

A PRELIMINARY STUDY OF THE ARYLATION OF STARCH
AND SOME OF ITS DERIVATIVES

by

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INTRODUCTION

Object of the Experiments

Although many reactions of starch have been recorded in the literature, a survey revealed no condensation reactions of starch or its derivatives with aromatic hydrocarbons. Such reactions would be of interest to the theoretical chemist for what knowledge may be learned of their nature and requisite conditions for their preparation and to the practical chemist for the products obtained. It is probable that such compounds as might be obtained would be of very high molecular weight and would have properties of gums or resins. Such products are welcomed by those who work in the field of synthetic organic chemistry. It is possible that a successful synthesis from a single aromatic hydrocarbon might serve as a basis for a whole series of reactions using other homologues of the aromatic series.

Method of Approach

The experimental work recorded in this research was made as a preliminary study of the arylation of starch and some of its derivatives. The particular reactions selected were modifications of some of those previously recorded in the literature in which compounds such as simple alcohols and esters were used to alkylate aromatic hydrocarbons of the benzenoid type in the presence of suitable catalysts. Suffice it to say that the alkylation of an aromatic hydrocarbon with an alcohol or ester is analogous to the arylation of starch or a starch ester with an aromatic hydrocarbon. A study was made of the relative effectiveness of dry natural starch, soluble starch, and starch acetate in the condensation with benzene in the presence of anhydrous aluminum chloride as a catalyst. Observations were made on the influence of the time factor, temperature, and the ratios of the molar quantities to find their apparent relationship to the products obtained. The catalytic effect of sulfuric acid in producing the same kind of condensation was also studied and an attempt was made to condense benzene with tri-trichloroacetyl starch by using the Friedel-Crafts reaction.

SURVEY OF THE LITERATURE

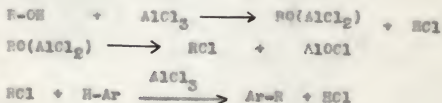
In a survey of the literature it was found that several methods had been used successfully for alkylating aromatic hydrocarbons. It was felt that one or more of these methods might be utilized in the arylation of starch.

Alkylation with Aluminum Chloride as a Catalyst

Alkylation with Alcohols. Perhaps the most complete investigation of the alkylation of aromatic hydrocarbons with alcohols has been made by Tsukervanik and his co-workers (1 to 5). In the work done by these men, aliphatic alcohols were condensed with aromatic hydrocarbons with aluminum chloride as a catalyst. It was found that hydrocarbons such as benzene and toluene could be condensed with all classes of aliphatic alcohols, including the cyclic secondary alcohols of which cyclohexanol is a typical example. In the presence of a suitable reaction vehicle, such as ligroin, naphthalene was condensed with primary, secondary, and tertiary alcohols. In general the tertiary alcohols were more reactive than the secondary alcohols,

which in turn were more reactive than the primary alcohols. Toluene was more easily condensed with alcohols than benzene and naphthalene reacted readily with all classes of alcohols, yielding up to 60 per cent of the theoretical of mixed alkyl naphthalenes. The temperatures necessary for these reactions were not all clearly defined. In general, the mixtures were warmed on a water bath at or below their boiling temperatures for several hours except in the case of the primary alcohols where it was necessary to maintain a temperature of 110 to 140° C. To give optimum yields, the tertiary alcohols required 0.5 mol of aluminum chloride per mol of alcohol; the secondary, 2/3 to 4/3 mol; and the primary, 1½ to 2 mols.

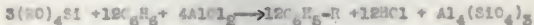
Morris and Ingraham (6) paralleled the work of Tsukervanik in part, but their study was made of the conditions necessary to produce optimum yields of asymmetrically substituted benzenes using aliphatic alcohols as alkylating agents. Methyl and ethyl alcohols were condensed with benzene and the following reaction mechanism was developed:



Huston and co-workers (7,8,9) carried out numerous experiments, condensed alcohols with aromatic hydrocarbons, and obtained yields that were somewhat smaller than those reported by Tsukervanik. No condensation was obtained with primary alcohols, but good yields were recorded for secondary and tertiary alcohols. Condensations were attempted with all the primary alcohols up to and including n-hexyl alcohol; failure to obtain alkylation products with them may have been because sufficiently high temperatures were not reached. Cycloalkyl carbinols were condensed with benzene. Increased yields of products were obtained when the reaction mixtures were heated. A large excess of benzene was used in these reactions (4-5 mols per mol of alcohol).

Alkylation with Esters. Esters of both organic and inorganic acids have been used successfully as alkylating agents in the presence of aluminum chloride as a catalyst. Kane and Lowy (10) used the alkyl esters of sulfuric, orthosilicic, and carbonic acids to alkylate benzene. They found that these compounds were all efficient alkylating agents. All of the condensing alkyl groups were primary. The temperatures used varied from room temperature to 80° C. The reactions were summarized by the following equa-

tions:



Berman and Lowy (11) found that compounds such as alkyl phosphates, alkyl acetates, and tertiary butyl hypochlorite were efficient alkylating agents. Temperatures from 20° C. to 80° C. were used, and more aluminum chloride than was required by the balanced equation was used to obtain the best yields.

