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THE ACTION OF TRIOXYMETHYLENE  
ON VARIOUS HYDROCARBONS  
IN THE PRESENCE OF  
ALUMINIUM CHLORIDE .

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A Thesis

submitted to the Faculty of the Graduate School  
of the

University of Minnesota

by

Vaman R. Kokatnur

in partial fulfillment of the requirements  
for the degree of  
MASTER OF SCIENCE.

May 1914.

REPORT  
of  
COMMITTEE ON THESIS

THE undersigned, acting as a committee of  
the Graduate School, have read the accompanying  
thesis submitted by Mr. Vaman R. Kokatnur,  
for the degree of Master of Science.

They approve it as a thesis meeting the require-  
ments of the Graduate School of the University of  
Minnesota, and recommend that it be accepted in  
partial fulfillment of the requirements for the  
degree of Master of Science.

G. B. Frankforter  
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May 26, 1914

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The Reaction of Trioxymethylene on Various Hydrocarbons in the Presence of Aluminium Chloride.

Every year, in fact every day adds a great number of organic compounds to the already voluminous list. The organic chemistry of to-day is an undying monument to the geni of men like Wöhler, Liebig, Baeyer, Berzelius, Berthelet and Fisher. Since the days of Wöhler and Liebig the number of artificial organic compounds has been tremendously increased, and to-day they number not less than one hundred thousand.

Yet everyone will admit that we are just on the threshold of this vast unexplored domain. The total number of compounds known to us to-day is but a tiny drop in the limitless ocean of possible ones yet to come. It has been shown mathematically by Cayley (Phil. Mag.(4) 47,444) that the number of hydrocarbon isomerides is enormous, even in case of compounds of simple empirical formula. He showed that Tredecane,  $C_{13}H_{28}$ , is capable of existing in 802 different isomeric forms. Triacontane,  $C_{30}H_{62}$  may exist in millions

of different forms, while Hexacontane,  $C_{60}H_{122}$ , according to the same logic, may form isomerides beyond human comprehension, and yet the innumerable derivatives and substitution-products are not included in this calculation.

The general methods used to build up these various organic compounds are known in chemistry as synthetic methods. Out of the many synthetic methods thus used, is one discovered by Friedel and Crafts. This historical reaction (Compt. rend. 84,1392) or (Ann.chim.Phys. (6) 1449), known after the names of its discoverers, is classed as one of the most important catalytic reactions.

Catalysis may be defined as a chemical change, either analytic or synthetic, brought about by the influence of the mere presence of a substance, but without that substance entering permanently into the chemical reaction; or, as stated by Ostwald, an increase in the reaction-velocity beyond the normal, by some substance which does not enter the reaction.

Such catalytic changes are classified under four heads: (1) addition, (2) polymerization, (3) substitution, and (4), condensation. Of these, the last two are of interest in the present paper. Most of the condensation reactions are either brought about by Friedel and Crafts' reaction or by the Baeyer's reaction, the one eliminating HCl and the other H<sub>2</sub>O.

Though these two reactions have been regarded as separate and distinct, they are in many cases identical as will be shown in the course of this paper. For, anhydrous aluminium chloride not only acts as a catalyzer by eliminating HCl but as a substitute for H<sub>2</sub>SO<sub>4</sub> in removing a molecule of water from the reacting compounds; This has been shown by Doctors Frankforter and Kritchevsky that when a hydrocarbon, presumably benzene, and an aldehyde, as chloral, are brought together in the presence of aluminium chloride at 0°, a reaction analogous to the Baeyer reaction takes place, (U. of M. Studies, Bull. No. 2).

Friedel and Crafts found that anhydrous aluminium

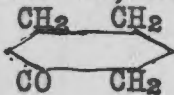
chloride when added to amyl chloride gave a vigorous reaction, liberating HCl and forming at the same time hydrocarbons which did not absorb bromine. When, however, the reaction was carried out in the presence of a hydrocarbon, a compound consisting of the two radicals, one of hydrocarbon and the other of amyl chloride, was formed, thus  $C_5H_{11}Cl + C_6H_6 + (AlCl_3) = C_6H_5-C_5H_{11} + HCl + (AlCl_3)$ .

Friedel and Crafts never attempted to explain their well-known reaction, and even to-day this question has not been satisfactorily solved. It was Gustavson (Bull. Soc. Chim., 42, 325 or Ber. 13, 157), however, who first drew attention to the explanation of Friedel and Crafts' reaction. He assumed that an organic aluminium compound was first formed as an intermediate product which further broke down, liberating the condensed hydrocarbon and regenerating the aluminium chloride thus:  $C_6H_6 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + HCl$ .



