

A STUDY OF THE REACTIONS OF CHLOROFORM  
WITH CARBONYL COMPOUNDS

by

ERNEST ALVA IKENBERRY

A. B., McPherson College, 1947

---

A THESIS

Submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1951

Docu-  
ment  
LO  
db68  
T4  
1951  
I4  
c.2

TABLE OF CONTENTS

INTRODUCTION . . . . .	1
LITERATURE REVIEW . . . . .	2
DISCUSSION . . . . .	6
Products from Potassium Hydroxide Catalyzed Reactions . . . . .	8
Products from Quaternary Base Catalyzed Reactions . . . . .	13
Polymer-plastics Obtained from Chloroform- crotonaldehyde Reactions . . . . .	19
Attempted Free-radical Type Reactions of Chloroform and Cinnamaldehyde . . . . .	20
EXPERIMENTAL . . . . .	21
Preparation of Starting Materials . . . . .	21
The Reaction of Chloroform and Croton- aldehyde in the Presence of Solid Potassium Hydroxide . . . . .	22
The Reaction of Chloroform and Cinnam- aldehyde and Mesityl Oxide in the Presence of Solid Potassium Hydroxide . . . . .	24
The Reaction of Chloroform and Croton- aldehyde in the Presence of an Organic Quaternary Base . . . . .	25
Attempted Free-radical Type Reactions of Chloroform and Cinnamaldehyde . . . . .	27
Number of Experiments Carried Out . . . . .	28
SUMMARY . . . . .	29
ACKNOWLEDGMENTS . . . . .	31
LITERATURE CITED . . . . .	32

## INTRODUCTION

Since Willgerodt (1) in 1881 reacted chloroform with acetone in the presence of solid potassium hydroxide to form trichloromethyl dimethyl carbinol, this reaction has been extended to a great number of aldehydes and ketones.



The mechanism is thought to follow the usual course of base catalyzed condensations in which addition occurs between the polarized carbonyl group and the base generated trichloromethyl anion.

This investigation was undertaken to study the reaction of chloroform with acrylaldehydes. In the acrylaldehyde system a double bond is conjugate with the carbonyl group.



The chloroform, as a trichloromethyl anion, could (a) add 1,2 in the usual manner giving an unsaturated alcohol; (b) add 1,4 to the polarized conjugate system giving a vinyl alcohol which would rearrange to the corresponding saturated aldehyde; (c) add 3,4 giving the saturated aldehyde directly; or (d) add in some other manner. The end product of (b) and (c) addition would be identical.

Chloroform could possibly add to the carbon-carbon double bond by a free radical mechanism, but under the experimental

conditions used in a majority of the reactions, low temperature and presence of a strong base, such a reaction does not seem likely.

Thus the scope of this investigation included: (a) the possibility of reactions of chloroform with acrylaldehydes, especially of 1,4 addition to the conjugate system, (b) the mode of the reaction, and (c) the identification of the addition products of the reaction of chloroform with acrylaldehydes.

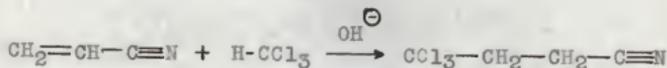
#### LITERATURE REVIEW

A review of the literature of the reaction of chloroform with carbonyl compounds showed that the reaction can be extended to a great many aldehydes and ketones. Most alkyl and aryl methyl ketones, and cyclic ketones will add chloroform. Alkyl aldehydes, if branched in the  $\alpha$ -position (2), give products. Aryl aldehydes will react unless the ring is deactivated by a substituent that can easily shift electrons in or out of the ring; e.g., -OH (3), -NO<sub>2</sub> (4), etc.

The scope of the reactions conducted by various authors may be summarized by the following tables. In Table 1, page 5, are summarized the condensations that were successful. In Table 2, page 5, are summarized the compounds that were shown not to react under the conditions used. The only reported addition of chloroform to an acrylaldehyde was the addition to cinnamaldehyde by A. Drboglav (5) in 1899 in which he postulated a 1,2 addition

giving trichloromethyl styryl carbinol. The reaction seems to follow the usual aryl aldehyde type reaction.

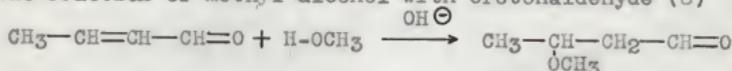
Chloroform was added to a conjugated system not entirely in the carbon system, and that addition was to acrylonitrile (6), (7).



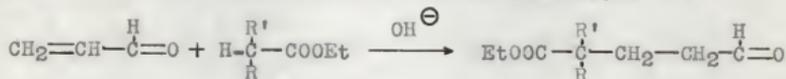
This reaction was catalyzed by either potassium hydroxide (6) or by tri-methyl benzyl ammonium hydroxide (7).

Also other anions have been added 1,4 to the acrylaldehyde conjugate system. The products were as if 3,4 addition had occurred. A few of these reactions are:

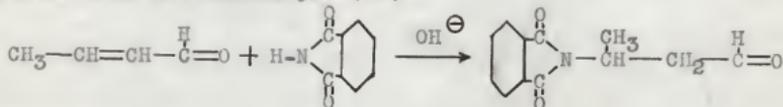
(a) the reaction of methyl alcohol with crotonaldehyde (8)



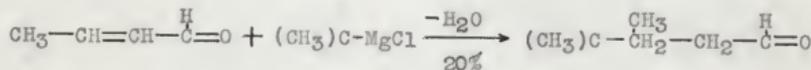
(b) the reaction of ethyl malonate with acrylaldehyde (9)



(c) the reaction of cyclic amides with acrylaldehydes, e.g., phthalimide with crotonaldehyde (10)



(d) the reaction of tertiary butyl magnesium chloride with crotonaldehyde (11)



A free radical addition of chloroform to a double bond has been shown by the reaction of chloroform with octene-1 (12)

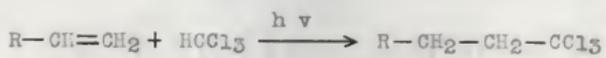


Table 1. Reactive compounds with chloroform,  $R_1-\overset{O}{\parallel}C-R_2$ .

