

REACTIONS OF DIHALOBENZENES WITH SALTS OF ORGANIC
ACIDS

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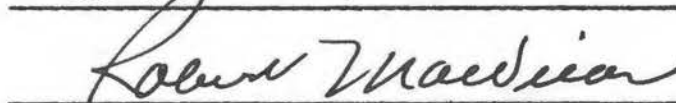
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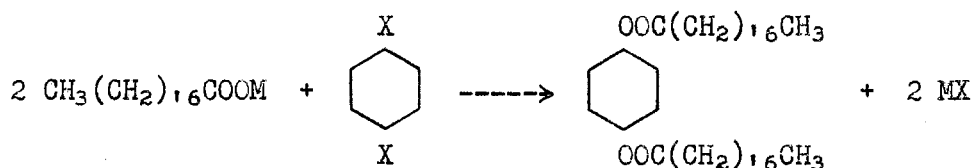
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INTRODUCTION

The original purpose of this research was to determine the feasibility of preparing the disubstituted esters of hydroquinone from the sodium salts of fatty acids and the dihalogen compounds of benzene.

The reaction was visualized as follows:



In the reaction, M was a monovalent metal, such as sodium, potassium or lithium. The halogen might be chlorine or bromine. Iodine compounds were excluded because of the expense of their preparation.

One of the principal reasons for investigating this reaction was an effort to find more uses for the dihalogen compounds of benzene. The dichlorobenzenes, in particular, can be obtained commercially at relatively low cost.

One possible insight to the use of this reaction, if it could be made to proceed, was the production of hydroquinone from p-dichlorobenzene. The diester could be saponified to give back the acid salt and hydroquinone. The acid salt could be recovered and used again. Therefore, the only reagent consumed would be the p-dichlorobenzene which is about 1/7 as expensive as hydroquinone on today's market.

This is only one example. Many other reactions could also make use of the dihalobenzenes, directly or indirectly, if this reaction could be made to go.

Since, in this investigation, the reaction was of greater interest than the actual products, the experimental portion was carried out with commercially available salts of the fatty acids. The dihalogen benzenes used were also from commercial supply.

HISTORICAL REVIEW

Very little has been recorded about a reaction of this type. In fact no references were found relating to halogen substitution on the benzene ring by this method. However, such a reaction with aliphatic chains has been described in beginning organic texts for some time.(5,6) Perhaps this particular reaction has not been thoroughly investigated, or it failed to proceed and thus was not reported.

As far as could be determined, work started on this particular reaction about 1940. At that time, Dr. H. P. Johnston (9), while working for Mallinckrodt Chemical Company, tried this reaction and obtained results which indicated that a reaction may have taken place. He recovered a small amount of benzene and also a small amount of monochlorobenzene. However, he did not pursue the reaction any further at that time.

About that same time, Monsanto Chemical Company is believed to have done some work along those lines. Also, Dow Chemical Company was reported to have tried some of these reactions. However, no references were found to back up any of these reports. It might be assumed that nothing came of the work being conducted at either place, and therefore, the results were never published.

In the absence of information on this specific type of reaction, the literature was consulted to see if the phenyl esters had been prepared by other means. This search was not as unprofitable as the material sought originally, but was not as rewarding as had been hoped,

because the identification and characterization of phenyl esters is very incomplete and the references are few in number. This made it exceedingly difficult to determine if the desired reaction was successful.

Rosenmund and Lohfert (16) were perhaps the first to prepare the phenyl esters in 1928. They were studying the rearrangement of simple phenol ketones by the Friedel Crafts reaction and found the two phenyl esters, pyrocatechol distearate, m.p. $83^{\circ}-5^{\circ}\text{C}$, and stearopyrocatechol, m.p. 70°C .