It is interesting to note in this connection that the

quantity of aluminium chloride required to bring about the reaction, is always greater than would be justified as a catalyzer.

Since the discovery of this great reaction, chemists have used it in various ways in order to bring about certain chemical changes, in some cases under entirely different conditions. It has been used to obtain ketones, aldehydes, and acids besides hydrocarbons. It has also been used for effecting internal condensation by Kipping (Trans.Chem.Soc.65, 484, Ibid. 75, 144), thus:  $C_6H_5 - CH_2 - CH_2 - CH_2 - CH_2 - COCl = C_6H_4$    $CH_2$ .

Further, Scholl and Seer have shown (Monatsh. 33,1) that anhydrous aluminium chloride in a few cases actually breaks off free hydrogen instead of free HCl. e.g.  $C_5H_{12} + Al_2Cl_6 = C_5H_{10} + H_2 + Al_2Cl_6$ . Recently Paye (Ann.chim. Phys. 225, 196) has shown that aluminium chloride possesses the power of transposing chlorine to certain organic compounds. It has been also shown by Jacobsen (Ber. 18, 339) that the condensation reaction is sometimes reversed under suitable conditions

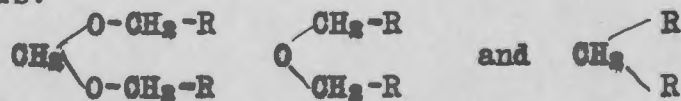


as is seen in case of Hexamethylbenzene when the methyl groups are successively detached forming all the lower homologues of benzene. Another very interesting behavior has been observed by Anschütz (Ann. 235, 177-192) in connection with this reaction, namely, that the methyl groups are simultaneously detached and transferred from one position of the hydrocarbon to another, both in building up and breaking it down. This has been independently verified in this paper.

The following research ~~was taken up~~ was taken up to study further, more thoroughly only one of the phases of this reaction, viz: the dehydrating action of anhydrous aluminium chloride. For this purpose experiments similar to those studied by Drs. Frankforter and Kritchevsky were begun, substituting trioxymethylene, however, for chloral. In each case the same general condensation-reaction took place. In a few cases the reaction seemed to be comparatively simple, while in others it appeared to be extremely complex. This variation seemed to be due largely to temperature, as a result

of the way in which the aluminium chloride was added, either fast or slow, or as to whether the whole mass was kept in a freezing mixture during the reaction. Finally, it was hoped that in addition to studying the reaction itself some light might be thrown on the constitution of trioxymethylene.

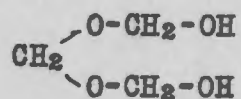
The molecular structure of trioxymethylene is generally accepted as a ring compound in which the oxygen and the methylene groups are symmetrically arranged. In case the accepted theory is a fact, it was hoped to prepare condensation products by breaking the ring and substituting hydrocarbon radicals for one or more of the oxygen atoms as may be indicated by the following compounds:



where R represents either benzene or one of its homologues.

On going over the literature of trioxymethylene it was found that Grassi and Masselli (Gaz., 28,477) had

had prepared compounds analogous to those which we had hoped to prepare by breaking the ring and substituting inorganic radicals for the oxygen. Thus by treating trioxymethylene with acetic acid and water, they obtained trioxymethylene hydrate,



Then, by treating the hydrate with hydrochloric acid, the trioxymethylene chloride was formed. And finally, by treating the chloride with benzene, they obtained diphenylmethane. They assumed that the hydrochloric acid broke the ring compound down into formaldehyde at the same time forming a hydrochloride,  $\text{ClCH}_2\text{OH}$ . This compound then reacted with the benzene forming the diphenylmethane. They failed to prepare any of the oxycompounds.

As has already been stated, the reaction between trioxymethylene and the hydrocarbons varies widely, depending upon the conditions under which the reaction takes place. Under none of these conditions, however, were we able to prepare any of the oxycompounds although

various complex hydrocarbons were prepared, as will be shown later. Notwithstanding the fact that no oxycompounds could be isolated, the truth remains that trioxymethylene acts differently from formaldehyde in the presence of aluminium chloride. This fact may mean that some of the oxycompounds are actually formed in the reaction and are broken down into the various hydrocarbons before equilibrium is finally reached.

