ciated most frequently with red autumn colors and flavones most frequently with purplish autumn colors, the methods of analysis employed here ought to be a valuable guide to the plant breeder. For example, *Acer rubrum* is frequently purplish red in Ithaca in the autumn and contains both precursors in quantity. By breeding out flavones it may be possible to produce a red variety containing no purple while by breeding out leuco-anthocyanin a purple variety may result. The starting point for the production of the red variety would be specimens containing smaller amounts of flavone. Specimens containing smaller amounts of leuco-anthocyanin would be selected in attempting to produce the purple variety. The data suggest many other breeding experiments such as the above. These possibilities make it desirable to increase further the precision of the analytical methods.

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Conclusions

The following conclusions are drawn from the results obtained.

1. Of 86 species of plants belonging to 50 genera which have been analyzed for leuco-anthocyanin and flavone, 84% contained demonstrable quantities of both precursors of the anthocyanins.

2. The probable precursor of the autumn color was found to be a flavone in 38% of the cases and a leuco-anthocyanin in 14% of the cases. Both precursors were present in quantity in 48% of the cases.

3. It is suggested that in a few cases a phlobaphene may be mistaken for a leuco-anthocyanin.

4. These results necessarily apply only to Ithaca and vicinity in the autumn of 1938.

5. In some cases all the species examined of a genus contained the same type of precursor of the autumn color. In other cases the genera were not homogeneous in this respect.

6. Leuco-anthocyanins appear to give rise to red autumn colors more frequently than purplish colors. The reverse appears to be the case when a flavone is the probable precursor because of a co-pigmenting effect of the flavone.

7. The apparent relationship between type of precursor and autumn color suggests a criterion based on analyses for flavone and leuco-anthocyanin for selecting plants from which to breed red or purple varieties.

8. This same method can be applied to fruits which develop anthocyanin pigments. The author hopes to be able to report this year on the precursors of the anthocyanins in strawberries, currants, cherries, barberries, raspberries, blackberries, peaches, apples, plums, grapes, etc.

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The Formation of Intermediate Compounds in Hydrocarbon Syntheses by the Friedel and Crafts Reaction, and the Preparation of Certain Symmetrical Trialkylbenzenes

BY JAMES F. NORRIS AND DAVID RUBINSTEIN[1]

In order to obtain more information in regard to the mechanism of the Friedel and Crafts reaction, certain of the substances described by Gustavson[2] as complexes of aluminum chloride and aromatic hydrocarbons have been studied. Menschutkin[3]

(1) From the thesis of David Rubinstein submitted in partial fulfilment for the degree of Doctor of Philosophy, 1934.

(2) G. Gustavson, *Ber.*, **11**, II, 1841 and 2151 (1878); *ibid.*, **16**, 784 R (1883); *J. prakt. Chem.*, [2] **42**, 250 (1890); [2] **68**, 209 (1903); [2] **72**, 57 (1905).

(3) Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **3**, 41, 1089 (1909); *Chem. Centr.*, **81**, I, 167 (1910); Kablukow and Saashanow, *Chem. Centr.*, **81**, I, 912 (1910).

showed earlier that aluminum bromide did not form a compound with toluene, but the fact is not significant in this connection, because the complexes described by Gustavson were formed in the presence of hydrogen chloride or hydrogen bromide.

In the study of the complexes aluminum bromide was used in most cases, because the compound is readily soluble in toluene, whereas aluminum chloride is insoluble or only slightly soluble. When dry hydrogen bromide was passed

into a solution of aluminum bromide (40.5 g.) in toluene at room temperature, drops of a heavy oil were formed almost immediately. The reaction was complete in twelve minutes. This oil after repeated washing with toluene was analyzed and was found to have the composition very near that represented by the formula $Al_2Br_6 \cdot 6C_6H_5CH_3$. A sample of this oil was kept at room temperature under a pressure of 10 to 11 mm. From time to time the loss in weight was determined and the weight of the residue was plotted against time. The smooth curve so produced approached after twenty-two hours a constant weight which was that of a complex having the composition $Al_2Br_6 \cdot C_6H_5CH_3$. No crystals separated. The product changed to a glassy solid when cooled with solid carbon dioxide and acetone. Next, a solution which contained the components in the proportion $Al_2Br_6 + 6C_6H_5CH_3$ and had not been treated with hydrogen bromide was evacuated under the conditions used before. As the evacuation proceeded crystals of aluminum bromide separated and at the end of one hour all the hydrocarbon had been removed.

A sample of the oil was evaporated at 11 mm. and the hydrocarbon recovered was condensed and studied. It boiled constantly at 111°. The hydrocarbon which remained in combination with the aluminum bromide was recovered; it boiled constantly at 111°. Evidently the toluene had not changed to any measurable degree into other hydrocarbons. When the complex which contained aluminum chloride (30 g.) and toluene was prepared, the materials had been heated for forty-five minutes to obtain it. In this case a part of the toluene was converted into benzene, xylenes, and other hydrocarbons.

