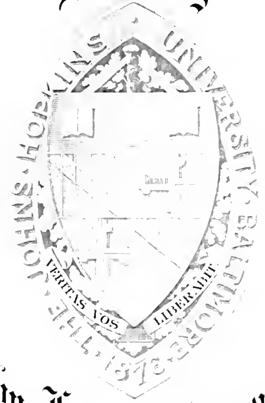
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THE ALKYLATION OF BENZENE, TOLUENE AND NAPHTHALENE AND THE CHLORINATION OF ACETYLENE

DISSERTATION

Submitted to the Board of University Studies of
The Johns Hopkins University in Conformity
with Requirements for the Degree of
Doctor of Philosophy

by

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The author welcomes this opportunity to express his deepest sense of gratitude to Doctor Reid, under whose direction the first part of this work was done, and to Doctors Frazer, Patrick, Lovelace and Thornton for the inspiration received in the lecture room and laboratories.

Appreciation is also extended to the authorities of The Chemical Warfare Service for permission to publish the work on the chlorination of acetylene, which work was done at Edgewood Arsenal.

THE ALKYLATION OF BENZENE, TOLUENE AND NAPHTHALENE.

Friedel and Crafts and later workers have shown that benzene may be alkylated by treating it with an alkyl halide in the presence of anhydrous aluminum chloride -

$$RCl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5R + HCl$$

Balsohn[1] in preparing ethyl benzene modified the Friedel and Crafts reaction slightly. Instead of using ethyl chloride, he used ethylene and hydrochloric acid in proportions to give ethyl chloride -

$$C_2H_4 + HCl \longrightarrow C_2H_5Cl$$

Since ethyl chloride and benzene react in the presence of aluminum chloride to liberate hydrochloric acid, the total amount of hydrochloric acid required in comparison with that of ethylene is very small since it undergoes a cyclic process

$$\begin{tikzcd}
C_2H_4 + HCl \arrow[r] & C_2H_5Cl \\
 & + \\
 & C_6H_6 \arrow[d] \\
 & HCl + C_6H_5C_2H_5\ ;
\end{tikzcd}$$

in fact Balsohn later found that even traces of water vapor in the ethylene used were sufficient, on reacting with the aluminum chloride, to furnish the required amount of hydrochloric acid.

Balsohn's method consisted in bubbling ethylene through

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[1] Bull. Soc. Chim. (2) 31, 539 (1879).

a mixture of benzene and aluminum chloride at 70°- 90° C. Under these conditions ethylation takes place very slowly; consequently the practical importance of the reaction was at that time not realized.

According to McDaniels[1] 1 volume of benzene at 80°C. dissolves two volumes of ethylene. Since this solubility is small it is important that the benzene be saturated continuously with ethylene if the best results are desired. This point was recognized by Milligan and Reid[2] who used high speed stirring to maintain a condition of saturation; as a result they found that the obscure and apparently unimportant method of Balsohn was, in reality, a very practical one - a reaction which when performed with the aid of high speed stirring, far outrivaled the usual method in which a previously prepared alkyl chloride is employed.

THE PRESENT INVESTIGATION.

1. To study more thoroughly certain features of the Friedel and Crafts reaction.

2. To apply the method of Balsohn in the alkylation of Benzene, Naphthalene and Toluene, using high speed stirring.

3. To study the chlorination of acetylene, using stirring.

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[1] J. Phys. Chem. 15, 605

[2] J. Am. Chem. Soc. 44, 206

APPARATUS .

The stirrer as is shown in Figure I consists of a disc two inches in diameter and three sixteenths of an inch thick with holes three sixtyfourth of an inch in diameter bored radially around its periphery and terminating inside of a small cone at the bottom of the disc. The disc is screwed onto a tool-steel shaft which is connected by means of belts and an intermediate pulley to a 1700 R.P.M. motor. With the size of pulleys which were used speeds as high as 13,000 R.P.M. could be obtained. The gas to be used was, after preliminary drying and purification, introduced by an inlet tube ending just under the cone and thrown out through the small holes by the centrifugal force of the rapidly rotating disc. A rather closely fitting iron tube was placed around the stirrer shaft and connected by suitable means to the frame of the stirrer. This tube passed through the rubber stopper of the reaction bottle and dipped below the surface of the liquid contained therein; in this way a perfectly gas-tight reaction chamber was obtained. Baffle plates were used to decrease the gyratory motion of the liquid.

A condenser was attached at one end by means of an adapter to the reaction bottle, while the other end was connected to a receiver for unused gas.

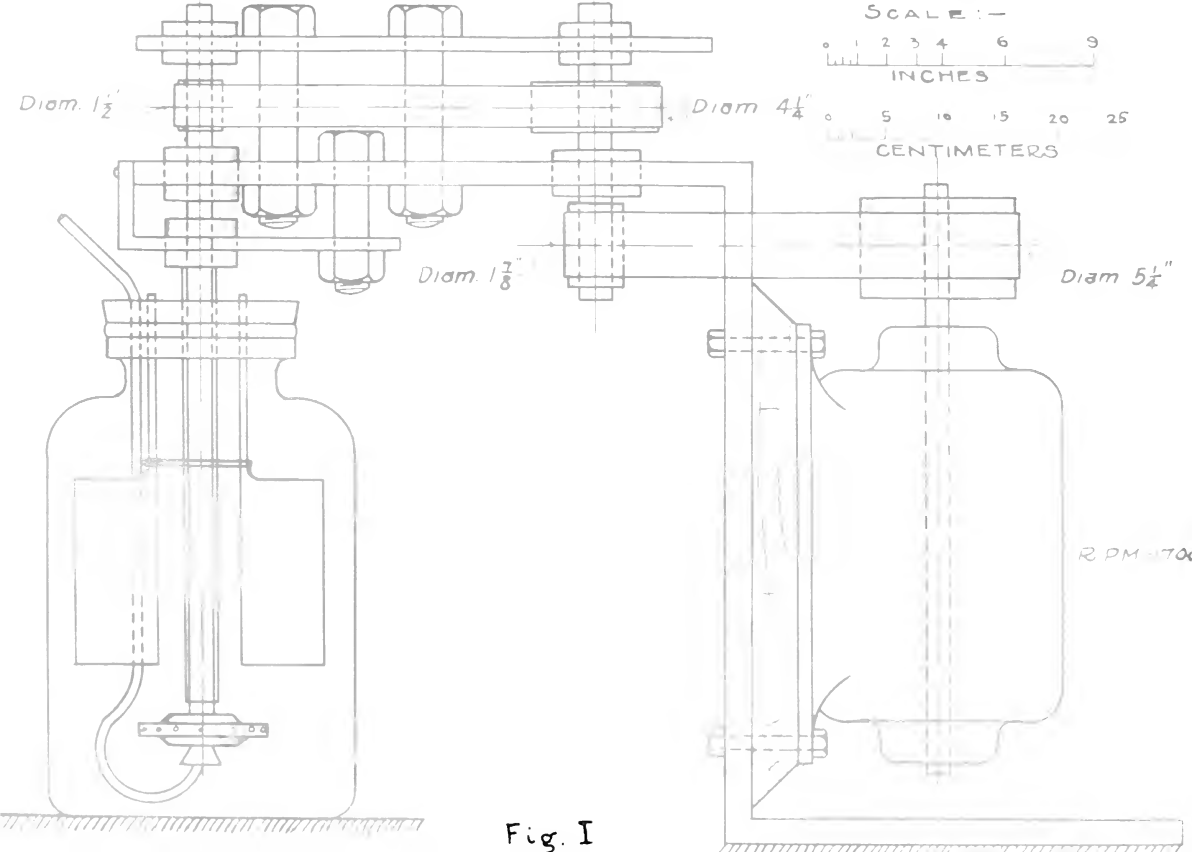
SCALE :—
0 1 2 3 4 6 9
INCHES
0 5 10 15 20 25
CENTIMETERS
Diam. 1½"
Diam 4¼"
Diam. 1⅞"
Diam 5¼"
RPM 170

Fig. I

THE ETHYLATION OF BENZENE.