$R_1$	$R_2$	Common name	Reference
Methyl	Methyl	Acetone	(1)
Methyl	Ethyl	Methyl ethyl ketone	(13)
Methyl	t-butyl	Methyl t-butyl ketone	(2)
Methyl	Phenyl	Acetophenone	(2)
		Cyclohexanone	(2)
		Cyclopentanone	(14)
Hydrogen	Iso-propyl	Iso-butylaldehyde	(2)
Hydrogen	Heptyl	2-ethyl hexanaldehyde	(2)
Hydrogen	Phenyl	Benzaldehyde	(3)
Hydrogen	Furyl	Furfuraldehyde	(3)
Hydrogen	p-chloro phenyl	p-chlorobenzaldehyde	(4)
Hydrogen	o-chloro phenyl	o-chlorobenzaldehyde	(4)
Hydrogen	m-chloro phenyl	m-chlorobenzaldehyde <sup>a</sup>	(4)
Hydrogen	o-methyl phenyl	o-tolualdehyde	(4)
Hydrogen	m-methyl phenyl	m-tolualdehyde	(4)
Hydrogen	p-methyl phenyl	p-tolualdehyde	(4)
Hydrogen	p-methoxy phenyl	anisaldehyde	(4)
Hydrogen	o-methoxy phenyl	o-methoxybenzaldehyde	(4)
Hydrogen	m-methoxy phenyl	m-methoxybenzaldehyde	(4)
Hydrogen	stryl	cinnamaldehyde	(5)

a-considerable amounts of m-chlorobenzoic acid were also formed.

Table 2. Non-reactive compounds with chloroform,  $R_1-\overset{O}{\parallel}C-R_2$ .

$R_1$	$R_2$	Common name	Reference
Ethyl	Ethyl	Diethyl ketone	(15)
n-propyl	n-propyl	Di-n-propyl ketone	(15)
Ethyl	n-propyl	Ethyl propyl ketone	(15)
Phenyl	Phenyl	Benzophenone	(2)
Phenyl	$\alpha$ -Naphthyl	Phenyl $\alpha$ -naphthyl ketone <sup>a</sup>	
Hydrogen	Hydrogen	Formaldehyde	(3)
Hydrogen	Methyl	Acetaldehyde	(3)
Hydrogen	Ethyl	Propionaldehyde	(3)
Hydrogen	n-propyl	n-Butyraldehyde <sup>b</sup>	(3)
Hydrogen	s-butyl	Iso-valeraldehyde <sup>b</sup>	(3)
Hydrogen	o-hydroxy phenyl	Salicylaldehyde	(3)
Hydrogen	o-nitro phenyl	o-Nitrobenzaldehyde <sup>c</sup>	(4)
Hydrogen	p-nitro phenyl	p-nitrobenzaldehyde <sup>c</sup>	(4)
Hydrogen	o-phenyl phenyl	o-phenylbenzaldehyde <sup>c</sup>	(4)

a-found unreactive by the author in experiments with both trimethyl benzyl ammonium hydroxide and potassium hydroxide.

b-gave chlorine containing tars.

c-underwent Cannizzaro reaction.

## DISCUSSION

A base catalyzed reaction was found to occur between chloroform and crotonaldehyde, cinnamaldehyde and mesityl oxide. No chlorine containing products could be found from the reaction of chloroform and acrylaldehyde. In this case only polymers of acrylaldehyde were obtained.

Since Weizman et al. (2) discovered that the use of acetal as a solvent in the reaction of chloroform and acetone increased the yields of trichloromethyl dimethyl carbinol from 25 per cent to 98 per cent, the early experiments with chloroform and cinnamaldehyde and crotonaldehyde were carried out using acetal as the solvent.

The reactions using crotonaldehyde were outstanding in that they gave chlorine-containing constant boiling liquid products. Although the yields of these liquids were low, good yields of polymeric resins were always obtained. The polymeric resins from these reactions contained about 1.5 per cent chlorine.

In the reactions using cinnamaldehyde, only very small amounts of distillable liquids containing chlorine could be obtained. None of the products had the properties reported by Drboglaw (5) for 1,1,1-trichloromethyl styryl carbinol.

The high boiling products obtained from mesityl oxide were very small amounts of unstable liquids. These liquids gave a positive qualitative test for chlorine.

In the above experiments solid potassium hydroxide was used as the basic catalyst. Mole ratios of base to aldehyde of

from 1/20 to 2/1 were used. A 1/1 ratio was found to give the best results. A temperature of 0° to 5° C. was maintained during the reaction. In all cases a side reaction occurred in which chloroform and/or the product was consumed giving potassium chloride.

A final experiment with crotonaldehyde using dry ether as the solvent and a 50 per cent methanol solution of trimethyl benzyl ammonium hydroxide as the catalyst, gave much better yields of constant boiling product. Two chlorine containing liquids were obtained in 14.5 and 22 per cent yields. A lower boiling product that only contained a trace of chlorine, 3.2 per cent, was also found. This product was saturated and had a methoxyl content of 26 per cent. The structures of these new products will be discussed later. This experiment, although using a different catalyst, supports the general trend of the findings of Bergman et al.(4) in which they found that in the reactions of chloroform with benzaldehyde and substituted benzaldehydes, the use of acetal as a solvent caused decreased yields of addition products.

The products obtained in all the crotonaldehyde experiments were clear to light yellow oils. All of these liquids gave positive tests for carbonyl with 2,4 dinitrophenylhydrazine reagent. These products were all distillable liquids at 1-2 mm pressure. All of the products contained organically bound chlorine except the lowest boiling product obtained from the reaction in which ether and the quaternary base was used as the catalyst. In all cases, the chlorines were tightly bound, since no silver chloride precipitate was formed even upon boiling with alcoholic silver

nitrate. Upon boiling with alcoholic potassium hydroxide, a precipitate of potassium chloride was formed, and the compounds were decomposed into tars. Quantitative hydrolysis of the chlorines by standard alcoholic potassium hydroxide was not successful. The amount of base consumed was found to increase as the length of heating was increased.

Many of the products were found to contain traces of organic acid. This acid was not hydrogen chloride as in no case did the products give a positive test with silver nitrate solution. As carbon dioxide or dilute sulfuric acid was used to neutralize the basic catalyst, these acids would not be found in the product after vacuum distillation. Titration with 0.01768 N alcoholic potassium hydroxide gave neutralization equivalents of from 1,081 to 2,250, which therefore indicated that only an acid impurity was present. Many of the products were unsaturated, as will be delineated later.

#### Products from Potassium Hydroxide Catalyzed Reactions

It was noted that two types of products were obtained from crotonaldehyde using solid potassium hydroxide as the catalyst. One was a higher boiling fraction, b.p.  $58^{\circ}$  -  $61^{\circ}$ C. at 6.8 mm, Product I. This was a clear oil which upon standing turned light yellow. It was much more stable than the lower boiling fraction, Product II, b.p.  $50^{\circ}$  -  $56^{\circ}$ C. at 0.9 mm. This was a light yellow oil which was quite unstable.

The higher boiling fraction, Product I, had an aromatic sharp odor and the following physical and chemical properties as listed in Table 3.

Table 3. Physical and Chemical Properties of Product I.