An attempt was made to determine the molecular weight of the complex containing aluminum bromide and toluene. It was found that the lowering of the freezing point of p-dichlorobenzene could be used. The constant of the solvent was determined. The molecular weight of aluminum bromide was found to correspond to the formula Al_2Br_6 and that of toluene to $C_6H_5CH_3$. The molecular weight of the oil which approached the composition $Al_2Br_6 \cdot 6C_6H_5CH_3$ (mol. wt. 1086) was found to be 174. If the components of the oil had affected the freezing point separately the lowering of the latter would have given the average molecular weight 155. The results are in accord with the view that the oil in solution in p-

dichlorobenzene separated into toluene and a complex containing less than six molecules of the hydrocarbon. If the complex had the composition represented by the formula $Al_2Br_6 \cdot C_6H_5CH_3$ the freezing point lowering would have corresponded to the average molecular weight 181; the value found was 174.

The results of the behavior of the oil at a low pressure and the determination of its molecular weight showed that if the oil that approaches the composition $Al_2Br_6 \cdot 6C_6H_5CH_3$ is a true complex it is very easily decomposed. The results also indicate that a stable complex $Al_2Br_6 \cdot C_6H_5CH_3$ probably is formed. It is possible that in each case a relatively small percentage of combined hydrogen bromide is present. This point will be investigated. Complexes with other aromatic hydrocarbons are now being studied as to their composition, structure, stability and behavior with reagents.

The work indicated that stable complexes are formed in which $1Al_2Cl_6$ or $1Al_2Br_6$ is combined with 1 mole of aromatic hydrocarbon. It appeared of interest to determine how such complexes react with certain alkyl halides. Previous syntheses had been effected with relatively small proportions of aluminum chloride. Syntheses were carried out in which the molecular ratio of the aluminum chloride to hydrocarbon was varied. The results of these experiments are given later in this paper. The striking fact was discovered that when the molecular ratio of Al_2Cl_6 to benzene was one to one a yield of 85 to 90% of symmetrical triethylbenzene was obtained. The utilization of toluene gave 85% of symmetrical methyldiethylbenzene, and the methylation of crude m-xylene 50% of mesitylene: in this case the trimethylbenzene fraction contained 87% mesitylene.

The fact was surprising that such high yields of meta compounds were formed. It was evident from the results of the experiments in which the molecular ratios of the reactants were varied that the relative proportions of the aluminum chloride and hydrocarbon were a determining factor in the orientation of the alkyl groups introduced. In methylation temperature had a marked effect. At 0° the trimethyl derivative formed from benzene was largely pseudocumene whereas at the boiling point mesitylene was the chief product. In ethylation this effect of the temperature was not observed; the product was symmetrical triethylbenzene at low or high temperatures.

It appeared to be probable that meta orientation might result from the rearrangement of ortho and para compounds first formed. It is well known that rearrangement of alkyl groups in aromatic hydrocarbons is brought about by heating the latter with aluminum chloride. Experiments were undertaken with o-xylene and p-xylene to determine to what extent rearrangement took place. A relatively low temperature (55°) and short time (ten minutes) were used in the experiments in order to avoid conversion of the hydrocarbons into benzene, toluene and higher alkylated products. In the study of these rearrangements it was necessary to analyze mixtures of the three xylenes. The methods given in the literature are only roughly quantitative and are time consuming. The method used was based on the lowering of the freezing points of o-xylene and of p-xylene produced by a sample of the mixture to be analyzed. The freezing point of the o-xylene was not affected by the o-xylene in the mixture but was lowered by the p- and m-xylenes. p-Xylene was affected in a similar way. From the results in the two determinations the composition of the mixture could be calculated provided only xylenes were present. It was found that heating for ten minutes at 55° converted o-xylene into a mixture which contained 18.7% of m-xylene; under the same conditions the product from p-xylene contained 64.3% of the meta isomer.

Toluene was methylated at different temperatures and the xylenes formed were isolated and analyzed. At 0° when methyl chloride was used the xylenes formed contained 27.3% of the meta and 53.5% of the ortho isomer, at 106°, 98.2% meta and 1.8% ortho.

Experimental Details

Complex Containing Al_2Cl_6 and $C_6H_5CH_3$.—Thirty grams of aluminum chloride and 186 g. sulfur-free toluene dried over sodium (mol. ratio $1Al_2Cl_6$ to $4.5C_6H_5CH_3$) were placed in a three-necked 500-cc. flask provided with a glass stirrer, reflux condenser, and gas delivery tube leading to the bottom of the flask. The air was replaced by dry hydrogen chloride which was passed slowly through the mixture at 80–90°. The aluminum chloride gradually passed into solution and a heavy brown oil was formed. In about forty-five minutes when nearly all the chloride had dissolved the mixture was cooled and allowed to settle. A portion of the oil was separated and analyzed for aluminum and chlorine. Theoretical percentages for $Al_2Cl_6 \cdot 6C_6H_5CH_3$: Al, 6.58; Cl, 25.96. Found: Al, 6.55, 6.57; Cl, 24.80, 25.15. Ratio of Al to Cl, 1 to 2.88 and 1 to 2.90; ratio of Al_2Cl_6 to hydrocarbon 1 to 6.34 and 1 to 6.38.

The oil as decomposed with water and the hydrocarbon obtained was fractionated carefully. The fractions obtained were as follows: 7 cc. at 80°, 7 cc. at 80–111°. 86 cc. at 110.5–111°, 6 cc. at 111–139°, 10 cc. at 139°, 12 cc. which boiled up to 350°. The xylene fraction did not solidify at −70°; it evidently contained a large proportion of m-xylene.

These results showed that the method used did not yield a pure compound; they indicated, however, the possibility that a mixture of compounds had been formed and that the relation of the Al_2Cl_6 in them to hydrocarbon was 1 to 6.