The ethylene used was of commercial variety but of a very high grade of purity. It was first passed through a gas meter. The difference between the amount of gas as represented by the gas meter and the amount of recovered gas was taken as the amount which had reacted. After passing through the gas meter, the ethylene was purified and dryed by passing through two gas wash-bottles, one containing pyrogallic acid and the other sulphuric acid respectively; and then through two drying towers filled with soda lime and another containing phosphoric anhydride.

The gas was passed into the benzene-aluminum chloride mixture at such a rate as to allow only an occasional bubble to escape. This was found to be the method conducive to the best results, since if the amount of escaping gas is large, it carries appreciable quantities of hydrochloric acid along with it and the reaction slows down to a very marked degree. In some cases it was possible to restore the original reactivity by passing in small quantities of dry hydrochloric acid along with the ethylene.

In all of the experiments, the temperature was held at approximately 70°. It was found that the change of temperature coefficient of the reaction within the interval 60°-90°C. is approximately zero.

Throughout the work it was found that an incubation period of about twenty minutes before the passage of the ethylene, favored the reaction.

Experience has shown that at any given instant during the course of a reaction, a maximum rate of absorption of gas under the prevailing conditions can be obtained, only with one particular rate of stirring. If the rate of stirring be reduced below this point, a reduction in the rate of gas supply must be made; while on the other hand, if the rate of stirring is increased, a corresponding escape of gas takes place with the consequent loss of hydrochloric acid, and, as a result the reaction slows down to a very marked degree. The rates of stirring ranged between 8,000 and 10,000 R.P.M.

RATIO OF C_6H_6 TO $AlCl_3$

It was desirable to know the relative proportions of benzene and aluminum chloride which would afford a maximum rate of reaction. It is quite conceivable that if this ratio be either very large or very small a poor rate of reactions will be obtained. The inclination is to use a large amount of catalyst with the hope of insuring a good rate of reaction; it has however been found that an excess of aluminum chloride is just as detrimental to the rate of reaction as an insufficiency. The aluminum chloride used in all of the experiments in one set was from the same lot.

Since the usual course of a catalytic reaction is to increase up to a maximum and then decrease, a comparison of results can be obtained only by counting time from the instant at which the introduction of the ethylene is begun, since the rate of increase of reaction rate varies in the different experiments. In table I the rates of absorption for a period of 134 minutes after the introduction of the ethylene are listed for five different experiments in which varying relative amounts of aluminum chloride and benzene were used.

TABLE I

Exp.	Molal Ratio $AlCl_3 : C_6H_6$	ℓ. C_2H_4 Absorbed	Time	Average Rate of Absorption cc. C_2H_4/Mol C_6H_6/Min.
1	1 : 8.5	58.6	134	114
2	1 : 10	60.9	134	120
3	1 : 13	138.5	134	200
4	1 : 22	104.4	134	133
5	1 : 44	4.8	134	10

It thus appears that better results are obtained when the ratio of aluminum chloride to benzene lies between 1 : 13 and 1 : 22 . Ratios greater than 1 : 13 give poorer results while a ratio as small as 1 : 44 gives practically no results.

EXAMINATION OF THE TWO LAYERS.

Friedel and Crafts[1], Gustavson, Boeseken and others have found that in the Friedel and Crafts reaction, there are always two layers formed. A clear upper layer and a dark brown, very viscous lower layer. They state that the upper layer contains mostly benzene and the low boiling products, i.e. the lower substituted benzenes, while the lower layer contains materials boiling at much higher temperatures. An explanation for this phenomenon makes its appearance on consideration of the various theories which have been proposed to explain the mechanism of the Friedel and Crafts reaction. Friedel and Crafts' own theory was, that the aluminum chloride used combines with the benzene to form a compound $C_6H_5.Al_2Cl_5$ which later reacts with the alkyl chloride giving hydrochloric acid and a substituted benzene

$$C_6H_5Al_2Cl_5 + RCl \longrightarrow C_6H_5R + HCl$$

This theory was later abandoned for the theory proposed by Gustavson[2] who attributed the condensation to the formation of addition products of aluminum chloride with three molecules of benzene $AlCl_3.3\ C_6H_6$; products which have been isolated and analyzed. These addition products are attacked very easily by

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1. Ann. Chim. Phys. 6, (1), 449
2. B. 12, 853; 13, 157; 16, 784; 33, 767.

alkyl chlorides:

$$AlCl_3.3\ C_6H_6 + 3\ RCl \rightarrow 3\ HCl + AlCl_3.3(C_6H_5R)$$

$$\downarrow$$

$$AlCl_3 + 3\ C_6H_5R$$

Boeseken[1] has shown that Gustavson's intermediate is formed only in the presence of traces of moisture. He also shows that Gustavson's assumption, that one mol of $AlCl_3$ suffices for 3 mols of hydrocarbon and three mols of alkyl chloride, is not valid in certain cases, since in these one mol of $AlCl_3$ will condense only one mol of hydrocarbon and one mol of alkyl chloride. He contends that the aluminum chloride combines with the alkyl halide and has isolated some of these compounds

$$C_6H_5COCl.AlCl_3 + C_6H_6 \longrightarrow C_6H_5COC_6H_5.AlCl_3$$

Boeseken[2] points out that in the formation of homologues of benzene, a very small amount of $AlCl_3$ was sufficient to cause the reaction of a large amount of alkyl halide. This, he explained, was due to the inability of $AlCl_3$ to form very stable compounds with the reactants.

All of the theories which have been proposed assume that

1. Boeseken - A. ch. (6) 14, 167
2. Boeseken - Rec. Trav. 22, 301

aluminum chloride forms an addition product with the alkylated benzene. If this be true, then we should expect to find at the end of our reaction, the most alkylated benzenes in combination with the aluminum chloride.

This point was investigated by first separating the two layers, as well as possible, by siphoning off the upper layer. The two layers were then treated separately with water to decompose the aluminum chloride complexes. The amounts of these complexes, in the upper layer, are very small as is shown by treating with water; practically no heat is evolved and only very small amounts of aluminum hydroxide precipitate. The lower layer, on the other hand, contains practically the whole of the aluminum chloride used and has to be decomposed extremely slowly and with constant cooling. The upper and lower layers were fractionated separately through a Vigreux column. It was found that the lower layer contained, by far, a higher percentage of the more alkylated benzenes.

The following ratios will indicate the relative molecular amounts of the different ethyl benzenes appearing in the upper and lower layers. These calculations were made upon the basis of 1000 molecular weights of mono ethyl benzene appearing in the upper and lower layers respectively.

Run	Layer	Mono	Di	Tri	Tetra	Penta	Hexa
2	Upper	1000	583	122	47	26	32
	Lower	1000	1943	698	199	302	151
3	Upper	1000	588	354	177	59	59
	Lower	1000	325	354	177	1622	270
4	Upper	1000	94	42	—	—	—
	Lower	1000	354	125	—	—	—
12	Upper	—	1000	5253	1128	1204	1813
	Lower	—	1000	7169	3991	9018	71

From the data given, it is quite apparent that there is a marked difference in the composition of the two layers. In run #2 the reaction was stopped in its early stage, i.e. after considerable quantities of mono- and di-ethyl benzenes had been formed. Run #12 was carried much further toward completion and as a result higher percentages of the more ethylated benzenes were obtained. In all of the runs which were made, it was observed that an extraordinary high percentage of penta ethyl benzene was obtained in the lower layer as compared with that in the upper layer.

