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THE ADDITION OF CHLOROFORM AND BROMOFORM TO
M-TOLUALDEHYDE AND M-BROMOBENZALDEHYDE

by

Alvin R. Kincaid
B. A., Walla Walla College, 1934

Presented in partial fulfillment of the re-
quirements for the degree of Master
of Arts

Montana State University

1939

Approved:

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of Examiners.

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on Graduate Study

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INTRODUCTION

Problem

The problem which was investigated in preparation for this paper was concerned with the addition of chloroform and bromoform to some of the substituted benzaldehydes that have not yet been studied, and the preparation of the acetic, propionic, butyric, and benzoic esters of the resulting carbinols. The ones investigated were *n*-tolualdehyde and *m*-bromobenzaldehyde.

Purpose

The purpose of the investigation of this problem was to help complete the study of the addition of chloroform and bromoform to the different substituted benzaldehydes and to study some of the esters that can be prepared from the carbinol product of the addition.

History

The first work reported done on adding chloroform or bromoform to benzaldehyde was done by Jocietz² in 1897. He reported that chloroform would add to benzaldehyde in the presence of an alkali but gave no experimental data. In 1923 Yoder¹¹ reported the preparation of this carbinol and also the carbamic acid ester of it, but he gave no experimental details of how the carbinol was prepared. Howard³,

in 1925, found that by adding one-third the gram-molecular weight of benzaldehyde to one-half the gram-molecular weight of dry chloroform and adding four grams of powdered potassium hydroxide in small portions over a one-half hour period with constant mechanical stirring he could add chloroform to benzaldehyde. He could obtain the best results using these proportions.

In 1899 Siegfried⁸ reported that he had made tribromomethyl-phenylcarbinol from benzaldehyde and bromoform in the presence of an alkali, stating only that he had used the same method as Jocietz. Howard³, using the same method as before, succeeded in adding bromoform in place of chloroform to benzaldehyde. He also prepared the acetic, propionic, butyric, and benzoic esters of this carbinol.

The preparation of trichloromethyl-o-chlorophenylcarbinol and tribromomethyl-o-chlorophenylcarbinol was reported by Howard and Castles⁵ in 1935, also the acetic, propionic, butyric, and benzoic esters of both. The carbinols were synthesized by adding chloroform or bromoform to o-chlorobenzaldehyde in the presence of powdered potassium hydroxide.

In 1935 Howard⁶ reported the preparation of trichloromethyl--and tribromomethyl-p-chlorophenylcarbinol by the addition of chloroform and bromoform to p-chlorobenzaldehyde in the presence of potassium hydroxide. He

also prepared the acetic, propionic, butyric, and benzoic esters of the trichloromethyl-p-chlorophenylcarbinol and studied their properties. He attempted to prepare the same esters of the tribromomethyl-p-chlorophenylcarbinol by similar and different methods, but all efforts ended in failure. The carbinol in each case was recovered unchanged.

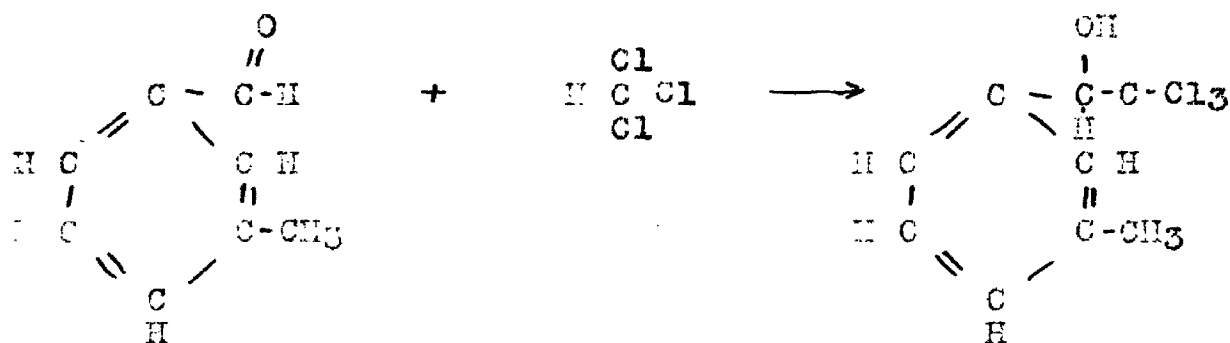
Howard and Stephens⁷ in 1938 reported the preparation of trichloromethyl--and tribromomethyl-m-chlorophenylcarbinol, by adding chloroform or bromoform to m-chlorobenzaldehyde in the presence of powdered potassium hydroxide. They also reported at the same time the preparation of trichloromethyl--and tribromomethyl-p-tolylcarbinol by adding chloroform or bromoform to tolualdehyde in the presence of powdered potassium hydroxide. They too, reported the preparation of the acetic, propionic, butyric, and benzoic esters of each of the four carbinols they had prepared together with some of their properties.

Stephens⁹ in 1938 reported attempting the addition of chloroform and bromoform to m-bromobenzaldehyde but did not obtain any positive results. He had an accident in which most of the products formed were lost before he had them purified.

THEORETICAL

Carbinol Preparation

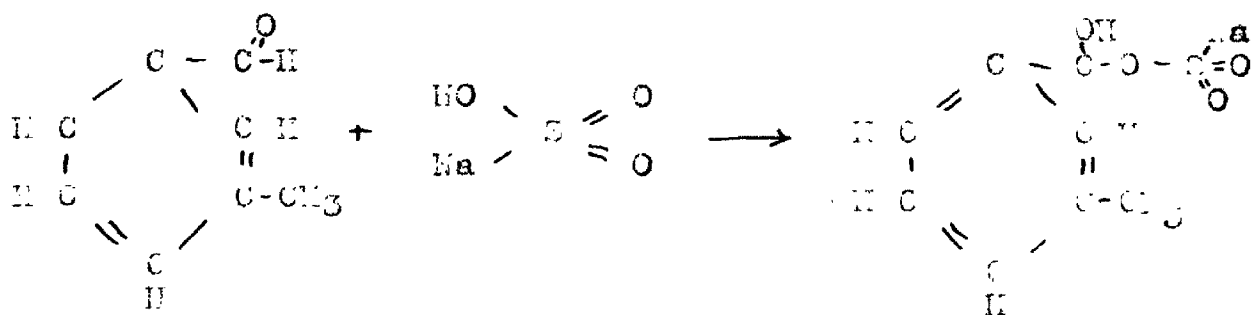
The trichloromethyl- α -tolylcarbinol was prepared by the reaction between dry chloroform and α -tolaldehyde in the presence of finely powdered potassium hydroxide. The reaction shown by equation is:



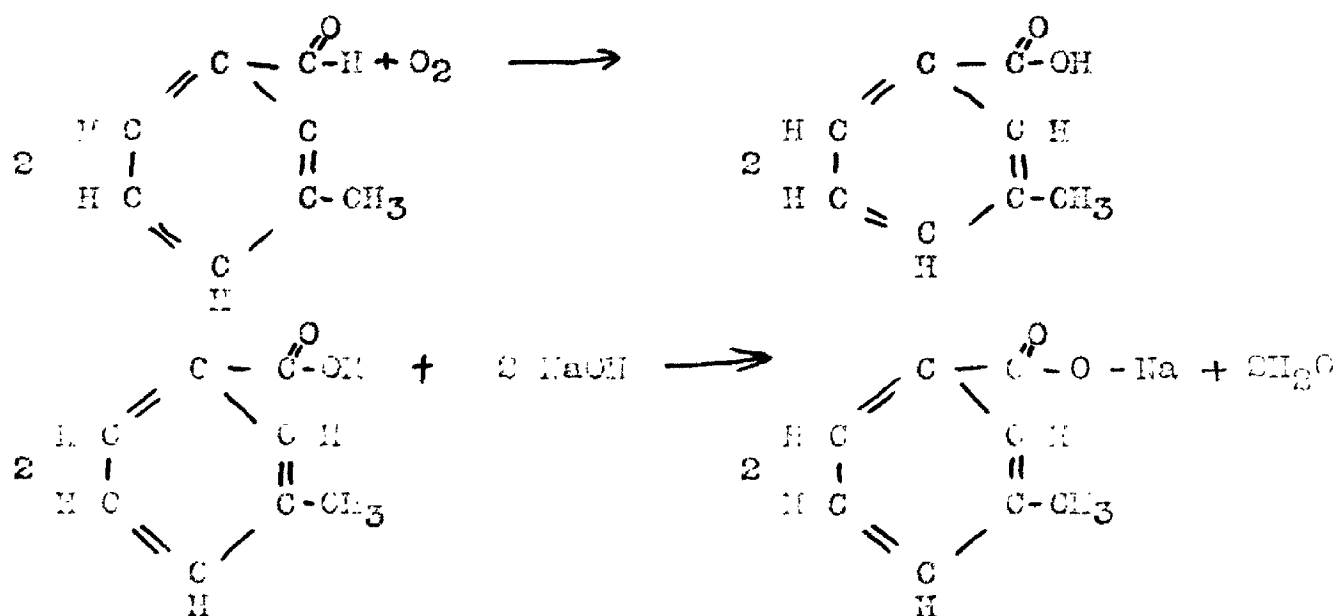
The entire reaction was carried out in a three necked flask fitted with a mechanical stirrer and a mercury seal in the center neck. A calcium chloride tube was fitted in another neck to allow for expansion and contraction of gases and the other neck was closed with a rubber stopper except when materials were added. The purpose was to carry on the reaction under the most anhydrous conditions possible.

One-third the gram-molecular weight of the aldehyde and one-half of the gram-molecular weight of dry chloroform were poured into the flask and the stirrer started. Powdered potassium hydroxide was added in one-half to one gram portions over a period of about one-half an hour. The

amount of potassium hydroxide added and the rate of adding was controlled by the heat of the reaction. Just enough was added to keep the temperature of the reacting mixture around 50° C. When the reacting mixture no longer warmed on adding potassium hydroxide it was discontinued, from four to seven grams generally being used. The stirring was continued for about two more hours, then the reacting mixture was allowed to stand for another hour. Ether was added, the mixture filtered, and the residue was washed twice with fresh ether. The ether and unreacted chloroform was then distilled off and the residual mixture steam distilled to remove any remaining chloroform or unreacted aldehyde. The steam distillate was saved for later recovery of the aldehyde. The part that was non-volatile with steam was ether extracted and the extract washed in a separatory funnel with a saturated solution of sodium bisulphite to remove any remaining unreacted aldehyde. The sodium bisulphite will add to the aldehyde forming an insoluble salt that precipitates as a flaky layer between the ether and water solution. The equation for this reaction is:



After all the aldehyde was removed the extract was washed with a two percent solution of sodium hydroxide, (until basic to litmus paper) to remove any free acid that might have been formed by the oxidation of the aldehyde. The resulting sodium salt was insoluble in ether and was separated with the water. The reactions for the oxidation and neutralization are as follows:



Each of the filtrates from the washings were extracted with ether again to recover any of the new compound that may have been lost by the washings. This ether extract was added to the original ether extract and the combined extracts washed with water, then dried over five grams of anhydrous sodium sulfate for three hours. The ether was then filtered into a Claisen distilling flask to remove the so-

dium sulphate. The ether was distilled off and the remaining liquid was fractionated under diminished pressure. A small amount of tarry residue remained in the flask and would not distill without decomposition.

An analyses for the chlorine content of the highest fraction was attempted by the Parr peroxide bomb method and later accomplished by the Carius method.

The percentage of chlorine in trichloromethyl-*m*-tolylcarbinol calculated from $C_9H_9OCl_3$ is 44.42%.

In preparing the tribromomethyl-*m*-tolylcarbinol almost the same procedure was followed. Bromoform was used instead of chloroform and one run was made under anhydrous conditions and the other run was made in an open necked flask without much difference in results.

Some decomposition occurred on distillation of the carbinol even under diminished pressure. Portions of the freshly distilled high boiling fraction were analysed by the Carius method.

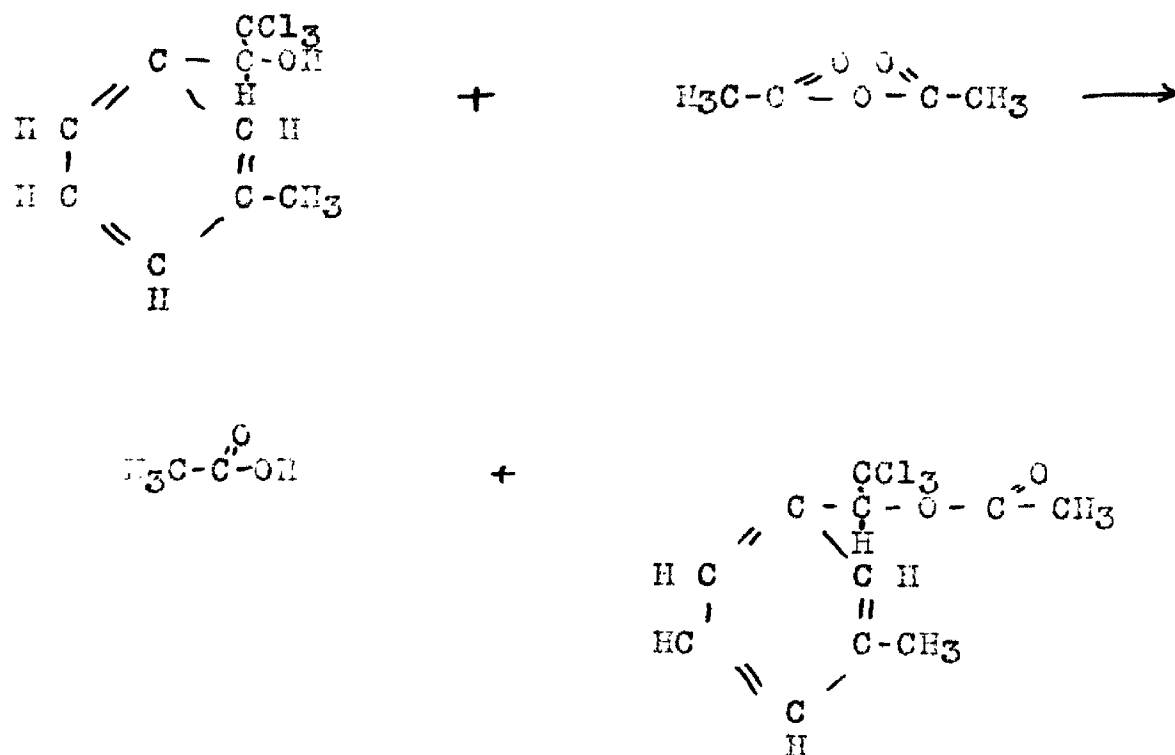
The percentage of bromine in tribromomethyl-*m*-tolylcarbinol calculated from $C_9H_9OBr_3$ is 64.31%.

