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Addition of chloroform and bromoform to substituted benzaldehydes: p-Tolualdehyde m-Bromobenzaldehyde m-Nitrobenzaldehyde

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THE ADDITION OF CHLOROFORM AND BROMOFORM TO SUBSTITUTED BENZALDEHYDES

p-Tolualdehyde
m-Bromobenzaldehyde
m-Nitrobenzaldehyde

by

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B.A., Montana State University, 1934

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1936

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Chairman of Board
of Examiners.

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Chairman of Committee
on Graduate Study

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HISTORICAL

In 1897, Jocicz[1] reported that chloroform would add to benzaldehyde in the presence of an alkali, forming the corresponding trichloromethyl carbinol. However, he gave no expetimental details. Yoder[7] has also reported the preparation of this carbinol, and the carbamic acid ester of it, but he gave no experimental data on the preparation of the carbinol. Howard[2], in 1925, undertook to find the best experimental conditions under which this condensation would take place. He found that by using one-third the gram molecular weight of the aldehyde, one-half the gram molecular weight of dry chloroform and adding four grams of powdered potassium hydroxide slowly over a one-half hour period with constant mechanical stirring, he obtained the best results.

Siegfried[6], in 1899, investigated and reported on the condensation of benzaldehyde and bromoform in the presence of alkali, stating only that he had used the method of Jocicz, to form tribromomethyl-phenylcarbinol. Howard[3] repeated his own experiment, using bromoform in place of chloroform and thus again prepared the bromoform addition carbinol. He also prepared the acetic, propionic, butyric, and benzoic esters of this carbinol.

Howard and Castles[4] have reported the preparation of trichloromethyl-o-chlorophenylcarbinol and tribromomethylo-chlorophenyl carbinol as well as the acetic, propionic, butyric and benzoic esters of each. These carbinols were prepared by the addition of chloroform and bromoform to o-chlorobenzaldehyde in the presence of potassium hydroxide.

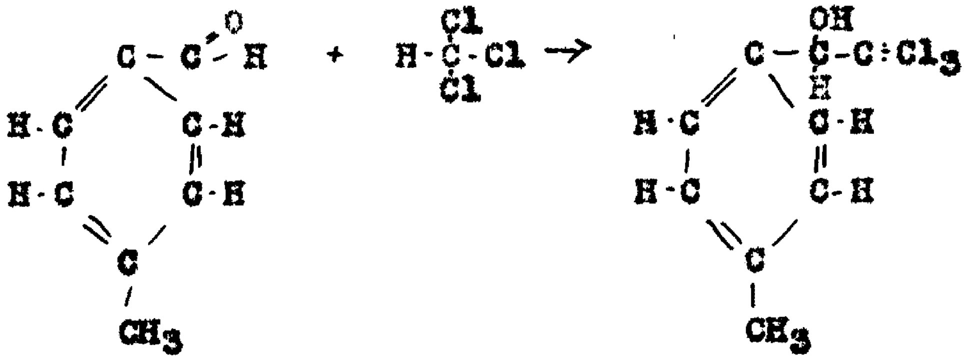
Howard[5] reported the preparation of trichloromethyl- and tribromomethyl-p-chlorophenylcarbinol by the addition of chloroform and bromoform to p-chlorobenzaldehyde in the presence of potassium hydroxide. Also, the acetic, propionic, butyric and benzoic esters of the trichloromethyl-p-chlorophenylcarbinol were prepared and their properties studied. Several attempts to prepare the esters of the bromoform addition compound, by similar and different means, were made, but all ended in failure as the carbinol in each case came through unchanged.

The problem which was investigated in preparation for this paper was concerned with the addition of chloroform and bromoform to some more of the substituted benzaldehydes, and the preparation of the acetic, propionic, butyric and benzoic esters of the resulting carbinols. The specific ones investigated were; p-tolualdehyde, m-bromobenzaldehyde, and m-nitrobenzaldehyde.

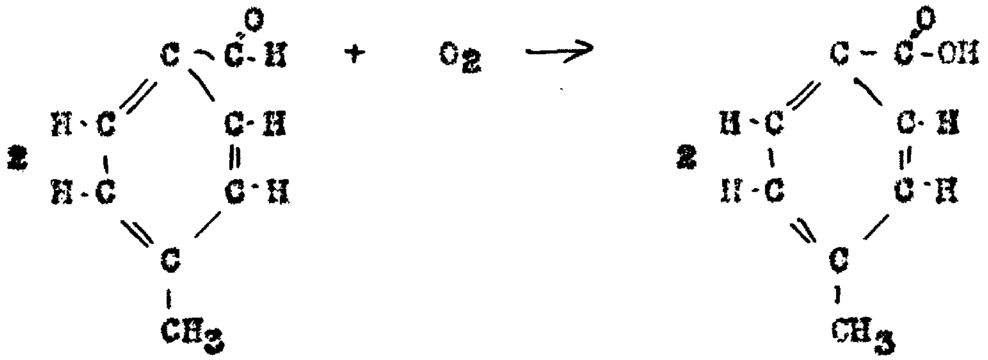
THEORETICAL

Carbinol Preparation

The trichloromethyl-p-tolylcarbinol was prepared by the interaction of chloroform and p-tolualdehyde in the presence of powdered potassium hydroxide, according to the reaction,



The entire reaction was carried out in a three necked flask. In the center neck was fitted a mercury sealed mechanical stirrer. Through the other necks were introduced the reagents used. First, one-third the gram molecular weight of the aldehyde, then one-half the gram molecular weight of dry chloroform. The stirrer was started and dry powdered potassium hydroxide was added in small amounts over a one-half hour period. From time to time, as the hydroxide was added, heat was generated in the flask, showing evidence of reaction. The rate at which the hydroxide is added controls the rate of the reaction. After the hydroxide was added, the stirring was continued for about one hour longer. The reacting mixture was allowed to stand for at least three hours before ether was added and the mixture filtered. The ether and some of the chloroform was then distilled off and the residual mixture was steam distilled to remove any remaining chloroform and the unchanged aldehyde. The part which was non-volatile with steam was extracted from the condensed steam with ether, and the extract treated in a separatory funnel with a three percent sodium hydroxide solution to remove any free acid which might have been formed by the oxidation of the aldehyde, by converting it to the sodium salt.