Property	Observed	Calculated
Physical Property		
Boiling point <sup>a</sup>	58-61° C./0.8 mm	-----
Refractive index (25°C.)	1.4936	-----
Density (20°/4°C.)	1.104	-----
Per cent chlorine	21.0 <sup>b</sup>	21.05
Molar refraction	44.57	45.04
Tests with		
Br <sub>2</sub> /CCl <sub>4</sub>	weak positive <sup>c</sup>	negative
Aq. KMnO <sub>4</sub>	positive	positive
2,4-dinitrophenylhydrazine	positive	positive
Fehling's solution	positive	positive
Product I/CHCl <sub>3</sub> and AlCl <sub>3</sub> <sup>d</sup>	orange-red color	orange-red color
Al. AgNO <sub>3</sub>	negative	negative

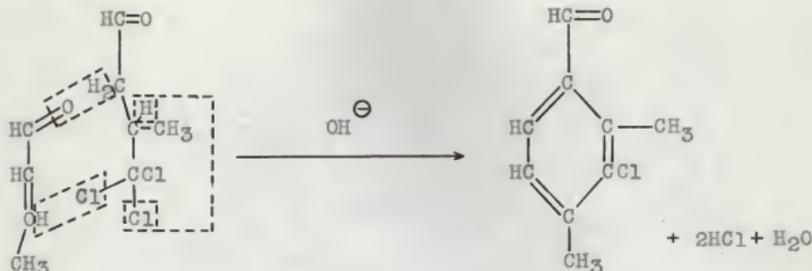
a-Decomposed before boiling at atmospheric pressure.

b-Average of four determinations.

c-Caused probably by a trace of impurity.

d-Qualitative test for the presence of an aromatic ring. Orange to red color is characteristic for benzene and its homologs and aryl halides (16).

A structure that could be postulated for this product which fits its physical and chemical properties, is 2,4-dimethyl 3-chloro benzaldehyde. This compound could possibly be formed from the condensation of crotonaldehyde with the addition product of 1,4 addition of chloroform with crotonaldehyde followed by the elimination of 2 moles of hydrogen chloride and one mole of water.



This compound also shows the characteristic absorption in the ultra violet of a carbonyl conjugate with a benzene ring, Table 4 and Fig. 1.

Table 4. Comparison of Ultraviolet Absorption Spectra

Compound	$\lambda$ max. $m\mu$	$\log \epsilon_{\text{max}}$
Benzaldehyde and Acetophenone (17)	320	1.7
	278	3.02
Product I	317	1.85
	278	3.16

Since the substituent methyl groups and chlorine atom can only exert inductive or second order resonance effects, the absorption characteristics should be similar. Resonance effects seem to play the major part in the determination of relative position of absorption (18).

The lower boiling product, Product II, was a much less stable liquid. Upon standing, the product turned dark brown and a precipitate formed. Upon redistillation, the refractive index changed from 1.5083 to 1.5042. The boiling point was 51-56° C.

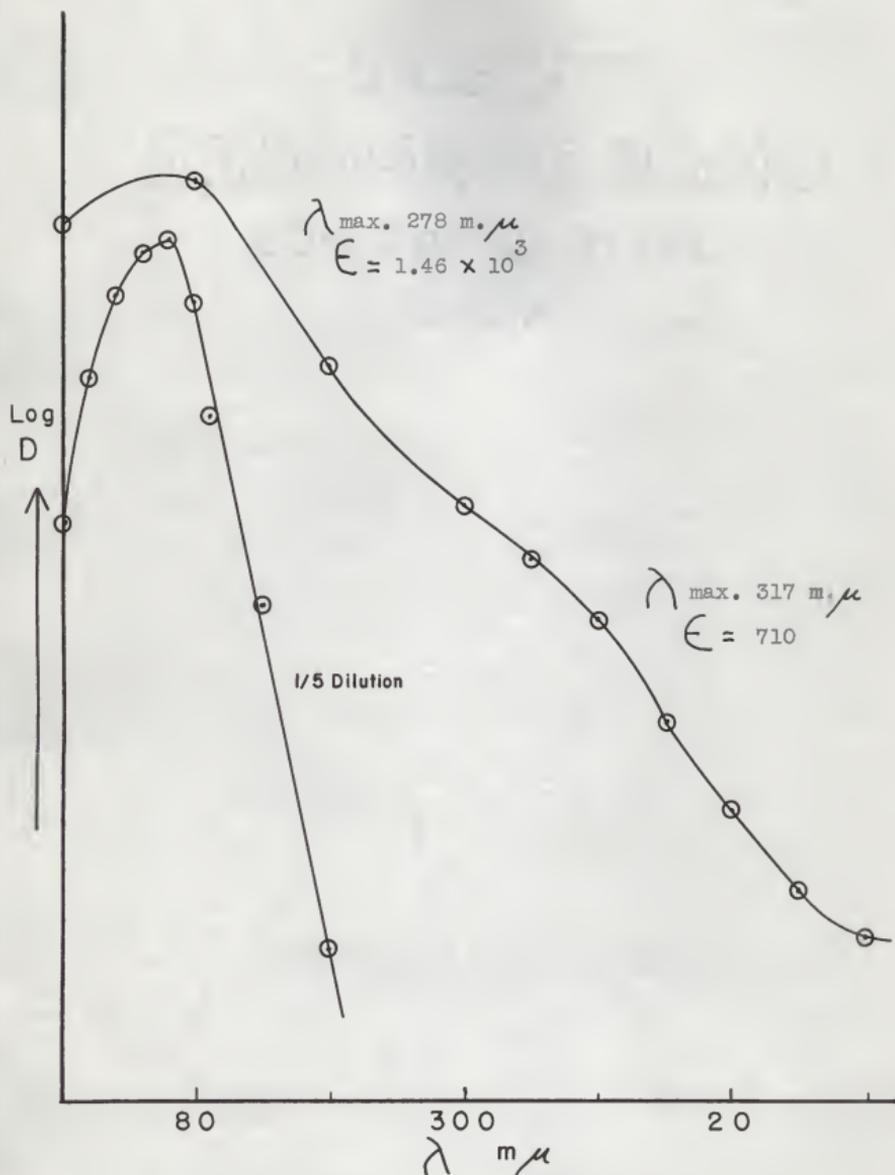


Fig. 1. Ultraviolet absorption of Product I in Skelly B.

at 1-0.9 mm. Satisfactory chlorine determinations were difficult to obtain via the usual analytical procedures. The highest value obtained was 27.5 per cent chlorine.

The purified lower boiling product had the physical and chemical properties listed in Table 5.

Table 5. Physical and Chemical Properties of Product II.

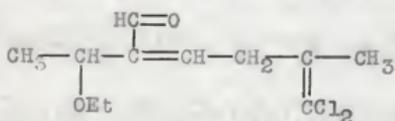
Property	Observed	Calculated
Physical Property		
Boiling point <sup>a</sup>	51-56° C./1-0.9 mm	-----
Refractive index (29°C.) <sup>b</sup>	1.5043	-----
Per cent chlorine	27.5 <sup>c</sup>	28.2
Tests with		
Br <sub>2</sub> /CCl <sub>4</sub>	positive	positive
Aq. KMnO <sub>4</sub>	positive	positive
2,4-dinitrophenylhydrazine	positive	positive
Fehling's solution	positive	positive
Al. AgNO <sub>3</sub>	negative	negative
Product II/CHCl <sub>3</sub> and AlCl <sub>3</sub>	negative	negative

a-Boiling point in first fractionation.

b-Refractionated once.

c-Highest value obtained.