When an attempt was made to prepare a similar oil from benzene and aluminum chloride, a product was formed after refluxing the mixture for about nine hours. Analyses showed that complex decompositions had taken place.

Complex Containing Al_2Br_6 and $C_6H_5CH_3$.—Nitrogen was passed through 120 g. of dry sulfur-free $C_6H_5CH_3$ to remove dissolved air, 40.5 g. of resublimed Al_2Br_6 added, and pure hydrogen bromide was bubbled slowly through the rapidly stirred mixture at room temperature. The amount of hydrogen bromide used was about 0.5 mole based on the Al_2Br_6 used. The separation of the oil was complete in twelve minutes. The oil was shaken five times with toluene in the absence of air and moisture to remove any excess of Al_2Br_6 and hydrogen bromide. It was found that 1 cc. of the complex dissolved in about 60 cc. of toluene.

Samples of the oil made at different times gave the following results. Theoretical for $Al_2Br_6 \cdot 6C_6H_5CH_3$: Al, 4.97; Br, 44.2. Found: I, Al, 4.70; Br, 44.8, 44.8; ratio Al to Br, 1 to 3.2; Al_2Br_6 to $C_6H_5CH_3$, 1 to 5.94. Found: II, Al, 4.61, 4.58; Br, 44.8, 44.8; ratio Al to Br, 1 to 3.28; Al_2Br_6 to $C_6H_5 \cdot CH_3$, 1 to 5.94. The results are in satisfactory agreement with the formula indicated for the complex with the exception that the values for aluminum are low. It is possible that the complex contains a small percentage of hydrogen bromide. This possibility will be investigated.

Behavior of the Complex $Al_2Br_6 \cdot 6C_6H_5CH_3$ under Diminished Pressure.—Twenty-two grams of the complex was placed in a flask attached by a ground glass joint to a stopcock connected to a trap immersed in a mixture of carbon dioxide snow and acetone. The system was evacuated by a pump to 10–11 mm. At intervals of fifteen minutes the evacuation was stopped, the flask filled with dry nitrogen and weighed. The weights of the material in the flask when plotted formed a smooth curve. The complex used contained 4.70% Al. At the end of three and one-half hours the material in the flask contained 8.06% Al; after twenty-two hours, 8.35% Al. The complex $Al_2Br_6 \cdot C_6H_5CH_3$ contains 8.63% Al. The results of the analyses are in accord with the determinations of the loss in weight of the original complex. The final residue in the flask did not crystallize when held for one hundred and thirty-five minutes in a mixture of carbon dioxide snow and acetone.

When a mixture of Al_2Br_6 and toluene was evaporated in the same way all the hydrocarbon was lost and the aluminum halide was obtained.

A sample of the complex made from 29 g. of Al_2Br_6 and 31 g. of toluene was prepared. It was not washed with

toluene, as it was thought that such treatment might remove any decomposition products formed. It was held at 10–11 mm. and the hydrocarbon volatilized was distilled through a 13-turn Davis column. The first 5 cc. was again fractionated in order to detect the presence of benzene. All the material recovered boiled at 111°. The stable complex in the flask was decomposed by ice and hydrochloric acid. The hydrocarbon obtained measured 6.5 cc. and was slightly yellow in color but boiled constantly at 111°.

Molecular Weight of the Aluminum Bromide–Toluene Complex.—It was necessary to select as the solvent a compound that did not react or form a compound with aluminum bromide. p-Dichlorobenzene was found to suit the conditions. The freezing point lowerings produced by Al_2Br_6 and C_6H_6 were determined and the constant was found to be 72.3.

The lowering of the freezing point of the solvent produced by a definite weight of the bromide was first determined. Benzene was added and the lowering noted. The solutes acted independently and the lowerings of the freezing points in each case gave the correct molecular weights of the two solutes. It was evident that no complex was formed. The results were as follows: p-dichlorobenzene 18.14 g., Al_2Br_6 0.4818 g., depression 0.356°. Theoretical mol. wt. Al_2Br_6 534, found 539. Benzene added: I, 0.1138 g., depression 0.588°; II, 0.2644 g., depression 1.333°. Theoretical mol. wt. C_6H_6 78, found 77.1 and 79.1.

With the use of the constant 72.3 the molecular weight of the complex $Al_2Br_6\cdot6C_6H_5CH_3$ was determined. p-Dichlorobenzene 23.47 g.; complex, 0.1427, 0.2713, 0.4608; lowerings 0.242, 0.458, 0.802°. Mol. wts., 181, 182, 177. Results with a second preparation gave mol. wt. 164, 168.

The molecular weight of the complex $Al_2Br_6\cdot6C_6H_5CH_3$ is 1086; it evidently did not exist in solution. The conclusions drawn from these experiments are given in the first part of this paper.

The Ethylation of Benzene with Ethyl Bromide.—Gustavson was of the opinion that a stable complex was formed which contained aluminum chloride and s-triethylbenzene in the molecular ratio $1Al_2Cl_6$ to $1C_6H_3$-$(C_2H_5)_3$. It appeared to be of interest to determine whether the compound was formed when Al_2Cl_6, C_6H_6, and C_2H_5Br in the molecular ratios 1:1:3 were allowed to react. The experiment is described in detail because the yield of 1,3,5-triethylbenzene was about 90% of the theoretical and the procedure used was that followed in a number of experiments, the results of which are reported in tabular form.