The majority of the work which has been done on these phenyl esters has been performed since 1937 when Carlo Marangoni (11) prepared them from the phenols and the acid chlorides. Marangoni prepared the acid chlorides by the reaction of thionyl chloride or phosphorus pentachloride on the fatty acids. From the reaction of the acid chlorides and the phenols, he isolated the following esters and determined their melting points: hydroquinone distearate $\text{C}_{42}\text{H}_{74}\text{O}_4$, m.p. 97°C , pyrocatechol distearate $\text{C}_{42}\text{H}_{74}\text{O}_4$, m.p. 68°C (instead of $83^{\circ}-5^{\circ}\text{C}$ as reported by Rosenmund and Lohfert).

The most recent work was done by David Aelony (1) of General Mills, Inc. in 1955. His method of preparation involved the direct esterification of fatty acids and the phenols. Up until that time it was stated in most of the organic text books that the direct esterification of phenols was impossible. (3) The direct esterification of phenols with fatty acids was the outgrowth of an attempt to devise a method for estimating the phenolic hydroxyl groups present in a particular substituted phenol-formaldehyde resin. By the use of such catalysts as sulfuric acid, phosphoric acid, lead stearate, and several others, Aelony prepared several of the phenyl esters. Among them were: p-chlorophenyl stearate, m.p. $59^{\circ}-63^{\circ}\text{C}$, b.p. $195^{\circ}\text{C}/75\mu$; p-diphenylstearate, m.p. $74^{\circ}-$

76°C, b.p. 245°C/50μ; resorcinol distearate, m.p. 64°-65°C, b.p. ----; resorcinol dioleate, m.p. ----, b.p. ----.

There are two other references of interest which should be mentioned. Shonle and Row (17) patented a process for producing the esters of oleic acid and stearic acid from the sodium salts and benzyl chloride. This is of interest because it is the same type of reaction. However, the bonding of the halogen is so different there is no real comparison. In the case described by Shonle and Row, the chlorine is bonded to the chain where conjugation of the double bonds in the ring does not play as important a role and the halogen should be relatively easy to replace.

The other reference was by G. Malcolm Dyson. (4) He reported that "In some cases where esterification is precluded by ordinary methods -- especially those with substituted halogen or nitro groups -- it is possible to make the ester by refluxing the silver salt of the acid with alkyl iodide." This may be formulated as follows:



Here, again, the same type of reaction is seen, except for the halogen being on the aliphatic chain instead of on the ring. So, to date, some of the phenyl esters have been prepared, but by other types of reactions. This type of reaction has been performed in reverse, but never by pulling the halogen off the benzene ring.

EXPERIMENTAL

Attempted Preparation of the Diester from Sodium Stearate and p-Dichlorobenzene:

Run I. Sixty-one and three-tenths grams of sodium stearate (0.2 mole) and 14.7 grams (0.1 mole) of p-dichlorobenzene were placed into a round bottom flask which was equipped with a reflux condenser. The reagents were heated to a steady reflux and the temperature maintained for 72 hours. During the refluxing, considerable foaming occurred, indicating the presence of water in the reacting vessel. The melt became darker as the time increased, indicating decomposition of the stearate chain.

At the end of the reflux period, the reaction mixture was cooled and observed. Two solid layers formed and were separated physically by means of a spatula. The upper layer was white and appeared, by observation, to be mostly p-dichlorobenzene. The lower layer was a chocolate brown and, by observation, appeared to be sodium stearate.

It was reasoned that if the reaction took place, free chloride ions would be present. If so, a test with silver nitrate solution should give a precipitate with the chloride ions. The upper layer gave a negative halogen test. The lower layer showed a fairly strong trace of halogen. However, this trace could be attributed to impurities in the sodium stearate.

Ether and toluene extracts were made of both layers. The solutions were checked qualitatively for reaction products with the Infra-

red Spectrometer. A study of the spectra revealed only the original reactants.