The ether extract was again washed with water and then dried over anhydrous sodium sulfate. After drying, the ether was distilled off in a Claison distilling flask and the remaining material fractionated under diminished pressure.

The analysis for the chlorine content was made by the Parr peroxide bomb method in the higher boiling of the two fractions collected. After each fractionation, there was a comparatively small amount of tarry residue left in the distilling flask, and this was discarded. The steam distillate was saved for later recovery of the unchanged aldehyde.

The percentage of chlorine in trichloromethyl-p-tolylcarbinol, calculated from $C_9H_9OCl_3$ is 44.42% Cl.

In the preparation of the tribromomethyl-p-tolylcarbinol, exactly the same procedure was followed with the exception that bromoform was substituted for chloroform. In the fractionation of the carbinol under diminished pressure, the distilling flask must be heated very rapidly, as extended heating at low temperatures appears to decompose the carbinol, even under diminished pressure.

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

The same general procedures were followed in the preparation of trichloromethyl- and tribromomethyl-m-bromophenylcarbinol, using m-bromobenzaldehyde in place of p-tolualdehyde.

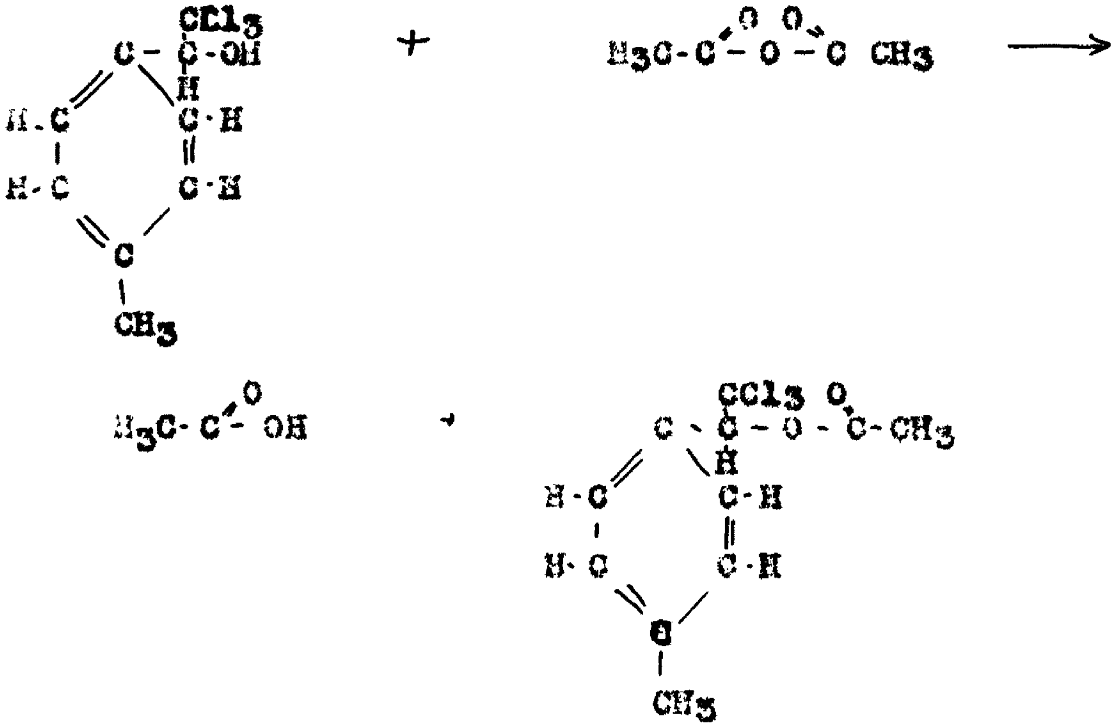
The percentage of halogen in trichloromethyl-m-bromophenylcarbinol, expressed as chlorine equivalent and calculated from $C_8H_6OBrCl_3$ is 50.22% Cl equivalent.

In the attempted preparation of trichloromethyl-m-nitrophenylcarbinol, the same procedure was tried again with the exception that three-fourths of the gram molecular weight of chloroform was used instead of one-half as the m-nitrobenzaldehyde would not dissolve in the smaller amount. As the m-nitrobenzaldehyde is not very volatile with steam, the material was treated with a saturated sodium bisulfite solution to remove the aldehyde. This was done just before the ether extract was dried. Exceptional care had to be taken in the addition of the alkali in the mixing flask, as there seemed to be a tendency for the mixture to overheat and char.

The percentage of chlorine in trichloromethyl-m-nitrophenylcarbinol calculated from $C_8H_6O_3NCl_3$ is 39.33% Cl.

Ester Preparation

In the preparation of the acetic and propionic esters, the method used was the one in which the carbinol was allowed to react with the acid anhydride. The reaction for the preparation of the acetic ester of trichloromethyl-p-tolylcarbinol is shown in the following equation.