The same general procedure was followed in the preparation of the trichloromethyl-*m*-bromophenylcarbinol using *m*-bromobenzaldehyde instead of *m*-tolualdehyde. Part of the

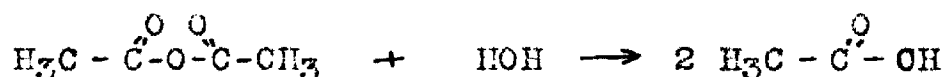
time the reaction was carried on under anhydrous conditions and part of the time in an open necked flask without any noticeable changes in results. Heating the mixture while the potassium hydroxide was being added and also increasing the amount of potassium hydroxide added was tried without any noticeable changes in results.

Ester Preparation

The Acetic ester of trichloromethyl-*m*-tolylcarbinol was prepared by allowing it to react with one and one-half the theoretical amount of acetic anhydride needed for the reaction. The equations for the reaction are as follows:



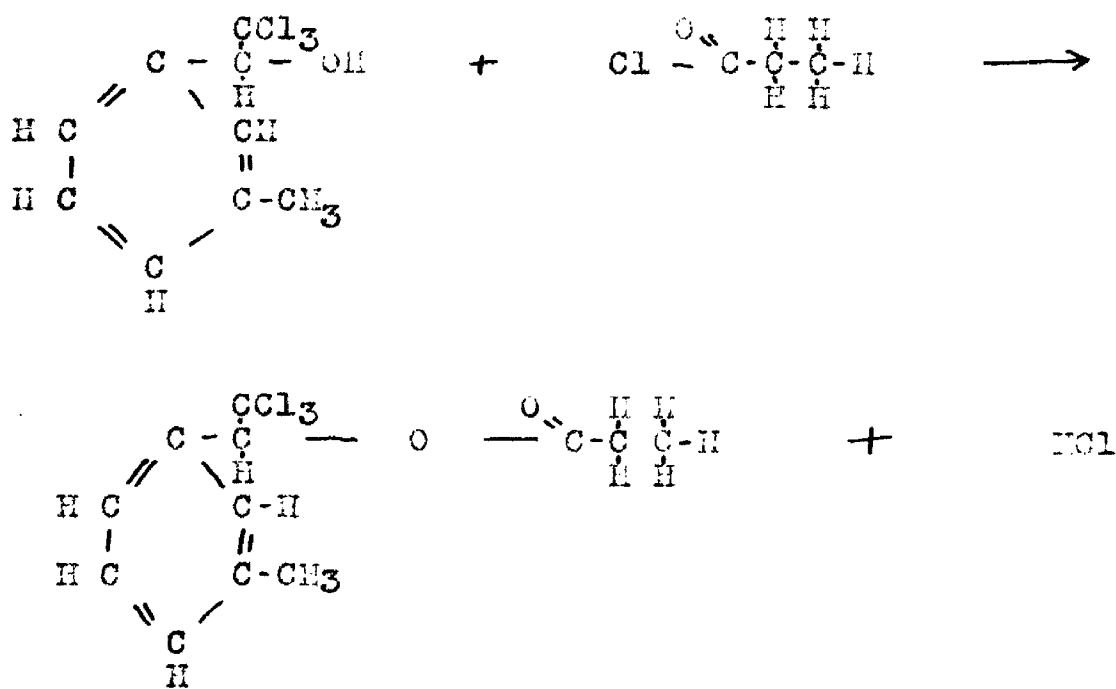
Five grams of the carbinol and five grams of acetic anhydride were placed in a 50 ml. flask. It was attached to a reflux condenser and refluxed for two hours at a temperature that caused the mixture to boil vigorously. A calcium chloride tube was placed in the open end of the Condenser to keep atmospheric moisture from hydrolyzing the anhydride to the acid. About 30 mls. of water were added to the mixture after refluxing, then it was allowed to stand for an hour to hydrolyze any excess anhydride.



The mixture was then washed in a separatory funnel until slightly alkaline with three percent sodium hydroxide to change the free acid formed from the above hydrolyses to the sodium salt of the acid and thus keep it from dissolving in the ether that was used in the next process. The ester was ether extracted, washed with water until neutral to litmus paper, then put in a 50 ml. flask with three grams of bone black. The mixture was attached to a reflux condenser and refluxed for twenty minutes to remove any impurities that could be adsorbed. The mixture was filtered to remove the charcoal and was again put in a separatory funnel and washed with a three percent sodium hydroxide solution and then a saturated solution of sodium bisulphite to neutralize and precipitate any acid or alde-

hyde that may have been formed by decomposition. The extract was dried over sodium sulphate and the ester remaining after the ether was distilled off was recrystallized from 6 N. acetic acid.

The halogen content of the esters was determined by the Parr peroxide bomb method. The amount of halogen in the acetic ester of trichloromethyl-*m*-tolylcarbinol was calculated from $C_{11}H_{11}O_2Cl_3$ and found to be 37.79% chlorine. The bromine in the tribromomethyl-*m*-tolylcarbinol was calculated from $C_{11}H_{11}O_2Br_3$ and found to be 57.79%. The propionic and butyric esters were prepared by exactly the same procedure as was used in preparing the acetic esters. Propionyl chloride and butyryl chloride were used with the carbinol instead of the anhydride according to the following reaction:



The esters were liquid and showed no signs of solidifying so they were distilled under diminished pressure and their halogen content determined by the Carius method.

The amount of halogen in the propionic and butyric esters of trichloromethyl-*m*-tolylcarbinol was found to be as follows:

Propionic ester calculated from $C_{12}H_{13}O_2Cl_3$ is 36.00% Cl

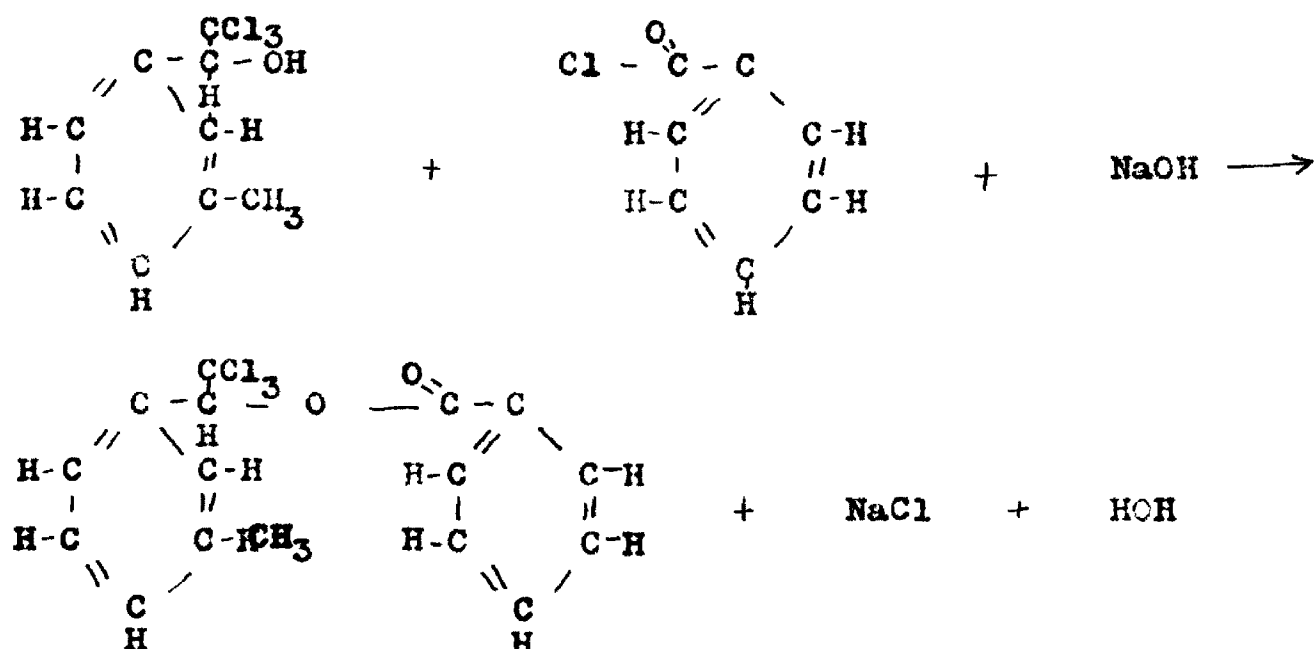
Butyric ester calculated from $C_{13}H_{15}O_2Cl_3$ is 34.37% Cl

