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### A study of the synthesis of 4-chlorobutanal.

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UNIVERSITY OF LOUISVILLE

A STUDY OF THE SYNTHESIS OF 4-CHLOROBUTANAL

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

CARL E. MOORE

1947

75711



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**NAME OF STUDENT** Carl E. Moore

**TITLE OF THESIS** A Study of the Synthesis  
of 4-chlorobutanol

**APPROVED BY READING OF COMMITTEE COMPOSED OF THE  
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**DATE:** June 5, 1947

## ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Dr. Max I. Bowman, Assistant Professor of Chemistry, College of Arts and Sciences, University of Louisville, for his counsel and guidance and for his kind cooperation in carrying out the literature searches. Appreciation is also expressed to his wife, Mary Agnes Moore, for her generous contribution of helpful suggestions and criticisms concerning the preparation of the manuscript.

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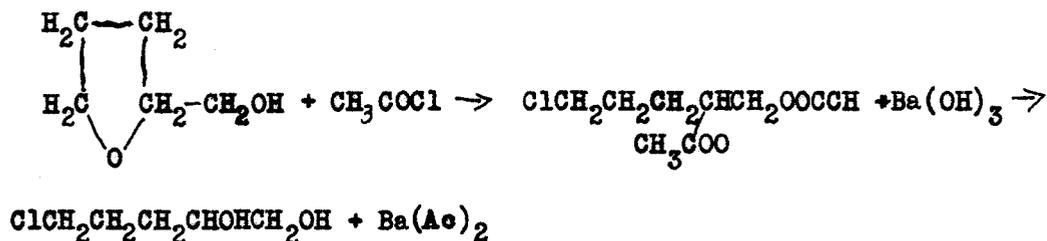
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## PURPOSE

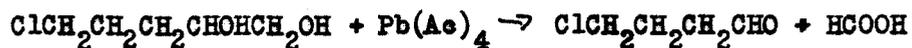
The original purpose of this research was to prepare gamma-chlorobutyraldehyde in yields sufficient for use in further synthesis. Preparative difficulties, however, made it necessary to alter this purpose to include a more general study of aldehyde synthesis in order to accomplish a satisfactory preparation of the compound. Thus the final intent of this undertaking was to evaluate existing synthetic methods in respect to the compound desired and to investigate new methods of aldehyde synthesis.

## HISTORY OF 4-CHLOROBUTANAL

4-chlorobutanal was first reported in 1942 by Paul (10), who prepared the compound from tetrahydrofurfuryl alcohol, which has recently become easily available. Recent researches (9) have established that tetrahydrofurfuryl alcohols may be prepared with good yields by starting with furfural, a material obtained as a by-product in the cereal industry. The ring of tetrahydrofurfuryl alcohol was opened by reacting with acetylchloride, yielding 5-chloro-1,2-pentanediacetate, which was hydrolyzed by barium hydroxide to 5-chloro-1,2-pentanediol:



The 5-chloro-1,2-pentanediol was oxidized with lead tetraacetate to give gamma-chlorobutyraldehyde:



Paul also prepared the aldehyde by the use of sodium iodate but without advantage.

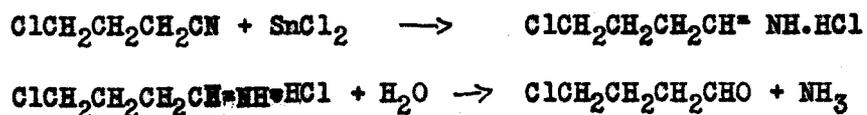
The article by Paul reported that 4-chlorobutanal is a colorless liquid of penetrating odor (b.p. 50°C- 60°C at 13mm;  $D_{15}^{8.5}$  1.107;  $M_D^{8.5}$  1.44662). It gave the following derivatives: p-nitrophenylhydrazone, m.p. 110; 2,4-dinitrophenylhydrazone, m.p. 134-135; oxime, m.p. 74.5, easily rearranged by Raney nickel to 4-chlorobutyramide, m.p. 99°C-100°C. The aldehyde polymerizes readily under the influence of heat. There was no yield figure given, just the statement that the reaction takes place with suitable yield.