In all of the experiments it was observed that the speed of the reaction increased up to a maximum, remained constant, and then began to decrease. Experiment #13 shows this rather clearly. In the following table the rates are given in cc. of ethylene absorbed with their respective periods of absorption.

Experiment

13

Period of Absorption Min.	cc. of C_2H_4 Absorbed per Min.
72	190
30	770
20	1300
30	1220
35	1350
15	1322
15	982
18	883

Fig. 2 is a graphic representation of these values.

The manner in which the benzene was dryed had considerable influence on the reaction. Calcium chloride-dryed benzene on being stirred with aluminum chloride gave rise to hydrochloric acid fumes which hovered above the surface of the benzene. After the reaction had progressed for some time these fumes gradually disappeared. Reactions in which calcium chloride dryed benzene was used appeared to be very sensitive to changes in temperature, rate of stirring and loss of hydrochloric acid, and further, maintained the maximum rate for only a

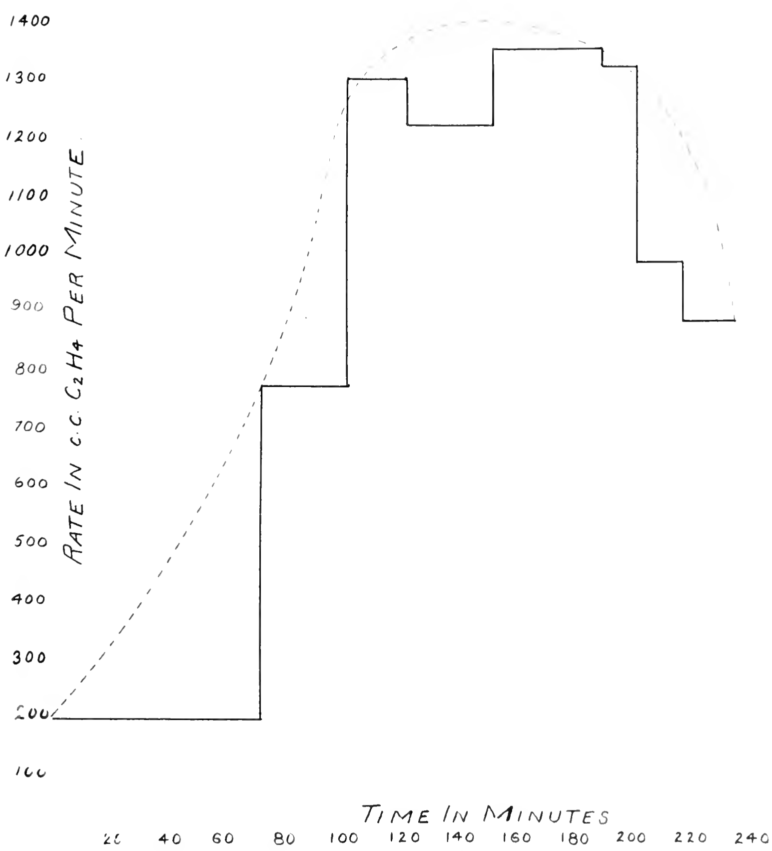

1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
RATE IN c.c. C_2H_4 PER MINUTE
TIME IN MINUTES
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 2.

short period as compared to sodium-dryed benzene, which did not yield white fumes of hydrochloric acid on being stirred with aluminum chloride.

Experiment #2 gives a fair idea of the rate at which benzene can be ethylated. 5.83 mols of benzene were ethylated with 139 ℓ. of ethylene, in the presence of 60 g. of $AlCl_3$ over a period of 134 minutes. The average rate of ethylatinn being 1034 cc. of ethylene per minute. The above amount of ethylene was calculated from the products obtained which were -

123 g.	Benzene
200 g.	Ethyl benzene
155 g.	Di ethyl benzene
42 g.	Tri ethyl benzene
18 g.	Tetra ethyl benzene
13.5 g.	Penta ethyl benzene
16 g.	Hexa ethyl benzene

It has been previously stated that the reactions were run so as to permit only an occasional bubble of ethylene to escape. In this experiment calculation shows that 97 % of the ethylene sent into the reaction bottle is present in the distilled products. In this experiment 3.85 mols. of benzene, 0.385 mols of $AlCl_3$ and 14.1 mols of ethylene were made to react over a period of 675 minutes. The products obtained were -

1/2	g.	Benzene
4	g.	Ethyl benzene
74½	g.	Di ethyl benzene
305	g.	Tri ethyl benzene
82	g.	Tetra ethyl benzene
31	g.	Penta ethyl benzene
154	g.	Hexa ethyl benzene.

It was not possible to ethylate the benzene directly to hexaethyl benzene with the apparatus which was used in this work, due to the increase in volume of the liquid mixture on ethylation. The volume change is about 100 % for an ethylation of about 80 per cent.

Experiment # 13 is interesting from the standpoint of the comparative ease of ethylation of benzene and diethyl benzene. A mixture of 2.24 mols of diethyl benzene and 0.385 mols of aluminum chloride was ethylated at a rate of 900 cc. per minute for 233 minutes. In this experiment benzene and aluminum chloride were employed in the ratio of 1 : 5.7 and the average rate at which the ethylene reacted for a period of the first 134 minutes amounted to 257 cc. per mol of diethyl benzene per minute. This is a much higher rate than would have been obtained had benzene and aluminum chloride been used in the above proportions. If diethyl benzene ethylates at the same rate as benzene we would have expected a lower rate of absorption. It appeared throughout this work that alkylated benzenes alkylate with somewhat greater

ease than does benzene; in other words it is harder to substitute the first alkyl group into the benzene ring than it is to substitute the second alkyl group. This experiment was stopped on account of the product solidifying in the reaction bottle and consequently preventing further stirring. There were obtained on separation -

447	g. Hexa ethyl benzene
32	g. Tetra ethyl benzene
4	g. Penta ethyl benzene
3	g. Residue

The amount of ethylene which reacted in this experiment represents 82½ % of the amount required to convert all of the diethyl benzene into hexa ethyl benzene. Of the amount of ethylene which reacted 86½ % was accounted for in the hexa ethyl benzene obtained after centrifuging out the included oils.

In experiment #14, 2.24 mols of tri-ethyl benzene were ethylated with 5.03 mols of ethylene; 0.385 mols of $AlCl_3$ were used and the reaction run for a period of 248 minutes. The average rate was 240 cc. per minute for the first 134 minutes as compared with 257 cc. per mol of diethyl benzene as was stated in the previous experiment. From these results it appears that tri-ethyl benzene can be alkylated at approximately the same rate as diethyl benzene but both of these at a greater rate than benzene. This reaction was

stopped before the products in the reaction bottle solidified. On separation there were obtained -

345 g.	Hexa ethyl benzene
10 g.	Penta ethyl benzene
70 g.	Tetra ethyl benzene
22 g.	Tri ethyl benzene

The amount of ethylene which reacted corresponded to 72½ % of the amount required to carry all of the tri-ethyl benzene to hexa-ethyl benzene; of this amount 80.1 percent went to form hexa-ethyl benzene.

It was expected that by stirring gaseous ethyl chloride into a mixture of benzene and aluminum chloride that the ethylation would take place somewhat faster, since a certain amount of time must be consumed in its formation from ethylene and hydrochloric acdi. Commercial ethyl chloride after drying was passed into a mixture of benzene and aluminum chloride. In this reaction one mol of hydrochloric acid is liberated from each mol of ethyl chloride which reacts; consequently the escaping hydrochloric acid carried large amounts of ethyl chloride along with it and as a result a large loss was involved. On the whole, this method was very unsatisfactory as compared with that in which ethylene was used.