Assuming that in the above, a reaction occurred similar to that later indicated for the same reactants employing ether as solvent and a quaternary base as catalyst, the following type structure for the product can be postulated. The following structure would have the properties as shown in Table 5.



Product II

Possible mechanisms for formation of Product II would be along the same lines as those postulated for the quaternary base catalyzed reaction dealt with later. In the present case ethyl alcohol from decomposition of acetal would be present to furnish the ethoxyl in Product II instead of methyl alcohol that was present in the later reaction. In fact, free ethyl alcohol was always isolated from reactions employing acetal as the solvent.

#### Products from Quaternary Base Catalyzed Reactions

In this case, the yields of products from the reaction of chloroform and crotonaldehyde were much better than where potassium hydroxide was employed. Product III was obtained in 22 per cent yield and Product IV was obtained in 14.5 per cent yield, calculated on the basis of chloroform that entered into the reaction. As in previous reactions, higher non-constant boiling products were also formed, and a non-distillable clear plastic residue was obtained. Besides Products III and IV, a low boiling, saturated aldehyde, b.p. 40-2° C./2 mm, 162° C. at atm., was also obtained. Its chemical and physical properties are listed in Table 8.

The higher boiling fraction, Product III, b.p. 83-85° C./2 mm, was a light yellow oil with a pleasant odor. It had the following physical and chemical properties as listed in Table 6.

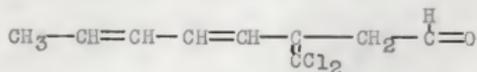
Table 6. Physical and chemical properties of Product III.

Property	Observed	Calculated
Physical Property		
Boiling Point	83-85° C./2 mm	-----
Refractive Index (25°C.)	1.4782	-----
Density (20 <sup>o</sup> /4 <sup>o</sup> C.)	1.252	-----
Unsaturation <sup>a</sup>	1.01	1.0 <sup>b</sup>
Per cent chlorine	35.03	34.6
	35.49	
Tests with		
Br <sub>2</sub> /CCl <sub>4</sub>	slow, but positive	positive
Aq. KMnO <sub>4</sub>	positive	positive
2,4-dinitrophenylhydrazine	positive	positive
Fehling's solution	positive	positive
Shiff's reagent	positive	positive
Bisulfite	positive	positive
Product III/CHCl <sub>3</sub> and AlCl <sub>3</sub>	negative	negative

a-Using Br<sub>2</sub>/CCl<sub>4</sub> at dry ice temperature and crotonaldehyde as a reference.

b-Assuming 1,4 addition to unsubstituted conjugate double bond.

More than one structure could be postulated for this Product III. The most likely structure seems to be:



This could be formed by aldol condensation of crotonaldehyde and then 1,4 addition of chloroform to the aldol accompanied by splitting out hydrogen chloride and loss of water upon heating.

The ultra violet absorption maxima for this compound was found to be 266.5 m $\mu$ . (Fig. 2, Page 15) A conjugate triene gives an absorption maxima of about 260 m $\mu$  (17). Since the carbonyl is not conjugate with the double bond system, it would

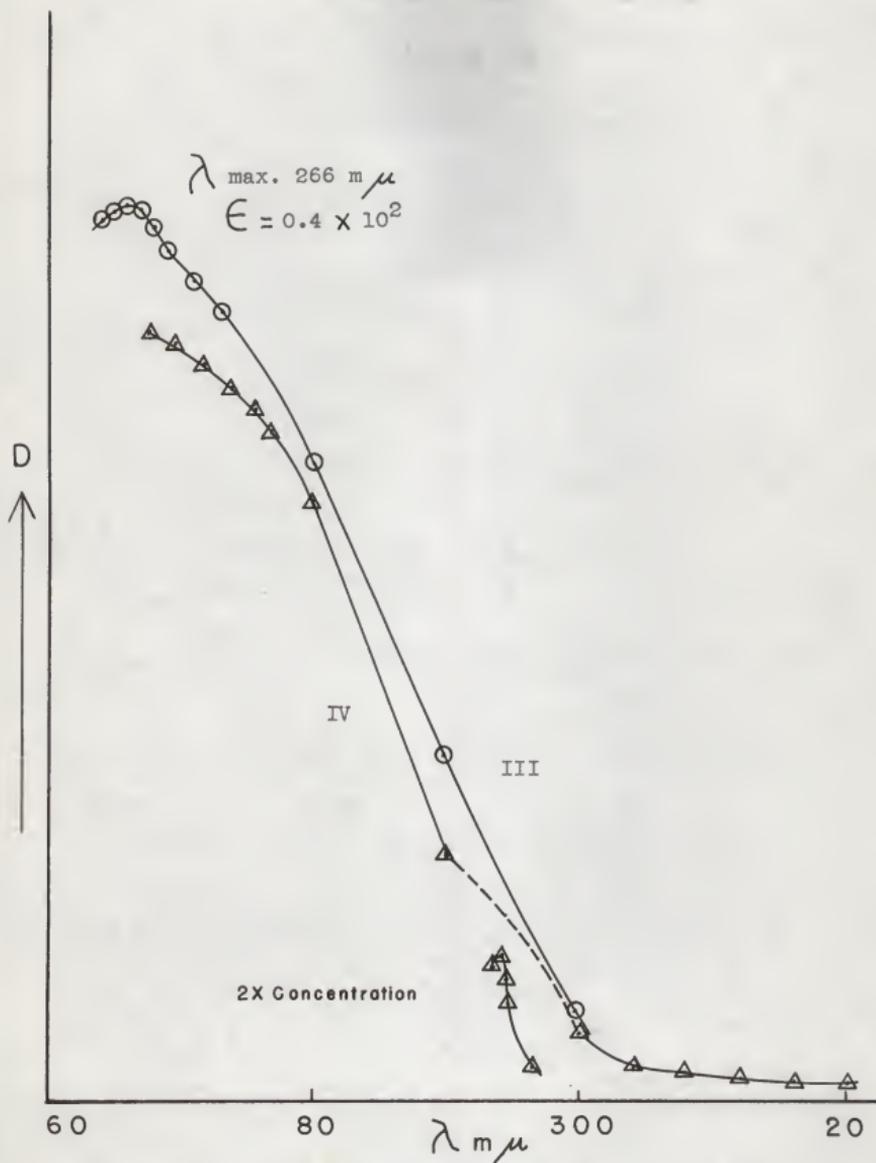


Fig. 2. The ultraviolet absorption of Product III and IV in Skelly B.

have no direct resonance effect on the absorption. There is a weak absorption maxima at about  $280 \text{ m}\mu$  which is the position at which a carbonyl should absorb. Substitution on a conjugate system tends to shift the absorption maxima to a longer wave length (18). The molar extinction was low,  $\epsilon:0.4 \times 10^2$ , but this probably was caused by partial polymerization of the compound. The polymerized product would have a much lower absorption maxima at this wave length. This would in effect only decrease the apparent concentration of Product III which would in turn decrease the molar extinction observed.