Run II. The reagents for this run were prepared in the same manner as for Run I, with the exception of adding 125 ml. of benzene. It was hoped that any water adsorbed on the acid salt would be removed as a benzene-water azeotrope. The reaction pot was heated to reflux and the azeotrope collected in a Dean-Stark water trap. Approximately 1.2 ml. of water was trapped. After the water was removed, the benzene was distilled into the trap and removed.

The pot temperature reached only 114°C . This was probably due to a small amount of benzene remaining in the system which refluxed and held down the temperature. Silver nitrate gave a negative test for halogen. Toluene and ether extractions were made of the pot residue and qualitatively inspected by infra-red absorption methods. As with Run I, no products other than the original reagents were found.

Attempted Preparation of the Diester from Potassium Oleate and p-Dichlorobenzene:

Run I. Forty-eight grams (0.15 moles) of potassium oleate and 14.7 grams (0.1 mole) of p-dichlorobenzene were weighed into the reaction flask. To this was added 100 ml. of N,N'-dimethylformamide. The N,N'-dimethylformamide, which has a rather high boiling point, was added as a solvent in an effort to raise the reaction temperature. All reagents completely dissolved to give a homogeneous mixture. This mixture was then heated to a steady reflux and the temperature maintained for a period of 72 hours. At the end of the reflux period, the solution was cooled and observed. Two immiscible liquids separated along with a very small amount of a dusty-tan, solid precipitate.

The two liquids were decanted into a separatory funnel, shaken, and allowed to separate. Since the interface between them was very "lazy", it was assumed that the two liquids were nearly the same density. When shaken, several minutes were required to again establish the level surface of the interface.

While withdrawing the bottom layer, the two layers reversed themselves. The remainder of the bottom layer became the top layer. Suspecting that surface tensions might have caused the change, the upper layer and the remainder of the original bottom layer were centrifuged at 2000 r.p.m. for five minutes. Even after this treatment, the two liquids remained reversed.

Layer I. Addition of water caused a very dense soapy substance to precipitate. This precipitate filtered very slowly, even under vacuum. A few very small crystals were noticed on the filter paper and identified as p-dichlorobenzene (by observation). Through solubility tests, the major portion of the precipitate was identified as potassium oleate.

The filtrate from the above filtration was made acidic with nitric acid and treated with silver nitrate. The test indicated that there was no halogen present.

Layer II. The above tests were repeated on Layer II. The results were about the same: potassium oleate was precipitated upon the addition of water; p-dichlorobenzene was also observed in the solid residue; and the filtrate gave a negative test for halogen.

The original precipitate was apparently a potassium salt of some variety. The solid gave the following tests: insoluble in water, insoluble in ether, negative Beilstein test, insoluble in acetone, insoluble

in benzene, insoluble in hydrochloric acid, gives a very strong potassium flame test, and has a melting point above 300°C.

Positive identifications of these new compounds were not made at this time, because it was assumed that the solvent reacted with the potassium oleate and this was not the desired reaction.

Run II. Sixty-one grams (0.2 moles) of potassium oleate and three grams of p-dichlorobenzene (0.02 moles) were measured into a round bottom flask and the mixture heated to reflux. These amounts of reagents were used so as to make the potassium oleate the solvent when in the molten stage. During the reflux period, about 28 hours, much foaming occurred, indicating the presence of water in the reagents. The potassium oleate was not a good solvent because it decomposed too readily.

The reflux apparatus was cooled and disassembled. The final product was a very dark, viscous semiliquid which barely flowed under its own weight. It had a very strong odor of p-dichlorobenzene.

A water extract of the product was made. This extract was tested very carefully with silver nitrate solution for the presence of chloride ions. The test was negative. An ether extract was also made. When the ether solution was evaporated, a residue of p-dichlorobenzene remained.

From the above tests, it was concluded that no reaction took place.