Five grams of the carbinol and five grams of the anhydride were put in a fifty ml. flask connected to a reflux air condenser and refluxed for two hours in an oil bath at a temperature so controlled that the reacting mixture condensed about one-third to one-half the way up in the air condenser. A calcium chloride tube was put at the top of the condenser to keep out the atmospheric moisture. At the end of the reaction time, the mixture was poured into a beaker of water and allowed to stand for some time to hydrolize the excess anhydride.

$$H_3C-\overset{O}{C}-O-\overset{O}{C}-CH_3 + HOH \rightarrow 2\ H_3C-\overset{O}{C}-OH$$

After the hydrolysis was completed, the mixture was made slightly alkaline with dilute sodium hydroxide solution to convert the free acid formed in the hydrolysis to the sodium salt and thus keep it from dissolving in the ether used in the next operation. The ester was then extracted with ether, washed with water, and dried over anhydrous sodium sulfate.

The ether was evaporated off and the ester remaining after the evaporation was recrystallized and the halogen content determined by the Parr method.

The calculated values for the propionic and acetic esters of trichloromethyl- and tribromomethyl-p-tolyl-carbinol are as follows:

Trichloromethyl-p-tolylcarbinol

Acetic ester calculated from $C_{11}H_{11}O_2Cl_3$ is 37.79% Cl

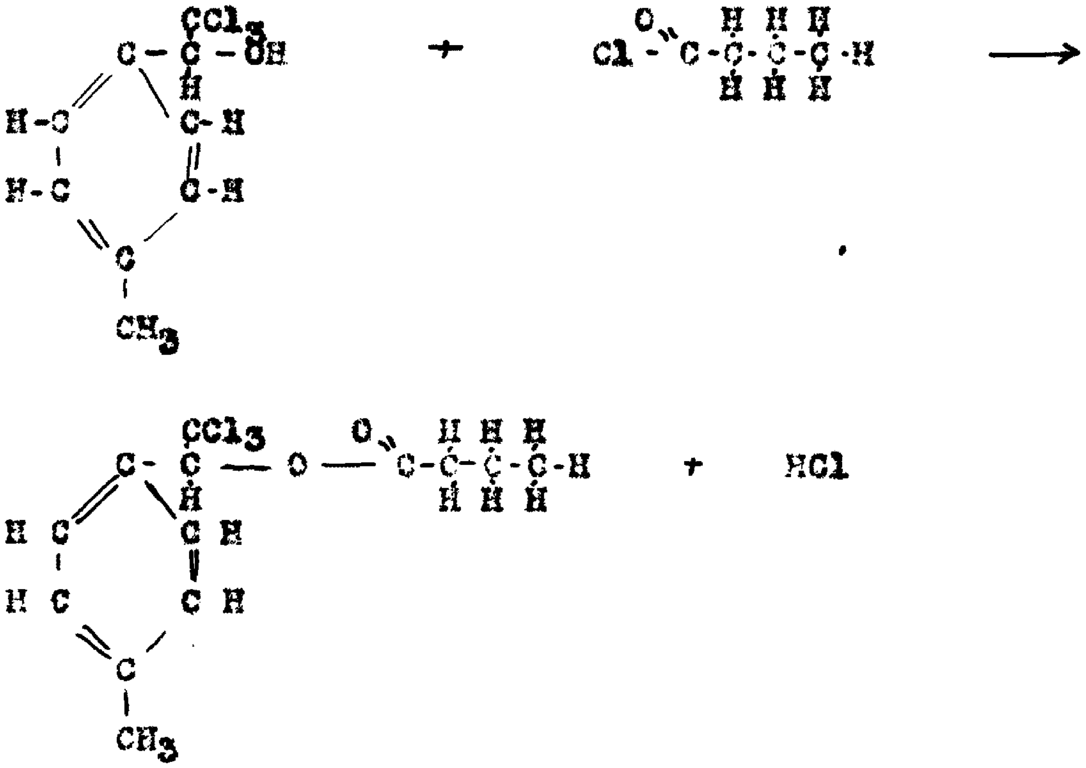
Propionic ester calculated from $C_{12}H_{13}O_2Cl_3$ is 36.01% Cl

Tribromomethyl-p-tolylcarbinol

Acetic ester calculated from $C_{11}H_{11}O_2Br_3$ is 57.81% Br

Propionic ester calculated from $C_{12}H_{13}O_2Br_3$ is 55.91% Br

In the preparation of the butyric ester, butyryl chloride was allowed to react with the carbinol according to the reaction,



The setup used and the procedure followed were the same as that in the preparation of the acetic and propionic esters. The butyric ester of the chloroform addition was a liquid, so could not be further purified by recrystallization.

The theoretical values calculated for the halogen content of the butyric esters are as follows:

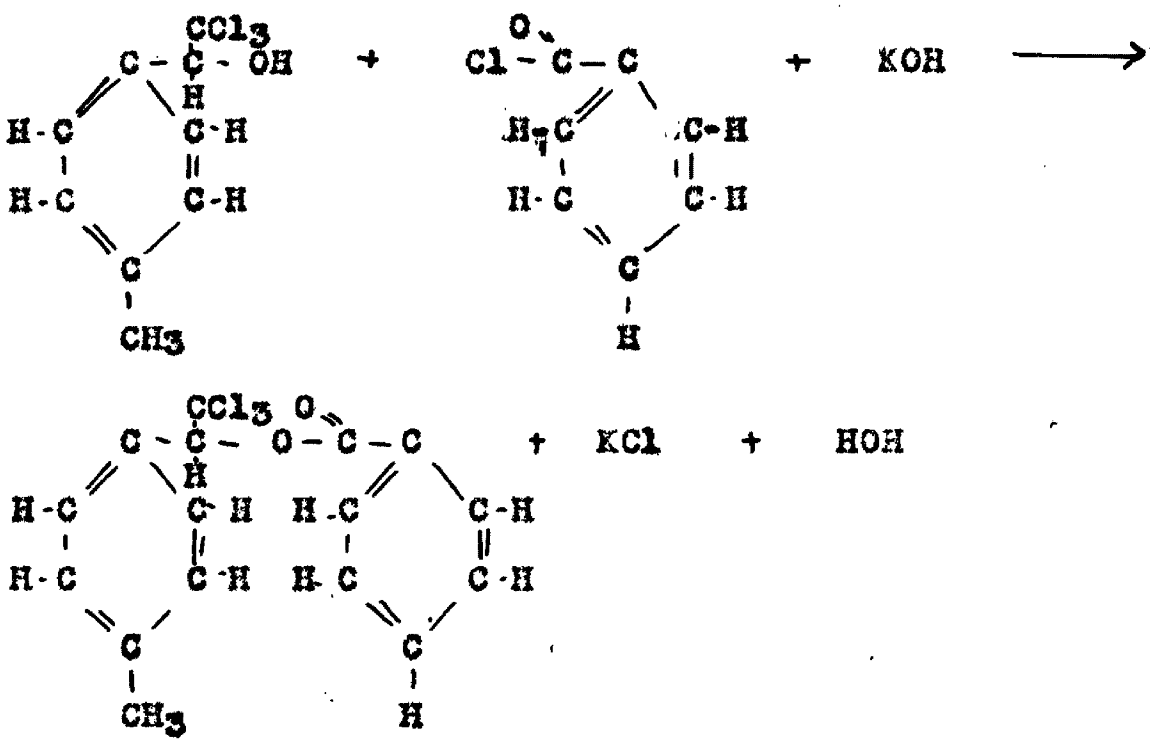
Trichloromethyl-p-tolylcarbinol

Butyric ester calculated from $C_{13}H_{15}O_2Cl_3$ is 34.36% Cl

Tribromomethyl-p-tolylcarbinol

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

In the preparation of the benzoic esters, the usual procedure of the Schotten-Bauman method was used. The equation for this method is,



The benzoyl chloride, the sodium hydroxide and the carbinol were all put in a 250 ml. erlenmeyer flask and shaken for at least one-half hour. When the reaction was completed, the ester was extracted with ether, washed, dried over anhydrous sodium sulfate, and the ether evaporated off. The solid ester which was left was recrystallized from hot 95% ethanol.

The theoretical values for the halogen content are as follows:

Trichloromethyl-p-tolylcarbinol
benzoic ester calculated from $C_{16}H_{13}O_2Cl_3$ is 30.97% Cl

Tribromomethyl-p-tolylcarbinol

Benzoic ester calculated from $C_{16}H_{13}O_2Br_3$ is 50.28% Br

Parr Peroxide Bomb

This method is one for determining the halogen content of organic compounds. Its success depends upon the fusion and decomposition of the material with sodium peroxide in a closed bomb and the precipitation of the halogen with silver nitrate. Approximately 0.2000 grams of the substance to be analyzed, 1.5 grams of potassium nitrate for an accelerator, 0.4 grams of lactose for fuel, and fifteen grams of sodium peroxide are put in a Parr bomb and very thoroughly shaken. When thoroughly mixed, the false top is removed and the top with the fuse wire is clamped into place. The entire bomb is immersed in water and an electric current is sent through the wire to ignite the charge. 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 usual method for the gravimetric analysis for halogen determinations is followed.

In some cases, especially if the halogen content was very high, better fusions resulted if 0.2 grams of benzoic acid was used in addition to the lactose for fuel.

Combustions

In the determination of the bromine content of tribromomethyl-p-tolylcarbinol by the Parr method, much difficulty was encountered in obtaining a good fusion, and because of this fact, the values found for the percentage of bromine did not check with each other. For this reason, it was thought that perhaps a hydrate had been formed, so the carbon and hydrogen content was determined.

The method used for the determination of the carbon and hydrogen content of tribromomethyl-p-tolylcarbinol was a combustion method, in which the carbon is converted into carbon dioxide and the hydrogen into water by forcing the material over hot copper oxide in a stream of oxygen, and absorbing the water formed in concentrated sulfuric acid and the carbon dioxide in a water solution of potassium hydroxide. As there was a halogen present in the carbinol, fused lead chromate was used in addition to the copper oxide in the combustion tube. The lead chromate was used to remove the bromine, because copper bromide is decomposed at a comparatively low temperature. A roll of silver foil was also placed at the exit end of the tube to remove any bromine which might have been driven past the lead salt.

The apparatus used in the combustion was as follows; an electric furnace with three elements, a combustion tube of hard, difficultly fusable glass filled for about one-half its length with copper oxide and about one-fourth its length with fused lead chromate, a tank of oxygen, a tube filled with soda lime, a sulfuric acid bubbler, a U-tube filled with glass beads and concentrated sulfuric acid to absorb the water formed in the combustion, and a Geissler bulb filled with potassium hydroxide solution to absorb the carbon dioxide.

The apparatus is arranged so that the oxygen is passed through the soda lime tube and the sulfuric acid bubbler before going through the combustion tube. The purpose of these absorbers is to remove carbon dioxide and water from the oxygen before entering the furnace. The hot gases which come out of the tube are driven first through the U-tube and then through the potash bulb.