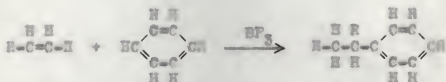
Kashtanov (12) used numerous esters of organic and inorganic acids with titanium chloride or aluminum chloride as a catalyst. Those esters which were successfully condensed with benzene when the latter catalyst was used were ethyl acetate, isomyl acetate, isomyl benzoate, and benzyl benzoate. The alkyl or aralkyl radical in each case was the part of the ester that condensed with the benzene. Large excesses of benzene were used, and the mixtures were refluxed.

The work of Bowden (13) was somewhat analogous to that which has already been discussed. He used alkyl esters of organic and inorganic acids, which included, in addition to the esters of the monocarboxylic acids up to

and including five carbons, some of the esters of benzoic, stearic, sulfuric, sulfurous, and oxalic acids. Three different procedures were used depending somewhat upon the ester being condensed. A large excess of benzene and some heat were required to obtain the best yields of products.

Alkylation with Boron Fluoride as a Catalyst

Alkylation of Benzene with Alcohols. McKenna and Sowa (14) alkylated benzene with various alcohols with the boron fluoride catalyst. Primary, secondary, and tertiary aliphatic alcohols, including benzyl alcohol, allyl alcohol, and cyclohexanol were used successfully as alkylating agents. Primary alcohols reacted with more difficulty than the secondary or tertiary alcohols. No reaction was obtained when methyl and ethyl alcohols were used for the alkylation. From 20 to 65 grams of catalyst per mol of alcohol and an equimolar mixture of benzene and alcohol were used. Room temperatures were used wherever possible, but heating was required in some cases. The following reaction mechanism was developed:



Alkylation of Naphthalene with Alcohols. Price and Ciskowski (15) used the same type of reaction as McKenna and Sowa to alkylate naphthalene. Secondary and tertiary aliphatic alcohols were condensed with naphthalene as well as benzyl alcohol. Support of the reaction mechanism developed by McKenna and Sowa was given through a successful alkylation of naphthalene with an olefine with the boron fluoride catalyst.

Alkylation by Alcohols with Sulfuric Acid as a Catalyst

Nightingale and Smith (16), employing a procedure outlined by Kirmann and Graves, found that sulfuric acid would catalyze the alkylation of aromatic hydrocarbons with alcohols. In this reaction a large excess of the hydrocarbon was treated with an alcohol in the presence of 85 per cent sulfuric acid and stirred continuously for several hours at room temperature. The procedure was satis-

factory for alkylation of benzene with iso-butyl and tertiary-butyl alcohols.

EXPERIMENTAL WORK

Apparatus

The apparatus used for the reactions recorded here consisted of a one liter three-necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser to which was attached a calcium chloride tube, and a thermometer that was extended into the reaction mixture. An electric heater served as a source of heat for those reactions which were carried out above room temperature.

Arylation of Dry Natural Starch with Aluminum Chloride Catalyst

Experiment I. The principal conditions and molar relationships are as follows:

Benzene	2.00 mols
Aluminum chloride	1.00 mol
Dry natural starch (dried <u>in vacuo</u>)	1.00 equiv.
Time	2 hours
Temperature	80° C.

One hundred seventy-four cubic centimeters of dry benzene

were placed in the reaction flask, and 183.3 grams of anhydrous aluminum chloride and 162 grams of dry, natural starch were added with constant stirring. The mixture was heated under reflux for two hours. The mass darkened, changing from brown to black; hydrogen chloride was evolved throughout the course of the reaction, and finally the mixture became too thick to stir; so it was cooled and set aside over night.

The black gummy solid was removed from the flask and stirred with 200 cc. of benzene for twenty minutes, filtered, and the filtrate evaporated. Some aluminum salts were obtained from this filtrate. The solid was then treated with three separate 200 cc. portions of benzene and the mixture digested on a water bath each time before filtering. The several filtrates, when evaporated, gave small amounts of gummy residues that did not exceed a gram each. The solid which had been digested showed evidence of containing considerable aluminum chloride, so a qualitative test was made. Aluminum chloride was present. It was removed by digestion of a twenty-three gram portion of the solid on a water bath with 95 cc. of absolute ethyl alcohol for thirty minutes at 75° C. This was followed by filtration. The process was repeated two more times, and the

residues remaining after evaporation of the filtrates consisted almost entirely of aluminum salts. The bulk of the solid which remained after removal of the aluminum chloride was light brown in color, gave a blue color characteristic of starch when its water paste was treated with aqueous iodine, reduced Fehling's solution, and left a small amount of inorganic ash when ignited in a crucible.

Experiment II. The principal conditions and molar relationships are as follows:

Benzene	2.00 mols
Aluminum chloride	0.50 mol
Dry natural starch (dried <u>in vacuo</u>)	0.50 equiv.
Time	7 hours
Temperature	80° C.

One hundred seventy-four cubic centimeters of dry benzene were placed in the reaction flask, and 81 grams of dry, natural starch and 66.5 grams of anhydrous aluminum chloride were added with constant stirring. The mixture was heated under reflux with an electric heater for seven hours within the temperature range of 77 to 80° C. It was observed that the mixture became brown and gradually darkened as heating was continued. Hydrogen chloride was evolved in considerable quantities for about two hours, after which only a small amount was liberated. At the end of the heating period the mixture had a red-brown color.

It was set aside over night.