The lower boiling fraction, Product IV, b.p.  $70-75^\circ \text{C}$ . at 2 mm, was a light yellow oil with a pleasant odor. It had the following physical and chemical properties as listed in Table 7.

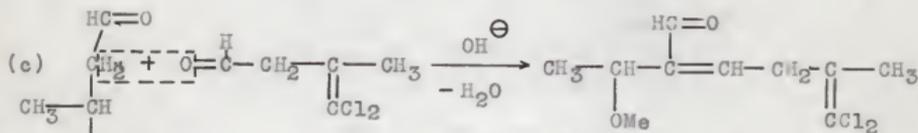
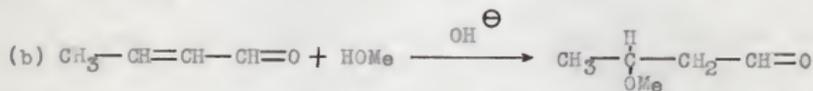
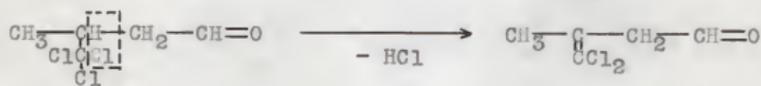
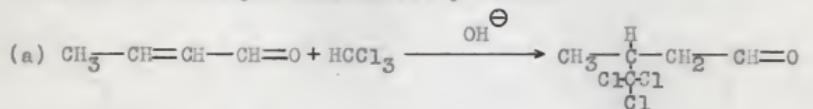
Table 7. Physical and chemical properties of Product IV.

Property	Observed	Calculated
Physical Property		
Boiling Point	$70-75^\circ \text{C}/2 \text{ mm}$	-----
Refractive Index ( $25^\circ \text{C}$ .)	1.4868	-----
Density ( $20^\circ/4^\circ \text{C}$ .)	1.228	-----
Unsaturation <sup>a</sup>	1.01	1 <sup>b</sup>
Per cent chlorine	28.51	29.90
	28.89	
Per cent methoxyl	12.6	13.08
Tests with		
$\text{Br}_2/\text{CCl}_4$	slow, but positive	positive
Aq. $\text{KMnO}_4$	positive	positive
2,4-dinitrophenylhydrazine	positive	positive
Fehling's solution	positive	positive
Shiff's reagent	positive	positive
Bisulfite	positive	positive
Product IV/ $\text{CHCl}_3 + \text{AlCl}_3$	negative	negative

a-Using  $\text{Br}_2/\text{CCl}_4$  at dry ice temperature and crotonaldehyde as a reference.

b-Assuming no addition to the double bond bearing two vinyl chlorine atoms, and other steric hindrance.

With the two different types of quantitative analyses obtained, only one combination of the reactants appears possible. This combination requires the reactions of two moles of crotonaldehyde and one mole of chloroform and one mole of methyl alcohol together with the loss of one mole of water and one mole of hydrogen chloride as shown in the equation below. On the other hand, more than one sequence of reactions seems possible. Aldol condensation could occur before or after the addition of chloroform and methyl alcohol. It may be postulated that a condensation occurred after (a) addition of chloroform to crotonaldehyde accompanied by loss of hydrogen chloride, and (b) addition of methyl alcohol to crotonaldehyde (8) and then, (c) an aldol condensation between the products of (a) and (b) as shown in the equations directly below.



Product IV

Although the ultraviolet absorption data on Product IV is not complete, a small absorption maxima was found at about 275 m $\mu$  (Fig. 2) and there is indication of a very large peak below 260 m $\mu$ . This could be indicative of an  $\alpha,\beta$  unsaturated aldehyde (19). The present ultraviolet absorption data was taken using Skelly B, as the absorption was expected at longer wave lengths.

Degradation studies and further ultraviolet absorption data will be necessary to show the exact sequence of reactions and structure of Product V. Further experiments of chloroform and crotonaldehyde in ether using a quaternary base are in progress. The physical and chemical properties of Product V, the low boiling saturated aromatic aldehyde are listed in Table 8.

Table 8. Physical and chemical properties of Product V.

Property	: Observed
Physical Property	
Boiling Point	162° C. 40-42° C./2 mm
Refractive Index (25° C.)	1.4966
Density (20°/4° C.)	0.995
Per cent methoxyl	26.0
Per cent chlorine	3.2
Tests with	
Br <sub>2</sub> /CCl <sub>4</sub>	negative
Aq. KMnO <sub>4</sub>	positive
2,4-dinitrophenylhydrazine <sup>a</sup>	positive
p-nitrophenylhydrazine <sup>b</sup>	positive
Product V/CHCl <sub>3</sub> + AlCl <sub>3</sub>	positive, orange coloration

a-m. p. 225.5-226.5° C.

b-m. p. 152-154° C.

## Polymer-plastics Obtained from Chloroform-crotonaldehyde Reactions

The highly viscous polymeric oils obtained as distillation residues from all the reactions of chloroform and crotonaldehyde had drying oil characteristics. Upon standing in air, they formed a tough surface film. Also when samples were dissolved in acetone and heated with a trace of dibenzoyl peroxide and spread on a test panel, the surface film dried to a hard, somewhat brittle film in about twenty-four hours. These oils when not catalyzed also set to clear glassy resins in a few weeks.

An ether solution of such an oil was found to undergo Diels-Alder type reaction with maleic anhydride, which proved presence of 1,3 unsaturation.

During the usual fractionation under reduced pressure, when the distillation flask temperature rose above 200°C., a rapid polymerization occurred which gave a clear, brittle, glassy plastic.

After the product had set to a semi-solid, the plastic would flow under slow stress, but would break leaving a glassy fracture under sudden stress.

This plastic product will be submitted to commercial firms for testing and experimental development, since this type product can be readily produced from commercially available raw materials.

Attempted Free-radical Type Reactions of  
Chloroform and Cinnamaldehyde

Three free radical initiators were used to attempt a reaction of chloroform with cinnamaldehyde. These initiators were: (a) heat and pressure, (b) dibenzoyl peroxide, and (c) ultraviolet light.

Under the conditions used, none of the reactions were successful and only reactants or non-chlorine containing polymers were obtained.