The reaction between ethylene and benzene in the presence of $AlCl_3$ is exothermic and a cooling coil was placed around the reaction bottle which was immersed in a water bath; this was used in case the mixture got above 70°C.

It was found that the reaction was aided by allowing the temperature to rise, at the beginning, until gentle refluxing was taking place. The refluxing was allowed to continue for several minutes, after which the mixture was cooled to 70°C. Refluxing for short periods of time tended also to revive the reaction after it had slowed down.

Two different boiling points are given in Beilstein for Hexa-ethyl Benzene namely 305°C. and 292°C. In this work a total of about 1400 grams of hexa-ethyl benzene were prepared; consequently, it seemed that advantage should be taken of this opportunity to obtain its boiling point. After 3 recrystallizations from hot alcohol, the boiling point as determined with a 400 g. sample was found to be 293°C. at 766 mm.

ETHYLATION OF TOLUNENE.

3.04 mols of toluene were treated with ethylene at a rate of 811 cc. per minute for a period of 81 minutes. This represents a rate of 266 cc. per mol of toluene per minute. This is a greater rate of ethylation than could be obtained with benzene. On fractionation of the product under ordinary pressure the following fractions were obtained:

Up to 120° C. = 45 g. - mostly toluene

$120 - 145^{\circ}$ = 42 g. - a mixture of dimethyl and ethyl benzenes

$145 - 160^{\circ}$ = 47 g. - ortho- and meta-methyl ethyl benzenes

$160 - 164^{\circ}$ = 74 g. - p. ethyl methyl benzene

$164 - 171^{\circ}$ = 33 g. 1 . 3 . 5 trimethyl benzene and
1 . 2 . 4 trimethyl benzene

$171 - 198^{\circ}$ = 28 g. 1 . 2 . 3 trimethyl benzene and
1.2.3.5 and 1.2.4.5 metaethyl dimethyl benzene

$198 - 203^{\circ}$ = 32 g. 3.5 diethyl -1-methyl benzene. This fraction had an intensive blue fluorescence.

$203 - 207^{\circ}$ = 33 g. 1.2.3.4 tetra methyl benzene

5 g. Residue.

The ethyl-methyl benzenes have been prepared by the Fettig synthesis[1].

ETHYLATION OF BROM BENZENE

2.83 mols of Brom Benzene were ethylated at a rate of 70 cc. per mol of brombenzene per minute for a period of 345 minutes using 0.375 mols of aluminum chloride. Toluene, on the other hand , was ethylated at a rate of 266 cc. per minute per mol of toluene under nearly the same conditions.

[1] Claus - B. <u>18</u>, 1121
Wroblewski - A. <u>192</u>, 198
Fittig & Glinzer - A. <u>136</u>, 312
Jannasch & Deickmann - B. <u>7</u>, 1513

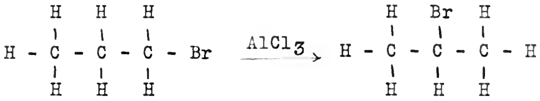
It appears that alkyl side chains increase the rate at which the benzene ring can be alkylated, while halogen substituents effect a retardation. Previous workers have shown, that $AlCl_3$ causes a shifting of halogen atoms in the benzene ring. This, as would be expected, took place in the ethylation of brombenzene. On fractionation of the product we obtained the following fractions:

Up to 140° C. = 15 g. - a mixture of benzene and ethylbenzene
140 - 180° = 135 g. Ethyl- & DiEthyl-Benzene
180 - 204° = 47 g. - 2 brom-1-ethyl benzene
204 - 215° = 39 g. - 4 brom-1-ethyl benzene
215 -221° = 45 g. - Triethyl benzene and dibrom benzene
221 - 240° = 35 g. Brom-diethyl benzenes.
240 - 250° = 35 g. Decomposed with liberation of hydrobromic acid.
Residue = 85 g. - Tar

PROPYLENE AND BENZENE

Gustavson[1] has shown, that when normal propyl bromide and isopropyl bromide react with benzene in the presence of aluminum chloride the same compound, namely isopropyl benzene, is obtained. It is evident from this that the aluminum chloride causes a transformation of the one form of propyl bromide into the other.

Kekule and Schrötter[2] have shown that normal propyl bromide under the influence of $AlCl_3$ splits off HBr and rearrangement is brought about giving isopropyl bromide:



$$\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{Br}\xrightarrow{\mathrm{AlCl_3}}\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$$

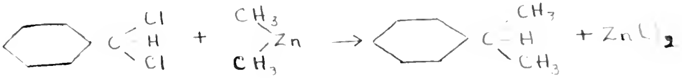
This action is a minimum at 0°C.

From 60 g. of propyl bromide and 80 g. of Benzene, Gustavson obtained 20 g. of isopropyl benzene, a yield of 34%.

Jacobsen[3] prepared isopropyl benzene by the Fittig method using 100 g. of isopropyl iodide and an excess of benzene. After a reaction period of 4 days he obtained 5 g. of isopropyl benzene, a yield of 7%.

1. B. 11, 1251
2. Bl. (4) 3, 726
3. B. 8, 1260

Liebman[1] prepared isopropyl benzene from benzal chloride and zinc methyl



Since isopropyl benzene can be prepared only very slowly by the above methods, which furthermore afford very low yields, it was hoped that the reaction between propylene and benzene in the presence of $AlCl_3$ would prove a better means for its preparation.

Propylene was generated from isopropyl alcohol by dropping it upon meta phosphoric acid at a temperature of 500°-700° C. This method, although it yields propylene of a very high degree of purity, is undesirable from the standpoint of the destructive action of phosphoric acid upon the glass reaction vessel at this temperature. The action was such as to gradually eat away the bottom of a pyrex flask in the course of ten hours under running conditions.

A slightly less pure grade of propylene (less reactive) can be obtained more readily, and in larger amounts, by passing isopropyl alcohol vapor over pumice impregnated with Al_2O_3 and held at a temperature of about 600°C. The pumice

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[1] Liebman - B. 13, 46

so impregnated may be used for a period of 6 - 8 months before yielding an undesirable grade of propylene. The propylene was collected in a tank over water and after passage through a gas-meter was purified as in the case of ethylene.

The rate of reaction between propylene and the benzene-aluminum chloride mixture was much slower than when ethylene was used. This might be explained as being due to the increase in weight of the isopropyl radical over that of the ethyl radical.

In experiment #18, 15 mols of benzene were treated with propylene at a rate of 122 cc. per minute or 8 cc. per minute per mol of benzene for a period of 1770 minutes in the presence of 1.1 mols of $AlCl_3$. This is a rate of about 1/25 that at which it was possible to ethylate benzene. The two layers on fractionation gave the following products:

Top Layer	Bottom Layer
35 g. up to 75°(b.p. 28°)	
188 g. Benzene	54 g. Benzene
550 g. Mono Isopropyl Benzene	82 g. 135 - 155°
369 g. Di Isopropyl Benzene	32 g. 200 - 220°
62 g. Tri " "	28½ g. 220- 255°
15 g. Tetra " "	16 g. 225 - 285°
15 g. Residue	75 g. Residue

The molal relationship of these products existing in the two

layers, calculated upon the basis of 1000 mols of mono-isopropyl benzene existing in each layer, is -

	Mono		Di		Tri		Tetra
Top	1000	:	497	:	66	:	13
Bottom	1000	:	285	:	200	:	100

From this relationship it is apparent, as was the case with the ethyl benzenes that the bottom layer is relatively richer in the more highly substituted benzenes than is the upper layer. The crude product in this experiment differs from that obtained in the ethylation of benzene in that a fraction boiling below 75° was obtained and that further, the bottom layer always contained a high percentage of tar. The isopropyl benzenes which appear in the literature at the present time are - mono-, ortho- and meta-di and 1:3:5 tri-isopropyl benzene. By a study of the temperature intervals existing between the boiling points of the ethyl benzenes a very good idea was obtained as to the temperature limits between which the higher substituted isopropyl benzene fractions should be taken; after the boiling points of several of these higher products had been obtained it was apparent that the fractions had been cut within the proper ranges.