In making the actual determinations, the following method was used. The Geissler bulb was filled with a fresh 25% potassium hydroxide solution, the apparatus put together, and the connections all made tight. The last two elements of the furnace turned on, and the heating continued until the copper oxide in the tube showed a dull red color. The oxygen was then started, and the rate of flow so controlled that there were about two or three bubbles per second through the bubbler. After the oxygen had passed through the tube for about one-half hour, the Geissler bulb and the U-tube were removed and, without interrupting the stream of oxygen through the furnace, weighed while still full of oxygen. The weighed tubes were then replaced and the flow of oxygen stopped while a porcelain boat containing about 0.2000 grams of the sample was placed in the front end of the combustion tube as far from the opening as the material in the tube would permit. The oxygen was again started and the first element of the furnace turned on and placed as near the opening as it was possible to get. When this element was hot, it was gradually moved down toward the others, thus distilling off the material in the boat. The combustion was continued for about four hours, or until the rate of the gas bubbling through the U-tube was the same as that going through the bubbler. Again the Geissler bulb and the U-tube were weighed while still full of oxygen, and from the weights of the gases absorbed, the percentage of carbon and hydrogen can be calculated. The theoretical values for this carbinol, calculated from $C_9H_9OBr_3$ are 28.97% C and 2.43% H.

Carius Method

As the Parr method was not satisfactory for the determination of the bromine content of tribromomethyl-p-tolylcarbinol, the Carius method was used.

The Carius method consists of heating the carbinol in a sealed tube with concentrated nitric acid and silver nitrate, and weighing the silver bromide formed. The determination is carried out in thick walled soda-glass tubes. One end of the tube is sealed off with a blunt seal, and the tube cleaned a and dried. When dry, approximately one and one-half grams of silver nitrate crystals are introduced, and then about one- and one-half ml. of concentrated nitric acid are added by means of a long pipette. About 0.2000 grams of the carbinol are then weighed into a two inch sodium decomposition tube and this introduced into the Carius tube without mixing the contents. The large tube is then sealed off with a thick seal, wrapped in paper and placed in a Carius furnace and heated for five hours at a temperature of 250-300°C.

At the end of this time, the pressure is released from the tube by heating one end with a needle point flame while the tube is still in the furnace. After this operation, the tube can be handled with safty, and is removed from the furnace, the end cut off, and the material washed into a beaker and all the large lumps broken up to dissolve the unchanged silver nitrate. When this is done, the silver halide is filtered through a weighed Gooch filter, washed very thoroughly, dried and again weighed. From the weight of the halide formed and the weight of the sample, the percentage of halogen is calculated.

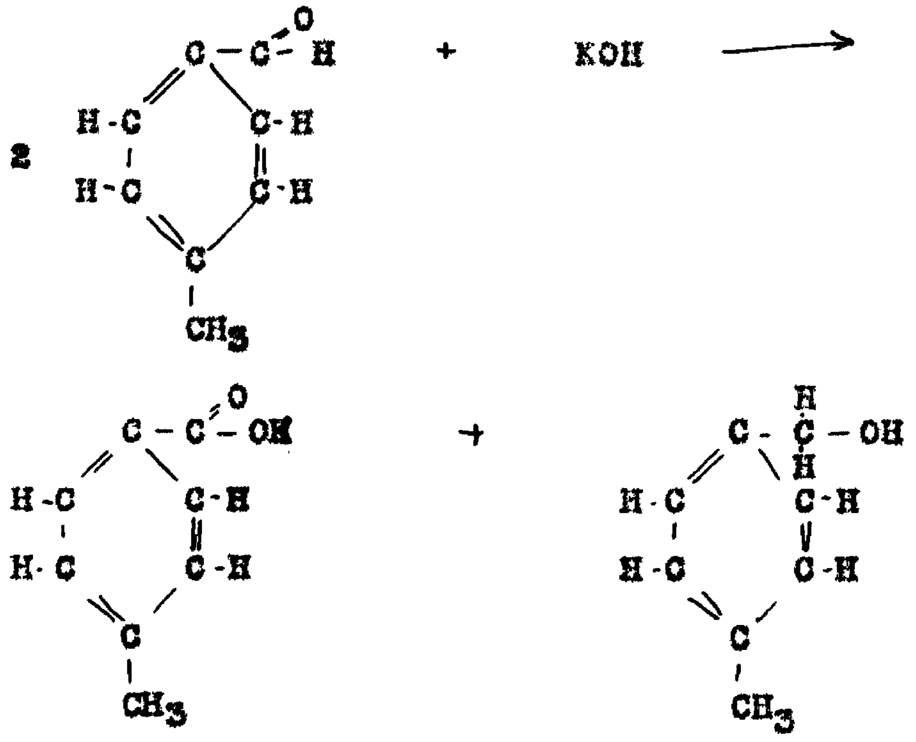
Solubilities

In the determination of the solubilities of the various products, 0.1 grams of a solid solute, or 0.2ml. of a liquid were used with 3 ml. of the solvent, according to the usual method of Qualitative Organic analyses.

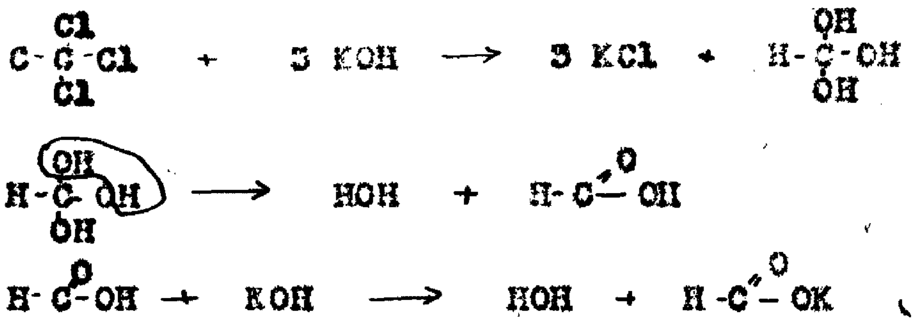
Yields

The yield in the case of the trichloromethyl- and the tribromomethyl-p-tolylcarbinol were quite low. There was a considerable amount of unchanged aldehyde, and there are several side reactions possible which might tend to 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 p-tolualdehyde may be represented by the following equation.



