[5] Henderson and Fernelius, "Inorganic Preparations," McGraw-Hill and Co., New York, N. Y., 1935, p. 24.

51 mm. and 80 mm. The inner tube was packed with 4-mm. glass beads to a depth of 1 meter. The 51-mm. tube was wound with enough no. 22 Nichrome wire to give a heater of approximately 300 watts. The three tubes were held in place by two hard wood discs having annular grooves 5 mm. deep to receive the ends of the tubes. The column was maintained at the desired temperature by the mercury-type thermoregulator 13, which, in conjunction with relay 10, 100-watt bulb 11, and variable transformer 12, controlled the amount of current supplied to the column heater winding.

Nitrogen under constant pressure in tank B forced catalyst solution from 3-liter flask C through a rotameter flowmeter E, regulating stopcock, preheater H, and into the column at N. The liquid flowed downward through the column and was collected in a graduated cylinder R, after passing through the condenser 17. The rate of withdrawal of liquid at Q was regulated to maintain a constant liquid level at N. The volume of catalyst solution present in the column during operation was approximately 100 ml. Nitrogen from B (dried by magnesium perchlorate in tube 7) forced the allyl chloride from the ice-water-jacketed 50 ml. buret F through the flowmeter G, regulating stopcock and vaporizer K into the bottom of the column through a coarse fritted glass plate. The tube from the vaporizer to the bottom of the column was electrically heated to prevent condensation of the allyl chloride at this point. Constant nitrogen pressure in B was maintained by assembly A. The pressure was that of a 254-mm. column of mercury. A decrease in pressure in B would break the upper contact which controlled the relay 5 and the solenoid 4 would be energized which in turn would open the stopcock 1, admitting nitrogen gas from the reducing valve of a commercial nitrogen tank. When the proper pressure had been restored, current to the solenoid would be interrupted and the spring 2 would return the stopcock to the closed position. The soft iron rod was attached to the spring by means of chain 3 which carried a ring through which the elongated stopcock handle passed. All stopcocks in the apparatus were held in place by springs.

Volatile materials from the column (such as unreacted allyl chloride, diallyl ether–water azeotrope, etc.) were condensed in receivers 15 and 16 immersed in ice water contained in Dewar S. The receivers were made from two halves of a Pyrex buret, and were affixed to the column head by 10/30 standard taper joints held in place by springs. All other standard taper joints in the apparatus were 24/40. Three-way stopcock 14 allowed rapid change of receivers at the beginning and end of a run.

The following general experimental procedure was used The desired quantity of cuprous chloride was dissolved in the proper amount of concd. hydrochloric acid and the solution was diluted to 2 liters with distilled water. Portions of this solution were poured into the flask C in such a way as to rinse its inner surfaces completely, allowing the rinsings to drain out through the three-way stopcock D. During rinsings and filling, the flask was swept continuously by carbon dioxide, injected through a glass tube inserted into the flask neck. The remainder of the catalyst solution was then poured into the flask, the carbon dioxide injector removed and the flask stoppered immediately. The apparatus was then flushed twice with the catalyst solution after which the rate of flow was reduced to 10 ml. per minute. At this rate ten minutes were required for a complete change of liquid in the column. The rate of flow of allyl chloride was set at 0.5 ml. per minute. At this time samples of catalyst solution were removed through stopcock D and analyzed for cuprous ion and acidity. A dry graduated cylinder was attached at R, buret reading recorded, three-way stopcock 14 turned to connect a dry cold-trap and the run started. Near the end of the hydrolysis run, samples of the catalyst solution were withdrawn and analyzed for cuprous ion. If the value obtained was lower than that at zero time, which was seldom the case, their average was taken as the concentration during the run. At the end of the time period (one to two hours) the hydrolysis take-off was stopped, the position of the stopcock to the cold-trap was reversed and the flow of catalyst solution and of allyl chloride was stopped. The hydrolysate was then analyzed for allyl alcohol and cuprous ion. The material collected in the cold-trap was analyzed for unreacted allyl chloride and diallyl ether.