The amount of halogen in the propionic and butyric esters of tribromomethyl-*m*-tolylcarbinol was found to be as follows:

Propionic ester calculated from $C_{12}H_{13}O_2Br_3$ is 55.90% Br.

Butyric ester calculated from $C_{13}H_{15}O_2Br_3$ is 54.14% Br.

The Schotten-Baumen method was used to prepare the benzoic esters. The equation for this method is as follows;



The benzoyl chloride, sodium hydroxide, and the carbinol were all placed in a 250 ml. Erlenmeyer flask and shaken for about half an hour. When the reaction was complete, as could be told by the temperature of the mixture rising to about 60° C, then cooling, the ester was ether extracted. The extract was next refluxed with three grams of bone black, washed successively with two percent sodium hydroxide, a saturated solution of sodium bisulfite, and water. It was then dried over anhydrous sodium sulfate. When dry the ether was evaporated and the thick liquid that remained was distilled under diminished pressure. After standing two days the distillate crystallized.

The tribromo ethyl-m-tolylcarbinol benzoic ester was not distilled but was recrystallized from hot 95% alcohol.

The theoretical values for the halogen content of these two esters are as follows:

Trichloroethyl-m-tolylcarbinol: Benzoic ester calculated from $C_{16}H_{13}O_2Cl_3$ 30.97% Cl.

Tribromoethyl-m-tolylcarbinol: Benzoic ester calculated from $C_{16}H_{13}O_2Br_3$ 50.20% Br.

Parr Peroxide Bomb

The Parr peroxide bomb is a device used to decompose organic compounds into simpler inorganic compounds. About 0.2000 grams of the substance to be analysed, 1.0 gram of potassium nitrate for an accelerator, 0.4 grams of lactose

for a fuel, and 15 grams of sodium peroxide are placed in the bomb and very thoroughly mixed by shaking. There are two lids for the bomb, one to be placed on only while mixing and the other to be used for igniting the explosive mixture. The latter is arranged so that an electric current can be passed through a fuse wire causing it to become red hot and to ignite the mixture. Great care must be taken in using only the correct amounts of materials, or the bomb may be bursted by too great an explosion. The fusion is carried out while the bomb is immersed in cold water.

After the fusion the fused mass is rinsed into a beaker, acidified with nitric acid, and filtered. An excess of silver nitrate is added to the filtrate and the halide is precipitated as silver halide. It is filtered, dried, and weighed. The amount of halogen can then be calculated from the weight of the silver halide and the weight of the sample.

The success of the Parr bomb method of analyses depends on a complete fusion and decomposition of the substance to be analysed.

Carius Method of analyses

The Parr bomb proved to be unsatisfactory for determining the halogen content of the liquids. It was difficult to get the liquids mixed thoroughly enough with the other solids used in the bomb to get a complete fusion so the Carius method was used. This method consists of heating the organic compound with fuming nitric acid and solid

silver nitrate in a sealed glass tube and weighing the silver halide that is formed. The determination is carried out in thick walled pyrex or soda-glass tubes.

One end of the tube is sealed off with a round blunt seal. The tube is then cleaned and dried. About one and one-half the theoretical amount of solid silver nitrate are introduced, then about one and one-half mls. of fuming nitric acid are added through a long pipette. The sides of the sealed glass tube must be kept dry until after sealing the upper end of the tube.

About 0.2000 grams of the carbimol are then weighed into a three inch test tube and this is carefully slid down to the bottom of the sealed tube. The carbimol must not come in contact with any acid or silver nitrate until the tube is completely sealed. The open end of the tube was then heated and drawn out to a five cm., thick walled, sealed capillary, the whole was wrapped in six thicknesses of wrapping paper and placed in a Carius furnace and heated for eight to ten hours at a temperature of 250°C .

After the tube has cooled the pressure is released from it by heating the end of the capillary with a needle point flame while the tube is still in the furnace. After the pressure bursts a hole in the tube it is then safe to handle. The capillary end was removed and the material washed into a beaker and diluted to 300 mls. It was heated

to boiling, allowed to cool in the dark and then filtered through a weighed Gooch filter, washed very thoroughly, dried, and weighed. From the weight of the silver halide formed and the weight of the sample the percentage of halogen was calculated.

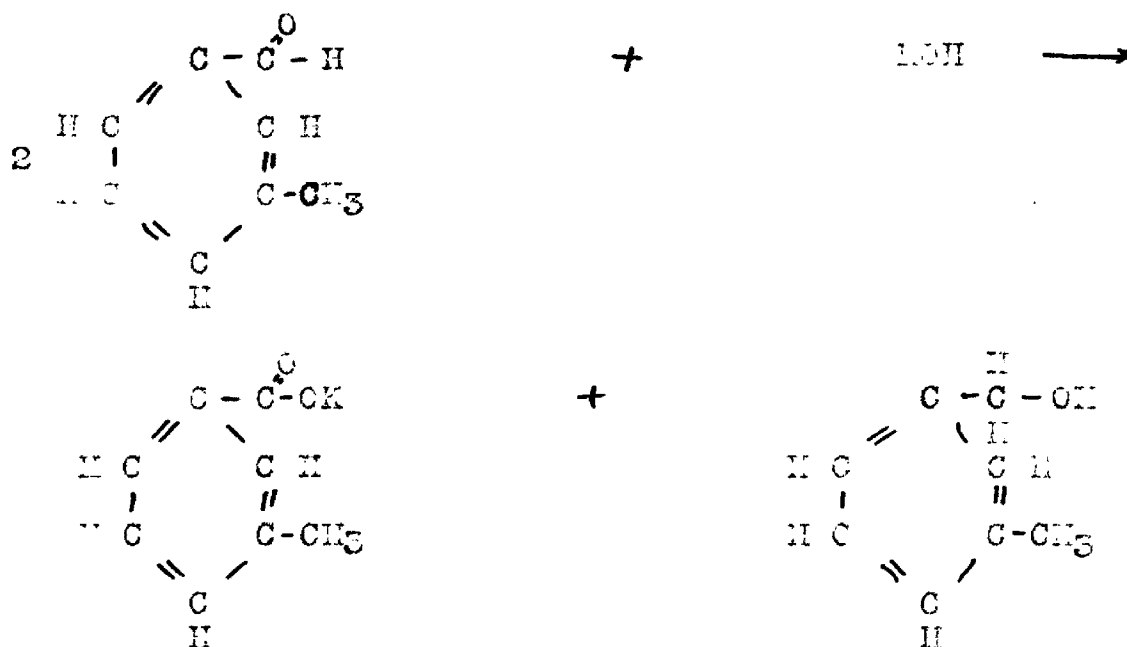
Solubilities

In determining the solubilities of the various products prepared 0.1 gram of a solid solute, or 0.2 mls. of a liquid were used with 3 mls. of the solvent, according to the usual method of qualitative organic analysis..