A portion of the dark, gummy product was placed in a Soxhlet extractor and extracted for four hours with 200 cc. of benzene. Upon evaporation of the extract a small amount of black, gummy material was obtained. It weighed 0.4 gram. Another portion of the crude product was treated with 100 cc. of absolute ethyl alcohol and stirred in the cold for 20 minutes. The mixture was filtered and the filtrate evaporated. This treatment was repeated six times before the last filtrate was free from aluminum salts. The solid obtained from the several alcoholic filtrates was mostly inorganic matter. Further extraction of this solid with 150 cc. of benzene in a Soxhlet extractor gave only a negligible quantity of organic matter. The black organic solid which had been partially purified by the alcoholic extractions was subjected to some qualitative tests. It was found that it formed a paste with hot water with difficulty; the paste gave a blue coloration when treated with aqueous iodine and reduced Fehling's solution. Ignition of a portion of this solid left a small amount of inorganic ash.

Experiment III. The principal conditions and molar relationships are as follows:

Benzene	5.68 mols
Aluminum chloride	0.625 mol
Dry natural starch (dried <u>in vacuo</u>)	0.083 equiv.
Time	.	.	.	(1 hr.)	35-80° C.
				(7 hrs.)	80° C.

Five hundred cubic centimeters of dry benzene were placed in the reaction flask, and 55.1 grams of anhydrous aluminum chloride were added with constant stirring. An initial temperature rise of 10° C. was observed. The stirring was continued, and 13.5 grams of dry, natural starch were added. The mixture was heated slowly on a water bath to 80° C. Hydrogen chloride was evolved after the temperature had reached 80° C., and the evolution of the gas was spontaneous when the temperature had reached 70° C. This observation was made upon removing the water bath for five minutes; the mixture bubbled constantly giving off hydrogen chloride while it was below the boiling temperature. The water bath was again placed under the flask, and the mixture was refluxed for seven hours. The color became brown and darkened. At the end of the reaction period the mixture had a maroon color. After removal from the flask, the mixture was poured into a beaker containing 400 cc. of

cracked ice and 50 cc. of concentrated hydrochloric acid and stirred. The top layer of benzene acquired a brilliant violet coloration, and the aqueous layer became turbid and milky. Much heat was evolved. The mixture was set aside over night, during which time the bright coloration disappeared leaving a red-brown layer. The benzene layer was separated and placed in a flask to dry over metallic sodium. After drying five hours the benzene was distilled off, and there remained a small amount of higher boiling liquid. This was transferred to a 25 cc. distilling flask and distilled in vacuo at about 2 mm. pressure. The following fractions were obtained:

<u>Temp.</u> <u>(°C.)</u>	<u>Volume</u> <u>(cc.)</u>
74- 80	3.5
80-170	2.2
170-206	1.5
Solid residue	1.45 grams

Experiment IV. The principal conditions and molar relationships are as follows:

Benzene	5.63 mols
Aluminum chloride	0.626 mol
Dry natural starch (dried <u>in vacuo</u>)	0.083 equiv.
Time	9.67 hours
Temperature	80° C.

Five hundred cubic centimeters of dry benzene were placed

in the reaction flask, and 85.1 grams of dry, natural starch were added with stirring. The flask was heated rapidly to 80° C. on a water bath. The evolution of hydrogen chloride in considerable quantities was observed for two hours after heating began, during which time the mixture had darkened to a rich brown. After refluxing for nine hours and 40 minutes the mixture, which was reddish in color, was poured into a beaker containing 400 cc. of cracked ice and 50 cc. of concentrated hydrochloric acid. The benzene layer acquired a bright, purple color which disappeared after 15 minutes of stirring leaving a reddish brown solution. The mixture was set aside over night. After standing 13 hours the benzene layer was separated from the aqueous layer and placed in a flask over metallic sodium to dry. After drying 48 hours the benzene was distilled off leaving a few cubic centimeters of higher boiling liquid. This was placed in a 25 cc. distilling flask and distilled under about 2 mm. pressure. The following fractions were collected:

<u>Temp.</u> <u>(°C.)</u>	<u>Volume</u> <u>(cc.)</u>
53- 90	2.4
90-170	1.2
170-203	0.6
Solid residue	0.56 gram

The aqueous layer was not filterable, but a portion of it gave a blue coloration when treated with aqueous iodine which was indicative of starch. No further tests were made.

Experiment V. The principal conditions and molar relationships are as follows:

Benzene	5.63 mols
Aluminum chloride	0.628 mol
Dry natural starch (dried <u>in vacuo</u>)	0.083 equiv.
Time	70 hours
Temperature	80° C.

Five hundred cubic centimeters of dry benzene were placed in the reaction flask, and 13.5 grams of dry, natural starch and 63.1 grams of anhydrous aluminum chloride were added with stirring. The flask was placed in a constant temperature bath and heated at 80° C. for 70 hours with constant stirring. Hydrogen chloride was evolved rather freely for about two hours. The solution gradually acquired a red-brown color, and there was some purple coloration on the sides of the flask for a time that looked much like there had been some complex formation. After the heating was stopped the contents of the flask were removed and the solid filtered off. Twenty-one grams of solid were recovered. The solid was decomposed by placing it in a beaker containing 86 grams of ice and 10 cc. of concentrated hydrochloric acid. Thereupon it was allowed

to stand over night. Attempts to filter the resulting suspension were unsuccessful so an equal volume of 95 per cent ethyl alcohol was added. A brown pasty mass precipitated. This was filtered from the liquid and dried for five days over concentrated sulfuric acid in a desiccator. This solid, which weighed 5.37 grams, formed a paste with hot water that produced a blue color characteristic of starch with aqueous iodine, and reduced Fehling's solution. Ignition of a small portion of the solid indicated the presence of a small fraction of inorganic matter. Oxidation of a 1.30 gram portion of the benzene insoluble solid with 9.5 grams of chromic oxide in 109 cc. of 25 per cent sulfuric acid for over 48 hours under gentle reflux gave no aromatic acid which indicated that there had been no condensation of the benzene with that portion of the recovered solid.