The substances used were: 78 g. C_6H_6 (1 mole), 335 g. C_2H_5Br (3 moles), and 267 g. Al_2Cl_6 (1 mole); theoretical yield $C_6H_3(C_2H_5)_3$, 162 g. The apparatus consisted of a 1-liter flask having three necks, which were fitted to a long water condenser, a thermometer, and a small separatory funnel. At the top of the condenser was a tube bent at two right angles, which dipped under a mixture of ice and water. This arrangement served to condense the ethyl bromide carried out of the reaction flask by the evolved hydrogen bromide. Toward the end of the reaction an amount of dry ethyl bromide equal to that recovered was

added to the flask. When benzene or ethyl bromide is added to the flask caution is necessary to avoid the introduction of water in the flask. The Al_2Cl_6 (Mallinckrodt) was added to the flask, which was cooled in an ice–salt mixture. About one-half to two-thirds of the ethyl bromide was next added to moisten the Al_2Cl_6 after shaking. The benzene was added slowly through the separatory funnel in the course of one-half hour. The bulb of the thermometer in the mixture registered below 0°. The rest of the ethyl bromide was added cautiously during about one-half hour. The flask was left in the freezing mixture and allowed to come to room temperature. It was shaken occasionally to facilitate the evolution of hydrogen bromide. The preparation should be started in the morning and left overnight at room temperature. An experiment showed that at the end of four hours the hydrocarbon formed boiled at 195–218°; when the reaction was allowed to proceed all night the product began to distil at 216°.

The clear yellow intermediate product was decomposed by pouring it with motor stirring into a 4-liter beaker one-eighth filled with crushed ice and 50 cc. of concentrated hydrochloric acid. Ice was added from time to time. The hydrocarbon was separated, shaken with sodium hydroxide, and dried with about 3 g. of calcium chloride.

The hydrocarbon was twice fractionated through a $12'' \times 1/2''$ (30 × 1.3 cm.) Vigreux column lagged with $2^1/_2''$ (6 cm.) magnesia pipe covering. The amount of triethylbenzene obtained boiling at 215–216° varied from 85 to 90% of the theoretical yield. By further fractionation the temperature range was reduced to 215–215.2° with a loss in weight of 5%.

On account of the large amount of Al_2Cl_6 required, an experiment was made in which the relatively cheap commercial chloride made by the Gulf Refining Company was used. The yield of triethylbenzene boiling at 215.2–216.2° was 85% when 1 mole C_6H_6, 3.3 moles C_2H_5Br, and 1.1 moles Al_2Cl_6 were used.

Preparation of Triethylbenzene from Ethyl Chloride, Benzene and Commercial Aluminum Chloride.—On account of the volatility of ethyl chloride it is necessary to condense and return to the reaction flask the part that is carried away by the evolved hydrogen chloride. A reflux spiral condenser cooled by carbon dioxide snow was used.

The materials were brought together at less than −50°. When the temperature reached −20° the reaction flask was placed in a salt–ice bath. In about four hours the temperature rose to 0°. After standing overnight at room temperature the product was decomposed.

In one experiment in which the reactants were in the mole ratio $1C_6H_6$, $3C_2H_5Cl$, $1Al_2Cl_6$, the yield of C_6H_3-$(C_2H_5)_3$ was 83.5%. The mole fractions of the hydrocarbon mixture were as follows: $C_6H_3(C_2H_5)_3$ 86.3%, C_6H_2-$(C_2H_5)_4$ 10.8%, $C_6H(C_2H_5)_5$ 2.9%. When the ethyl chloride was increased to 3.3 moles the corresponding figures were 75.6 and 78.7%, 18.1 and 3.2%.

Identification of the Triethylbenzene Formed in the Reaction.—The hydrocarbon used was that prepared from commercial aluminum chloride and ethyl chloride. The sample boiled at 215.2–216.2°. It was brominated at about 0°, in the absence of light, with the aid of a trace of iodine. The product was washed with a solution of so-

dium hydroxide, dried, and weighed. From 7.454 g. of hydrocarbon was obtained 18.30 g. which melted at 100–102°. The theoretical yield of tribromotriethylbenzene is 18.40 g. After recrystallization from alcohol 17.50 g. (m. p. 102.7–103.5°) was recovered. Three recrystallizations did not raise the melting point. The melting point of 2,4,6-tribromo-1,3,5-triethylbenzene is given in the literature as 105–106°[4] and as 103.5–104°.[5] The melting point of 3,5,6-tribromo-1,2,4-triethylbenzene is reported to be 88–89°.

When the hydrocarbon was nitrated nearly the theoretical yield of the trinitro derivative was obtained; it melted at 110.5–111.5°, the recorded melting point.

Trimesic acid was obtained as the result of the oxidation of the hydrocarbon. It melted at 362° (381° corr.). The recorded melting points are 360, 375–380, and 380° (corr.). The acid was shown to be tribasic; its trimethyl ester melted at 144–144.5° (recorded m. p. 142°, 142°, 144°). The recorded melting points of the corresponding esters of the isomeric tricarboxylic acids are 101° and −13°.

The triethylbenzene was condensed with carbamyl chloride. The triethylbenzamide melted at 155–156° and the acid prepared from it at 112–113°. These values agree with the recorded ones for 1,3,5-triethylbenzoic acid and its amide.