Trioxymethylene has never before been used with aluminium chloride, consequently no condensation products have ever been made; neither has it been studied in connection with concentrated sulphuric acid. As a matter of fact, formaldehyde itself has never been studied in this connection. It has been used, however, with concentrated sulphuric acid yielding compounds which in many cases ~~are the same as those obtained~~ are the same as those obtained with trioxymethylene and aluminium chloride.

### Experimental Part.

Benzene and Trioxymethylene.-- To 500 c.c. of benzene were added 35 g. of trioxymethylene, the mixture cooled to 0° and 170 G. of anhydrous aluminium chloride added piecemeal. An automatic stirrer was used, and the mixture stirred continuously while the aluminium chloride was being added. The temperature was never more than 20° though most of the time it was less than 10°.

After about 50 g. of aluminium chloride had been added, the color of the mixture changed to a reddish-brown and copious fumes of hydrochloric acid were liberated. The stirring was continued for some time after all aluminium chloride had been added. It required ten hours to complete the reaction. During this time hydrochloric acid continued to pass off. After the reaction had apparently ceased, the whole mixture was placed in a refrigerator for three or four days. At the end of that time it was removed and ice water added in order to decompose all aluminium chloride without rise in

temperature. After a sufficient quantity of water had been added an oily substance separated out and floated on the water. Some solid substance remained at the bottom of the flask. There was also some solid material which was lighter than water but heavier than the oil. This separated out and remained on the surface of the water just below the oily layer. The whole was then extracted with ether. All except the solid substance on the bottom of the flask dissolved. The ether solution was then separated from the water and the insoluble substance. This latter substance was set aside for further treatment. The ether extract was subjected to fractional distillation and the distillates were collected separately as follows: (a) between  $40^{\circ}$ - $80^{\circ}$ , (b)  $80^{\circ}$ - $130^{\circ}$ , (c)  $250^{\circ}$ - $280^{\circ}$  and (d)  $280^{\circ}$ - $360^{\circ}$ . A preliminary examination showed that distillate (a) was largely ether with some benzene. Distillate (b) was found to contain largely benzene with small amounts of toluene. From  $130^{\circ}$  the temperature rapidly rose to  $250^{\circ}$  and an aromatic liquid continued to distil over until a temperature of  $280^{\circ}$  was

reached. Then a white substance of somewhat waxy nature passed over and solidified on the walls of the condenser. This substance continued to distil over until the temperature had reached 360°. Distillation was then stopped as the tarry, resinous, solid material remaining in the flask showed signs of decomposition. A peculiar blue fluorescence was observed in the distillate. The resinous material was set apart for further treatment.

As the yield of products was not entirely satisfactory, the above experiment was repeated, varying the temperature and the proportion of trioxymethylene. In each case the same products were obtained, although the yield of the liquid and solid distillates (c) and (d) varied. In the above experiment the quantity of liquid distillate (c) was small. When 40 g. of trioxymethylene were used under exactly the same conditions, the yield of both (c) and (d) was greater, and when 50 g. were used there was a still larger yield of both the liquid and the solid distillates (c) and (d). On the contrary, when 100 g. of trioxymethylene were used, there was a

good yield of the liquid distillate (c) and no yield of the solid (d). Even when the temperature was allowed to rise to 40°-50° the same products were formed, although the yield varied.

The liquid distillate (c) was redistilled when it showed signs of crystallization. The redistilled oil was therefore cooled in a freezing mixture, when it crystallized in colorless prismatic needles. The melting point of the substance was found to be 26° -27°. It was at once suspected to be diphenylmethane. Hence it was compared with Kahlbaum's diphenylmethane in appearance, boiling point and other characteristics. Kahlbaum's diphenylmethane, although marked "c.p.", was found to be impure. It was a yellowish-colored liquid. It began to distil at 254° and continued to 261°. After distillation, however, it was colorless and at once crystallized in colorless, prismatic needles with a melting point of 26°-27°.

Our diphenylmethane distilled over between 259° and 262°. It was perfectly colorless and crystallized in colorless prismatic needles. The various tests indicated



that it was diphenylmethane. It also showed the characteristic blue fluorescence. Baeyer (Ber. 5,1099) first obtained diphenylmethane by treating benzene with formaldehyde in the presence of sulphuric acid; and later Nashroff, (J.Russ.Chem.Soc.,35, 825) on repeating Baeyer's experiments, showed that phenylformol was formed, and this substance by dry distillation yielded not only diphenylmethane but also toluene, xylene and anthracene.