Run III. Thirty-six and seven-tenths grams (0.25 moles) of p-dichlorobenzene and 15.2 grams (0.05 moles) of potassium oleate were used as a reacting mixture. As before, these reagents were placed in a reaction flask and heated to a steady reflux. This temperature was maintained for a period of 24 hours. The p-dichlorobenzene, being in excess, acted as the solvent in this run. However, it was not too desirable because it condensed to a solid and tended to plug the condenser.

Foaming was also a problem in this run. Even small amounts of adsorbed moisture seemed to cause an excess of foam to form with the potassium oleate. This foaming necessitated the use of tandem condensers stacked one on top of another to prevent overflow. The pot temperature did not exceed 170°C during the reaction.

The final product, after refluxing, was a white, soapy looking solid. The odor was strongly characteristic of p-dichlorobenzene. An ether extract of the pot mixture was made and evaporated. The soapy residue was a mixture of potassium oleate and p-dichlorobenzene. A chilled watch glass was placed over the container containing the soapy residue. Upon heating the residue, crystals of pure p-dichlorobenzene sublimed on the watch glass.

A water extract was made and treated with silver nitrate solution. The heavy white precipitate which formed was collected and boiled with sodium hydroxide. This was filtered again and the filtrate acidified with nitric acid. Addition of silver nitrate solution revealed a negative test for chloride ions.

From the above tests, it is concluded that no reaction took place.

Run IV. Forty-eight grams (0.15 moles) of potassium oleate and 15 grams (0.102 moles) of p-dichlorobenzene were placed in the reaction vessel. Five-tenths of a gram of copper powder was added in an effort to find a catalyst for this reaction. In order to combat the foaming, which was observed in the early experiments, the potassium oleate was dried in a vacuum oven at 60°C for a period of eight hours prior to use.

During the reflux period, the melt in the reaction pot reached a temperature of about 220°C . The vapor above the melt rose to 172°C .

A water extract of the products was obtained. When the extract was treated with silver nitrate solution, a light trace of chloride ion was detected.

An attempt was made to distill the reaction product. The distillation apparatus was set up and attached through a cold trap to an aspirator. Under a vacuum of about 30 mm., the temperature rose to 90°C and remained constant for a few minutes. At this point there was some foaming and a little mechanical carry-over. The temperature jumped quickly to 160°C where a small amount of product was distilled over. From observations, this appeared to be p-dichlorobenzene. The pot residue turned to a solid upon cooling and was identified as potassium oleate. It was concluded that if a reaction had taken place, the products were produced in such small quantities as to prevent detection.

Attempt to Prepare the Diester of Hydroquinone from Sodium Oleate and p-Dibromobenzene:

Run I. Forty-five grams of sodium oleate and eight grams of p-dibromobenzene were weighed into a three-neck flask and one gram of powdered copper added. The flask was equipped with a water condenser, a thermometer, and a ground-glass stopper. This apparatus was then heated to a steady reflux and maintained at this temperature for a period of eight hours.

The sodium oleate was dried in a vacuum oven for eight hours at 60°C, prior to use, in order to remove all moisture. Sodium oleate was substituted for the potassium oleate in this determination in order to avoid the decomposition and charring of the potassium salt. Potassium oleate has no melting point.

During the refluxing, the temperature of the melt in the pot reached 310°C and the vapor above the melt remained at about 240°C. No foaming

was observed at any time during the refluxing of this reaction. This was good evidence that all moisture had been removed.

As the reaction flask cooled, small cubic crystals were observed on the sides of the flask where the liquid had refluxed. Some of these crystals were extracted with a spatula and dissolved in water. A few milliliters of this solution were acidified with nitric acid and tested with silver nitrate solution. A very good test for halogen ions was observed. As a second check, a portion of the water solution was tested for bromide ion by the method set forth by Shriner and Fuson. (18) The pink color of eosin indicated a good positive test for bromide ions.

The p-dibromobenzene was checked for free halogen, and found not to contain even a trace of free halogen ions.