## EXPERIMENTAL

Preliminary experiments of reacting chloroform and acetone in the presence of powdered solid potassium hydroxide were carried out to familiarize the experimenter with the techniques involved in this type of reaction and to prepare a quantity of 1,1,1-trichloromethyl dimethyl carbinol; i.e., chloretone. The essential details of this work were submitted for publication to the Board of Editors of "Organic Syntheses" and given preliminary acceptance.

## Preparation of Starting Materials

Chloroform. U.S.P. chloroform was dried over anhydrous calcium chloride and redistilled, and the fraction, b.p. 60-61° C., used.

Crotonaldehyde. Eastman crotonaldehyde, 1878, was fractionated. The fraction boiling between 101-4° C. was used for the reactions. It was stored in the dark until used.

Potassium Hydroxide. Baker and Adams reagent grade potassium hydroxide, 2118, pellets were ground as rapidly as possible to a fine powder and stored in an air tight bottle.

Diethyl Acetal. Eastman acetal, P-512, was dried over anhydrous calcium chloride and fractionated. The material boiling between 98-101° C. was used. The acetal was stored with a trace of calcium oxide to suppress decomposition.

Ether. Commercial absolute ether was dried over sodium.

Cinnamaldehyde. Amend Drug and Chemical Company cinnamaldehyde, 46118, was fractionated at 2 mm, and the material used that boiled between 145-50° C.

Acrylaldehyde. Eastman material, stabilized with hydroquinone, 2037, was opened and filtered immediately before use.

Mesityl Oxide. Material by Paragon Testing Laboratories, 2407, was fractionated and the fraction boiling between 128-129° C. was used. This mesityl oxide was stored in the dark.

Trimethyl benzyl ammonium hydroxide. A 50 per cent methanolic solution of trimethyl benzyl ammonium hydroxide was used as supplied by Rohm and Haas Company.

#### The Reaction of Chloroform and Crotonaldehyde in the Presence of Solid Potassium Hydroxide

The reaction was carried out in a 500 ml three necked flask fitted with a reflux condenser and a Hershberg stirrer. In Experiment #14, 288 ml (2.0 mole) of acetal were added and cooled to 0° C. with an ice salt bath. Then, 28 gm (0.5 mole) of powdered potassium hydroxide were added slowly, keeping the acetal between 0° and -5° C. with rapid stirring. At the end of the addition, the reaction mixture was light yellow.

Then 160 ml (2.0 moles) of chloroform and 41 ml (0.5 mole) of crotonaldehyde were mixed and added through a dropping funnel over a period of two hours. The reaction mixture was stirred for another hour. During the addition of the chloroform-crotonaldehyde

mixture and during the stirring, after the addition was complete, the temperature of the reaction mixture was kept between  $0^{\circ}$  and  $5^{\circ}$  C. (Early experiments showed that temperatures above  $+5^{\circ}$  C. caused a rapid decomposition of chloroform and/or the addition products.)

Next, the reaction mixture was saturated with carbon dioxide gas and the potassium carbonate filtered, using 450 ml of dry ether to aid in filtering the paste and also to wash the reaction flask and paste. The resultant ether solution was light orange, and no tar formation was observed.

The ether and chloroform were removed by heating on a steam bath; the receiver was followed by a dry ice trap. The ethyl alcohol and acetal were taken off by distillation at water pump pressure (about 25 mm). Effluent volatile material from the distillation was passed through a dry ice trap. The foreruns of ether, chloroform and alcohol were later fractionated and the material boiling at  $50-70^{\circ}$  C., washed with water and redistilled, giving 155 gm of recovered chloroform.

The remaining residue from the reaction was fractionated at 0.8-1.5 mm pressure through a column 12.5 cm long with 15 mm diameter, packed with 3/16 inch glass helices. The distillation flask, column, still head and fraction-cutter were of Pyrex glass. The adiabatic column and special fraction-cutter were constructed by the experimenter. The distillation results are summarized in Table 9.

Table 9. Distillation of reaction products from the reaction of chloroform and crotonaldehyde in the presence of solid potassium hydroxide.

Fraction	b.p. °C.	P., mm	Color	wt., gm
C-III 1#	45-50	1	clear	0.2
C-III 2#(Product II)	51-56	0.9-1	lt. yellow	4.2
C-III 3#(Product I)	58-61	0.8	clear	2.4
C-III 4# <sup>a</sup>	105-18	0.9-1.5	yellow	4.2
C-III residue <sup>a,b,c</sup>	above 120	-	brown	16.5

a-Gave a qualitative chlorine test.

b-Soluble in acetone; partially soluble in dry ether. The ether insoluble residue was a spongy white solid.

c-Contained 1.5 per cent chlorine, originally a viscous oil which polymerized to a clear solid upon standing.

The weight per cent of combined reactants that appeared as Product I was 2.02 per cent and as Product II, 3.54 per cent. The chemical and physical properties of these products are listed in Tables 3 and 5.

Approximately fifty per cent of the crotonaldehyde was converted to the resin from crotonaldehyde and chloroform, termed C-III residue in Table 9.

#### The Reaction of Chloroform and Cinnamaldehyde and Mesityl Oxide in the Presence of Solid Potassium Hydroxide

The reactions of chloroform with cinnamaldehyde and mesityl oxide were carried out in a similar manner. Similar molar ratios were used except in the reaction using cinnamaldehyde in which 1/10 as much potassium hydroxide was used. In these experiments with cinnamaldehyde and with mesityl oxide, only traces of chlorine-

containing products were obtained. These traces were so small in amount as to make purification and identification impossible.

#### The Reaction of Chloroform and Crotonaldehyde in the Presence of an Organic Quaternary Base

The reaction was carried out in a 500 ml three necked flask fitted with a reflux condenser, a motor powered mercury sealed glass stirrer, and a dropping funnel. In experiment #19, 150 ml of dry ether were mixed with 50 ml of a fifty per cent methanolic solution of trimethyl benzyl ammonium hydroxide and cooled by an ice salt bath to 0-5° C. To this cooled basic mixture was added dropwise, with rapid stirring, a mixture of 160 ml (2.0 moles) of chloroform and 41 ml (0.5 mole) of crotonaldehyde over a period of forty-five minutes. During the addition of the chloroform and aldehyde and during a period of fifteen more minutes of rapid agitation, the reaction mixture was kept between 0-5° C.

The reaction mixture was neutralized with aqueous 5 per cent sulfuric acid until an acid reaction to litmus was obtained. The organic layer was separated and washed with two 250 ml portions of water and dried over anhydrous magnesium sulfate. The water layer was stored.

The ether, methyl alcohol, and chloroform were taken off by distillation from a steam bath.

A trace of crotonaldehyde was taken off at water pump vacuum at about 25 mm, raising the temperature of the distillation flask

to about 100° C. Then the residue was fractionated under 2-3 mm pressure. The distillation results are summarized in Table 10.