Potassium hydroxide will also react with chloroform to yield potassium formate, potassium chloride, and water. This reaction may be shown as taking place in the following steps.



$$C\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}Cl + 3\,KOH \longrightarrow 3\,KCl + H\text{-}\overset{OH}{\underset{OH}{C}}\text{-}OH$$

$$H\text{-}\overset{OH}{\underset{OH}{C}}\text{-}OH \longrightarrow HOH + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

$$H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + KOH \longrightarrow HOH + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OK$$

EXPERIMENTAL PART

Materials

The p-tolualdehyde, the m-bromobenzaldehyde and the m-nitrobenzaldehyde are obtainable from the Eastman Kodak Company. The chloroform and bromoform were of high chemical purity and the chloroform was dried over anhydrous calcium chloride for several days before use. The potassium hydroxide was C. P. grade and the ether used was 96% sulfuric. In the Parr and Carius analyses, all chemical's used were of the highest purity.

Trichloromethyl-p-tolylcarbinol Preparation

First run: 40 grams of p-tolualdehyde and 60 grams of dry chloroform were introduced into a three necked flask connected to a mechanical stirrer. The stirrer was started and four grams of powdered potassium hydroxide were added, a little at a time over a one-half hour period. At the end of this time, a pink jelly had formed in the flask and the stirrer was ineffective in mixing it, so it was stopped. The jelly was allowed to stand for three hours before it was ether extracted and filtered. The ether and some of the chloroform was distilled off, and the remaining material steam distilled to remove any remaining chloroform and the unchanged aldehyde. This left an orange solution which was extracted with ether, washed with water, and dried over sodium sulfate. When dry, the ether was distilled off in a Claison distilling flask and the residue distilled under diminished pressure. There were two fractions separated.

Fraction	I	135-150°C	17 mm
Fraction	II	150-167°C	17 mm

A small amount of tarry residue left in the distilling flask was discarded.

The second fraction contained a clear, yellow, oily liquid. A Parr analysis on this fraction showed 46.08% Cl. The calculated value for the desired carbinol is 44.42% Cl, indicating that some of the desired carbinol had been formed, but that some purification was necessary. The yield on this run was very small.

Second run: This run was made in exactly the same way as the first, except that there was better agitation in the flask and the stirring was continued for one-half hour after the potassium hydroxide had been added. There was no pink jelly formed and the reacting mixture did not heat as much as in the first run. The fractional distillation follows.

Fraction I 81-145°C 5 mm

Fraction II 145-149°C 5 mm

As the yield on the second run was much greater than that on the first, the two were combined and redistilled.

Fraction I 80-145°C 4½ mm

Fraction II 145-149°C 4½ mm

There were approximately 21 grams from the combined first two runs. The Parr analysis on the second fraction of this redistilled product showed 43.93% Cl.

After standing for about 48 hours, crystals started to form in the second fraction of the distillate. These were pressed out on filter papers, removing some yellow oily liquid, and leaving white crystals. These crystals were analyzed by the Parr method, and found to contain 44.21% Cl. This checks with the theoretical value of 44.42% Cl. A third run was made as a check on the yield and to obtain more of the carbinol for the preparation of the esters.

Third run: The procedure followed in this run was the same as that used in the second run. The potassium hydroxide was added over a forty-five minute period and the stirring was continued for one-half hour longer. The fractionation on this run was,

Fraction I 84-149°C 8½ mm

Fraction II 149-157°C 8 mm

The yield in the second fraction was about twenty grams, which is about 25% of the theoretical value.

The physical properties of the carbinol thus prepared are; a white crystalline solid, M. p. 57-59°C, B. p. 149-157°C at 8 mm pressure, insoluble in water, soluble in ehtanol, methanal, benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

Ester preparation

In the preparation of the acetic ester, five grams of the carbinol were mixed with five grams of acetic anhydeide in a fifty ml. flask immersed in an oil bath and refluxed at a temperature of 180-190°C for two hours and a half. At the end of this time, the mixture was poured into a beaker of water. A precipitate formed which did not dissolve. The mixture was stirred for some time to hydrolize the excess anhydride, and then a three percent sodium hydroxide solution was added until the mixture was alkaline. The mixture was then extracted with ether and the extract dried over sodium sulfate. The ether was evaporated off and the crystals which formed were recrystallized from hot 95% ethanol. The Parr analysis on the recrystallized acetic ester of this carbinol showed 37.45% Cl, which is in agreement with the calculated value of 37.79% Cl.

The physical properties of this ester are; a pale yellow crystalline solid, M. p. 105-106°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

The method used in the preparation of the propionic ester was the same as that used for the acetic ester. Five grams of the carbinol and five grams of the propionic anhydride were used and refluxed at 180-190°C for two and one-half hours. The propionic ester was recrystallized from hot 60% ethanol. The Parr analysis on the purified product showed 35.78% Cl, which is in agreement with the calculated value of 36.01% Cl.

The physical properties of this ester are; a white crystalline solid, M. p. 59-60°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, and carbon tetrachloride and carbon disulfide.