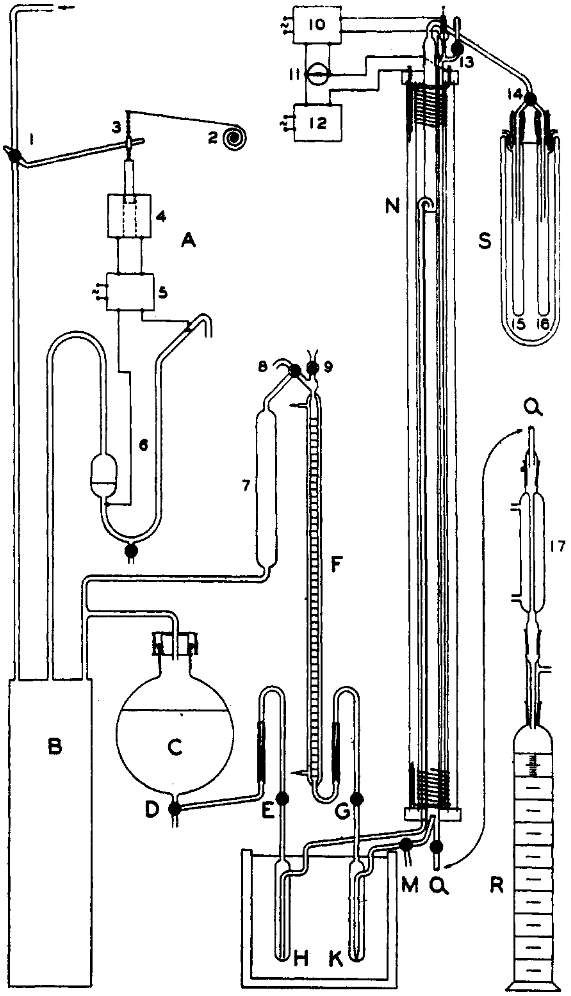

Fig. 1.—Apparatus for continuous catalytic hydrolysis of allyl chloride.

The column reactor was also used to determine the catalytic activity of the following metal chlorides: Cu^{II}, Sn^{IV}, Sn^{II}, Fe^{II}, Al^{III}, Mn^{II} and Co^{II}. The conditions were those which were optimum for cuprous chloride. The quantity of metal chloride used was that required to give a solution of the same molarity as 0.2 g. of cuprous per 100 ml. of catalyst solution. None of these ions showed any appreciable effect.

Batch Hydrolysis of Allyl Chloride in the Presence of Sodium Chloride.—The apparatus for batch hydrolysis consisted of a 250-ml. three-necked flask fitted with an efficient high-speed stirrer, thermometer, and reflux condenser through which ice-water was circulated. The catalyst solution was prepared by adding a solution of 0.5 g. of cuprous chloride in 8.25 ml. of concd. hydrochloric acid to a solution of the desired amount of sodium chloride dissolved in distilled water and diluting the resulting mixture to 250 ml. Using a pipet, 100 ml. of the catalyst solution was transferred to a 500-ml. volumetric flask for dilution and analysis for chloride ion. One hundred ml. was also transferred to the reaction flask. The flask was swept with carbon dioxide before and during the addition of the catalyst solution to lessen air oxidation of the cuprous ion.

Five ml. of allyl chloride was then introduced by pipet directly into the catalyst solution through a side neck of the flask and the neck was then closed with a stopper containing the thermometer. Rapid stirring was begun and the mixture was heated to 40° within less than one minute, and that temperature was held for the reaction time. Five ml. of allyl chloride was pipetted into a glass-stoppered flask and weighed to determine the weight of allyl chloride delivered to the reaction flask. At the end of the time period the mixture was cooled with an ice-bath to room temperature and transferred quantitatively to a 500-ml. volumetric flask, diluted and analyzed immediately for chloride ion. The increase in chloride ion was taken as an indication of the extent of hydrolysis. The results were reproducible to within 0.5%.

Analysis: Cuprous Ion.—The following procedure was used in the analysis of the catalyst solution and hydrolysate for cuprous ion. Twenty-five ml. of the cuprous ion containing solution was pipetted into 25 ml. of oxygen-free ferric ammonium sulfate solution, made by dissolving 33 g. of ferric ammonium sulfate in sufficient oxygen-free 3 *M* sulfuric acid to make 1 liter. (This quantity of the sulfate solution will titrate solutions containing up to 0.6% cuprous chloride.) Two hundred and fifty ml. of a solution containing 80 ml. of sulfuric acid and 25 ml. of phosphoric acid per liter was added. After the addition of 3 drops of a 0.2% solution of barium diphenylaminesulfonate the ferrous iron was titrated with 0.025 *N* potassium dichromate until the first permanent appearance of a purplish tinge. The precision of the method is ±0.1%.

Chloride Ion.—The Caldwell and Moyer[6] modification of the Volhard titration was used.