The benzene solution from which the solid had been filtered was poured into a beaker containing 400 cc. of chipped ice and 80 cc. of concentrated hydrochloric acid. A bright, purple color developed in the benzene layer and much heat was evolved. The bright color disappeared after stirring for a few minutes. The beaker was set aside over night. After standing 20 hours the benzene layer was removed from the aqueous layer and placed in a flask over

metallic sodium to dry. This solution was brown and possessed a blue fluorescence not unlike lubricating oil. After drying for 65 hours the liquid was filtered into a distilling flask, and the benzene was distilled off in a 12-inch fractionation column. After the removal of the benzene there remained about 15 cc. of higher boiling liquid which was transferred to a 25 cc. distilling flask and fractionated. The following fractions were collected:

Temp. (°C.)	Pressure (mm. Hg.)	Volume (cc.)
70-125	741.7	1.5
125-145	741.7	1.5
145-245	741.7	0.0
245-255	741.7	1.6
75-115	2.0	1.1
115-175	2.0	2.9
175-250	2.0	2.6
Solid residue	4.93 grams	

Experiment VI. The principal conditions and molar relationships are as follows:

Benzene	5.63 mols
Aluminum chloride	0.625 mol
Dry soluble starch (dried <u>in vacuo</u>)	0.083 equiv.
Time	8 hours
Temperature	80° C.

Five hundred cubic centimeters of dry benzene were placed in the reaction flask, and 15.5 grams of dry, soluble starch and 83.1 grams of anhydrous aluminum chloride were

added with stirring. The flask was heated rapidly to 80° C. on a water bath. When the temperature had reached 65° C., considerable hydrogen chloride was evolved, and this continued for about 30 minutes. During the heating the mixture changed to a rich brown color. After refluxing gently for eight hours the mixture was removed from the flask and poured into a beaker containing 400 cc. of chipped ice and 50 cc. of concentrated hydrochloric acid. Much heat was evolved, and the benzene layer developed a purple color which faded after a few minutes. The mixture was allowed to stand for 27 hours after which the benzene layer was separated from the aqueous layer and placed over metallic sodium to dry. After drying 72 hours the benzene solution was filtered into a distilling flask, and the benzene was distilled off leaving a few cc. of higher boiling liquid. This was placed in a 25 cc. distilling flask and distilled under 2 mm. pressure. The following fractions were collected:

Temp. (°C.)	Volume (cc.)
60- 90	0.8
90-170	1.4
170-210	1.8
Solid residue	1.41 grams

A small amount of brown solid was precipitated from a portion of the aqueous solution with 95 per cent ethyl alcohol.

This solid weighed 1.82 grams and gave a paste with hot water which turned blue when aqueous iodine was added; but it would not reduce Fehling's solution. Ignition of a small portion of the solid left a little inorganic residue.

Blank Reaction. The principal conditions and molar relationships are as follows:

Benzene	8.83 mols
Aluminum chloride	0.625 mol
Time	7 hours
Temperature	80° C.

This experiment was conducted to determine the effects of anhydrous aluminum chloride on benzene alone when the two are placed together under similar conditions to those used in the preceding experiments.

Five hundred cubic centimeters of dry benzene were placed in the reaction flask, and 83.1 grams of anhydrous aluminum chloride were added with stirring. The mixture was heated rapidly to 80° C. on a water bath with constant stirring, and that temperature was maintained for seven hours. The mixture became brown with heating, and some hydrogen chloride was evolved throughout the reaction period. After seven hours the contents of the flask were removed and poured with stirring into a beaker containing 400 cc. of chipped ice and 80 cc. of concentrated hydro-

chloric acid. The benzene layer developed a purple color which changed to brown on standing. After standing 15 hours the benzene layer was separated from the aqueous layer and placed over metallic sodium to dry. After drying 24 hours the solution was placed in a distilling flask and the benzene distilled off. There remained a small amount of higher boiling materials which was transferred to a small distilling flask and distilled under about 2 mm. pressure. The following fractions were collected:

Temp. (°C.)	Volume (cc.)
73- 90	1.1
90-170	1.9
170-206	1.2
Solid residue	1.28 grams

Arylation of Dry Swelled Starch with
Aluminum Chloride as a Catalyst

Experiment VII. The principal conditions and molar relationships are as follows:

Benzene	2.08 mols
Pyridine	0.76 mol
Aluminum chloride	0.231 mol
Dry starch (pyridine swelled)	0.033 equiv.
Time	8 hours
Temperature	83° C.