In the preparation of the butyric ester, five grams of the carbinol and five grams of butyryl chloride were refluxed at 110-120°C for two and one-half hours in the same way as in the acetic and propionic ester preparations. When the reacting mixture was hydrolized, a heavy oil separated out instead of a precipitate forming. This was extracted with ether, dried and the ether evaporated off. The Parr analysis on the residual liquid showed 34.13% Cl, which checks with the calculated value of 34.36% Cl. The physical properties of this ester are as follows; a clear, pale yellow oily liquid, B. p. 172-173½°C at 11 mm, d^{20}_{20} is 1.082, insoluble in water, soluble in ethanol, methanol, benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

The benzoic ester was prepared by the usual method of the Schotten-Baumen procedure. Twelve grams of 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 vigorously for more than one-half an hour. When the reaction was complete, an ether extract was made, dried over sodium sulfate, and the ether evaporated off, and the ester recrystallized from hot 95% ethanol. The Parr analysis on this product showed 30.71% Cl, which checks with the calculated value of 30.79% Cl.

The physical properties of this ester are; a white crystalline solid, M. p. 94-95°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

Tribromomethyl-p-tolylcarbinol

First run: 40 grams of p-tolualdehyde and 130 grams of bromoform were mixed in a three necked flask. The mechanical stirrer was started and four grams of powdered potassium hydroxide was added over a one-half hour period. The stirring was continued for one hour after the alkali had been added. The material in the flask was extracted with ether and the extract filtered. The ether was then distilled off and the residual liquid steam distilled. The steam distillate was saved and put with that from the chloroform addition. The material left in the distilling flask was extracted with ether, treated with a saturated sodium bisulfite solution, washed with water, dried, and the ether distilled off in a Claison distilling flask. The remaining liquid was fractionated under diminished pressure. Again, as in the case of the chloroform addition, two fractions were saved.

Fraction I 0-195°C 20 mm
Fraction II 195-198°C 20 mm

After the temperature reached 198°C, there was evidence of decomposition, and the temperature fell to 165°C, with some material being distilled at all times. There was also a fairly large residue left in the distilling flask and this was discarded. There were about 19 grams of the crude material in the second fraction, which did not crystallize.

Second run: This run was made in exactly the same way as the first, except for the fractions taken.

Fraction I 70-152°C 9-10 mm
Fraction II 152-190°C 13 mm

There was also much decomposition in this distillation, and the yield was quite low. The tarry residue that was left after the distillation was larger than in the first run, but was also discarded.

Third run: The third run was made in an effort to get enough of the combined second fractions to redistill. It was made in the same way as the first two, except for the distillation. It was thought that perhaps with slower heating, there would be less decomposition, so the distillation on this run was made with very gradual heating of the oil bath under the distilling flask. The fractions taken were,

Fraction I 77-146°C 5½ mm
Fraction II 146-109°C 5½ mm

There was even greater decomposition in this run than in the first two. After the temperature of 146°C was reached, it started to drop, and no amount of heating would make it rise again. The second fraction was very small, and was combined with those of the first two runs.

Fourth run: As the material from the first three runs was still insufficient for redistillation, another run was made in exactly the same way, except that the distilling flask was heated very rapidly.

Fraction I 0-178°C 4 mm
Fraction II 178-186°C 4 mm

The yield in the second fraction was very much greater than in any other run, and the decomposition was very slight.

The Parr analysis on the combined higher boiling fractions of the first four runs showed 20.69% Br. This is not in agreement with the calculated value of 64.31% Br.

The combined fractions were redistilled, and the following fractions taken.

Fraction I 0-183°C 4 mm

Fraction II 183-185°C 4 mm

After 24 hours, crystals started to form. These were pressed, and several Parr analyses were run, but failed to check with the calculated value or with each other. The product was recrystallized from hot 68. acetic acid, and white crystals were formed. These were dried, and the Parr analyses on them were no better. As the crystals darkened on standing in the sunlight, another run was made to see if the freshly distilled product would give any better results.

Fifth run: This run was made in the same way as the fourth.

Fraction I 0-178°C 4 mm

Fraction II 178-188°C 4 mm

The yield on this run was about 53 grams of crude distillate in the second fraction, which is about 25% of the theoretical value. The Parr analyses on the freshly distilled material was no better than the others.

As no positive results were obtained from the halogen determinations, it was thought that perhaps a hydrate had been formed, so the recrystallized product was analyzed by the combustion method to determine its carbon and hydrogen content. The average values found in the determinations were, 28.79% C, and 2.41% H. The calculated values for the desired carbinol are, 28.97% C and 2.43% H.

As the carbon and hydrogen checked with the calculated values for the carbinol itself, four Carius determinations were attempted in an effort to get the halogen content to check. The average value found from three of the determinations was 64.28% Br, which checks with the calculated value of 64.31% Br. Apparently the Parr method, as it now stands, is not satisfactory for all organic compounds, and will have to be modified in some way befor it can be relied upon in all cases.

Ester Preparation

The method used in the preparation of the esters of tribromomethyl-p-tolylcarbinol was exactly the same as that used in the preparation of the esters of the chloroform addition.

The acetic ester was prepared by refluxing five grams of the carbinol with five grams of acetic anhydride at 165-175°C for three hours, and pouring the mixture into water, and following the same procedure as in the preparation of the other esters. The crystals formed on the evaporation of the ether were recrystallized from hot 95% ethanol. From the Parr analysis of the recrystallized ester, it was found that it contained 57.63% Br, which is in agreement with the calculated value of 57.81% Br.

The physical properties of this ester are; a gray crystalline solid, M. p. 149-150°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

The propionic ester was prepared in a like manner, using five grams of the carbinol and five grams of propionic anhydride and refluxing at 165-175°C for three hours. The Parr analysis on the recrystallized product from hot 95% ethanol showed 55.85% Br, which is in agreement with the calculated value of 55.90% Br.