The Effect of the Change in Molecular Ratios of the Reactants on the Products Obtained as the Result of the Ethylation of Benzene.—The results of a number of experiments are given in Table I. The procedures used were similar to that described under triethylbenzene. The products were separated by careful fractional distillation. The breaks in the distillation curves were sharp.

TABLE I

The figures give the number of moles of the reactants and products formed compared with 1 mole of C_6H_6.

No. of expt.	1	2	3	4	5	6
C_2H_5Br	3.06	3.06	3.1	4.2	2.06	1.05
Al_2Cl_6	1.05	0.52	0.17	1	0.35	0.35
Products formed						
$C_6H_5C_2H_5$	...	.016	.066	..	.17	.08
$C_6H_4(C_2H_5)_2$	0.016	.02	.09	..	.06	.11
$C_6H_3(C_2H_5)_3$	.93	.79	.17	.79	.53	.24
$C_6H_2(C_2H_5)_4$	.018	.10	.11	.17	.01	.005
$C_6H(C_2H_5)_5$	...	...	.11	.02	..	...
$C_6(C_2H_5)_6$	...	...	.02	..	..	...

The conclusions that can be drawn from the table are as follows. I. The ratio of the moles of benzene to the moles of aluminum chloride has a marked effect on the products formed. This is clear from the comparison of experiments 1, 2, and 3. In experiment 3 all the possible ethyl derivatives were obtained. The result in this case is in accord with previous experience. II. The yield of triethylbenzene is determined largely by the amount of aluminum chloride used; the molecular ratio of benzene to ethyl bromide has a relatively small effect. In experiment 4, 4.2 moles of C_2H_5Br to 1 of C_6H_6 gave 79% triethylbenzene and higher substitution products. In experiment 5 in which the mole ratio was 1:2:0.35 there was

present only enough bromide to convert the benzene into diethylbenzene, yet the yield of triethylbenzene was 78% of that theoretically possible if all the bromide had been converted into triethylbenzene. In experiment 6 (mole ratio 1:1.05:0.35) the yield of triethylbenzene was 69% of that theoretically possible calculated from the ethyl bromide used. These results show clearly that triethylbenzene has a tendency to be formed and that the amount formed is largely dependent on the amount of aluminum chloride present with which it can unite. The results indicate that a complex is formed in which there are $1Al_2Cl_6$ and $1C_6H_3(C_2H_5)_3$.

The Ethylation of Toluene.—The experiments were carried out at −12 to −8°. The reactions were allowed to proceed overnight. The methyldiethylbenzene obtained after fractionation boiled at 199.8–200°. In an experiment 0.5 mole of toluene was used and the molar proportions were $1C_6H_5CH_3$, $2.08C_2H_5Br$, $1.1Al_2Cl_6$. The yield of methyldiethylbenzene was 78.4%. Based on 1 mole there was formed also 0.04 mole of ethyltoluene and 0.09 triethyltoluene. In a second experiment the molar proportions were $1C_6H_5CH_3$, $1.09C_2H_5Br$, and $0.5Al_2Cl_6$. Although the ethyl bromide used was only one-half of that required, the yield of diethyltoluene obtained was 82% of that theoretically possible.

A sample of the hydrocarbon was brominated in the way used with triethylbenzene. From 7.4882 g. of hydrocarbon 19.5537 g. of tribromo derivative was obtained which is a yield of 100.3% of the theoretical. The product before crystallization melted at 67–68°. After one crystallization in alcohol it melted at 68.2–68.8°; and five recrystallizations did not change the melting point. As this value was not in accord with the melting point given for the tribromo derivative of 1,3,5-methyldiethylbenzene, an analysis for bromine was made: calculated for 3Br atoms 62.30%; Br found 62.68, 62.68, 62.62.

Jacobson[6] prepared the hydrocarbon used by him by condensing methyl ethyl ketone. The bromo derivative, which was not analyzed, melted at 206°. Markownikoff[7] isolated the sample used by him from Russian petroleum. Its bromo derivative melted at 206.5°.

A nitro derivative of the methyldiethylbenzene was prepared; it was shown by analysis to contain $3NO_2$ groups, calcd. 14.84% N_2, found 15.07% N_2. The compound was not changed when it was heated with a boiling solution of sodium hydroxide (6 N). This fact showed that the nitro groups were joined to the ring. The nitro derivative melted at 106–106.5°. It is reported in the literature[8] that the trinitro derivative of 1,3,5-methyldiethylbenzene melts at 86–87°. The hydrocarbon used boiled over a range of 5° and no conclusive proof of its structure is given.

Attempts to prove the structure of our hydrocarbon by oxidation were not entirely satisfactory, because the product formed was shown by the determination of the neutralization equivalent not to be a pure tribasic acid. The methyl ester prepared from the crude acid melted at 139–141°. The recorded melting point of the trimethyl ester of trimesic acid (1,3,5) is 144°. From the crude acid

(4) Gattermann, Fritz and Beck, Ber., 32, 1122 (1899).

(5) Gustavson, J. prakt. Chemie, [2] 68, 212 (1903).

(6) Jacobson, Ber., 7, 1430 (1874).

(7) Markownikoff, Ann., 234, 107 (1886).

(8) Gattermann, Fritz and Beck, Ber., 32, 1122 (1899).

a sample was obtained by fractional crystallization which when mixed with an equal part of trimesic acid (m. p. 380–381°) melted at 378–379°. From the bromination and nitration experiments, which showed that the hydrocarbon which boiled within a 0.2° range was essentially uniform in composition, and from the results of the oxidation experiments, it is probable that the hydrocarbon has the symmetrical structure. Further study of the hydrocarbon is now in progress.