Allyl Alcohol.—The allyl alcohol content of the hydrolysate was determined by titration of unsaturation and by separation of the alcohol as its azeotrope with water. The amount of material capable of being titrated by bromine was determined by the Francis method.[7] It was necessary to make a correction for the cupric ion present, since its reaction with potassium iodide liberates an equivalent amount of iodine. The volume of standard thiosulfate equivalent to the cupric ion in 25 ml. of hydrolysate (determined by analysis of a separate sample) was subtracted from the volume used in back titration in the bromine number determination.

On known solutions containing 1.5% allyl alcohol this method for the determination of allyl alcohol gave 0.07% error.

Distillation of 1 to 2% allyl alcohol solutions to obtain the azeotrope with water gave a 5% error when a 36 inch 12 mm. vacuum-jacketed helix-packed column was used with a reflux ratio of 10 to 1. This method of analysis was used to supplement the data given by titration methods and to check the identity of the products. All data reported are based upon titration.

Diallyl Ether and Unreacted Allyl Chloride.—In every run an excess of allyl chloride was used and this excess collected in the cold traps along with the diallyl ether formed during the reaction. The amounts of diallyl ether and unreacted allyl chloride were determined by separating the water layer from the contents of the cold traps and determining the amount of saponifiable chlorine in the organic layer. This saponifiable chlorine corresponded to the allyl chloride. The amount of ether was determined by difference. This method can be used because of the insolubility of the chloride and ether in water and the absence of a significant amount of allyl alcohol.

Results

In the operation of the apparatus for continuous hydrolysis to determine the influence of a particular variable, such as hydrochloric acid or cuprous chloride concentration, on the yield of allyl alcohol it was necessary that as many as possible of the factors which might influence the reaction be kept constant. These variables are: (a) temperature, (b) rate of addition of allyl chloride, (c) rate of addition of catalyst solution and withdrawal of hydrolysate. The temperature used for hydrolysis was 80°, a temperature sufficiently high to assure removal of the diallyl ether (boiling point of the azeotrope with water = 78°) overhead but without significant loss of allyl alcohol (boiling point of the azeotrope with water = 88.6°). The rate of addition of allyl chloride (constant for all runs) was chosen so that a measurable amount would always escape unreacted. The rate of withdrawal of the hydrolysate was adjusted to maintain a constant level of catalyst solution (the continuous phase) in the column.

The reactions which are influenced by these conditions are

$$CH_2{=}CHCH_2Cl + H_2O \rightleftarrows CH_2{=}CHCH_2OH + HCl \quad (1)$$

$$CH_2{=}CHCH_2Cl + CH_2{=}CHCH_2OH \rightleftarrows CH_2{=}CHCH_2OCH_2CH{=}CH_2 + HCl \quad (2)$$

The effect on alcohol production of varying hydrochloric acid concentrations from 0.00 to 6.05 g. per 100 ml. of catalyst solution with a constant concentration of cuprous chloride is given in Table I. This table also contains the results obtained when the cuprous chloride concentration was varied from 0.00 to 0.36 g. per 100 ml. of catalyst solution while the hydrochloric acid concentration of the catalyst solution was maintained constant.

TABLE I

EFFECT OF HYDROCHLORIC ACID AND CUPROUS CHLORIDE UPON THE CATALYTIC HYDROLYSIS OF ALLYL CHLORIDE

Run no.	Component in 100 ml. of solution, g. HCl	CuCl	Allyl alcohol in 100 ml. of hydrolysate, g.
1	0.00[a]	0.19	1.22
2	1.00	.17	2.56
3	1.50	.17	2.67
4	3.05	.17	2.45
5	6.05	.18	1.94
6[b]	0.00	.00	0.12
7	3.15	.00	0.10
8	3.01	.08	1.88
9	3.05	.17	2.45
10	3.09	.36	2.69

[a] A solution containing 18 g. of sodium chloride per 100 ml. of water was used to dissolve the cuprous chloride.
[b] Distilled water alone was used in this run.