## THEORY AND DISCUSSION

## DISCUSSION OF ALDEHYDE METHODS

## Stephen Reduction

Of the various aldehyde methods considered, the Stephen Reduction (11) looked most promising because it is recognized to give excellent yields, except for a few compounds in the aromatic series. The basis of this method is the conversion of nitrile through the imino-chloride into the aldehyde with the same number of carbon atoms, the reducing agent being stannous chloride dissolved in ether saturated with hydrogen chloride. Gamma-chlorobutyronitrile was prepared by conventional methods (See Experimental Part.)



The reaction was first carried out according to Stephen's original directions (11) with negative results. It was decided to attempt the reaction again, using the drastic conditions recommended by King (6). The attempt was carried out by keeping the reaction mixture under reflux for 84 hours, with very little iminochloride forming. A drop

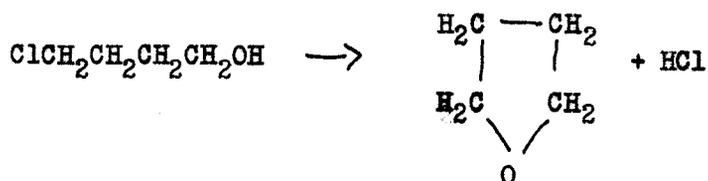
of water was added because Whitmore (12) reports that absolutely dry ether should not be used in this reaction. No yield of aldehyde was obtained. It is of interest to note that a small amount of what was probably iminochloride was formed under the more drastic conditions of the reaction. There is some indication, therefore, that this reaction might be favored by further intensifying the conditions by choosing a higher boiling ether than the ethyl ether used. Two other nitriles, alphanaphthonitrile and o-toluenitrile, were reported to have failed to respond to the more drastic treatment. However, other compounds, such as gamma-phthalimide-alpha-methylbutyraldehyde and gamma-phenoxybutyraldehyde can be obtained in good yield under the more drastic conditions (6).

#### Oxidation Methods

It was considered desirable to abandon the Stephen Reduction and to attempt to prepare the aldehyde from tetramethylenechlorhydrin because this compound is now easily obtainable from tetrahydrofuran (4), which E.I. DuPont De Nemours & Company is now producing in research quantities.



Attempts to oxidize the alcohol directly by means of air and catalyst (16) and pure oxygen and a catalyst were unsuccessful. The method using air and a catalyst failed to work because the temperature necessary for this reaction is so high that under the influence of the copper bronze and quinoline, hydrogen chloride split out, resulting in a recovery of the tetrahydrofuran.



Hydrogen peroxide has long been used successfully in oxidation methods in organic chemistry. However, there still appears to be a great deal to be learned about the chemistry of this useful reagent. A great step forward in this direction was made by Kharasch (5,7) in his work on the concept of free radicals in solution. Most of this work on the peroxides has dealt with the anomalies of peroxide-produced additions at

double bonds. Some oxidations have been explained by the peroxide effect, notably the Cannizzaro Reaction (13), in which benzaldehyde is converted into benzoic acid and benzyl alcohol. The fact that peroxides are formed easily with aldehydes and are readily oxidized to acids is a serious hindrance to this method for aldehyde preparation (14). Some difficultly prepared aldehydes may be obtained by the peroxide oxidation methods. Glyceraldehyde may be prepared by means of peroxide oxidation (15) where other methods fail. The most successful of the peroxide oxidative methods use a ferrous ion catalyst. The function of this catalyst is not fully explained. One author postulates an addition product of the hydrogen peroxide and ferrous ion (2). It has not been within the scope of this work to clarify the mechanism of the peroxide oxidation of alcohols to aldehydes.