Ethylation of *m*-Xylene.—Commercial "meta" xylene, ethyl bromide, and aluminum chloride in the mole ratio 1:1:1, respectively, and the procedure described above were used; the temperature was −10–0°. During the reaction neither hydrogen chloride nor hydrogen bromide was evolved. The hydrocarbon mixture obtained was fractionated through a 13-turn Davis column. The yield of hydrocarbon which boiled at 183.2° was 45%. When oxidized by dilute nitric acid a mixture of acids was obtained. Steam distillation separated a monobasic acid which was volatile. It melted at 165–166°, which is the melting point of mesitylenic acid.

The tribromo derivative prepared from a sample boiling within one degree was analyzed: calcd. 64.65% Br_2; found 64.80, 64.80%. It melted before crystallization at 87.5–88.5°. Three recrystallizations from 95% alcohol raised the melting point to 89–90°. Jacobson[8] gives 218° as the melting point of the tribromo derivative of 1,3,5-ethyl dimethylbenzene. Tohl and Geyger[9] also give 218°. They prepared from their hydrocarbon a sulfonamide which melted at 126°. The sulfonamide prepared from our hydrocarbon melted at 126°. Stahle[10] prepared the sulfonamides from 1,3,5- and 1,2,4-ethyl-*m*-xylene: the former melted at 126° and the latter at 148°.

The trinitro derivative of our hydrocarbon melted at 116.5 to 117.5°. Jacobson reports 238° as the melting point of the trinitro derivatives of his hydrocarbon which he considers to have the 1,3,5-structure. This melting point is checked by Tohl and Geyger. Further study is necessary to determine definitely the structure of the hydrocarbon.

The Methylation of Benzene.—Benzene (32.8 g.) was treated with CH_3Br and Al_2Cl_6 (mol. ratio 1:3:1) under the conditions used in the preparation of 1,3,5-triethylbenzene. The reaction was started at about −40°. The product (53 cc.) when fractionated through a 10″ Vigreux column yielded 23 cc. of trimethylbenzene (b. p. 168–171.5°). The low yield is due to the fact that a part of the methyl bromide was carried off by the escaping acid. Ten cc. of the hydrocarbon was sulfonated when it was heated on a steam-bath for twenty minutes with 10 cc. of concentrated sulfuric acid. On cooling the sulfonic acid crystallized. Three grams of the latter was heated with 10 cc. of concentrated hydrochloric acid for one hour. No hydrocarbon separated. A control experiment with the sulfonic acid derived from mesitylene showed that under these conditions mesitylene was formed. The sulfonic acid after crystallization from hot hydrochloric acid contains water of crystallization. After drying overnight it melted at 104–108°. The sulfonic acid derived from mesitylene melts at 77° and that from pseudocumene at 111–112°.

(9) Tohl and Geyger, *Ber.*, **25**, 1533 (1892).

(10) J. Stahle, *ibid.*, **23**, 988 (1890).

A sample of the hydrocarbon was oxidized by potassium permanganate. The yield of acid obtained was 50% of the theoretical. Without crystallization the acid melted at 218–220°. The 1,2,3-tricarboxylic acid derived from benzene melts at 190°, the 1,3,5 at 380°, and the 1,2,4 at 216–220°. These results show that the hydrocarbon obtained was largely the 1,2,4-trimethyl derivative. It is probable that a careful study would result in the development of a good method for the preparation of pseudocumene with a high yield.

The Orienting Effect of Methyl and Ethyl in the Friedel and Crafts Reaction.—The literature on this subject is voluminous and conflicting. Since the orienting effect of methyl and ethyl in our experiments appeared to be quite different, it seemed desirable to study the question further. It was discovered that change in the temperature at which the reaction is carried out has a marked effect. Experiments were carried out under conditions which would lead to the formation of the xylene from toluene. It was necessary to determine the proportions of the three xylenes formed under different conditions. The method used is outlined in the first part of this paper. The constant for *p*-xylene (m. p. 12.9°) was determined by using toluene as the solute. It was found to be 41.6. The constant for *o*-xylene was 41. The method was tested by analyzing known mixtures. The mixtures formed in the experiments were separated by fractional distillation. They were shown to consist of xylenes only by determination of their molecular weights (106).

Toluene was methylated under the conditions which would lead to the largest amounts of xylenes and the smallest amounts of higher substitution products. The time during which the reaction took place was as short as was consistent with a satisfactory yield.

An excess of toluene was used in all the experiments. The amounts of reagents were as follows: $C_6H_5CH_3$ 200 cc. (1.9 moles), 60 g. Al_2Cl_6 (0.45 mole), and CH_3Br 59 g. (0.62 mole). In the experiment at −5° the reactants were cooled to −40° and allowed to rise in temperature to −3° and then held at −5° for one hour. The product was treated with ice water, the hydrocarbon isolated and fractionated with a Davis column. The xylene fraction (139–143°) amounted to 17 cc.

In an experiment at 94° the vapor of methyl bromide was passed into the mixture of toluene and aluminum chloride which had been heated on a steam-bath. At the end of twenty minutes the reaction appeared to be complete and the product was decomposed. The refractionated xylene (b. p. 138–139.8°) amounted to 21 cc. From this was obtained 17 cc. which boiled at 139–139.8° and yielded crystals at −74°.