In experiment #21, 14 mols of benzene were treated with 100 cc. of propylene per minute (7 cc. per min. per mol of benzene) for a period of 2551 minutes in the presence of 1.1 mols of $AlCl_3$. The crude products yielded -

Upper Layer		Lower Layer
22 g.	up to 75°	2 g.
252 g.	Benzene	53 g.
720 g.	Mono Isopropyl Bnezene	119 g.
293 g.	Di " "	30 g.
29 g.	Tri " "	20 g.
—	Tetra " "	5 g.
16 g.	Residue	77 g.

Molal Ratio

Upper Layer	1000	:	299	:	23	:	—
Lower Layer	1000	:	180	:	100	:	50

It was noted throughout this work that the complexes of $AlCl_3$ with the isopropyl benzenes were decomposed more slowly by water than were the complexes between $AlCl_3$ and the ethyl benzenes.

It became the additional object of this work at this point to prepare some of the higher isopropyl benzenes. It is apparent from the data so far presented that mono- and di- isopropyl benzene may be prepared in large amounts by the reaction between benzene and propylene. After several attempts to carry the reaction to such a stage that the products would consist largely of the higher alkylated benzenes it was found that time was saved by first isolating the lower products and then retreating these with propylene in the

presence of $AlCl_3$. It was also interesting to find out whether or not the isopropyl benzenes and propylene react with greater ease than benzene and propylene.

In experiment #23, 3 mols of mono isopropyl benzene were treated with 42 cc. of propylene per minute (14 cc. per mol of mono isopropyl benzene per minute) for a period of 1655 minutes. From these results it is again apparent that an alkyl benzene may be alkylated with greater ease than benzene. The two layers on fractionation yielded the following:

Top Layer			Bottom Layer
10	g.	up to 75°	———
7	g.	Benzene	———
2½	g.	Mono Isopropyl Benzene	½ g.
20	g.	Di " "	½ g.
419½	g.	Tri " "	33 g.
12	g.	Tetra " "	7 g.
2	g.	White Solid	———
10	g.	Residue	5 g.

The percentage of each product occurring in each layer is :

	Mono	Di	Tri	Tetra
Top	0.73 %	4.38%	93.4%	1.85%
Bottom	2.04	1.5	82.1	14.3

In this experiment a total of 452½ grams of the tri isopropyl benzene was prepared. This product contains about 92% of the propylene used in the experiment.

In experiment #22, 10.6 mols of mono- isopropyl benzene were treated with propylene at a rate of 16 cc. per mol of propylene per minute (total of 170 cc. per minute) for a period of 1388 minutes in the presence of 60 g. of $AlCl_3$. The total products from the two layers were fractionated and refractionated several times to gain an idea of the relative isomeric yields. The fractions obtained were:

17 g.	up to 75°		at 766 mm.
20 g.	Benzene	75 - 90 °	
½ g.	___	90 - 152	
220 g.	Mono	152 - 156	(B.P. 152 - 154)
25 g.	Mono- Di-	156 - 201	
33 g.	Mono- Di	201 - 203½	
410 g.	Mono- Di	203½ - 204½	(B.P. 204)
22 g.		204½ - 205½	
23 g.		206 - 206½	
23 g.		206½ - 208½	
119 g.	Ortho- Di	208½ - 209½	(B.P. 209)
20 g.		212 - 215	
35 g.		215 - 220	
12 g.		220 - 225	
11 g.		225 - 230	
6 g.		230 - 233	
256 g.	1.3.5 Tri	233½-234½	(B.P. 234)
56 g.		234½ - 235½	
46 g.		235½ - 236½	

47 g.	236½ - 237½
6 g.	238 - 239
9 g.	239 - 240
15 g.	240 - 241
3 g.	242 - 243
16 g.	243 - 246
61 g.	above 246°

It appears from this data that about 65% of the di-isopropyl benzenes formed is the meta. Of the tri-isopropyl benzenes fromed, about 75% is symmetrical tri-isopropyl benzene.

250 g. of 1.3.5 tri-isopropyl benzene was treated with 56 l. of propylene in the course of 12 hours. This reaction went at an exceptionally high rate; it being possible to cause an absorption of 80 cc. of propylene per minute. The reaction was not allowed to go to completion. On cooling the products in the reaction bottle solidified. On purification it was found that a white solid had been formed which was identical with the 2 grams of white crystalline compound obtained in experiment #23. The fractions obtained from the crude material were:

5 g.	234 - 236
48 g.	236 - 245
14 g.	245 - 260

24 g.	260 - 265
15 g.	265 - 270
110 g.	above 270
26 g.	White crystals.

Several runs were made using tri-isopropyl benzene and it was found to be possible to run the reaction until the products solidified completely. A total of 65 grams of the white crystalline material was prepared. It was centrifuged free of included oils and recrystallized several times from alcohol. The material crystallized in the form of long white needles which had a melting point of 117° and a boiling point of 260° at 775 mm. This material was oxidized with a 7% solution of permanganate on a water bath for one month and an acid melting at 282° was obtained. This could have been either mellitic acid of m.p. 286° or the dianhydride of 1.2.4.5 tetra carboxylic acid of melting point 286° C.; however it would not be expected that the anhydride of this acid would be formed under the given conditions.

The silver salt of this acid was prepared and gave an analysis 65.42 % Ag, the theoretical for silver mellitate being 65.82 %, while the theoretical for the silver salt of benzene tetra carboxylic acid is 63.32 %. The boiling point of the hydrocarbon (260° at 775 mm.) indicates that it is tetra isopropyl benzene rather than hexa isopropyl benzene since its boiling point lies far below that of hexa ethyl

benzene (294°); also oils boiling above this were obtained ($265\frac{1}{2}$° and 270°C.) which are thought to be tetra isopropyl benzenes. Mixtures of oils boiling even higher than 270° were obtained but in insufficient quantities for separation. The 1.2.4.5 tetra methyl benzene boils below its two isomers, it being a solid while the isomers are liquids at room temperature. The boiling points of the hexa alkyl benzenes increase with increasing complexity of the alkyl groups as would be expected, hexamethyl benzene boiling at 264 ° and hexaethyl benzene at 294°; therefore we should expect hexaisopropyl benzene to boil higher than 294°C. A combustion was made on this hydrocarbon and the following analysis obtained.

	Sample	Theoretical For		
		Hexa	Penta	Tetra
% C	87.43 87.60	87.18	87.41	87.72
% H	12.43 12.61	12.82	12.59	12.28

Since p. diisopropyl had not been made, considerable time was spent in trying to locate it within the range of the boiling points of the meta and ortho diisopropyl benzenes. The attempt to isolate this material failed, however, although it is thought that it boils between 212° and 216° since such

a fraction was obtained which was quite resistant to further separation. Not enough of this fraction was obtained, however, to effect an adequate separation.

An attempt was made to synthesize para diisopropyl benzene by means of the Fittig synthesis. 240 grams of isopropyl benzene were brominated with 321 grams of bromine in the presence of 30 g. of iodine at 0°C. On fractionation of the product there were obtained 290 g. of para bromisopropyl benzene and 40 grams of ortho brom isopropyl benzene. Isopropyl chloride was obtained by refluxing isopropyl alcohol with an excess of concentrated hydrochloric acid, using a Hempel column mounted by a 40" Vigreux column. By using this arrangement and carrying on the distillation so that the material does not distill above 50° a fairly rapid preparation of isopropyl chloride may be obtained. The para brom-benzene was mixed with its molecular equivalent of isopropyl chloride and the mixture treated with the calculated quantity of sodium. The product on being separated yielded

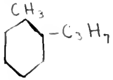
75 g. of a fraction 150°-157°C.