A study was undertaken to establish the best conditions for the oxidation of tetramethylenechlorhydrin to gamma-chlorbutyraldehyde after the method used for preparing glyceraldehyde (2) failed to give aldehyde in sufficient amount to permit yield measurements. It was decided to conduct a series of experiments in which the mole ratios of  $\text{Fe}^{+2}$  /ROH and  $\text{H}_2\text{O}_2$ /ROH and the temperature were varied and

the resulting products analyzed for the per cent aldehyde produced. The mole ratios of  $\text{Fe}^{+2}/\text{ROH}$  and  $\text{H}_2\text{O}_2/\text{ROH}$  were set at 0.1 and 0.25 respectively. The temperature was varied from  $10^\circ$  to  $100^\circ$  and the yields determined (See Table 1). With the optimum temperature and the alcohol and peroxide ratios constant, the best  $\text{Fe}/\text{ROH}$  ratio was determined (See Table 2).

The above experiment was repeated, using manganese dioxide to destroy the excess peroxide. This change resulted in an improved yield. It also demonstrated that the reaction was practically instantaneous. In cases where no ferrous catalyst had been used and a large excess of ferrous ion added to destroy the peroxide immediately, no change was noted in the yield. When no ferrous ion was used and a large excess of manganese dioxide added to destroy the hydrogen peroxide, no aldehyde was formed. By selection of the optimum reaction conditions it was found possible to increase the aldehyde yield to 28% based on the hydrogen peroxide used.

Glacial acetic acid was next chosen as a likely solvent for the peroxide oxidation because of its strong solvent properties, even though certain acids are known to inhibit the breakdown of hydrogen peroxide (8). The reaction was then run in glacial acetic acid, using the optimum mole ratios previously

determined for aqueous solutions, except that the ferrous ion was added in the form of solid ferrous sulfate. An unusual reaction took place with the peroxide attacking the chlorine on the gamma carbon and liberating chlorine gas quite easily at room temperature. This is perhaps another of the anomalies of the peroxide chemistry. The solutions were tested and no aldehydes were found to have resulted.

In the general consideration of oxidative methods it was felt desirable to investigate glacial acetic acid as a possible solvent medium for the oxidation of tetramethylene-chlorhydrin with potassium dichromate because glacial acetic acid is an excellent solvent for many organic materials and a limited number of inorganic salts. The potassium dichromate was finely powdered and dissolved in boiling glacial acetic acid, where it formed a deep red solution. It was found that the potassium dichromate was soluble in excess of three grams per hundred grams. (CAUTION!! No attempt has been made as yet to determine the upper limits of the solubility of potassium dichromate in glacial acetic acid. This operation may involve explosive hazards.) On addition of an alcohol to the hot dichromate glacial acetic acid solution, an almost immediate reduction of the dichromate to chromic ions took place, and the solution turned from red to light green. A series of experiments was carried out to determine the optimum reaction

temperature and time(See Table 6 and 7). The yields based on tetramethylenechlorhydrin were highly satisfactory, being 63.5% under optimum conditions. The dichromate oxidation method was then applied to various available alcohols that were considered representative types. These yields were also highly satisfactory and compare quite favorably with other published yields.

## SYNTHESIS

## THE STEPHEN REDUCTION OF NITRILES

The Stephen Reduction was carried out in the following manner: Constant boiling hydrobromic acid was reacted with trimethylenechlorhydrin to give trimethylenechlorobromide. Then the trimethylenechlorobromide was reacted with potassium cyanide to give gamma-chlorobutyronitrile. The latter was reacted with anhydrous stannous chloride to give the iminestannichloride addition product, which was decomposed in water.

## Preparation of Constant Boiling Hydrobromic Acid

One pound of hydrobromic acid (34%, 1.31 Sp. Gr.) was distilled until the boiling point reached 126°C. The resulting constant boiling solution gave the following: 1.49 Sp. Gr., 47.8% hydrobromic acid.