Sixty cubic centimeters of dry pyridine were placed in the reaction flask with 5.4 grams of dry pyridine-swelled starch. There was added 155 cc. of dry benzene and 30.75 grams of anhydrous aluminum chloride. Upon adding the aluminum chloride much heat was evolved, the temperature of the reactants rose to 80° C., and considerable hydrogen chloride was evolved. The mixture was heated on a water bath at 83° C. for eight hours, during which time very little hydrogen chloride was evolved. At the end of the reaction period the contents of the flask were poured into a beaker containing 300 cc. of chipped ice and 10 cc. of concentrated hydrochloric acid. No color change was observed. After standing 18 hours the entire mixture was filtered, and the benzene layer was separated from the aqueous layer and washed with 5 per cent sodium carbonate solution to remove acid, then with water to remove excess alkali. The benzene solution was then placed over anhydrous calcium chloride to dry. After drying 24 hours the benzene was distilled off, and there remained a small amount of brown solid weighing 1.50 grams which is about 2.5 times the weight of solid obtained from a corresponding amount of starch under analogous conditions where pyridine was not used (Experiment III). The solid filtered from the

reaction mixture was dried and weighed 7.62 grams. It had a dirty, white color, gave a blue color when aqueous iodine was added to its paste with hot water, did not reduce Fehling's solution, and contained some inorganic matter determined by ignition.

Arylation of Dry Swelled Starch
with Sulfuric Acid as a Catalyst

Experiment VIII (a). The principal conditions and molar relationships are as follows:

Benzene	2.08 mols
Sulfuric acid (85 per cent)	
H_2SO_4	4.52 mols
H_2O	4.33 mols
Dry starch (pyridine swelled)	0.097 equiv.
Time	44 hours
Temperature	20-25° C.

The apparatus used in this experiment was modified slightly. The reflux condenser was replaced by a dropping funnel, and the reaction was carried out at room temperature (20-25° C.). One hundred eighty-five cubic centimeters of benzene were placed in the reaction flask, and 15.7 grams of dry, pyridine-swelled starch were added with stirring. A solution of 85 per cent sulfuric acid made by mixing 265 cc. of concentrated sulfuric acid in 55 cc. of distilled water was added over a period of one hour through the

dropping funnel. After 17 hours of stirring at room temperature the benzene layer was no longer visible, and the mixture appeared black. The stirring was stopped after 44 hours, the mixture removed from the flask and poured into a beaker containing 300 cc. of distilled water, and the resulting mixture filtered through a Buchner funnel. The solid was washed with benzene which removed some soluble material; the benzene portion of the filtrate was separated, washed with sodium carbonate solution and water, then dried over metallic sodium. The solid product, which weighed 12.5 grams, was extracted with 150 cc. of benzene in a Soxhlet extractor for four hours and the extract combined with the dried benzene washings. Upon evaporation of the combined solutions, there was obtained 1.42 grams of a red-brown solid which is ether soluble but insoluble in ligroin. The original solid was then extracted with 150 cc. of acetone for four hours. Evaporation of the acetone extract gave 0.1 gram of a brown gummy solid.

A portion of the red-brown solid weighing 1.30 grams was oxidized gently for over 48 hours with 9.5 grams of chromic oxide in 109 cc. of a 25 per cent sulfuric acid solution. The mixture was cooled and extracted with ether three times. The extracts were evaporated and the residue

dissolved in 5 per cent sodium hydroxide and filtered. The filtrate was acidified with concentrated hydrochloric acid, and a small amount of yellowish white solid was precipitated. This solid was filtered off and extracted with ether four times. Evaporation of the ether extract left a white solid weighing 0.2926 gram. This solid was recrystallized from boiling water and the crystals filtered off and dried. They were white in color, and gave some smoke when ignited on a platinum spoon. No melting point was obtained at temperatures up to 275°C ., but the solid darkened and partially decomposed. It is possible that this solid is one of the phthalic acids or trimesic acid which sublime instead of melt.

Experiment VIII (b). The principal conditions and molar relationships are as follows:

Sulfuric acid (85 per cent)					
H_2SO_4	:	:	:	:	4.52 mols
H_2O	:	:	:	:	4.33 mols
Dry starch (pyridine swelled)	:	:	:	:	0.097 equiv.

The following reaction was a blank that was run under the same conditions as the preceding experiment except that the benzene was omitted. To the cooled sulfuric acid solution in the flask there was added 15.7 grams of dry, pyridine-swelled starch. The mixture was stirred for 44 hours.

During the course of the reaction the mixture darkened and became black. At the end of the 44 hours the contents of the flask were removed and poured with stirring into 300 cc. of distilled water. This mixture was filtered with suction through a Buchner funnel. There was obtained a dark filtrate which became transparent upon dilution with water and showed no evidence of solid particles. The precipitate recovered was washed three times with 400 cc. portions of distilled water and the washings filtered from the solid each time; then the solid was washed in the Buchner funnel with 400 cc. more of distilled water to remove the last traces of acid. Thereupon, the solid was dried in a desiccator over concentrated sulfuric acid. This solid did not form a paste with hot water, gave no blue color with aqueous iodine which would have been indicative of starch, and did not reduce Fehling's solution. The solid was extracted for one hour in a Soxhlet extractor with 150 cc. of benzene, and the extract evaporated. Only a trace of solid was obtained from the extract. The solid was then extracted with 150 cc. of acetone for four hours, and evaporation of this extract left 0.1 gram of a brown, gummy material.