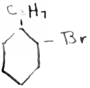
300 g. of an earthy material.

The fraction 150°-157° was oxidized with permanganate, and benzoic acid of melting point 121°-122° obtained. It is evident from this that the bromine of para brom-isopropyl benzene was replaced by a hydrogen atom. This evidently came about as a result of the splitting off of hydrochloric

acid from isopropyl chloride which then reacted with the para brom benzene through the agency of the sodium to give isopropyl benzene. It was noticed while the reaction was taking place that a gas was being liberated, this gas was evidently propylene.

The earthy material was very light in weight, had a dark brown color and was insoluble in all of the common organic solvents; even on extraction with xylene for several days using a Soxlett apparatus nothing dissolved. The material burned in a manner much like cork and emitted a grayish smoke having a peculiar odor. This material is likely a polyphenyl compound.

Jacobsen[1] states that it is very hard to put even one isopropyl group into the benzene ring by the Fittig Synthesis, since the isopropyl halide is attacked with difficulty by sodium. After allowing brombenzene and isopropyl iodide to react for four days in the presence of sodium he obtained only a 5% yield. Sprinkmeyer[2] tried to prepare ortho isocymol 

from ortho brom toluol, isopropyl iodide and sodium but failed to get any of the desired product; he was however able to prepare small amounts of it from ortho bromcumol 

, methyl iodide and sodium.

1.3.5 Triisopropyl benzene has been prepared [3]. The

[1] Jacobsen - Ber. 8, 1260

[2] Sprinkmeyer - Ber. 34, 195

[3] Compt. rend. 140, 940 ; C 1905 (11) 379;
J. prak. Chem. 2 72, 57

1.2.4 isomer was obtained as a result of the present work by refractionating the triisopropyl benzene fraction a number of times in a vacuum using a pressure regulator. A total of 300 grams of this oil was obtained having a boiling point of 237°-237½° at 752.5 mm. and 97°- 97½° under 4 mm. It was oxidized for five days on a water bath by a 7 percent solution of permanganate. An acid melting with anhydride formation at 214° was obtained, this evidently is 1.2.4 benzene tri-carboxylic acid. The oil had a specific gravity of 0.87644 at 0°C. and of 0.85928 at 25°C. It had a color of + 18 as determined by the method recommended by the American Society for Testing Materials using a viscosity of 21.7 seconds at 100°F. for 30 cc. using a Sabolt Universal Viscosimeter; 30 cc. of water under the same conditions gave a viscosity of 17.4 seconds. The index of refraction was found to be 1.4855 at 25°C. The oil gave a flash point of 205°F. and a fire test of 245°F.

200 grams of another oil were isolated. This had a boiling point of 270°C. at 766 mm. It had a color of -12 and flash and fire points of 240° and 280°F. respectively. The specific gravity was found to be 0.91283 at 0°C. and 0.89658 at 25°C. Its refractive index at 25°C. was found to be 1.5060. Its viscosity as determined with 30 cc. of oil was 43.7 seconds at 100°F.; the same amount of water at this temperature required 17.4 seconds. This oil was oxidized

with permanganate and an acid having a melting point of was obtained.

About 60 grams of another oil was isolated. It had a boiling point of 265½°C. at 755.7 mm. and 102½°C. at 4 mm. and refractive index 1.4969. Color -7.

The fraction boiling below 75° was refractionated and found to be composed of two substances one boiling at 28°C. and the other from 56°- 59°. The latter is likely diisopropyl which has a boiling point of 58°C. The former had a specific gravity of 0.70949 at 0°C.

2.5 dibrom isopropyl benzene was prepared by brominating 120 grams of isopropyl benzene with 325 grams of bromine in the presence of iodine at a low temperature. 235 grams of a liquid boiling at 258°- 259° and having a refractive index of 1.5718 at 25° was obtained. This oil was oxidized with permanganate and an acid having a melting point of 151°C. was obtained; this is evidently 2.5 dibrom benzoic acid which melts at 151°-153°.

PROPYLENE AND TOLUENE

Kelbe[1] states that by treating toluene with isopropyl iodide in the presence of aluminum chloride meta isocymol is obtained. Fittig attempted to prepare para methyl isopropyl benzene from para bromtoluol, isopropyl iodide and sodium but failed to get the desired product[2]. However, Widman[3] prepared it by the Fittig synthesis using para-brom-isopropyl benzene and methyl iodide.

7.2 mols of Toluene were made to react with 2¼ mols of propylene at a rate of 75 cc. per minute in the presence of 100 g. of $AlCl_3$. It is to be noted that this reaction goes somewhat faster than that between propylene and benzene. The product after purification was fractionated into the following:-

5 g.	Benzene		
370 g.	Toluene	105°-120°	
17 g.	Xylene	120°-145°	
25 g.		145°-170°	A mixture of trimethyl benzene and ortho cymene
161 g.		170°-185°	of meta isocymene (175-176) and cymene (para methyl isopropyl benzene) 175°-176°
60 g.		above 185°	

If the fraction 170°- 185° be a mixture of meta-and para-

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1. Ann. 210, 10
2. Ann. 149, 337
3. Ber. 24, 450

methyl isopropyl benzenes , a possible separation could not be obtained merely by distillation, since both boil at the same temperature. The mon- brom derivatives of these compounds however, boil at about ten degrees apart; that of the meta compound at about 224° and those of the para at about 234°.

136½ grams of the fraction 175-176, obtained by redistillation of the original 170°-185° fraction, was brominated in the cold, using 10 g. of iodine as a carrier, with 162 grams of bromine. The product after being washed and dryed gave the following:

3.7 g. - 160°-195° C.
11.2 g. - 195°-220° C.
para 160 g. - 228°- 240°C
6 g. - 240°-247°C.
25 g. - Residue

The fraction 228°-240°C. represents a yield of 80% of the brom derivatives of para- methyl isopropyl benzene. Kelbe[1] states that by the Friedel and Crafts reaction using toluene isopropyl iodide and AlCl$_3$ he obtained meta methyl isopropyl benzene. He obtained only a small quantity of his product and his method of identification which consisted in observing the solubility of barium salt of the corresponding di-carboxylic acid was unsatisfactory.

[1] Ann. <u>210</u>, 10

PROPYLENE AND NAPTHALENE

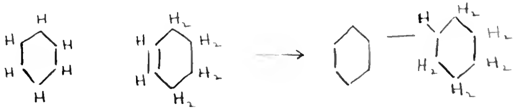
Since ethylene and napthalene react only very slowly in the presence of $AlCl_3$, it was to be expected that propylene and napthalene would react even slower. Instead of propylene, diisopropyl benzene was used.

217 grams of napthalene was stirred with 132 g. of diisopropyl benzene in the presence of 50 g. of $AlCl_3$ at a temperature of 90°C. for a period of 4½ hours. The product on fractionation gave the following:

72 g. mono isopropyl benzene 150°-185°
72 g. of napthalene 185°- 250°
15 g. isopropyl napthalene (264°-266°)
9 g. 266°-300° probably diisopropyl napthalene.
50 g. of an oil boiling above 300° C.