## Synthesis of Trimethylenechlorobromide (1)

One and a half moles of trimethylenechlorhydrin was treated with three moles of hydrobromic acid (47.8%), and three moles of sulfuric acid was added gradually. The mixture was

refluxed for one hour and distilled until no water insoluble product appeared. The water insoluble layer was separated and washed with water, then with 50g of cold concentrated sulfuric acid, and finally with sodium carbonate (50g in 500cc of water). The resulting compound was separated, dried with 10g calcium chloride, and distilled.

#### Data

10cc containing water over at about 145°C

Temperature up to 149°C-162°C (main fraction over)

Tailings over at 166°C

Theoretical yield 238g

Actual yield 202g

Percentage yield 85

#### Preparation of Anhydrous Stannous Chloride

To one mole of hydrated stannous chloride two moles of acetic anhydride was added cautiously since much heat was evolved. The resulting salt was washed free of acetic acid and excess acetic anhydride with dry ether and preserved in a dessicator.

#### Preparation of Gamma-Chlorobutyronitrile

1.2 moles of potassium cyanide and 126cc of water were put in a round bottom flask and warmed with stirring until dissolved. To this mixture was added 492cc ethyl alcohol and

1.4 moles of trimethylenechlorobromide and refluxed one and a half hours. 630cc of water was added, and the gamma-chlorobutyronitrile was collected in 112cc of chloroform and removed from the aqueous solution. The chloroform solution was washed with 200cc calcium chloride solution (1+1 of saturated calcium chloride and water). The solution was dried over fused calcium chloride and distilled in a modified claisen flask until the temperature reached 120° C. The resulting product was fractionated.

Data

40°-80°	25mm	First fraction
84°-92°	22mm	Main fraction
97°-107°	19mm	Tailings
Percentage yield		26

Reduction of Aldimine Stannichloride of Gamma-Chlorebutyronitrile

One and one-half moles of anhydrous stannous chloride was added to dry ether, forming a suspension. The suspension was saturated with dry hydrogen chloride until two layers formed, and the nitrile was then added. The hydrogen chloride was prepared by adding concentrated sulfuric acid to sodium chloride and scrubbing the gas with concentrated sulfuric acid. The reaction failed to give an addition product immediately. However, after sixteen hours refluxing, a white oily emulsion appeared at the interface of the two layers. The emulsion broke up on addition of cold

water. The ethereal solution had a characteristic odor resembling an ester. A light blue color developed with fuchsin aldehyde reagent after standing several hours. Tests with Fehling Solution were inconclusive. A sodium bisulfite addition product was attempted, at the same time running a sample of normal butyraldehyde as a control. No addition products were formed. The absence of the crystalline aldiminestannichloride and the failure of a definitely positive aldehyde test to be obtained made it necessary to make a second run, varying the experimental conditions.

Run two was made up similar to the first but was refluxed for eighty-four hours and allowed to stand two weeks at room temperature. A small quantity of white solid appeared at the interface of the two liquids. This solid was increased by the addition of a drop of water, which was added following Whitmore's line of reasoning (12). The solid which separated out was dissolved in water. The filtrate was evaporated free of ether and excess hydrogen chloride, then extracted with ether to recover the unreacted nitrile and any aldehyde that might have been formed in the solution due to hydrolysis. The mixture was vacuum fractionated and yielded no satisfactory indication of aldehyde.

## OXIDATION METHODS

The oxidation methods were carried out on tetramethylenechlorhydrin, which was derived from tetrahydrofuran. The four methods employed used pure oxygen and a catalyst, air and a catalyst, hydrogen peroxide, and finally potassium dichromate.

### Preparation of Tetramethylenechlorhydrin

Dry hydrogen chloride produced from sodium chloride and concentrated sulfuric acid and scrubbed through concentrated sulfuric acid was run into 100.8g tetrahydrofuran and cooled in an ice bath until the solution was saturated. The mixture was put under reflux until the temperature of the solution reached 93°C. This reaction required an overall time of six hours. The solution was distilled at atmospheric pressure until it was freed of tetrahydrofuran. The remaining liquid was fractionated at 14mm, and the fraction coming over at 81°-83°C was retained.