Arylation of Starch Triacetate
with Aluminum Chloride as a Catalyst

Experiment IX. The principal conditions and molar relationships are as follows:

Benzene	5.63 mols
Aluminum chloride	:	:	:	:	:	0.538 mol
Starch triacetate	0.0833 equiv.
Time	30 hours
Temperature	.	.	.	(28 hrs.)		20-25° C.
				(2 hrs.)		80° C.

Five hundred cubic centimeters of dry benzene were placed in the reaction flask, and 24 grams of starch triacetate and 71.7 grams of anhydrous aluminum chloride were added with stirring. The mixture was stirred at 20-25° C. for 28 hours. At the end of this time there was only slight evidence of reaction, that being the appearance of a light brown color. The mixture was then heated rapidly to 80° C., that temperature being maintained for two hours. Much hydrogen chloride was evolved during the heating, and the mixture darkened in color. At the end of the reaction the solution had a red color when viewed before a light. The mixture was removed from the flask and poured with stirring into a beaker containing 400 cc. of chipped ice and 50 cc. of concentrated hydrochloric acid. The benzene layer acquired a brilliant red coloration which changed to orange

after stirring 30 minutes. This solution had an odor unlike that of benzene. The mixture was set aside over night and after standing for 24 hours it was filtered to remove the solid, and the benzene layer was washed twice with 5 per cent sodium carbonate and several times with distilled water, then placed over anhydrous calcium chloride to dry. Metallic sodium was used later to complete the drying. After drying 24 hours over sodium the solution was filtered, and the benzene was distilled off leaving a few cubic centimeters of higher boiling material. This was placed in a 25 cc. distilling flask and fractionated under 15 mm. pressure. The following fractions were obtained:

<u>Temp.</u> <u>(°C.)</u>	<u>Volume</u> <u>(cc.)</u>
65- 80	2.3
80-120	1.8
120-190	1.0

There remained no undistillable residue.

The solid separated from the reaction mixture was dried in air but possessed an odor of acetic acid, so it was placed in 200 cc. of warm distilled water (80° C.), and solid sodium carbonate was added until the solution was slightly basic to litmus. The solid was filtered from the liquid, washed with liberal quantities of distilled water to remove the alkali, then dried in a desiccator over sul-

furic acid. This crumbly, brown, amorphous solid gave a weak reduction test with Fehling's solution, but would not readily form a paste with water nor give a blue coloration with aqueous iodine when boiled in a small amount of water and cooled. Observations on ignition of the solid indicated that it contained some inorganic matter.

Arylation of Tri-trichloroacetyl Starch Using the Friedel-Crafts Reaction

Experiment I. The principal conditions and molar relationships are as follows:

Benzene	1.13 mols
Aluminum chloride	:	:	:	:	:	0.0126 mol
Tri-trichloroacetyl starch	0.0056 equiv.
Time	1.5 hours
Temperature	:	:	(1/4 hr.)	:	:	25-30° C.
			(1 1/4 hrs.)	:	:	30° C.

One hundred cubic centimeters of dry benzene were placed in the reaction flask, and 3.33 grams of tri-trichloroacetyl starch and 1.68 grams of anhydrous aluminum chloride were added with constant stirring. No temperature or color changes were noticed, and no hydrogen chloride was evolved. The mixture was then heated rapidly on a water bath to 30° C., this requiring about 20 minutes. Hydrogen chloride was evolved in moderate quantities for about 20 minutes after

the temperature had reached 65° C. The mixture was refluxed for 75 minutes and gradually became brown. At the end of the reaction period the mixture was removed from the flask and filtered, and a small amount of solid was recovered. This solid was mostly inorganic and weighed 0.37 gram. The liquid portion of the mixture was placed in 100 grams of ice containing 5 cc. of concentrated hydrochloric acid and allowed to stand for five hours. The benzene layer was removed, filtered, washed with 5 per cent sodium carbonate solution and water, and dried over anhydrous calcium chloride. After drying for 48 hours the benzene was distilled off at temperatures that did not exceed 80° C., and there remained a brown substance that hardened to a crumbly resinous solid on drying. This solid weighed 2.55 grams. Ignition of a small amount of it indicated the presence of some inorganic material. The solid was ground in water in a mortar, filtered in a Buchner funnel, and washed repeatedly with 50 per cent ethyl alcohol solution until the washings contained no free chloride ion. After drying the product, an analysis was run for chlorine in a Farr bomb. The drop in the percentage of chlorine corresponded to the replacement of one chlorine atom per formula weight by a phenyl group. Oxidation of a 1.30 gram sample

of the product with 9.5 grams of chromic oxide in 100 cc. of 25 per cent sulfuric acid for over 48 hours gave little evidence of oxidation. Only a trace of solid was obtained from extraction with ether, and this was insufficient to permit purification and melting point determination.

DISCUSSION OF RESULTS

Although the results of the reactions recorded in this paper were mostly negative, an analysis and comparison of the data obtained will give further significance to the work as a whole.