TETRAHYDRO BENZENE AND BENZENE

Since tetrahydro benzene contains an ethylene linkage it was thought that it would react with benzene in the same manner as has been shown in the case of ethylene and propylene. The product expected was phenyl cyclohexane



3.54 mols of tetra-hydro benzene were mixed with 3.54 mols of benzene and treated very gradually with 60 grams of $AlCl_3$. On the addition of the $AlCl_3$ a violent reaction took place with the liberation of large amounts of heat. After the 60 grams of $AlCl_3$ had been added, the reaction bottle was connected with the stirrer. The mixture could not however be stirred for periods longer than 30 seconds, as the amount of heat liberated was such as to cause the liquid to boil. As the reaction proceeded the mixture could be stirred for increasing periods of time. After about 45 minutes it was possible to stir the mixture continuously and this was done for a period of five hours; during which the temperature of the mixture remained at about 55 degrees. At the end of five hours of stirring the temperature began to fall. The reaction product was purified and dryed and on distillation gave the following fractions:

30 g. up to 230° - mostly benzene, cyclohexyl chloride (141.3) and tetrahydro benzene
50 g. 230°-245° Phenyl cyclohexane
125 g. above 245° - likely diphenyl cyclohexane and small amounts of dihexyl .

Kursanoff[1] prepared phenyl cyclohexane from cyclohexyl chloride, benzene and $AlCl_3$.

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[1] Ann. <u>318</u>, 310

To 100 grams of benzene and 10 grams of $AlCl_3$ he added slowly 50 grams of $AlCl_3$ he added slowly 50 grams of cyclohexyl chloride and obtained the following products:

10 g. up to 130° mostly benzene

34 g. 130°-132° (10 mm.) Phenyl cyclohexane

1 drop 132°-200° (10 mm.)

16 g. 200°-315° (20 mm.) diphenyl cyclohexane

He showed that the latter was an ortho compound by preparing it from ortho dichlorcyclohexane.

Kursanoff states that the more $AlCl_3$ used the lower the percentage of phenyl cyclohexane obtained while the higher the percentage of higher boiling products. As an example of this he obtained a 11 percent yield of phenyl cyclohexane by using 30 g. of $AlCl_3$, 20 g. of chlor cyclohexane and 40 g. of benzene whereas by using 0.1 g. of $AlCl_3$ under the same conditions he obtained a 68 percent yield of phenyl cyclohexane. This might explain why in the present work such a high percentage of higher boiling products were obtained.

An effort was made to prepare phenyl cyclohexane by the Fittig synthesis. To 15 grams of finely divided sodium 65 cc. of alcohol free dry ether were added. A mixture of 35 g. of brom benzene and 35 g. of cyclohexyl bromide were then added. The reaction began immediately and cooling

was necessary for its control. After standing over night the product was distilled. A yield of 6-7 grams of phenyl cyclohexane was obtained which corresponds to about 18% - 20% of the theory.

Phenyl cyclohexane has also been prepared by reducing diphenyl with hydrogen in the presence of catalytic nickel[1].

SUMMARY

1. Benzene, Toluene and Napthalene may be alkylated readily by Olefine and Polymethylene hydrocarbons in the presence of aluminum chloride with the aid of high speed stirring. By this method these alkyl compounds may be prepared more rapidly than is possible by the ordinary Friedel and Crafts reaction.

2. The rate at which alkylation will take place depends largely upon the relative amounts of aromatic hydrocarbon and aluminum chloride used.

3. The two layers which are always obtained in the Friedel and Crafts reaction differ widely in the percentage of products present. The $AlCl_3$ which is found almost wholly in the lower layer retains the higher boiling or more alkylated products.

4. The lower alkyl benzenes may be alkylated with

[1] C(1912) 11, 191

greater ease than benzene.

5. The larger the alkyl group the more difficult is its entrance into the benzene ring.

II.

THE CHLORINATION OF ACETYLENE

The object of this work was to prepare tetra- and hexa-chloretharies from chlorine and acetylene using a liquid medium into which the two gases could be dispersed by means of a high speed stirrer. It was thought that saturation with water vapor, of the gases included within the minute bubbles occasioned by the vigorous stirring, might cause a change in the usual course of the reaction. The reaction usually proceeds with explosive violence to give hydrochloric acid and free carbon.

Chlorine and acetylene were introduced into the cone of the stirrer simultaneously by different inlet tubes.

EXPERIMENTAL

500 cc. of water was placed in the reaction bottle and a run made at room temperature. Explosions took place continuously from the start which gave rise to numerous scintillations throughout the liquid. It was thought that by using a large excess of one of the gases that the explosions could be prevented, but this was found not to be true. Explosions took place in every case irrespective of the richness of the mixture. It was then decided to pass the gases into boiling water with the view that the increase

in water vapor would tend to dilute the gases and thereby reduce the violent action. Explosions did not occur in any case with temperatures above 65° C.

Sometime after this work was completed there appeared an English patent #174,635[1] in which it was stated that the chlorination of acetylene could be controlled in the presence of steam superheated to 400°-500° C.

Mouneyrat[2] has studied the action of chlorine on acetylene. He states that ethylene dichloride in the presence of aluminum chloride at 70°-75° decomposes to give acetylene and hydrochloric acid

$$(1) \quad C_2H_4Cl_2 \longrightarrow C_2H_2 + 2\ HCl$$

He chlorinated $C_2H_4Cl_2$ under these conditions and got $C_2H_2Cl_4$. Assuming that reaction (1) does take place he accounts for the fact that no explosions occurred on chlorination by saying that there was a total absence of oxygen. If the presence of oxygen be the cause of the explosions then we would expect that on passing the gases through water, the dissolved oxygen would be expelled and that the explosions would gradually cease. This, however, was not the case.

[1] Chem. Abs. 16, 1779

[2] Bull. soc. chim. 19, 448

After the water had been stirred for one hour at a temperature of 80° using 350 cc. of Cl_2 and 1400 cc. of C_2H_2 per minute, an emulsion was formed and very effective stirring was taking place. A current of air had to be directed on the end of the exhaust pipe to prevent the exhaust gases from igniting. The fact that the exhaust gases after leaving the reflux condenser would catch fire, while no explosions were occurring in the reaction bottle seems to indicate that water vapor had a great influence in preventing explosions in the chamber; or that due to the heating practically all of the oxygen was driven out. Refluxing began at 76° C. After two hours at the above rates of flow the product was fractioned. Three drops of a colorless oil, heavier than water, having a boiling point at about 90° were obtained. This oil has an odor which at first is etherial but on further inhalation becomes extremely pungent. The odor was identical with that of dichloracetaldehyde. It is known that acetylene and water react slightly to give acetaldehyde

$$C_2H_2 + H_2O \longrightarrow CH_3CHO$$

It is likely that a small amount of this compound was formed, which on chlorination gave dichlor-acetaldehyde.

After the water fraction had come over 50 g. of a colorless, odorless oil, boiling at 109° and having a specific

gravity of 1.0889 was obtained. These physical data do not check with those of any of the compounds which could be expected.

THE CHLORINATION OF ACETYLENE
BY THE USE OF SULPHUR DICHLORIDE

Since acetylene could not be chlorinated under the conditions as set forth above, work was undertaken to study its chlorination by the use of sulphur dichloride according to the method of Michel[1] . This consists in alternately passing chlorine and acetylene into a mixture of sulphur monochloride and 2% hydrogen reduced iron. Michel simply allowed these gases to bubble through the mixture; he states that a good yield of hexa-chlorethane can be obtained in this way. The reactions which take place are:

(1) $S_2Cl_2 + Cl_2 \rightarrow 2\ SCl_2$

(2) $C_2H_2 + 4\ SCl_2 \rightarrow C_2H_2Cl_4 + 2\ S_2Cl_2$

(3) $C_2H_2 + 6\ SCl_2 \rightarrow C_2Cl_6 + 3\ S_2Cl_2$

In the first experiment the temperature was so regulated that gentle refluxing took place. Since the reaction

$$S_2Cl_2 + Cl_2 \rightarrow 2\ SCl_2$$

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1. Zeit. Angew. Chem. 19, 1095

is exothermic and since further the boiling point of SCl_2, which is being formed, is lower than that of S_2Cl_2, a cooling coil was placed around the reaction vessel and the whole immersed in an oil bath. The temperature at the beginning was held at 125°. Chlorine was stirred into 1057 g. of S_2Cl_2 at a rate of 1500 cc. per minute for 10 minutes; total absorption taking place. At the end of this period the entire contents of the reaction vessel was forced out of the liquid seal with explosive violence. This could have been due to the instability of sulphur dichloride or to the clogging of the exhaust line. The latter was found not to have been the cause.