#### Data

Theoretical yield	152 g
Actual yield	66.8g
Percentage yield	44

### Oxidation by Means of Pure Oxygen

Five grams of tetrahydrofuran and one gram of activated charcoal were added to 100cc carbontetrachloride, and oxygen was bubbled through a capillary tube into the solution for six hours. The solution was tested for aldehydes with negative results.

### Oxidation by Means of Copper Bronze Catalyst

Two grams of tetramethylenechlorhydrin, 1.8g quinoline, 2g meta-dinitrobenzene, 0.5g copper bronze, 10g 4,4'-dichlorodiphenyl were put into a 100cc distilling flask equipped with a bubbler and connected to the vacuum line. The flask was placed in an oil bath and the temperature raised to 150°C. Immediately tetrahydrofuran began distilling over. The method was considered useless for the compound desired and was abandoned.

### Oxidation with Hydrogen Peroxide

Two grams of ferrous sulfate was dissolved in as little water as possible by heating and then put into a round bottom flask. 20g of tetramethylenechlorhydrin was weighed into the flask and 20cc of water added. 154cc of 6% hydrogen peroxide derived from 29% superoxol was added from a dropping funnel.

The temperature went up rapidly to 35° C on the addition of the first hydrogen peroxide. The reaction mixture was cooled by immersing in a water bath. A light red color appeared in the solution. After vigorous stirring of several hours, almost all the alcohol was in solution except a little around the surface perimeter, where it had a polymeric appearance. A penetrating characteristic odor was noted soon after the first addition of hydrogen peroxide. After all the hydrogen peroxide was added, the mixture was stirred vigorously and allowed to stand overnight at room temperature. After 48 hours the mixture had lost its red color but had retained an aldehyde odor. The solution was acid to methyl red. The aqueous solution was extracted with ether. No aldehyde was recovered.

Further study of the hydrogen peroxide oxidation was made, using ferrous sulfate as a catalyst. A series of samples was run to establish the optimum conditions for the reaction, varying temperature and the mole ratios of ferrous ion, alcohol, and hydrogen peroxide. The reactions were carried out in a borate testing tube, using a mechanical stirrer with a glass rod as agitator. The alcohol and ferrous ion in the form of a ferrous ammonium sulfate solution were added from Mohr pipettes in the desired mole ratios and the hydrogen peroxide slowly added to the mixture being agitated. The reaction time was arbitrarily

set at twenty minutes.

The aldehyde solutions resulting from the various oxidations were made up to 200cc with isopropyl alcohol. A suitable aliquot was chosen and added to 200cc of a saturated solution of 2,4-dinitrophenylhydrazine in 2 molar hydrochloric acid. 200cc of 2 molar hydrochloric acid was added, and the solutions were allowed to digest a minimum of two hours. The resulting precipitates were collected in tared Gooch crucibles and washed twice with 2 molar hydrochloric acid and with distilled water until free of chloride. The precipitates were then dried for two hours at 100°C, cooled, and weighed.

TABLE I

Effect of Reaction Temperature on Yield, Using Superoxol

Temperature	Moles ROH	Moles Fe <sup>++</sup>	Moles H <sub>2</sub> O <sub>2</sub>	Yield (Based on H <sub>2</sub> O <sub>2</sub> )
10°C	.00690	.000940	.00320	0 %
25°C	.00690	.000940	.00190	27.5 %
40°C	.00690	.000940	.00204	24.0 %
75°C	.00690	.000940	.00208	19.5 %
100°C	.00690	.000940	.00124	0 %

TABLE II

Effect of Ratio of Fe/ROH on yield, using 6% Hydrogen Peroxide and Destroying Excess H<sub>2</sub>O<sub>2</sub> with Ferrous Sulfate