The physical properties of this ester are; a brown crystalline solid, M. p. 170°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

The butyric ester was also prepared in a similar manner. Five grams of butyryl chloride and five grams of the carbinol were refluxed at 125-130°C for three hours. The product left after the evaporation of the ether was a solid, and was recrystallized from hot 95% ethanol. The Parr analysis on the recrystallized product showed 53.90% Br, which checks with the calculated value of 54.14% Br.

The physical properties of this ester are as follows; a white crystalline solid, M. p. 63°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulfide.

The benzoic ester was prepared by the Schotten-Baumen method. 12 grams of benzoyl chloride and five grams of the carbinol were used, and the product was recrystallized from hot 95% ethanol. The Parr analysis on this purified product showed 50.11% Br, which is in agreement with the calculated value of 50.28% Br.

The physical properties of this ester are as follows; a white crystalline solid, M. p. 126°C, insoluble in water, slightly soluble in ethanol and methanol, and soluble in benzene, acetone, ether, chloroform, carbon tetrachloride, and carbon disulgide.

Trichloromethyl-m-bromophenylcarbinol

The general method of procedure used in this preparation was the same as in the preparation of the other carbinols.

First run: 60 grams of m-bromobenzaldehyde and 60 grams of chloroform were put in a three necked mixing flask, and four grams of powdered potassium hydroxide were added with constant stirring over a one-half hour period. After the mixture had stood for several hours, it was extracted with ether, filtered, and the ether distilled off.

The mixture was then steam distilled to remove the excess chloroform and aldehyde. After the steam distillation, it was again extracted with ether, treated with saturated sodium bisulfite solution, washed, dried, and the ether distilled off. The remaining liquid was fractionated under diminished pressure.

As the yield was very small, a second run was made in the same way as the first, and the two combined and redistilled.

Several Parr analyses on the higher boiling fraction of the distillate were made, and these showed evidence of containing some of the desired carbinol, but in an impure form.

Two runs on the bromoform addition compound were also made. After all the available aldehyde had been used in making these four runs, an accident occured which caused the loss of all the products formed.

Although the results on these additions were not positive, the evidence is that probably both the chloroform and the bromoform additions took place to form the corresponding carbinol.

Trichloromethyl-m-nitrophenylcarbinol

First run: 50 grams of m-nitrobenzaldehyde and 90 grams of chloroform were put in the mixing flask and four grams of powdered potassium hydroxide were added over a one-half hour period.

In the fractionation, the following fractions were taken.

Fraction I 0-180°C 11 mm

Fraction II 180-190°C 11 mm

The tarry residue left in the distilling flask was comparatively small, and was discarded.

The Parr analysis on the second fraction showed only 9.35% Cl, which does not agree with the calculated value of 39.33% Cl.

As this did not look very encouraging, a second run was made in an attempt to get enough of the material to redistill.

The second run was made in the same way as the first, and as there was not enough to redistill, another run was made in the same way as the first two. These three runs were combined and redistilled.

Fraction I 168-180°C 11 mm

Fraction II 180-190°C 11 mm

The Parr analysis on the first fraction showed only 5.97% Cl, and that on the second fraction showed 10.75% Cl.

Although there is a possibility that some of the compound sought was formed, the amount was so small that further investigation along this line was discontinued.

Summary

In this summary are tabulated the quantitative results obtained in the investigation of p-tolualdehyde.

Compound prepared	B. p.	Press.	M. p.	Analysis	
				Calc'd	Found
Trichloromethyl-p-tolylcarbinol	145-153°C	4½mm	57-59°C	44.42%Cl	44.21%Cl
Esters of above					
Acetic	----	----	105-6°C	37.79%Cl	37.48%Cl
Butyric	172-173°C	11mm	----	34.36%Cl	34.13%Cl
Propionic	----	----	59-60°C	36.01%Cl	35.78%Cl
Benzoic	----	----	94-95°C	30.97%Cl	30.71%Cl
Tribromomethyl-p-tolylcarbinol	183-185°C	4 mm	62°C	64.31%BR	64.28%Br
Esters of above					
Acetic	----	----	149-50°C	57.81%Br	57.63%Br
Butyric	----	----	63°C	54.14%Br	53.90%Br
Propionic	----	-----	170°C	55.90%Br	55.85%Br
Benzoic	----	----	126°C	50.28%Br	50.11%Br

Conclusion

Trichloromethyl- and tribromomethyl-p-tolylcarbinols as well as the acetic, propionic, butyric, and benzoic esters of each have been prepared and some of their properties studied.

. Chloroform and bromoform will probably add to m-bromobenzaldehyde to give the corresponding carbinols, but no positive results were obtained.

Chloroform will not add to m-nitrobenzaldehyde under the same conditions that it will to p-tolualdehyde.

BIBLIOGRAPHY

1. Jocicz, *Chemisches Centr.* 48, I (1897) p. 1013.

2. Howard, J. W., "The Addition of Chloroform to Aldehydes," *The Journal of the American Chemical Society* 47, II (1925) p. 455-456.

3. Howard, J. W., "Some Esters of Tribromomethylphenylcarbinol", *The Journal of the Ametican Chemical Society* 52, III (1930) p. 5059-60.

4. Howard, J. W., and Castles, I., "The Addition of Chloroform and Bromoform tooo-Chlorobenzaldehyde," *The Journal of the American Chemical Society* 57, (1935) p. 376-377.

5. Howard, J. W., "The Addition of Chloroform and Bromoform to p-Chlorobenzaldehyde," *THe Journal of the American Chemical Society* 57, (1935) p. 2317-2318.

6. Siegfried, *Chemisches Centr.* 70, I (1899) p. 606.

7. Yoder, L., "Urethane from Chlorine Substituted Secondary and Tertiary Alcohols," *The Journal of the American Chemical Society* 45, I (1923) p. 475-479.

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