The products in the bottom of the reaction flask were solid, but did not have the brick-like qualities of the earlier reactions. In fact, the solid was rather soft and slightly "gummy". A distillation apparatus was set up and an attempt was made to separate any products which might have been produced.

Fraction I. This fraction contained everything that came over up to 97°C. Most of the material came over at 94°C where the temperature remained constant for a few minutes. About one milliliter of distillate was collected and it was almost colorless.

Fraction II. This fraction included everything from 97°C to 200°C. The boiling point range seemed to be 170°-3°C. One milliliter of very light yellow liquid was collected.

Fraction III. Materials caught in this fraction were collected between 210°C and 255°C. There was no constant boiling point, only a steady rise in temperature. The material being distilled came over

as a heavy white vapor. About six milliliters of dark brown liquid were collected.

Fraction IV. This was all the remaining products that came over below 240°C under the vacuum of an aspirator. The material which came over was a very heavy brown vapor. Approximately 20 mls. of liquid were collected. The liquid was a very dark brown with a greenish tinge which made it resemble motor oil.

Pot Residue. A black solid residue remained. It appeared to be mostly carbon. This residue gave a good test for bromide ions, both with silver nitrate solution and the specific bromide ion test.

In an effort to get a better separation of the materials obtained from the distillation, the four liquids were poured together in a micro distillation apparatus and the mixture was again fractionated. However, the second distillation did not duplicate the temperatures obtained in the first fractionation.

Fraction I. This included everything up to 110°C. Constant boiling temperature was 91-2°C. The product was colorless until the temperature of 97°C was reached. At this point, the few drops that came over were rather blue in color. Approximately two milliliters were collected.

Fraction II. This temperature was of the range between 110°-150°C. The boiling point was at 125°C. The liquid of this fraction was a vivid blue-green in color. The color faded to a dark brown after standing at room temperature for three days. Three milliliters of this liquid were collected.

Fraction III. This fraction was collected between 150°C and 186°C. The boiling range was around 174°C. The product had a slight blue color which was probably due to the material of Fraction II. Three milliliters of this material were collected.

Fraction IV. This fraction was collected between 186°C and 240°C. Four milliliters were collected and it was completely colorless.

Pot Residue. The residue contained all products boiling above 240°C. Approximately 20 mls. of this greenish-brown liquid remained.

A sodium fusion test for halogen was performed on each fraction. The refractive index was also recorded.

FRACTION	REFRACTIVE INDEX	HALOGEN	BOILING POINT
I	1.4165	none	91°-2°C
II	1.4728	light trace	125°C
III	1.4626	strong trace	174°C
IV	1.3338	strong trace	238°C
Pot Residue (liquid from fractionation)	1.4834	light trace	above 238°C
Pot Residue (solid from original dis- tillation)	-----	Good test, al- though no better than test with a water extraction	-----

The original pot residue was extracted in turn with ether, toluene, acetone, and dioxane. These extracts were checked qualitatively for the dioleate ester with the Infra-red Spectrometer. After examining the spectras of the extracts, it was concluded that none of the diester had been formed.

Run II. This run was performed as described in the first run except the copper catalyst was omitted. The same test methods were used. Halogen ions were not present. Therefore, it was concluded that no reaction had taken place.

Run III. This run was performed in an effort to duplicate and extend the information found in Run I. The same reagents were used in approximately the same proportions. The quantity of copper powder was raised from one gram to five grams.

The apparatus was similar to that used in Run I. A trap filled with reagent grade sodium hydroxide was added to the top of the reflux condenser. It was believed, from the results of Run I, that bromine was being lost during the reflux period, perhaps as hydrogen bromide. Therefore, if hydrogen bromide was given off, it should have been caught by the sodium hydroxide.