Any consideration of the products obtained from the reactions of starch and benzene with aluminum chloride catalyst must be made with care, and the results of the blank reaction with benzene and aluminum chloride must be borne in mind. The amount of benzene soluble material obtained from the blank run for seven hours compared favorably with similar material obtained from the experiments where condensation was attempted, except in the experiment in which pyridine was used, where the amount of solid obtained was about 2.5 times as great, the comparison being made for identical weights of starch. However, it is likely that some differences existed in the undistillable

benzene soluble residues, although this was not evident. A marked increase in the amount of undistillable benzene soluble residue was observed for the reaction which ran for 70 hours. Only about 40 per cent of the weight of original starch was recovered which is indicative of some reaction. However, it was impossible to ascertain whether or not the undistillable solid residue was composed in part of condensation products of starch and benzene without the development of a method of separation of the chemical individuals in the solid. It must be remembered that mere oxidation of the product and isolation of the resulting acids would be no criterion for judging the extent of the reaction unless there was a noticeable increase in products over that observed in the blank reaction. Moreover, the acids obtained from such oxidations would be similar to those from the blank itself if the products were oxidized.

It was evident from the first two experiments that a large excess of benzene was advisable in order to keep the reaction mixture as nearly uniform as possible and facilitate the separation of the inorganic and organic products of the reaction. The absence of a suitable extraction solvent for the organic products increased the problem of separation. Ethyl alcohol was found to be effective in re-

moving aluminum salts, but no satisfactory method was found for separating insoluble oxides from the organic materials. When large excesses of benzene were used and the products of the reaction were decomposed in ice and hydrochloric acid, most of the inorganic material was removed by the aqueous solution. Even so, the insoluble organic solids recovered usually contained some inorganic material.

In the reaction in which pyridine was used as a dispersion agent there was a marked difference in the amount of hydrogen chloride evolved which may be attributed to the formation of pyridine hydrochloride. Although some hydrogen chloride escaped, there was a strong exothermic reaction characteristic of the formation of this salt when the aluminum chloride was added. The combination of the hydrogen chloride with the pyridine effectively decreases the acidic properties of the mixture which would increase the stability of the starch. A low concentration of hydrogen chloride may also decrease the side reactions of the benzene and aluminum chloride which are generally favored by the presence of HCl. The hydrogen chloride was probably formed by the reaction of the aluminum chloride with the starch to form a complex. Since pyridine hydrochloride has been used successfully to activate such groups as the hydroxyl group, and organic sulfites, it is thought

that some conditions of temperature and pressure may be reached at which it can activate the starch complex without rupturing any of the glucosidic linkages. The increased stability of starch in basic media together with the possibility of desirable catalytic effects of the pyridine hydrochloride make this reaction worthy of further investigation.

The formation of brilliant red to violet colors in the benzene layer when the benzene-starch-aluminum chloride mixtures were decomposed in ice and hydrochloric acid can not be attributed entirely to the presence of a starch complex, for a similar coloration was observed with the products of the blank reaction. A marked decrease in the rate of evolution of hydrogen chloride after about two hours was noticed in all but the first two reactions with starch. This decrease was not noticed in the blank reaction where the gas came off throughout the reaction. Moreover, the evolution of hydrogen chloride in the case of the starch reactions was accompanied by a rapid darkening color within the two hour period, whereas in the blank this occurred more slowly. This seems to be indicative of some chemical reaction with the starch. In any case the evolution of hydrogen chloride and the color changes were simul-

taneous.

In the reaction of starch and benzene with sulfuric acid as a catalyst the benzene soluble product obtained was doubtlessly the result of some condensation of the starch with the benzene since no corresponding product was obtained from the sulfuric acid and starch alone under the same conditions. This belief was further substantiated by oxidation of the benzene soluble product which gave some acid that melted or sublimed at a high temperature. However, the yield was quite small and much more remains to be done to determine the conditions necessary for optimum yields.

Efforts to condense benzene with starch triacetate may be considered unsuccessful. There was no high boiling or undistillable residue obtained, and the volatile products were similar to those obtained from the blank with aluminum chloride and benzene.

The failure to obtain any benzoic or other acid from oxidation of the product from the tri-trichloroacetyl starch reaction may be because no condensation occurred, or more probably because the product was not oxidized under the conditions employed. There was little evidence of any reduction of the chromic acid in the experiment, and the

solid showed little evidence of oxidation. The drop in chlorine content gives reason to believe that some condensation has occurred; however, there is no confirmation of this in the fact that the product is soluble in ether and benzene since the original starch ester had similar solubility in these solvents.

Condensation reactions in which starch is a reactant present obstacles that may or may not be surmountable. One such obstacle is the lack of a suitable dispersion medium for starch which can penetrate the molecular aggregate enough to reach the reactive groups. Moreover the activation energies of the hydroxyl groups of the starch or starch-catalyst complexes may be higher than those of the glucosidic bonds. Even under mild conditions of temperature and pressure in the presence of acids the glucoside bonds are preferentially attacked. Apparently successful condensations with starch require catalytic conditions which increase the reactivity of hydroxyl groups of the starch or starch complexes.

SUMMARY AND CONCLUSIONS

In conclusion it may be said that starch will not condense with benzene to any great extent under the conditions used in these experiments. However, the results offer encouragement toward further research in an attempt to find the necessary conditions for the desired reactions. The failures may be due, in part, to the lack of a suitable dispersion medium for the starch and improper adjustment of variables such as temperature, time, and concentrations. The presence of hydrocarbons that result from side reactions of benzene and aluminum chloride increases the problem of separation and characterization of any products resulting from the proposed condensation. Blank reactions with benzene and aluminum chloride alone for comparison constitute a partial solution of this difficulty. The use of dry pyridine, as a dispersion agent, was not satisfactory under the conditions used. The pyridine apparently inhibited the effects of the catalyst in producing side reactions with benzene, but gave a relatively larger amount of benzene soluble solid and decreased the extent of starch degradation.