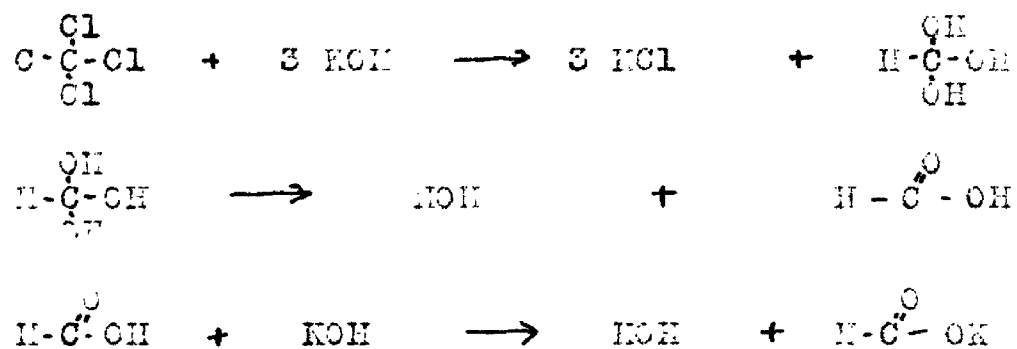
Yields

The yields obtained in preparing the trichloromethyl- and tribromomethyl-*m*-tolylcarbinol were very low, being only 15% and 12% respectively. There was always at least one half of the aldehyde that came through unchanged and could be reclaimed. There was always considerable decomposition of the carbinol during its distillation under diminished pressure, especially in the case of the tribromomethyl-*m*-tolylcarbinol.

There are two side reactions possible that might cut down the yield. Potassium hydroxide will react with a benzaldehyde to form an alcohol and the potassium salt of an acid. This reaction for *m*-tolu aldehyde is shown by the following equations:



Potassium hydroxide will also react with chloroform to give potassium formate, potassium chloride, and water. This reaction is shown in the following steps.



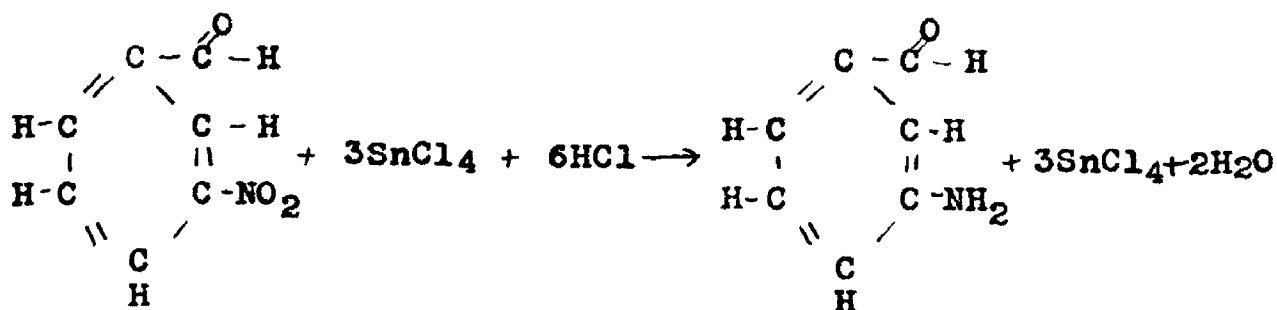
Much better yields were obtained in the preparation of the esters. The solid esters averaged 80% of the theoretical amount and the liquid esters averaged 50% of the Theoretical yields. There was always some decomposition in distilling the liquids, even under diminished pressure. Some of the liquid was always lost in the condenser and in fractionating the distillate.

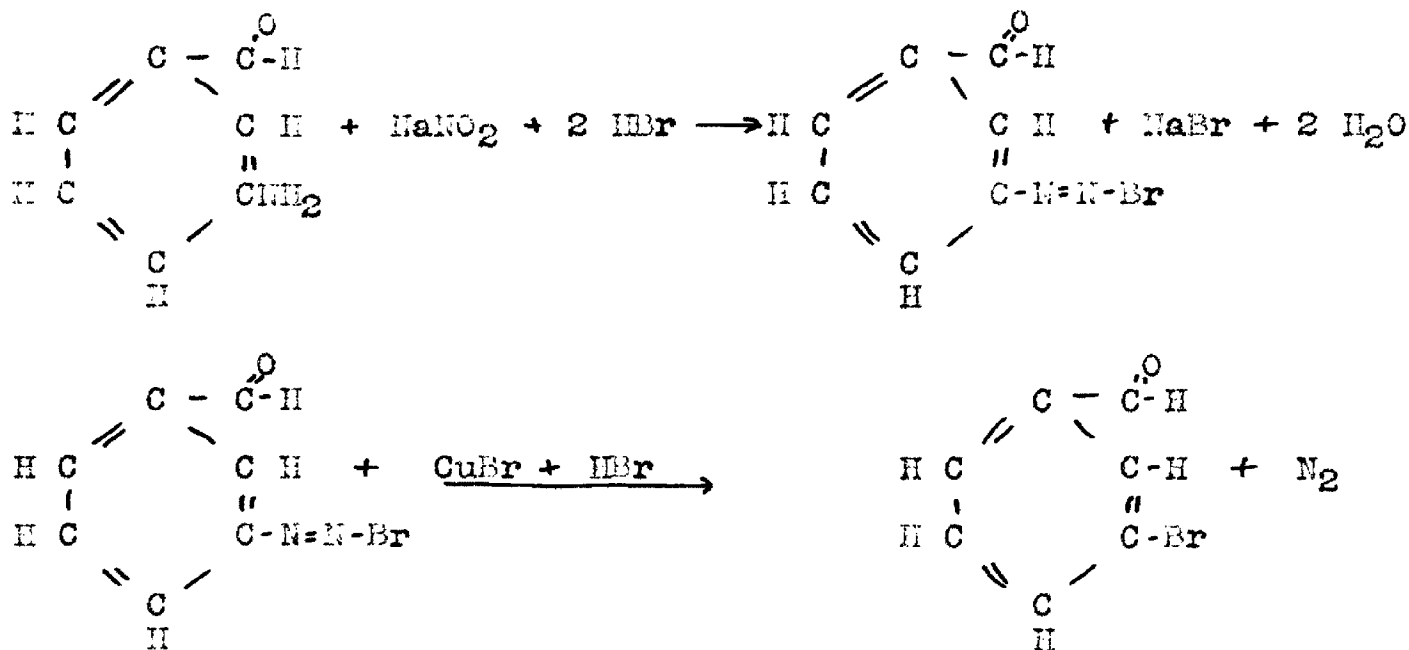
EXPERIMENTAL PART

Materials

The m-tolualdehyde which was used in synthesizing the trichloromethyl--and tribromomethyl-m-tolylcarbinol can be purchased from the Eastman Kodak Company, Rochester, New York at \$6.00 per kilogram. The chloroform and bromoform were C.P. grade and the chloroform was dried over calcium chloride several days before using it. The potassium hydroxide was of C. P. grade and in the pellet form. It was powdered with a mortar and pestle. The ether was 96% sulfuric U. S. P. grade containing about three percent alcohol. All the other chemicals used were of C. P. grade except the sodium bisulfite.