The reagents were heated to reflux and the temperature maintained for a period of ten hours. During this period, the vapor temperature reached 230°C and the melt averaged about 310°C. Vacuum dried sodium oleate was again used in order to prevent foaming. During the reflux period, there seemed to be no refluxing of the p-dibromobenzene as in previous runs. A layer of heavy white vapors covered the molten reagents. From time to time, a small amount of very low boiling liquid formed. Periodically a drop of this liquid would fall from the end of the condenser and cause a mild explosion in the flask.

The sodium hydroxide trap, at the top of the reflux condenser, began to collect something almost as soon as the reaction started. The sodium hydroxide turned a light tan color and a layer of fluffy, dirty-white material built up around each sodium hydroxide pellet.

The reaction flask was cooled and the gas trap removed. The sodium hydroxide was dissolved in water and a portion of the solution acidified with nitric acid. Addition of silver nitrate did not reveal even a trace of halogen. A specific test for bromine with fluorescein was also performed, and the results were negative.

The products in the reaction flask, as in Run I, were solid, but rather soft and gummy. These products were placed in a distillation apparatus equipped with a vacuum pump. It was hoped that a separation under vacuum would hold pyrolysis to a minimum. A vacuum of 0.1 mm. was obtained and the distillation started. No effort was made to separate fractions on the first distillation.

In the distillation the temperature was raised under a vacuum of 0.1 mm. At 112°C a few drops came over. The temperature climbed at a very irregular rate to 222°C. Below this temperature about 1.5 mls. of distillate were collected. The temperature then rose rapidly to 242°C where very bright green vapors began to flood the distilling system. For about 20 minutes a temperature of 245°C was maintained. During this time, the system was being flooded with the bright green vapors. The temperature suddenly dropped to 110°C and the distillation was stopped. Twenty milliliters of distillate had been collected in the receiver and three milliliters were removed from the cold trap in front of the vacuum pump. The distillate was a dark, viscous liquid. It had a green cast, which made it resemble motor oil. The material in the cold trap appeared to be the same product, and had probably not condensed in the condenser due to the system being flooded.

The residue was removed from the flask and crushed with a mortar and a pestle. This gave a black granular solid. The solid was extracted with warm water and tested with silver nitrate. The result was a very strong test for halogen ions. This was immediately followed with a specific test for bromide ions with fluorescein. This test was also very strongly positive.

Three separate attempts were made to saponify any esters which might have been left in the pot residue. The first two attempts were

entirely unsuccessful. On the third attempt, the pot residue was added to a 25% solution of sodium hydroxide and the mixture was allowed to stand three days at room temperature. Then the carbon residue was filtered and the filtrate acidified with sulfuric acid. This was allowed to stand for a period of three hours. At this time a small amount of light brown precipitate was observed suspended in the solution. An attempt was made to separate the precipitate, but it was lost in the filter paper and was not recovered. The precipitate was adsorbed on the filter like some kind of an oil.

A sodium fusion test was run on the distillate. When this was checked with silver nitrate, a very light trace of halogen was indicated. A specific test for bromide ion was performed, and the results were so faint that they were almost unobserved.

The solubility of the distillate was determined and the following properties were found: insoluble in water, insoluble in base (a small portion dissolved because the base acquired a light brown cast), insoluble in hydrochloric acid, soluble in sulfuric acid, and only slightly soluble in phosphoric acid.

A ferric chloride test was performed to check for phenols. The ferric chloride solution was not miscible with the distillate, but with shaking, the water solution took on a violet color.

An acid chloride test for phenols was also performed, but the results were rather inconclusive. The entire solution was a turbid brown and was insoluble in sodium hydroxide.

Hydroxyl amine-hydrochloride reagent was added to the distillate. This test for ketones was negative.

Three drops of the distillate were added to five milliliters of purple potassium permanganate solution. The reaction was immediate and the potassium permanganate solution was readily discolored.

At this point an effort was made to separate the products in the original distillate. The vacuum distilling apparatus was modified so as to catch separate fractions without breaking the vacuum. A vacuum of 0.1 mm. was obtained and the distillation started.