Table 10. Distillation of reaction products from the reaction of chloroform and crotonaldehyde in the presence of an organic quaternary base.

Fraction	b.p. ° C.	P., mm	Color	wt., gm
C-VI 1# (Product V)	40-2	2	clear	2.5
C-VI 2# (Product IV)	70-5	2-3	lt. yellow	3.0
C-VI 3# (Product III)	83-5	2	lt. yellow	3.9
C-VI 4#	85-90	2	yellow	2.5
C-VI 5#	98-120	2	orange yellow	3.4
C-VI 6#	above 120	2	orange	0.7
C-VI residue <sup>a</sup>	-	-	-	10.0

<sup>a</sup>-Soluble in acetone. Originally a viscous oil which partly polymerized upon heating at 100° C. for four hours with a trace of dibenzoyl peroxide; upon standing, the initiated polymerization continued, and a clear brown solid resulted in about one day.

The fore-runs of methyl alcohol and chloroform were combined and washed well with several portions of water and fractionated, giving 150 ml of chloroform.

A 10 ml aliquot of the original acid water solution was titrated with 0.0833 N silver nitrate and it was found that an equivalent of 4.53 g of chloroform had been decomposed during the reaction.

The yield of Product III was 22 per cent, and of Product IV was 14.5 per cent based upon the amount of chloroform consumed.

The chemical and physical properties of Products III, IV, and V, that were found, are listed in Table 6, Table 7, and Table 8.

Attempted Free-radical Type Reactions  
of Chloroform and Cinnamaldehyde

Three types of reactions were carried out. (a) Heat and pressure (b) dibenzoyl peroxide, and (c) ultraviolet light were used in attempts to force reaction of chloroform with cinnamaldehyde.

(a) Heat and pressure reaction: In two Pyrex glass Carius tubes were sealed 120 ml of chloroform (1.5 moles) and 44.5 ml (0.375 mole) of cinnamaldehyde. These tubes, in a series of experiments, were heated up to temperatures of 200-240° C. for up to forty hours without obtaining reaction. In all cases, the tubes exploded when the temperature was raised above 255° C. for any length of time.

(b) Dibenzoyl peroxide reaction: In this reaction 30 ml (0.25 mole) of cinnamaldehyde was dissolved in 285 ml of kerosene. To this mixture was added, dropwise at room temperature, 40 ml (0.5 mole) of chloroform in which 1.54 g of dibenzoyl peroxide was dissolved. Then the reaction mixture was refluxed under nitrogen for forty hours.

Fractionation of the reaction mixture gave no chlorine containing products other than reactants.

(c) Ultraviolet light reaction: This reaction was carried out in a shallow Pyrex glass dish which was blanketed by dry nitrogen during the reaction. A mixture of 160 ml (2.0 moles) of chloroform and 9 ml (0.076 mole) of cinnamaldehyde was irradiated for forty minutes with an ultraviolet source (Speri

Inc., Cincinnati, Ohio. Model P100. 100-20 v. A. C.; 500 watts.) Fractionation of the reaction mixture gave 5.2 ml recovered cinnamaldehyde and a plastic residue which contained no chlorine.

#### Number of Experiments Carried Out

In the course of this investigation, besides the numerous characterization and analytical experiments that were done, synthesis experiments found necessary to establish successful conditions amounted to ten experiments on reactions of chloroform with acetone, and twenty experiments on reactions of chloroform with acrylaldehydes and ketones.

## SUMMARY

Chloroform was found to react with substituted acrylaldehydes and ketones in the presence of a strong base.

The major products of the reactions were found to be plastic materials which contained some organically bound chlorine.

Two constant boiling liquids, Product I and II, were obtained from the reaction of chloroform and crotonaldehyde in the presence of potassium hydroxide with acetal as solvent. Product I and II contained 21-27.5 per cent chlorine. Three constant boiling liquids, Products III, IV, and V, were obtained from the reaction of chloroform with crotonaldehyde in dry ether using a quaternary base as the condensing agent. Product III contained 35 per cent chlorine, and Product IV contained 28.9 per cent of chlorine. Product V had an impurity which could not be removed under the circumstances.

No isolatable pure products were obtained from the basic condensation of chloroform with cinnamaldehyde and with mesityl oxide using acetal as a solvent.

Acrylaldehyde itself was found to give only polymeric products which contained no chlorine.

Free radical type reactions of chloroform and substituted acrylaldehydes, under the experimental conditions used, gave no chlorine containing products.

Although acetal, as a solvent, has been reported to increase yields in the base catalyzed reaction of ketones and chloroform (2), it was found to decrease yields in the reactions of substituted

acrylaldehydes and chloroform.

The probability of 1,4 addition of chloroform and substituted acrylaldehydes was shown by the type products found. Possible modes of reaction and postulated structures of the products were outlined in the thesis.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Donald G. Kundiger, Assistant Professor in the Department of Chemistry, for his advice, constructive criticism, and encouragement throughout the course of research and in preparation of this manuscript: to Mr. Eugene E. Richardson for methoxyl determination, to all the Chemistry staff and fellow students who by their kind interest and suggestions assisted in this investigation, and to my wife, Mrs. Leona Dell Ikenberry for her continued cooperation and aid in preparation of the manuscript.

## LITERATURE CITED

- (1) Willgerödt, C.  
Ueber die einwirkung atzender alkalien auf halogenirte  
verbindungen in acetonlosungen. Deut. Chem. Gessel.  
Ber. 14:2451-60. 1881.
- (2) Weizmann, Ch., and E. Bergman, and M. Sulzbacher.  
Preparation of acetonechloroform and its homologs. Amer.  
Chem. Soc. Jour. 70:1189-91. 1948.
- (3) Howard, J.W.  
The addition of chloroform to aldehydes. Amer. Chem.  
Soc. Jour. 47:455-6. 1925.
- (4) Bergman, Ernest D., and D. Ginsburg, and Davie.  
Aryltrichloromethyl carbinols. Amer. Chem. Soc. Jour.  
72:5012-14. 1950.
- (5) Drboglow, A.  
Ueber die synthese des trichlormethylstyrylcarbinols und  
die einwirkung von funfprozentiger wasseriger losung  
von kaliumhydrat auf dasselbe. Chem. Zentbl. II: 328-  
9. 1900. Abstract from Zhur. Obsheh. Khim. 32:218-?.  
1900. Original not seen.
- (6) Niederhauser, Warren, and H.A. Bruson.  
Title not known, U.S. Pat. 2,379,097. June 26, 1945.  
Original not seen. Abstract in Chem. Abs. 39:4618. 1945.
- (7) Bruson, Herman A., and others.  
The chemistry of acrylonitrile. VI cyanoethylation of the  
haloforms. Amer. Chem. Soc. Jour. 67:601-2. 1945.
- (8) Farbenind, I.G. (Max Heyse, inventor).  
Title not known. Ger. Pat. 554,949. Aug. 5, 1930.  
Original not seen. Abstract in Chem. Abs. 26:5964. 1932.
- (9) Warner, Don T., and Owen A. Moe.  
1,4 addition of ethyl malonate to acrolein. Amer. Chem.  
Soc. Jour. 70:3470-2. 1948.
- (10) Moe, Owen A., and Don T. Warner.  
1,4 addition of cyclic imids to  $\alpha, \beta$  unsaturated aldehydes.  
Amer. Chem. Soc. Jour. 71:1251. 1949.
- (11) Stevens, Philip G.  
The addition of organomagnesium halides on  $\alpha, \beta$ -unsaturated  
aldehydes. Amer. Chem. Soc. Jour. 57:1112-7. 1935.