In the following experiments the temperature during chlorinations was held at 40°; this seemed to help rather than hinder the rate of chlorination. The absorption of acetylene however occurred more rapidly at somewhat more elevated temperatures. The heat liberated during the absorption of acetylene was used to raise the temperature of the mixture to about 80° C.

It was not found necessary to remove the excess of acetylene by means of an inert gas such as CO_2 before a new chlorination.

The flow of chlorine was measured by a calibrated flowmeter, the acetylene by means of a wet meter.

The chlorination of sulphur monochloride took place

with extreme ease; it being possible to get 1299 g. of the monochloride to absorb as high as 7000 cc. of chlorine per minute.

In the case of the absorption of acetylene the reaction proceeded in a manner which is often found when working with catalysts, namely that the reaction had to gradually "build itself up". By this is meant that although at the beginning the catalyst might be distributed throughout the sulphur chloride medium rather homogeneously, the acetylene would not be taken up at the same rate at which it would be, after the reaction had been in progress for sometime. The rate of absorption of acetylene would always increase to a maximum and then gradually decrease. This phenomenon is not to be explained as being due to the presence of small amounts of the chlorethanes, for even when they were present at the beginning, the reaction exhibited the same behavior. It is likely, however, that this behavior can be explained as being due to the formation of an intermediate compound between Fe and C_2H_2; which compound later catalizes the reaction.

After the reaction slowed down, the sulphur monochloride was chlorinated to the dichloride and this was distilled off. The remaining liquid was steam-distilled; this served to carry off the liquid tetrachlorethane from the solid hexachlorethane. In several experiments the sulphur chlorides

were decomposed with water, the liberated hydrochloric acid neutralized with Na_2CO_3, and the mixture steam-distilled. The residue consisting of sulphur and hexachlorethane was then extracted with ether.

In order to get a closer estimate of the relative yields, two runs were made and the resulting products were worked up together.

RUN # 1

1299 g. S_2Cl_2 = 9.61 mols.

25 g. Fe

CHLORINE				ACETYLENE			
Time Min.	Flowmeter P	Rate cc.	Total Cl_2 l.	Time	Flowmeter P	Rate cc.	Total C_2H_2 l.
35	8	2550	89.3	30	14	1000	30
61	6	2130	129.9	78	14	1000	78
96			219.2	45	14	1000	45
				60	20	1220	73.2
				213			226.2
110	6	2130	234.3	15	20	1220	18.3
2	11	3100	6.2	5	15	1040	5.2
16	24	4800	76.8	4	15	1040	4.2
				13	8	750	9.8
128			317.3	37			37.5
11	42	7000	77	5	20	1220	6.1
20	20	4350	80.7	52	20	1220	63.4
				23	12	912	21
31			157.7	80			90.5
27	24	4800	130	42	20	1220	51.2
				65	20	1220	79.3
				107			130.5
282			824	437			484.7

Average rate of chlorination = 2920 cc. per min. or 2.25 cc. Cl_2 per g. S_2Cl_2 per minute.

The average rate of acetylene absorption = 1100 cc. per minute, or 0.85 cc. C_2H_2 per g. S_2Cl_2 per minute.

The relative rates of chlorine uptake to acetylene uptake are apparently 3 : 1. Weight of product = 1410 g.

RUN # 2

934 g. S_2Cl_2
25 g. Fe
Temp. 40°

CHLORINE				ACETYLENE				
Time	Flow-Meter P.	Rate at P.	Total Cl_2 ℓ.	Time	Flow- Meter P.	Wet Meter ℓ.	Total C_2H_2 Flow-meter ℓ.	Rate Flow P. cc.
45	14	3.55	160	3	15		3.1	1040
				101	8	89.2	75.8	750
46	14	3.55	155	87	8	61.5	65.3	750
52	14	3.55	184.6	102	8	72.2	76.5	750
57	14	3.55	202.3	82	8	57.1	61.5	750
200			701.9	374		280	282.2	

Yield of mixture of $C_2H_2Cl_2$
$C_2H_2Cl_4$
C_2HCl_5 = 1035 g.
C_2Cl_6

The total products from both runs amounted to 2445 g. which on separation gave the following percentage by weight.

	B. P.	Yield	%
C_2Cl_6	Sublimes	76 g.	3
C_2HCl_5	158°	49 g.	2
$C_2H_2Cl_4$	147°	1887 g.	77
$C_2H_2Cl_2$	84°	108 g.	4

It is quite evident that this method gives only a very small relative amount of hexachlorethane; the main product being s-tetrachlorethane.

The tetrachlorethane thus prepared was further chlorinated to hexachlorethane in the presence of $AlCl_3$. This procedure is similar to that used by Mouneyrat by which he chlorinated ethylene dichloride to hexachlorethane.

The chlorine was passed into the mixture at 120° C. The density increased with the chlorine absorption until a point was reached where the entire contents of the bottle <u>solidified</u> and could no longer be stirred. The hexachlor-ethane was freed as much as possible from the tetrachlor-ethane by suction and the former then recrystallized from alcohol. The yield of C_2Cl_6 calculated upon the basis of the amount of chlorine used amounted to 63%.

The effects of stirring at a rate of 8000 R.P.M. on the

rate of absorption of chlorine by tetrachlorethane in the presence of $AlCl_3$ was investigated at a point in the chlorination where the chlorine was being taken up at a rate of 1400 cc. per minute. The stirring was stopped with the result that the flow-meter pressure on the chlorine line dropped from 3 cm. indicating a rate of 1400 cc. per minute to 1 cm. indicating a rate of 750 cc. per minute. The latter rate is necessarily greater than it would have been, had not the liquid been previously stirred, since as soon as the stirring was stopped the $AlCl_3$ was still rather homogeneously distributed throughout the liquid.

CONCLUSIONS.

1. Chlorination of acetylene in the presence of 2% catalytic iron gives s-tetrachlorethane almost exclusively.

2. s-Tetrachlorethane can be chlorinated in the presence of $AlCl_3$ using high speed stirring until the reaction mixture solidifies, thus giving a yield of 63% hexachlorethane.

3. The effect of high speed stirring was to double the rate of chlorination of s-tetrachlorethane to hexachlorethane.

4. Chlorine and acetylene may be made to react without violence in the presence of water vapor above 65° C.

BIOGRAPHY

The author of this dissertation was born in Charles Co., Maryland, February 8, 1897. He received his early education in the public schools of Baltimore and graduated from The Johns Hopkins University in 1920 with the degree of Bachelor of Science. In the fall of 1920 he entered the Johns Hopkins Graduate School of Chemistry, taking as his subordinate subjects Physical Chemistry and Mathematics. In June 1922 he received the degree of Master of Arts, the title of his thesis being:- "The Friedel and Crafts Reaction."

During the years 1921-22 and 1922-23 he was part-time instructor in Organic Chemistry at the Mt. Vernon College of Baltimore and the University of Maryland respectively.

He was appointed a Hopkins Scholar for the years 1920-21, 1921-22 and 1922-23.