The m-bromobenzaldehyde used in the preparation of the trichloromethyl-m-bromophenylcarbinol could not be purchased, unless specially prepared, which is very expensive, so the materials for making it were purchased and it was synthesised according to the directions given by Buck and Ide and checked by Johnson and Vittum. The reactions are shown by the following equations:





Sixty grams of the 252 grams of *m*-bromobenzaldehyde prepared in this way were used to react with chloroform and form the trichloromethyl-*m*-bromophenylcarbinol. An analysis by the Parr bomb showed it to be about two per cent low in halogen content.

Before more carbinol was prepared from this *m*-bromobenzaldehyde Tyson¹⁰ found that the above method would not prepare just *m*-bromobenzaldehyde but a mixture of *m*-bromo-- and *m*-chlorobenzaldehyde would result. He however, gave a method for preparing pure *m*-bromobenzaldehyde which was almost the same except he used stannous bromide instead of stannous chloride and hydrobromic acid instead of hydrochloric acid for all the reactions concerned with these two chemicals.

More *m*-bromobenzaldehyde was prepared by this new method to be used in making the carbinols.

Trichloromethyl-m-tolylcarbinol Preparation

First run: 40 grams of m-tolualdehyde and 60 grams of dry chloroform were introduced into a one liter three necked flask. The flask was fitted to a mechanical stirrer with a mercury seal. Another neck was closed with a calcium chloride tube and the remaining neck was stoppered and used for adding materials. The stirrer was started and seven grams of powdered potassium hydroxide were added over a period of thirty minutes. The heat generated by the reaction indicated how fast the hydroxide could be added. If it was added too fast or in too large a portions the mixture would char in spots. It was added at a rate so that the temperature of the mixture never rose much above 50° C. A pink jelly mass formed after twenty to thirty minutes stirring which was difficult to stir, but stirring was continued for another hour. It was then allowed to stand for two more hours before all the ether soluble products were extracted with ether and filtered. Filtering was slow and difficult. The ether and chloroform were distilled off and the remaining liquid was steam distilled to remove any unreacted aldehyde and remaining chloroform. This left a dark red brown liquid which was ether extracted from the condensed steam. It was then washed with a saturated solution of so-

dium bisulfite to remove any aldehyde that might still remain and with a two percent solution of sodium hydroxide. The red brown color was removed by the hydroxide solution leaving a dark amber colored liquid. The remaining ether extract was dried over sodium sulfate for three hours, then it was filtered into a Claisen distilling flask and the ether distilled off. The residue was distilled under diminished pressure. There were three fractions separated as follows:

Fraction I 140-150° C. 9mm yield 6 grams

Fraction II 151-161° C. 3mm yield 11 grams

Fraction III 162-170° C. 9mm yield 3 grams

A small amount of tarry residue and decomposed charred material was left in the flask.

The light amber second fraction was analysed with the Parr bomb and found to contain 44.10% Cl and 43.86% Cl on the two out of three analyses that checked the closest.

The calculated value for the desired carbinol is 44.42% Cl, indicating that the carbinol was prepared but needed some purification. This fraction was used to synthesize esters of the carbinol which checked alright with the theoretical values for chlorine content.

Second run: This run was made exactly the same as

the first run except that instead of 60 grams of dry chloroform enough more was used to keep the pink jell in a solution thin enough so that it could be stirred to an advantage mechanically. Stirring was continued for about three hours and the mixture was allowed to stand over night. The mixture was then filtered by suction through a Buchner funnel.

The fractional distillation was as follows:

Fraction I	140-151° C.	14mm.	yield 3 grams
Fraction II	152-164° C.	14mm.	yield 14 grams
Fraction III	164-170° C.	14mm.	yield 4 grams

The Parr analyses of the middle fraction showed it was evidently the desired carbinol in an impure state, the results being 44.13% Cl and 42.35% Cl. It was also used to make esters of the carbinol which checked closely with the theoretical amount of chlorine.

Third run: The procedure followed in preparing this run was exactly the same as was used in the second run. The fractional distillation of this run was as follows:

Fraction I	140-148° C.	8mm.	yield 2 grams
Fraction II	140-154° C.	8mm.	yield 10 grams

Decomposition occurred at a higher temperature, then the temperature fell.

A Parr analyses of the second fraction showed the chlorine content to be still low, being 42.69% and 42.76%.

After the fusions of the Parr bomb an oily film could be noticed on the lid of the bomb. It was thought that the fusions might be incomplete so the Carius method was used to analyse the same fraction. The results showed 42.30% Cl and 42.40% Cl. These were the two results that checked closest out of three analyses that were made.

The fraction was then redistilled and fractionated as follows:

Fraction I 159-162° C. 9gms.

Fraction II 163-165° C. 3gms.

This freshly distilled higher boiling fraction was analysed by the Carius method and found to contain 44.39% Cl and 44.35% Cl which agrees well with the theoretical value of 44.42% Cl.

The physical properties of this carbinol are: a light, amber, viscous liquid; B. p. 163-165° C. under 9gms. of pressure; $d_{25/25}$ is 1.3684; insoluble in water and carbon tetrachloride; very soluble in absolute ethanol, methanol, benzene, acetone, ether, chloroform and carbon disulphide.

Esters of Trichloroethyl-*n*-tolyloxyalcohol

Five grams of carbinol and five grams of acetic anhydride were refluxed at 130 to 150° C. in a 50 ml. flask for two hours. Thirty ml. of water was added and the mixture was then allowed to stand for one and one-half hours.

Then the mixture was transferred to a separatory funnel. Some of the ester was solidifying and had to be extracted with ether in order to get it into the separatory funnel. A two percent solution of sodium hydroxide was added until the mixture was alkaline. More ether was added, the then solid ester was dissolved and the lower alkaline layer separated. The ether was distilled off and crystallization was attempted from hot 95% alcohol with not much success. A thick, sticky, amber colored liquid is all that would result. The liquid was again extracted with ether, charcoal was added and the mixture refluxed for twenty minutes to remove impurities by adsorption. After filtering the ether extract was dried over anhydrous sodium sulfate. The mixture was filtered, the ether distilled off, and another attempt was made to crystallize the now thick, white liquid from 95% alcohol. This attempt was unsuccessful so the alcohol was evaporated. 100 ml. of water and 25 ml. of 6N. acetic acid were added and the liquid crystallized into a solid mass. The acid was neutralized with two percent sodium hydroxide and the mass was broken up and washed with water. The solid was dried several days between filter paper in a desiccator under diminished pressure. The yield was five grams.

A Parr analyses for the chlorine content showed 37.75% and 37.52% which checked closely with the theoretical

value of 37.79,5 Cl.