The solid distillate (d) which passed over between 280°-360° was finally dissolved in amixture of hot benzenecontaining a little alcohol, as this mixture was found to give best results. On cooling the solution a leafy,white substance crystallized out. This was filtered off, washed with alcohol several times to remove the last traces of diphenylmethane and recrystallized three or four times. The pure crystals thus obtained were dried and the melting point was found to be 210°-211°. The crystals were monoclinic plates of pearly lustre, and both in solution and out of it showed a beautiful fluorescence. Analysis gave

numbers for anthracene, although the melting point was a little low. It gave all the reactions for anthracene and an oxidation gave anthraquinone, leaving no doubt as to its identity. The yield of both diphenylmethane and anthracene was exceptionally good.

The fact that diphenylmethane and anthracene are the two principal compounds formed in the reaction throws some light on the nature of the reaction. From the amounts of these two compounds obtained, it is evident that equal molecular quantities are formed. In view of this fact the equation may be represented as follows:

$$4 \text{ C}_6\text{H}_6 + (\text{CH}_2\text{O})_3 + \text{AlCl}_3 = \text{CH}_2(\text{C}_6\text{H}_5)_2 + \text{C}_{14}\text{H}_{10} + 3 \text{ H}_2\text{O} + \text{AlCl}_3.$$

As equal molecular quantities of diphenylmethane and anthracene are formed in this reaction we were at first led to believe that the trioxymethylene molecule is not symmetrical, the methylene group forming the diphenylmethane having different molecular nature from the other two groups in the molecule. On the contrary, Baeyer obtained diphenylmethane from benzene and formaldehyde by means of sulphuric acid; and Nashroff

by the same reaction obtained both diphenylmethane and anthracene. These facts scarcely permit such a conclusion although the reaction is none the less interesting.

Baeyer (Ber.6,222) showed that when diphenylmethane was further treated with formaldehyde and sulphuric acid condensation occurred, forming dihydroanthracene. In order to determine whether or not trioxymethylene would act the same as formaldehyde, 50 g. of diphenylmethane and 9 g. of trioxymethylene were treated with 20 g. of aluminium chloride according to the method already given. On examining the products after the reaction had been completed a considerable quantity of diphenylmethane was recovered. There was left in the flask after distilling off the diphenylmethane a tarry mass which does not contain anthracene. This was set aside for examination later. Therefore, trioxymethylene does not act, in the presence of aluminium chloride, like formaldehyde in the presence of sulphuric acid.

In order to show whether or not trioxymethylene forms the same compound with the benzene homologues

in the presence of aluminium chloride which formaldehyde does in the presence of sulphuric acid, a series of experiments was made using toluene, xylene and mesitylene instead of benzene.

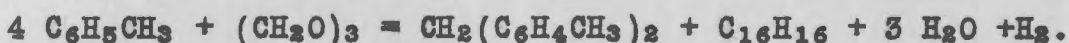
Toluene and Trioxymethylene.-- Fifty g. of trioxymethylene were dissolved in 400 c.c of toluene and 100 g. of aluminium chloride, added piecemeal. A large amount of heat was liberated but the temperature was not allowed to go above 65°. The whole mass changed to a reddish-brown color and fumes of hydrochloric acid were given off. The upper layer showed a deep blue fluorescence. The whole mass was kept in a cool place for four days, when ice-water was added, and subjected to the same process described under benzene. Distillate (a) passed over between 50° and 120°, (b) between 390° and 310° and (c) between 310° and 400°. After the small quantity of (a), which, on examination was found to be a mixture of ether, toluene and benzene, had passed over the temperature immediately rose to 290°. At this

an  
point, oil began to distil over and continued until a temperature of 310° was reached. The distillate then began to solidify on the walls of the condenser. The solid continued to pass over until a temperature of 400° was reached. Owing to decomposition the distillation was stopped. A dark, resinous substance remained in the flask. This material was reserved for further investigation.

On redistilling the oil which was collected between 290° - 310° most of it passed over between 285°-287°. It showed a brilliant blue fluorescence. It was further purified and analyzed. Analysis and physical and chemical properties checked well for ditoluylmethane.