In the methylation of toluene (1.5 moles) at 106° with methyl chloride (0.4 mole) the latter was passed very rapidly into the mixture of the hydrocarbon and aluminum chloride (1.5 moles) which had been heated on a steam-bath. The temperature rose to 106°. The introduction of 30 g. of methyl chloride required from three to four minutes: very little of the chloride passed through without reacting. The mixture was cooled and decomposed. There was obtained 32 cc. of xylene (b. p. 137–140°). Six cc. of higher boiling products was obtained.

In the methylation with methyl chloride at 55° the re-

action was allowed to take place for six minutes. The xylene fraction (b. p. 136–143°) measured 47 cc. when the quantities used were the same as those at 106°.

In the methylation with methyl chloride at 0° the reaction was allowed to proceed for two hours; 28 cc. of xylene (b. p. 138–146°) was obtained. The proportions of the three xylenes obtained in these experiments are given in Table II.

TABLE II

| Methylating agent | Temp., °C. | Per cent. xylenes | | |
		Ortho	Para	Meta
CH₃Br	−3	44.5	27.5	28.0
CH₃Br	5–18	45.6	28.0	26.4
CH₃Br + AlBr₃–	−3	49.1	20.4	30.5
Toluene complex				
CH₃Br	94	8.4	9.0	83.6
CH₃Cl	0	53.5	19.2	27.3
CH₃Cl	55	12.2	0.7	87.1
CH₃Cl	106	1.8	0.0	98.2

From the table it can be seen that the temperature has a marked effect on the position taken by the methyl radical when introduced into toluene. At the higher temperatures the product was largely the meta isomer. It seemed improbable that the relatively slight change in temperature would change methyl from an ortho–para to a meta orienting group. Since it has been shown frequently that aluminum chloride produces a rearrangement of the xylenes, experiments were carried out to determine whether under the conditions of our experiments the rearrangement of ortho and para xylenes to the meta isomer could take place. The change was studied at 55° in the presence of hydrogen chloride, since the latter was present during the formation of the xylenes from toluene. The xylene (15 g.) and aluminum chloride (19 g.) each heated to 55°, were mixed and held at that temperature for ten minutes while a stream of hydrogen chloride (1 to 2 bubbles per second) was passed through the mixture which was shaken. In the case of o-xylene about two-thirds of the aluminum chloride passed into solution; in the case of p-xylene all the chloride had changed to a brown oil in five minutes. The products were decomposed by water and the hydrocarbons fractionated through a Davis column. No toluene or trimethylbenzene was found. The mixtures were analyzed by the method outlined above. o-Xylene yielded a mixture which contained 81.6% ortho, 0.0% para, and 18.7% meta. p-Xylene gave 0.6% ortho, 35.1% para, and 64.3% meta.

Preparation of Mesitylene.—The methylation of benzene at 0° yielded chiefly pseudocumene. From the results obtained in the experiments on the rearrangements of the xylenes, it appeared possible to prepare mesitylene if higher temperatures and the proper amount of aluminum chloride were used. The preparation is described in detail because it is the only method of preparing mesitylene, with a satisfactory yield, by methylation with a methyl halide.

Eastman technical m-xylene was used. It was found by analysis to contain 15.2% o-xylene, and 23.8% p-xylene. The remaining 61% was m-xylene plus the small amounts of other substances present in commercial m-xylene. Commercial aluminum chloride was used. It is denser than the pure white variety and forms a mixture with the hydrocarbon that can be stirred.

The reaction was carried out in a 1-liter flask with 3 necks. The large central opening was equipped with a stirrer which passed through a closely fitting glass bearing the lower end of which was below the surface of the liquid in the flask. Through one of the side openings a gas delivery tube passed to the bottom of the flask. The other opening was fitted to a condenser by means of an adapter containing a thermometer.

Two moles of technical m-xylene (212 g.) was added to the flask and heated to 120°. One mole of technical aluminum chloride (540 g.) was added. The mixture was stirred and when the temperature was 100° the source of heat was removed and methyl chloride was introduced from a tank which was placed on a scale. The methyl chloride passed through concentrated sulfuric acid and a tube filled with cotton and then into the flask. The rate was about 1.5 g. per minute. In from thirty to sixty minutes 91 g. (1.8 moles) was added. The methyl chloride caused the aluminum chloride to go into solution rapidly. The significant observation was made that no hydrogen chloride was evolved until about two-thirds of the methyl chloride had been added. The cause for this behavior will be studied.

The brown oil formed was decomposed in the usual way and the hydrocarbons washed, dried and distilled through a 10″ (25 cm.) Vigreux column. The fraction boiling at 150–175° measured 200 cc. From the fraction 175–191° (9.5 cc.) was recovered 5 cc. boiling up to 175°. The 205 cc. was sulfonated by heating with 275 cc. of concentrated sulfuric acid. The mixture was heated for two hours. The contents of the flask were allowed to cool slightly and before the sulfonic acids crystallized the mixture was poured into 700 cc. of concentrated hydrochloric acid in a flask cooled by ice water. The flask was attached to a reflux condenser and stirred and heated on a steam-bath. Hydrolysis was complete in about one hour. The method is simpler than the one recommended in the literature. The separation of mesitylene from lower boiling hydrocarbons was so complete that the oil on fractionation through the 10″ (25 cm.) column begins to boil at 164.5°. The cut boiling at 164.5–167° measured 148 cc. From the next cut (13 cc. 167–175°) was recovered by a second distillation 10 cc. boiling up to 165.5°. The total product was 158 cc. which boiled over a 2° range. Of this 95% boiled within 1.5°, and 84% within 1°. Based on the methyl chloride, the yield was 63% of the theoretical.