The physical properties of this ester are: a white solid mass, m. p. 40-50° C.; insoluble in water; soluble in absolute ethanol and methanol; very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

The method used in the preparation of the propionic ester was about the same as that used for the acetic ester. Five grams of the carbinol and five grams of propionic anhydride were used and refluxed at a temperature that kept the boiling mixture condensing about one-third the way up the condenser. When water was added to hydrolyze the excess anhydride a liquid separated out instead of a precipitate. The liquid was extracted with ether and refluxed with three grams of bone black for 15 minutes to remove the impurities that could be adsorbed. It was filtered and the ether was distilled off. The residue was distilled under diminished pressure and all came over in one fraction boiling at 105-100° C. under 0.5 mm. pressure. The yield was three grams. The first analyses by the Carius method showed two out of three samples were slightly low in chlorine content so the fraction was redistilled. One sample checked alright with the theoretical value. It came over at 103 to 100° C. at 0.5 mm. pressure. A carius analyses on this fresh fraction

showed 35.93% Cl and 35.95% Cl which agreed well with the theoretical value of 36.00% Cl.

The physical properties of this ester are: light amber, slightly viscous liquid; B. p. 163-166° C. at 7mm. pressure; $d_{25/25}$ is 1.2819; insoluble in water; very soluble in absolute ethanol, methanol, benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

In preparing the butyric ester the same procedure was used with five grams of carbinol and five grams of butyryl chloride as was used in preparing the propionic ester with about the same corresponding results. The liquid was distilled under diminished pressure and came over at 174 to 177° C. at 10mm. The yield was four grams.

A Parr analyses was tried on this ester because it was not a viscous liquid and it was thought a good fusion may be possible; but the results were 33.75% Cl and 33.69% Cl which did not agree closely enough with the theoretical value of 34.37% Cl. The same fraction was now analysed by the Carius method and three out of three samples checked very closely with the theoretical. The results showed 34.42% Cl, 34.40% Cl and 34.34% Cl.

The physical properties of this ester are: light amber, thin liquid; B. p. 174 to 177° C. at 10mm.; $d_{25/25}$ is 1.2507; insoluble in water; soluble in methanol, benzene, acetone, chloroform, carbon tetrachloride and carbon disulfide; very soluble in absolute ethanol and ether.

The benzoic ester was prepared by the method of the Schotten-Bauman procedure. 12 grams of the benzoyl chloride, five grams of the carbinol and 100 ml. of 3N. sodium hydroxide solution were placed in a 250 ml. Erlenmeyer flask and shaken for about one-half hour. When the reaction was complete, as was told by the temperature of the mixture cooling down, an ether extract was made. It was dried over sodium sulfate, filtered, the ether distilled off, and the liquid that remained was distilled under diminished pressure. It came over at 222-225° C. at 9mm. The yield was five grams. A Carius analyses was made that showed the chlorine content to be 30.77% and 30.65% which agreed well with the theoretical value of 30.97%.

On standing two days the liquid crystallized.

The physical properties of this ester are: a very viscous, amber colored liquid; boiling point 222-225° C. at 9mm.; when solidified it was a white soft crystalline substance like gum caplor; m. p. 33-36° C.; insoluble in water; soluble in absolute ethanol and methanol; very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

Tribromomethyl-m-tolcarbinol Preparation

First run: 40 grams of m-tolylaldehyde and 85 grams of bromoform were introduced into a one liter round bottom

flask. It was connected to a mechanical stirrer and stirred for two hours while four grams of powdered potassium hydroxide were added in portions over a period of one hour. The temperature went up to about 50° C. which showed evidence of reaction. The mixture turned a light tint of brown in color. After standing over night the mixture was ether extracted and filtered. The ether was distilled from the filtrate and the residue now remaining was steam distilled to remove any unreacted aldehyde and bromoform. About 500 ml. of distillate came over. The residue was ether extracted and washed with a saturated solution of sodium sulfite to remove any remaining aldehyde. Then it was washed with two percent solution of sodium hydroxide to remove any acid that may have been formed. After washing again with water and drying over sodium sulfate for three hours the ether extract was filtered into a Claisen distilling flask and the ether was distilled off. The residue was distilled under diminished pressure. Three fractions were collected as follows:

- Fraction I 90-100° C. 11ms. yield 4 grams
- Fraction II 101-105° C. 11ms. yield 9 grams
- Fraction III 106-107° C. 11ms. yield 3 grams

Decomposition began at 107° C. and the temperature fell. There was some dark vapor coming over most of the time after 100° C. that was evidence of decomposition beginning.

The middle fraction was analysed by the Carius method immediately after distillation. The three analyses made all checked closely with the theoretical calculated amount of 64.31% Br. They were 64.22%, 64.30%, and 64.16%. Both the second and third fractions were used in synthesizing esters which checked alright.

Second run: 40 grams of *n*-tolylaldehyde and 65 grams of bromoform were treated exactly as the first run except that seven grams of powdered potassium hydroxide were used and added over a period of one hour. Potassium hydroxide was added until the reaction stopped warming up when a small portion was added. The color remained white instead of light brown tint in this second run. On distillation under diminished pressure the following fractions were obtained:

Fraction I 88-100° C. 9grams.

Fraction II 107-100° C. 9grams, yield 13 grams

Decomposition started then and the temperature dropped. The second fraction was used in preparing esters of the carbinol. It was not analysed for bromine content.

The physical properties of this carbinol are as follows:

a viscous, dark, red brown liquid; B. p. 131-135° C. at 11mm. $d_{25/25}$ is 1.3640; insoluble in water; soluble in absolute ethanol, methanol, acetone, chloroform, carbon tetrachloride, carbon disulfide; very soluble in benzene

and ether.

Esters of Tribromomethyl-m-tolylcarbinol

The method used in preparing the esters of the tribromomethyl-m-tolylcarbinol was almost the same as was used in preparing the esters of the trichloromethyl-m-tolylcarbinol.

The acetate ester was prepared by refluxing four grams of acetic anhydride for two hours, hot enough so the liquid condensed about one-fourth the way up in a water condenser. After cooling water was added to hydrolyze the anhydride to the acid. After standing one hour a dirty brown solid had formed. It was ether extracted, refluxed with three grams of bone black for twenty minutes, filtered, washed with a saturated sodium bisulfite solution, and two percent solution of sodium hydroxide until alkaline to litmus paper. The ether extract was dried over sodium sulfate, filtered, the ether was then distilled off. When the residue cooled it crystallized. It was recrystallized from hot 95% ethanol and dried between filter paper until thoroughly dry. There was five grams of the acetate. On analyses with the Parr bomb the solid ester showed 57.96% Br. and 57.76% Br which agrees well with the calculated theoretical value of 57.79% Br.

The physical properties are: a white crystalline solid; m. p. is 92-93° C; insoluble in water; slightly

soluble in absolute ethanol and methanol; very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulphide.

The propionate ester was prepared by the same procedure as was used in the acetic ester, using five grams of the carbinol with five grams of propionic anhydride. It came out as a light amber liquid that would not crystallize so was distilled under diminished pressure. The following fractions were collected:

Fraction I	175-181° C.	7ms.
Fraction II	182-185° C.	7ms.