These data indicate that an acid concentration between 1 and 2% and a cuprous chloride concentration of 0.2 to 0.3% represent the optimum operating conditions. The hydrolysis of allyl chloride using these optimum conditions gave results in essential agreement with those reported by Williams.[2]

The effect of chloride ion concentration upon the reaction could not be studied satisfactorily in the continuous flow apparatus and was determined

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[6] Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[7] Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

by the use of the batch reactor. Data indicating the linear relationship between chloride ion concentration and chloride ion formation in the catalytic hydrolysis of allyl chloride is given in Table II. This table also contains data pertaining to the influence of time on the chloride ion formation in the presence of an appreciable chloride ion concentration. These data indicate that chloride ion influences the rate of reaction but apparently does not enter into an equilibrium reaction with the products of the reaction. This was further substantiated by subjecting allyl alcohol to the same catalyst solution and temperature as in runs 5, 6, 7 and 8, Table II. Four hours of contact gave no diminution of chloride ion in solution. Ten and twenty grams of sodium perchlorate per 100 ml. of catalyst solution had no effect on the extent or rate of reaction (88% after ten minutes for each concentration). This indicated that it was the chloride ion alone which affected the reaction.

TABLE II

EFFECT OF SODIUM CHLORIDE ON THE CATALYTIC HYDROLYSIS OF ALLYL CHLORIDE

Run	NaCl in 100 ml. of cat. solution[a]	Time, min.	Moles of allyl chloride Used	Moles of allyl chloride Reacted	% Reacted
1	0 g.	10	0.060	0.052	87
2	5	10	.060	.042	70
3	10	10	.060	.033	55
4	16	10	.060	.021	35
5	25	30	.061	.029	48
6	25	60	.060	.042	70
7	25	120	.060	.051	85
8	25	240	.060	.054	90

[a] Catalyst solution contained 0.2 g. CuCl and 1.5 g. HCl per 100 ml.

The following series of reactions is proposed to explain the observed effect of cuprous chloride and chloride ion on the hydrolysis of allyl chloride in an acid solution

$$\mathrm{CuCl} + \mathrm{Cl}^- \rightleftarrows \mathrm{CuCl_2}^- \tag{3}$$

$$\mathrm{CH_2{=}CHCH_2Cl} + \mathrm{CuCl_2}^- \longrightarrow [\mathrm{CH_2{=}CHCH_2Cl{\cdot}CuCl_2}]^- \tag{4a}$$

$$[\mathrm{CH_2{=}CHCH_2Cl{\cdot}CuCl_2}]^- \longrightarrow [\mathrm{CH_2{=}CHCH_2{\cdot}CuCl_2}] + \mathrm{Cl}^- \tag{4b}$$

$$[\mathrm{CH_2{=}CHCH_2{\cdot}CuCl_2}] + \mathrm{OH}^- \longrightarrow \mathrm{CH_2{=}CHCH_2OH} + \mathrm{CuCl_2}^- \tag{5}$$

These reactions are in accord with the generally accepted theory[8] of a unimolecular ionization reaction with the rate controlling step being the ionization of the alkyl halide. This type of reaction would predominate in a neutral or acid solution and the ionization would be inhibited by chloride ion.

In the catalytic hydrolysis of allyl chloride the ionization step is accelerated by the formation with the cuprous chloride-chloride ion complex, $\mathrm{CuCl_2}^-$, of an intermediate association complex or transition state which causes the chlorine to be more easily removed as an ion. That the catalyst is the complex ion and not cuprous chloride is indicated by the fact that the reaction rate was increased by increasing the cuprous content of the catalyst solution (Table I). The amount of solid cuprous chloride dissolved was always appreciably greater than the amount which would dissolve as cuprous chloride in water containing no added chloride ions. Since any cuprous chloride which dissolved in the catalyst solution in excess of the amount soluble in chloride-ion-free water did so as the complex ion, any increase in reaction rate with increased cuprous content must be attributed to the complex ion and not to the dissolved cuprous chloride, the concentration of which either remained constant or decreased.

The effect of increased hydrochloric acid on the yield of alcohol noted in Table I may be explained by the equilibrium represented by equation (1). The establishment of this equilibrium is catalyzed by cuprous chloride.[4] The equilibrium constant is a function of both the hydronium and chloride ion concentration and is probably but slightly affected by chloride ion concentration alone.

Summary

1. The effect of several variables on the cuprous chloride catalyzed acid hydrolysis of allyl chloride has been investigated.

2. A series of reactions have been proposed to explain the observed effects of chloride ion, cuprous chloride-chloride ion complex and hydrochloric acid.

3. The following metal ions showed no catalytic effect on the acid hydrolysis of allyl chloride: $\mathrm{Cu^{II}}$, $\mathrm{Sn^{IV}}$, $\mathrm{Sn^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Al^{III}}$, $\mathrm{Mn^{II}}$, and $\mathrm{Co^{II}}$.

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[8] Bateman, Hughes and Ingold, THIS JOURNAL, 60, 3080 (1938).