Fraction I. The first drops came over about 32°C. This fraction was collected to a temperature of 60°C. About ten drops were produced.

Fraction II. The temperature range was from 60°C to 100°C. Two milliliters were collected.

Fraction III. The vacuum dropped to 0.8 mm. The products collected boiled below 168°C. About one milliliter was collected.

Fraction IV. The temperature dropped to 70°C and could not be raised with the hottest flame of the bunsen burner. Distillation was stopped here to prevent further pyrolysis. The products were assumed to be about the same as Fraction III.

While Fraction IV was being collected, a small amount of material solidified in the condenser. It was collected and recrystallized from acetone. About 0.25 gram of white crystalline solid was obtained.

Pot Residue. This material was a very viscous brown liquid. About four milliliters remained.

Cold Trap. Two milliliters of material were retained in the cold trap. This consisted of three mutually immiscible liquids. The top layer was a light yellow color, the middle layer was colorless, and the bottom layer was a brown color.

Analysis of Fraction I. There was no material to analyze because the few drops that were produced were retained in the condenser.

Analysis of Gold Trap (middle layer). This layer was colorless and had a very low refractive index (1.3470). Very few liquids, other than water, have an index of refraction this low. A drop of the liquid in question was placed on a piece of metallic sodium. Immediately there was a very vigorous reaction.

A color test was performed with a crystal of cobalt chloride dissolved in absolute methyl alcohol. The color change was from blue to pink. From these tests, the liquid was concluded to be water.

Solid Residue (from condenser during fractionation). This material was washed from the condenser and recrystallized from acetone. The melting point range was 65°-7°C. The crystals were white and had a "soapy feel". The Beilstein test was negative, indicating the absence of halogen. The material did not form a bromination derivative and the aluminum chloride test did not indicate a benzene ring. The ferric chloride test was negative.

A small amount of these crystals was added to a 25% potassium hydroxide solution and boiled on a steam bath for six hours. Upon cooling, the white crystals solidified on the top of the solution. These crystals were filtered and the filtrate was acidified with sulfuric acid. Upon standing, a small amount of a flocculent precipitate formed. The quantity was too small to filter.

The analysis of the remainder of the fractions and also the contents of the cold trap are tabulated on the following page.

Table I: Analysis of the Fractions

Qualitative Tests	Fractions			Gold Trap	
	II	III	IV	Top Layer	Bottom Layer
Refractive index	1.4555	1.4655	1.4711	1.4439	1.4948
Boiling point	242°C	168°C/0.8 mm.	Above 270°C	170°C	180°C
Melting point	-22°C to -23°C	-15°C to -20°C	---	Below -50°C	5°-6°C
Litmus paper	neutral	neutral	neutral	neutral	acid
Ferric chloride test (phenols)	negative	negative	negative	negative	positive (blue-violet)
α -naphthylurethan (phenols)	white ppt. melts 285°C	---	---	---	white ppt. melts 129°-30
Bromination	cryst. ppt. melts 83°-5°C	decolorized sol. no ppt.	decolorized sol. no ppt.	decolorized sol. oil is liq. to -20°C	---
KMnO ₄ solution (unsaturation)	reduced	reduced	reduced	reduced	---
Phenylhydrazone (aldehydes + ketones)	no reaction	no reaction	no reaction	no reaction	---
Beilstein test (halogen)	negative	negative	negative	negative	negative
Metallic sodium	no reaction	no reaction	no reaction	no reaction	reacts readily
Aluminum chloride test (test for ring structure)	negative	trace test	positive	negative	positive

DISCUSSION

The first reactions were unsuccessful as far as the desired product was concerned. The major effort was to find the best method of refluxing the reagents. Even though these attempts were unsuccessful, they provided some valuable information.