The yield from the above two fractions was four grams. An analysis of the higher boiling fraction by the Carius method showed it to be slightly low in bromine content. The calculated theoretical value of bromine is 55.91%, but the analyses showed 55.11% Br and 54.75% Br.

The lower boiling fraction was then analysed and found to have a still lower bromine content, so the higher fraction was redistilled. This time, with the exception of the first seven or eight drops, it all came over at 7ms. pressure and 183-184° C. These first drops were collected separately. As an attempt was being made to determine the density of the liquid it crystallized into a white, gum like, crystalline mass. This mass was pressed between filter paper, then analysed by the

Carius method. The two best analyses showed it to contain 55.40% and 55.28% Br. These results were still slightly low and the ester should have been recrystallized from some solvent and another analyses made, but there was none left to work with.

The physical properties of the ester are: a white, soft, crystalline mass; M. p. 30° C.; B. p. $103-104^{\circ}$ C.; insoluble in water; soluble in absolute ethanol, methanol, and carbon disulfide; very soluble in benzene, acetone, ether, chloroform, and carbon tetrachloride.

The butyric ester was prepared according to the same procedure used in preparing the acetic and propionic esters, using five grams of carbimol and five grams of butyryl chloride. The liquid resulted was distilled under diminished pressure and the following fractions were collected:

Fraction I	$55-1.5^{\circ}$ C.	9ms.
Fraction II	$101-105^{\circ}$ C.	0ms.

The yield was three grams of an amber colored liquid. A Carius analyses showed the product to contain 54.06% and 54.12% Br. which agreed well with the calculated theoretical value of 54.14% Br.

The physical properties of this ester are as follows: an amber colored, viscous liquid; B. p. $101-105^{\circ}$ C. at 0ms. pressure; $d_{25/25}$ is 1.7840; insoluble in water; soluble in absolute ethanol, methanol, benzene,

acetone, chloroform, carbon tetrachloride, and carbon disulfide; very soluble in ether.

The benzoic ester was prepared by the regular Schotten-Baumen method. 100 ml. of 5N. sodium hydroxide, 12 grams of benzoyl chloride, and five grams of the carbinol were placed in a 250 ml. flask and shaken vigorously for 30 minutes. A thick, white liquid, a mass solid, settled out on standing. The liquid was decanted, the benzoate extracted with ether, refluxed with three grams of bone black for 20 minutes and then filtered. The filtrate was washed with a saturated solution of sodium bisulfite and two percent sodium hydroxide until the solution reacted basic to litmus paper. The ether was evaporated and a yellowish-white, solid mass formed on standing over night. It was recrystallized from hot 95% ethanol. The yield was five grams.

A Carius analyses of the product showed it to contain 50.4% and 50.33% C. These amounts agree with the calculated theoretical amount of 50.33% C.

The physical properties of this ester are as follows: a white crystalline solid, m. p. is 36-37° C.; insoluble in water; slightly soluble in absolute ethanol and methanol; very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

Trichloromethyl-n-bromophenylcarbinol Preparation

The preparation of this carbinol was attempted by using almost the same methods as were used in preparing the trichloromethyl--and tribromomethyl-n-tolylcarbinol but with almost no success. Four runs were made and one factor was varied each time with no change in results. Always just two to three grams of the thought to be desired product would distill over, and it didn't come over at a constant temperature. On distillation under diminished pressure the liquid would begin coming over at about 160° C. and 7-8 mm. pressure. It would continue to come over in steady drops and the temperature would steadily rise until about $165-170^{\circ}$ C. decomposition would begin at this temperature and there was always quite a bit of tarry charred mass left in the distilling flask. From 155° C. to about 170° C., instead of an amber liquid distilling over, a yellowish-white semi-solid mass would collect in the air condenser and remain there until removed by heating hot enough so it would run down. There was never less than two grams or more than three grams of this higher boiling fraction. The lower fractions combined always contained from six to ten grams of the amber viscous liquid.

Sixty grams of m-bromobenzaldehyde with 60 grams of chloroform were introduced into a round bottom flask and stirred mechanically while four grams of powdered potassium hydroxide were added over one half hour period. The temperature caused by the reaction did not rise over 45° C., which was evidence of not much reaction taking place. Potassium hydroxide reacting with chloroform gives off about that much heat.

It was thought that atmospheric moisture may be hindering the reaction, so the second run was carried out in a three necked flask fitted with a mercury sealed mechanical stirrer. One of the other two necks was fitted with a calcium chloride tube and the other was stoppered. All the other conditions were kept the same as in the first run. There was no noticeable change in results.

It was thought that if more potassium hydroxide were used better results would be obtained. The third run was carried out under the same conditions as were used in the second run except that seven grams of powdered potassium hydroxide were added over an hour period of stirring. There was still no noticeable change in results.

The fourth run was made like the second except that while the four grams of potassium hydroxide were being added the mixture was kept at a temperature of about 60 to 65° C. by heating with an electric hot plate. No better results were obtained than before.

Always from one-half to two-thirds of the aldehyde used would be recovered unchanged in the steam distillation, and more would be precipitated with sodium bisulfite later. This was evidence that the chloroform did not react and add on to the aldehyde, or was decomposing again during the steam distillation.

The four small higher boiling fractions were combined and redistilled under diminished pressure and collected as follows:

Fraction I	107-155° C.	9gms.	1 gram yield
Fraction II	156-170° C.	9gms.	3 gram yield

It was thought that the higher boiling fractions of white semi-solid mass would crystallize, but at the end of two months it was still the same. The wide boiling range of the small fractions resulting was indication that a pure compound had not been prepared.

SUMMARY

A summary of facts concerning the investigation of adding chloroform and bromoform to m-tolaldehyde and the

preparation of esters from the resulting carbinols are tabulated in the chart below.

Compound prepared	B. p.	Press.	l. p. or d. 25/25	Analyses	
				Calc'd	Found
Trichloromethyl- m-tolylcarbinol	183-185°C	9 mm	---	44.42%Cl	44.39%Cl 44.35%Cl
Esters of above					
Acetic	---	---	43-50°C	37.79%Cl	37.52%Cl 37.73%Cl
Propionic	163-166°C	8 mm	1.2319	36.00%Cl	35.93%Cl 35.95%Cl
Butyric	174-177°C	10 mm	1.2307	34.37%Cl	34.42%Cl 34.40%Cl
Benzoic	222-225°C	9 mm	63-66°C	30.97%Cl	30.77%Cl 30.85%Cl
Tribromomethyl- m-tolylcarbinol	191-195°C	11 mm	1.3340	64.31%Br	64.30%Br 64.22%Br
Esters of above					
Acetic	---	---	32-35°C	37.79%Br	37.96%Br 37.76%Br
Propionic	163-164°C	7 mm	33°C	55.91%Br	55.40%Br 55.20%Br
Butyric	191-195°C	8 mm	1.7340	54.14%Br	54.12%Br 54.06%Br
Benzoic	---	---	36-37°C	50.20%Br	50.40%Br 50.33%Br

CONCLUSION

Trichloromethyl--and tribromomethyl-m-tolylcarbinol as well as the acetic, propionic, butyric, and benzoic esters of each can be prepared by the methods shown in this paper. The carbinols are rather unstable compounds and seem to decompose somewhat on standing for a long time or at high temperatures. The esters seem to be more stable on standing and at high temperatures.

Chloroform will not add to m-bromobenzaldehyde in amounts large enough to be practical under the same conditions that it will add to some of the other aldehydes.

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