Temperature	Moles ROH	Moles Fe <sup>++</sup>	Moles H <sub>2</sub> O <sub>2</sub>	Yield
30°C	.0132	.00152	.00380	19.1 %
30°C	.0132	.000760	.00380	17.8 %
30°C	.0132	.000504	.00380	19.3 %
30	.0132	none	.00380	19.6 %

TABLE III

Effect of Ratio of Fe/ROH on yield, using Manganese Dioxide to Destroy Excess Peroxide

Temperature	Moles ROH	Moles Fe <sup>++</sup>	Moles H <sub>2</sub> O <sub>2</sub>	Yield
30°C	.0132	.00152	.00380	28.0 %
30°C	.0132	.00076	.00380	22.8 %
30°C	.0132	.000504	.00380	18.6 %
30°C	.0132	.000260	.00380	5.2 %
30°C	.0132	None	.00380	None

TABLE IV

Effect of Mole Ratio of  $H_2O_2$ , Using Manganese Dioxide to Destroy the Excess Hydrogen Peroxide

Temperature	Moles ROH	Moles Fe <sup>++</sup>	Moles $H_2O_2$	Yield
30°C	.0132	.000940	.00152	none
30°C	.0132	.000940	.00750	16.2 %
30°C	.0132	.000940	.00990	12.3 %
30°C	.0132	.000940	.00380	28.0 %

TABLE V

Determination of Degree of Aldehyde Formations in Glacial Acetic Acid, Using Superoxol

Temperature	Moles ROH	Moles Fe <sup>++</sup>	Moles $H_2O_2$	Yield
30°C	.0132	Saturated solution	.0264	none
30	.0132	Presence of solid $FeSO_4$	.0264	none

#### Potassium Dichromate Oxidation

Potassium dichromate was dissolved in boiling glacial acetic acid and used as an oxidizing agent for the preparation

of gamma-chlorbutryaldehyde and various other higher aldehydes. The oxidizing mixtures were made by dissolving one gram of powdered potassium dichromate in 50cc of boiling acid.

TABLE VI

Effect of Reaction Temperature

Time	Moles ROH	Moles $K_2Cr_2O_7$	Temperature	Acetic acid	Yield
3 min.	.0100	.00340	105°C	50cc	60 %
3 min.	.0100	.00340	95°C	50cc	57.5 %
3 min.	.0100	.00340	85°C	50cc	49 %

TABLE VII

Effect of Reaction Time

Time	Moles ROH	Moles $K_2Cr_2O_7$	Temperature	Acetic acid	Yield
3 min.	.0100	.00340	105°C	50cc	60%
8 min.	.0100	.00340	105°C	50cc	63.5%
15 min.	.0100	.00340	105°C	50cc	61.0%
30 hrs.	.0100	.00340	30°C	50cc	13.9%

TABLE VIII

Determination of Aldehydes Formed From Various Alcohols,  
Using the Potassium Dichromate Acetic Acid Procedure

Time	Moles ROH	Moles $K_2Cr_2O_7$	Temperature	Acetic acid	Yield
<u>Allyl Alcohol</u>					
3 min.	.0100	.00340	105°C	50cc	102%
<u>Benzyl Alcohol</u>					
3 min.	.0100	.00340	105°C	50cc	86%
<u>2-Ethylhexanol</u>					
3 min.	.0100	.00340	105°C	50cc	68%
<u>Amyl Alcohol</u>					
3 min.	.0100	.00340	105°C	50cc	65%

## S U M M A R Y

A study has been made of various possible methods of synthesizing gamma-chlorobutyraldehyde. The Stephen Reaction under normal conditions has been found unsuitable for the synthesis but giving indications of a possible favorable reaction at higher temperatures. Oxidation methods have been investigated and the optimum reaction conditions established for the use of potassium dichromate and hydrogen peroxide as oxidizing agents. Gamma-chlorobutyraldehyde has been synthesized by two methods not hitherto reported. A new technique has been developed for the preparation of aldehydes. The yields by this new method on samples of representative alcohols have been found to vary from 63 to 100 per cent.

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