It was learned that the reagents had to be anhydrous. Even small amounts of moisture adsorbed on the reagents caused the long chain acid salts to foam excessively. This problem was solved by drying the fatty acid salts in a vacuum oven for a period of six hours at 60°C. The dihalobenzene compounds did not lend themselves to this type of drying because they sublimed too readily. However, it was not necessary to dry them because they did not adsorb an appreciable amount of water.

Secondly, the temperature had to be raised high enough to cause the reaction to take place. A high boiling solvent was considered as a means of raising the temperature. However, inert solvents with a sufficiently high boiling point were difficult to obtain. This problem was solved by using the reagents in such quantities as to make one of them the solvent when in the molten state.

Paradichlorobenzene was replaced with p-dibromobenzene because the bromine should be more easily replaced than the chlorine. Neither of the halogens should be easily replaceable. In the benzene ring where there is such strong conjugation, the resonance effect is so great

that the halogen is very tightly bound. The second halogen on the benzene ring makes both of these atoms less easily replaced.(14)

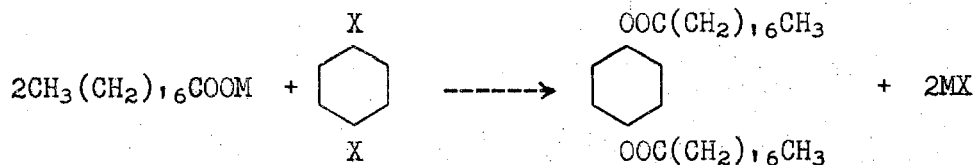
From the analysis of the products formed in the p-dibromobenzene reaction, several facts stand out. No dibromobenzene was recovered. In fact, no organic halogen was found at all. All the bromine was located as an inorganic salt in the pot residue.

Reaction products were characterized mainly as unsaturated hydrocarbons. One component in particular was identified as decylene. The other compounds appeared to be unsaturated hydrocarbons with slightly longer chains. This is in keeping with the results reported by Pectet and Potok.(13) They reported the pyrolysis of sodium oleate to give a greenish colored distillate which consisted principally of a mixture of olefins corresponding to C_9H_{18} , $C_{10}H_{20}$, $C_{11}H_{22}$, and $C_{13}H_{26}$.

A substituted phenol was also isolated from among the products. The phenol was found to have an aliphatic side chain containing roughly four to nine carbon atoms. Due to the lack of recorded characteristics of these phenols and also the excessively small quantities of the product recovered, the definite characterization of the phenol was not possible.

The micro-quantities of the products collected were a hindrance to the identification of all products.

The original reaction,



was impossible to obtain due to the pyrolysis in the reaction. Indications are that the disappearance of the p-dibromobenzene was in part due to the formation of the diester. However, the temperature at which

this occurred was well above the pyrolysis temperature of the ester produced. This meant that decomposition of the ester occurred as fast as it was formed. The presence of the phenol is a good indication of this. With phenol present and water formed in the pyrolysis, the thermal decomposition probably occurred at a lower temperature than would normally be expected.

This reaction, as it stands now, is of no practical value. Some method must be devised to raise the temperature high enough to get the reaction to take place, but not so high as to cause pyrolysis of the products as they are formed.

SUMMARY

The original purpose of this research was to study the reaction in preparing the diester of hydroquinone from the p-dihalobenzenes and the salts of fatty acids. The first few attempts were unsuccessful because of two things: moisture in the reaction caused excessive foaming, and the reaction temperature could not be raised high enough. These difficulties were overcome by choosing an acid salt with a high boiling point and drying it in a vacuum oven. This eliminated both problems at once.

Even though the reaction, as originally stated in the introduction, was impossible to obtain due to pyrolysis, it was indicated that the disappearance of the p-dibromobenzene was in part due to the formation of the diester. However, the temperature at which this occurred was well above the pyrolysis temperature of the ester. The phenol which was isolated, is a good indication of this. Before this reaction would be feasible, some method must be found to acquire the high reaction temperature without causing pyrolysis of the products.

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