The semisolid substance which came over between 310° - 400° was then dissolved in a mixture of alcohol and benzene from which it was obtained in well crystallized form. It was recrystallized several times by this means, when the constant melting point of 225°-226° indicated that it was pure. Analysis and general properties checked well for dimethylantracene, a com-

pound prepared by Friedel and Crafts (Ann.Chim. Phys. (6) 11, 266) by treating toluene and methylene dichloride with aluminium chloride. As their reaction is evidently an exact duplicate of the reaction with benzene, it may be represented as follows:



It is also interesting to note that Anschütz (Ann. 235, 176) obtained the same dimethylantracene by treating toluene with acetylene tetrabromide and aluminium chloride.

Xylene and Trioxymethylene.-- To a mixture of 500 g. of o-xylene B.P. 142 and 50 g. of trioxymethylene, were added with constant stirring, 100 g. of aluminium chloride. The temperature rose to 65° and copious fumes of hydrochloric acid were liberated. The mass seemed to divide into two layers, the upper one showing a deep, greenish-blue fluorescence, the lower one being dark-brown. The whole was allowed to stand at ordinary room temperature for three days, at the end of which time the reaction seemed to be complete. The whole

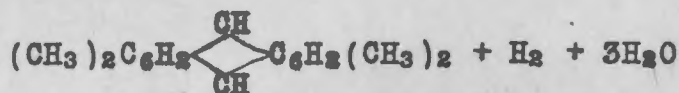
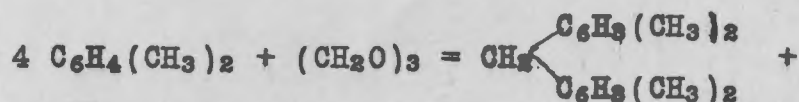
mass was treated with ice-water, allowed to stand for some time and finally extracted with ether. The extract was drawn off, the ether removed, and the residue distilled at ordinary pressure. The distillates were collected as follows: (a) between 70° and 150°, (b) 200° and 230° and (c) between 330° and 400°. After these distillates had been removed there remained in the flask a tarry substance. After removing distillate (b) an air condenser was used and the solid distillates were thus easily collected for further examination. The first distillate (a) consisted of a mixture of hydrocarbons, benzene, xylene, and possibly some toluene. Distillate (b) was redistilled, when a large part passed over between 311°-313°. It was wonderfully fluorescent, more so even than diphenylmethane and ditoluylmethane. Analysis of the purified substance gave numbers for  $C_{17}H_{20}$  or dixylylmethane. This compound has evidently never before been made, although a substance of the same empirical formula (Ann.Chim.Phys.(6) 1, 516) a duryl benzyl compound has been prepared.

Tetramethylanthracene.-- Distillate (c) or that which passed over between 330°-400° was now examined. It was a semi-solid, evidently composed of two or more compounds. It was purified by washing with chloroform. This rapidly took out the oily substance leaving behind most of the solid substance. The latter was then recrystallized from a mixture of benzene and alcohol. By repeating the process several times the substance was obtained in pure form. It crystallized in yellow monoclinic plates of pearly lustre. In solution it possessed an intense green fluorescence. It does not appear to have a melting point but decomposes at 233°-235°. It can be sublimed, however, without difficulty, forming crystals with wonderful iridescence.

Analysis gave C = 92.23 and H. 7.22. Theoretical C = 92.3 H = 7.7. Friedel and Crafts (Ann. chim. Phys. (6) 11, 268) prepared a tetramethylanthracene from m-xylene with a melting point of 162° - 163°, while Anschütz (Ann. 235, 174) obtained from m-xylene an entirely different tetramethylanthracene with a melting point of



above 280°. Dewar and Jones (J.Chem.Soc. 85,213) obtained the same compound described by Anschütz which they designated 2:4:6:8 derivative. Anschütz also obtained from o-xylene a tetramethyl compound with a melting point of 280°, almost the same as the m compound. It is evident that the one prepared above is an isomeric form, the exact structure of which has not yet been obtained. From what has already been stated concerning these reactions this one may be represented as analogous to those already given:



Mesitylene and Trioxymethylene,-- Two Hundred grams of mesitylene were brought together with 30 g. of trioxymethylene at ordinary temperature and 55 g. of aluminium chloride added with constant, vigorous stirring. The temperature rose to 50°, hydrochloric acid gas was

liberated and the color changed to a dark red. Two layers again appeared, the upper one having a deep violet fluorescence. After allowing it to stand for two days at ordinary room temperature, water was added, and finally the whole mass was extracted with ether. The addition of ether precipitated an amorphous substance which was at first thought to be an aluminium compound, but which was found to be entirely organic. It was removed and recrystallized from a mixture of benzene and chloroform. The purified substance melted at 286°-287°. It was a light-yellow crystalline powder. Analysis gave the following:

C = 89.60 and H = 8.45    Calc. C = 91.60 and H = 8.40

It gave all the general characteristics of an anthracene derivative, notwithstanding the fact that Dewar and Jones (J.Chem.Soc., 85, 218) were unable to prepare anthracene derivatives from mesitylene by the Friedel Crafts reaction. It seems perfectly evident that hexamethylantracene cannot be made from mesitylene and any other reagent. On the contrary, a tetramethyl

compound is not impossible as two of the methyl groups, one from each of two mesitylene molecules, might be the means of connecting the two molecules as an anthracene derivative. This seems to have happened forming a tetramethylantracene which must necessarily be either 1:3:6:8 or a 2:4:7:9 derivative. It is interesting to note that the melting point corresponds closely with the melting point of tetramethylantracene.

The filtered ether extract was then distilled and the distillates collected in two parts, the first between 90°-200° and the second between 200°-350°. Above this practically nothing would distil over. At a very high temperature it began to decompose. The first distillate consisted of small amounts of benzene, toluene, xylene and mesitylene. The second distillate at first appeared as an oily liquid from which crystals formed on standing. These were separated out by adding ether when the oily substance immediately dissolved, leaving the crystals behind. They were removed, washed with ether and recrystallized from a mixture of hot alcohol and ether. Thus obtained, the crystals appeared as white

monoclinic plates with a melting point of 129°-130°.

Analysis and general characteristics showed that the substance was dimesitylmethane prepared by Baeyer (B., 5, 1098) from mesitylene, formaldehyde and sulphuric acid.

The ether solution containing the oil was warmed in order to remove the ether and then distilled. The first fraction, boiling between 170°-325°, was so small that no attempt was made to examine it.

Durene.-- The distillates between 325° and 355° which had solidified were put together. The crystals were mixed with some oil and could not be separated from it. Both the oil and the crystals were extremely soluble in all the solvents. Mixtures of solvents also did not work, so it was thought the oil might be partially removed by putting the oily crystals on unglazed procelain. After two days, much of the oil was absorbed by the procelain plate, and the fleecy, white, silken needles were seen on the plate. They were removed from the plate, dissolved in 95 per cent. alcohol, using

a very small quantity, and crystallized from the solution. They are extremely soluble in alcohol and much more in other solvents. The melting point of the crystals was found to be 79-80°.

A microscopic examination proves that these crystals are different from dimesitylmethane and monoclinic, with a melting point of 130°. They show beautiful colors when nicols are crossed showing that they are anisotropic. They are biaxial with parallel extension, Dimesitylmethane also shows colors when nicols are crossed, but the crystals are certainly different and their axes could not be determined.

An analysis of these crystals (melting point 79°-80°) gave 90.22 per cent. for C and 9.65 per cent. for H, which is very close to 89.60 per cent C and 10.40 per cent. H of Durool. It was first suspected to be dimethylantracene, melting point 71°, but it could not be that as the analysis is far from that of dimethylantracene, 93.20 per cent. C and 6.80 per cent. H. Besides when oxidized by chromic acid it evolves CO<sub>2</sub> and

does not give dimethylanthraquinone, melting point  $157^{\circ}$ . Its dibrom-compound agrees with that of durene, melting point  $199^{\circ}$ - $200^{\circ}$ . Its dinitro-compound, melting point  $205^{\circ}$ - $207^{\circ}$  also proves it to be durene.

The production of durene from mesitylene is extremely interesting. In fact, mesitylene has been found almost inert. Dewar and Jones (Trans.Chem.Soc. 85,213-22) find it impossible to condense it to anthracene by the action of nickel carbonyl in the presence of  $Al_2Cl_6$ . Baeyer obtained only dimesitylmethane, nothing else, by the action of  $H_2SO_4$  on mesitylene and formaldehyde. It is possible in the present case that as hexamethylanthracene could not be formed, two methyl groups, one each from two molecules of mesitylene, were detached by the action of  $Al_2Cl_6$  and were further added to the other two molecules of mesitylene, hence changing them into two molecules of tetramethylbenzol. This tetramethylbenzol must have been changed to durene by the further action of  $Al_2Cl_6$  in splitting the methyl groups and replacing the same in other positions(See Anschütz, Ann. 235, 179-192).