- (12) Kharasch, M.S., and Elwood V. Jensen, and W.H. Urry.  
Reaction of atoms and free radicals in solution. X The  
addition of polyhalomethones to olefins. Amer. Chem.  
Soc. Jour. 69:1100-5. 1947.
- (13) Ekeley, John B., and Carl J. Klemme.  
The addition products of methyl ethyl ketone with  
chloroform, bromoform, and iodoform. Amer. Chem. Soc.  
Jour. 46:1252-4. 1924.
- (14) Garland, C.E., and W.A. Welch.  
Notes: Trichloromethylcyclopentanol-1. Amer. Chem.  
Soc. Jour. 53:2414-5. 1931.
- (15) Howard, J.W.  
Some alcohols containing the trichloromethyl group.  
Amer. Chem. Soc. Jour. 48:744-5. 1926.
- (16) Shriner, Ralph L., and R.C. Fuson.  
The systematic identification of organic compounds.  
New York: John Wiley and Sons, 1948. 88-90 p.
- (17) Morton, R.A., and A.L. Stubbs.  
Absorption spectra of hydroxy-aldehydes, hydroxy-ketones,  
and their methyl ethers. Jour. Chem. Soc. (London).  
Pt. II:1347-59. 1940.
- (18) Ferguson, Lloyd N.  
Relationships between absorption spectra and chemical  
constitution of organic molecules. Chem. Rev. 43:385-446.  
1948.
- (19) Woodward, Robert Burns.  
Structure and the absorption spectra of  $\alpha, \beta$ -unsaturated  
ketones. Amer. Chem. Soc. Jour. 63:1123-6. 1941.

A STUDY OF THE REACTIONS OF CHLOROFORM  
WITH CARBONYL COMPOUNDS

by

ERNEST ALVA IKENBERRY

A. B., McPherson College, 1947

---

AN ABSTRACT OF A THESIS

Submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1951

A study of the reactions of chloroform with acrylaldehyde and substituted acrylaldehydes was undertaken (a) to investigate particularly the 1,4 addition of chloroform to acrylaldehyde and substituted acrylaldehydes and (b) to produce new chlorinated organic compounds. If trichloromethyl groups were found intact in these chlorinated compounds, they could be of significant interest and importance since they might possess important hypnotic and insecticidal properties. Indeed, chloroform itself has been used as an anesthetic and as an insecticide. However the trichloromethyl group may or may not cause anesthetic and insecticidal effects. Thus, *p,p'*-dichlorodiphenyl trichloromethyl methane, DDT, to be toxic requires its trichloromethyl group. On the other hand, chlorethone, with its trichloromethyl group, is non-toxic and non-insecticidal.

Chloroform has been shown to react in the presence of a strong base to give 1,2 addition to the carbonyl group in most methyl ketones, cyclic ketones, aryl aldehydes, and alkyl aldehydes, if branched in the  $\alpha$ -position. Since many base initiated 1,4 additions are known to occur with the acrylaldehyde system, it was reasoned that a similar type reaction might occur with chloroform and a suitable acrylaldehyde. Chloroform has been shown to react by 1,4 addition with the conjugate system in acrylonitrile. The only reported reaction of chloroform with an acrylaldehyde, was the reaction of chloroform with cinnamaldehyde. In this case the reaction was direct 1,2 addition to the carbonyl group.

This investigation has shown that it is possible to add chloroform to substituted acrylaldehydes, and that the addition is probably 1,4 to the conjugate system. As acrylaldehydes are quite reactive

under the conditions of the reaction, the addition products are condensation products of the acrylaldehydes with themselves and with chloroform. In every case large amounts of polymeric products were obtained which contained organically bound chlorine. In every case some chloroform and/or reaction product reacted with the base present to form chloride salts.

It was also shown that acetal, although reported by others to be a good solvent for 1,2 addition of chloroform to a carbonyl group, gave decreased yields of lower molecular weight products in the case of a typical acrylaldehyde, crotonaldehyde.

The postulated structures for the products obtained from the reaction of chloroform with crotonaldehyde in the presence of solid potassium hydroxide, using acetal as solvent, were shown by physical and chemical data to be:

- (a) 2,4-dimethyl-3-chlorobenzaldehyde, b.p. 58-61° C./0.8 mm, Product I, calculated per cent chlorine 21.05, found as the average of four analyses 21.0 and:
- (b) 2(1-ethoxoethyl)-5-methyl-6,6-dichloro-2,5-hexadien-1-al, b.p. 51-56° C./1-0.9 mm, Product II, or another addition product of crotonaldehyde with itself, chloroform, and ethyl alcohol with subsequent elimination of water and hydrogen chloride.

Three constant boiling liquid products were obtained from the reaction of chloroform with crotonaldehyde in the presence of methanolic trimethyl benzyl ammonium hydroxide, using dry ether as solvent. These products were Product III, b.p. 83-85° C./2 mm;

Product IV, b.p. 70-75° C./2 mm; and Product V, b.p. 162° C. (40-42° C./2 mm). The postulated structures for the two higher boiling products are as follows:

(c) 3-(dichloromethylene)-4,6-octadien-1-al, Product III, calculated per cent chlorine 34.6, found 35.1; and

(d) 2-(1-methoxoethyl)-5-methyl-6,6-dichloro-2,5-hexadien-1-al, Product IV, calculated per cent chlorine 29.9, found 28.7, and calculated per cent methoxyl 13.08, found 12.6.

No structure was postulated for the lower boiling Product V. This was a saturated aldehyde which contained a trace of chlorine, 3.2 per cent, and 26 per cent methoxyl content.

Possible sequences of reactions in equation form were outlined in the thesis.

No isolatable pure products were obtained from the basic condensation of chloroform with cinnamaldehyde and with mesityl oxide using acetal as the solvent.

Acrylaldehyde itself was found to give only polymeric products which contained no chlorine.

Attempted free radical type reactions of chloroform and acrylaldehyde, and substituted acrylaldehydes under the experimental conditions used, gave no chlorine containing products.