In order to determine the purity of the mesitylene a cooling curve was made. The hydrocarbon was fractionated through a Davis column and 158 cc. yielded 147 cc. which boiled at 164.5–164.8°. A cooling curve of this sample showed that it was at least 99.7% mesitylene. The product from another preparation (1 mole technical m-xylene, 0.83 mole CH₃Cl, and 1 mole Al₂Cl₆) was fractionated repeatedly before sulfonation. The numbers of moles of the components of the mixture were as follows: C₆H₆ 0.006, C₆H₅CH₃ 0.038, C₆H₄(CH₃)₂ 0.209, C₆H₃(CH₃)₃ 0.49, C₆H₂(CH₃)₄ 0.11.

Summary

1. The heavy oil that separates when a solution of aluminum bromide is treated with hydrogen bromide at room temperature has a composi-

tion that closely approaches that represented by the formula $Al_2Br_6 \cdot 6C_6H_5CH_3$.

2. When this oil is evaporated at room temperature at 10 to 11 mm. pressure the non-volatile product appears to have the formula $Al_2Br_6 \cdot C_6H_5CH_3$.

3. The results of the determination of the molecular weight of the oil indicate that the latter when dissolved was converted into toluene and the complex $Al_2Br_6 \cdot C_6H_5CH_3$.

4. The ethylation of benzene with ethyl chloride and ethyl bromide when the molecular ratio of Al_2Cl_6 to C_6H_6 was 1 to 1 gave yields of s-triethylbenzene from 85 to 90% of the theoretical.

5. Excellent yields of s-ethyldimethylbenzene and s-diethylmethylbenzene were obtained.

6. A series of experiments showed that the molecular ratios of Al_2Cl_6 to hydrocarbon was the determining factor in the relative proportions in which the several alkylated products were formed.

7. At 0° the chief product of the methylation of benzene with 3 moles of halide is 1,2,4-trimethylbenzene; at 100° the product is chiefly 1,3,5-trimethylbenzene.

8. The rearrangement of o-xylene and p-xylene to a mixture of the three isomers was studied.

9. The influence of temperature on the structure of the xylenes formed when toluene is methylated showed that the low temperature favors the formation of the ortho and para compounds; at 100° the chief product is the meta isomer. In ethylation the product was largely meta at the two temperatures.

10. Detailed directions are given for the preparation of the symmetrical tri derivatives because the methods give much higher yields and purer products than have been obtained in the past.


Relative Reactivities of Organometallic Compounds. XXVI.* Interconversion of Bismuth and Alkali Metals

By Henry Gilman, H. L. Yablunky and A. C. Svigoon

Interconversion reactions are related to the relative reactivities of organometallic compounds.[1] Incidental to studies on the metalation of radicals attached to heavy metals,[2] we have now observed that when triarylbismuth compounds react with organoalkali compounds the following typical interconversion occurs.

$(p\text{-}CH_3C_6H_4)_3Bi + 3n\text{-}C_4H_9Li \longrightarrow$
$3p\text{-}CH_3C_6H_4Li + (n\text{-}C_4H_9)_3Bi$
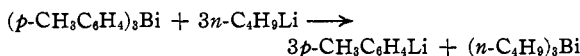
The reaction probably takes place step-wise with the intermediate formation of unsymmetrical organometallic compounds.[2] Pertinent illustrations of the formation of unsymmetrical compounds in interconversions of bismuth compounds are to be found in studies by Challenger and Ridgway.[3] These authors observed that tri-α-

naphthylbismuth and diphenylmercury gave not only di-α-naphthylmercury and triphenylbismuth, but also diphenyl-α-naphthylbismuth. They also noted that triphenylbismuth and tri-α-naphthylbismuth reacted readily to give diphenyl-α-naphthylbismuth.

Tri-p-chlorophenylbismuth was one of the several triarylbismuth compounds examined in this study. This compound was selected because recent studies have shown that metalation of a polynuclear compound occurs preferentially in that nucleus having a so-called negative atom or group. For example, metalation of p-bromodiphenyl ether takes place in the bromophenyl and not in the phenyl nucleus.[4] The absence of metalation in the several typical triarylbismuth compounds investigated indicates that metalation is without promise as a possible indirect means of introducing water-solubilizing groups into triarylbismuth compounds.

The interconversion is probably an equilibrium

(*) Paper XXV, This Journal, 61, 957 (1939).

(1) For a general discussion of interconversion reactions of organometallic compounds, see pp. 481–485 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938.

(2) Gilman and Bebb, This Journal, 61, 109 (1939).

(3) Challenger and Ridgway, J. Chem. Soc., 121, 104 (1922). These unsymmetrical compounds can be prepared conveniently in liquid ammonia by interaction of R_2BiNa with $R'X$ compounds. The R_2BiNa compounds are first prepared from R_2BiX compounds and sodium in liquid ammonia.

(4) Gilman, Langham and Jacoby, This Journal, 61, 106 (1939). See, also, Wittig, Pockels and Dröge, Ber., 71, 1903 (1938); and Gilman, Cheney and Willis, This Journal, 61, 951 (1939).