Although the 88 per cent sulfuric acid was effective as a catalyst, the yield was too small to predict the ultimate value of this method. It is possible that other effects of the sulfuric acid on the starch outweigh the catalytic effects in the condensation.

Starch triacetate did not react under the conditions used, but it cannot be concluded that the reaction is impossible from a single experiment for others have observed that variables such as temperature, time, and concentrations may not be described in general statements, since these factors differ for different esters. This suggests a more extended study of this reaction.

From the results of the oxidation of the product from tri-trichloroacetyl starch it could not be proved that any condensation had occurred, but from the apparent resistance of the solid to oxidation it is thought that perhaps the oxidizing agent was not strong enough to oxidize off any aryl groups present. The drop in the percentage of chlorine indicated the substitution of one phenyl group for a chlorine per formula weight. It is believed that the condensation can be carried out by increasing the time factor and perhaps the amount of catalyst since the quantities used were based on those used for simple alkylation re-

actions with alkyl halides which may not provide a proper environment for the condensation of a complex molecule with extraordinary properties.

In general, the success of any of the reactions that have been proposed will be dependent upon the dispersion of the starch aggregate to an extent that will enable the potentially active groups to become available for reaction, and upon the presence of the necessary energy for the reaction to occur. It seems justifiable to attribute the failures to lack of penetration of the starch and its esters by the other reactants, and to the absence of enough energy to activate a large number of such groups because of their spatial positions.

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LITERATURE CITED

- (1) Tsukervanik, I. P.
Condensation of alcohols with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. I. Condensation of tertiary aliphatic alcohols with benzene and toluene. J. Gen. Chem. (U. S. S. R.), 5:117-20. 1935.
- (2) Tsukervanik, I. P. and Tokareva, K.
Condensation of alcohols with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. II. Condensation of secondary alcohols with benzene and toluene. J. Gen. Chem. (U. S. S. R.), 5:567-70. 1935.
- (3) Tsukervanik, I. P. and Vikhrova, G.
Condensation of alcohols with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. III. Condensation of primary alcohols with benzene and toluene. J. Gen. Chem. (U. S. S. R.), 7:632-6. 1937.
- (4) Tsukervanik, I. P. and Terent'eva, I.
Condensation of alcohols with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. IV. Condensation of aliphatic alcohols with naphthalene. J. Gen. Chem. (U. S. S. R.), 7:637-40. 1937.
- (5) Tsukervanik, I. P. and Sidorova, M. G.
Condensation of alcohols with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. V. Condensation of cyclohexanol with benzene and toluene. J. Gen. Chem. (U. S. S. R.), 7:641-5. 1937.
- (6) Norris, J. F. and Ingraham, J. W.
Condensation of aliphatic alcohols with aromatic hydrocarbons. I. Preparation of mesitylene and *s*-tristhyl benzene. J. Am. Chem. Soc. 60:1421-3. 1938.

- (7) Huston, R. C. and Goodenoot, K.
Effect of strain in cycloalkyl carbinols on their reactivity with benzene in the presence of aluminum chloride. *J. Am. Chem. Soc.* 58:2432-4. 1936.
- (8) Huston, R. C. and Esieh, T. Y.
Condensation of aliphatic alcohols with aromatic compounds in the presence of aluminum chloride. *J. Am. Chem. Soc.* 58:439-41. 1936.
- (9) Huston, R. C., Fox, W. D. and Binder, M. W.
Condensation of aliphatic alcohols with aromatic compounds in the presence of aluminum chloride. II. Tertiary aliphatic alcohols and benzene. *J. Org. Chem.* 3:251-60. 1938.
- (10) Kane, Howard L. and Lowy, Alexander.
Reactions of alkyl sulfates, tetraethyl orthosilicate, and diethyl carbonate in Friedel-Crafts syntheses. *J. Am. Chem. Soc.* 58:2605-8. 1936.
- (11) Berman, Nathan and Lowy, Alexander.
Reaction of trialkyl phosphates, alkyl acetates, and tertiary butyl hypochlorite in Friedel-Crafts syntheses. *J. Am. Chem. Soc.* 60:2596-7. 1938.
- (12) Kashtanov, L. I.
Reactions of esters with aluminum chloride and thallium chloride in benzene. *C. A.* 27:275. 1933. [*J. Gen. Chem.* (U. S. S. R.), 2:515-23. 1932.]
- (13) Bowden, Everett.
Alkylation of benzene by esters by the Friedel-Crafts reaction. *J. Am. Chem. Soc.* 60:1645-7. 1938.
- (14) McKenna, James F. and Sowa, Frank J.
Organic reactions with boron fluoride. XIII. The alkylation of benzene with alcohols. *J. Am. Chem. Soc.* 59:470-1. 1937.
- (15) Price, Charles C. and Ciskowski, Joseph M.
Alkylation of naphthalene with alcohols and boron fluoride. *J. Am. Chem. Soc.* 60:2499-2502. 1938.
- (16) Nightingale, Dorothy and Smith, Lee Irvin.
The action of aluminum chloride on aromatic hydrocarbons. I. The 1,3-dimethyl-4-butyl benzenes. *J. Am. Chem. Soc.* 61:101-4. 1939.