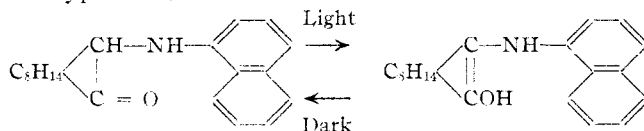


of solutions it is untenable. The change in this case is very probably due to a change in the chemical structure of the molecule. For instance, in the case of α -naphthylamino-camphor the change may be represented as the keto-enol type thus,



The colorless solution probably contains the keto compound, whereas the green solution is due to the change of the keto to the enol form. The imino-derivatives in each of the above 3 cases do not show this phototropic behavior. The effect is produced only when the imino compound is transformed into the amino derivative, in which case alone the tautomeric change is possible. This may be regarded as a proof for the view put forward as to the mechanism of the change, but in the preliminary survey of a new field which is now presented, it is not possible to prove definitely the occurrence of dynamic isomerism of the above type. The true explanation of the change must, however, wait until the experiments, which have been instituted with this end in view have been completed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER.]

THE CONDENSATION OF ACETYLENE WITH BENZENE AND ITS DERIVATIVES IN THE PRESENCE OF ALUMINUM CHLORIDE.

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Received August 23, 1920.

The first and most important work on this condensation was that of Varet and Vienne.¹ They passed acetylene through a mixture of benzene and aluminum chloride, and reported the formation of a product containing 80% phenyl ethylene (styrene), 15% *unsym.* diphenylethane and 5% *sym.* diphenylethane (dibenzyl). Neither the actual amounts obtained, referred to the reacting materials, nor the conditions under which the runs were made, were stated.

Since the results of some work in this laboratory tended to throw considerable doubt on the correctness of these conclusions, this investigation was begun to ascertain, if possible, the general conditions governing the action of acetylene on benzene and benzene derivatives, and to determine the products formed by these reactions.

Work of a somewhat similar nature, but under entirely different con-

¹ Varet and Vienne, *Compt. rend.*, **164**, 1375 (1886).

ditions, was done by Parone.¹ He reported that ethylbenzene, styrene, dibenzyl and anthracene were produced by the action of nascent acetylene on benzene.

We proceeded to duplicate the experiment of Varet and Vienne as nearly as possible and, in attempts to modify the reaction, were led to substitute for the benzene some of its derivatives. In all cases the yields were low and variable. The only influence of the substituted groups was to vary the intensity of the reaction as a whole, rather than to produce any change in the nature or relative proportions of the products. The normal course of the reaction is the union of 2 molecules of benzene with one of acetylene to form a diphenylethane, and the combination of a portion of this with more acetylene to produce an anthracene. The union of one molecule of benzene with one of acetylene to produce styrene either takes place to a slight extent only, or, more probably, the unsaturation of the compound formed leads to its immediate condensation with another molecule of benzene and the formation of the diphenylethane. At any rate, at no time was more than a trace of styrene obtained.

Experimental.

General Operations.

All runs were carried out in much the same way. The acetylene, after it was purified by passing it through a solution of chromic acid, was washed and stored in gasometers from which it was led at a nearly constant rate (20 liters per hour) through a drying bottle to the reaction flask containing the anhydrous aluminum chloride and the benzene or substituted benzene. This flask was provided with an efficient return condenser through which the unabsorbed gas was discharged to a large bottle where its volume was measured approximately. In some runs no gas was permitted to escape, while the pressure was 150 mm. above atmospheric pressure. Provision was made for heating or cooling the reaction flask and the mixture was shaken frequently during the course of the reaction.

Various grades of aluminum chloride were used. These ranged from an impure commercial product to the freshly prepared, nearly pure material made in the laboratory. The fresh product was found to be much too active, but, in the course of 2 weeks to 6 months, if it was stored in sealed bottles its activity was modified to such an extent that almost any intensity of reaction could be obtained.

After passing 30 to 45 liters of acetylene through the reaction mixture, the product, a reddish-brown material typical of those obtained by the Friedel-Craft reaction, was hydrolyzed and distilled with steam to remove the excess of unchanged liquid. The amount of acetylene absorbed

¹ Parone, *L'Orosi*, **25**, 148 (1904).

varied from 25 to 30% of that passed through, and of this amount from 50 to 75% is accounted for in the final products, including the tar.

I. Condensation with Benzene.

In the majority of these runs, the temperature was held within a few degrees' variation of a given point. When the mixture was left undisturbed, the temperature gradually rose to about 70° to 80° as the reaction proceeded, and, after about 3 hours, started to diminish. The condensation product consisted of a dirty yellow oil. When this oil was hydrolyzed and distilled with steam, it gave 2 volatile fractions and a black tarry residue.

The first fraction was unchanged benzene, together with some toluene and xylene, formed by the action of the aluminum chloride on benzene itself. A small portion of a material, b. p. 140–145°, was also obtained. This gave evidence of the presence of styrene, which, however, was not present in sufficient quantity to be isolated.

The second fraction, which came over very slowly (in from 4 to 6 hours), when dried, boiled at 280° to 290° and was identified as *unsym.* diphenylethane, b. p. 286°, by oxidation to benzophenone and the formation of benzophenone oxime, m. p. 140°.

The residue, dried and distilled, gave 2 principal fractions. One consisted of some diphenyl-ethane which had not come over with steam. The other fraction, which distilled above 360°, solidified, and, after several recrystallizations from alcohol, yielded long brown needles, m. p. 181°. On oxidation, it gave anthraquinone. It is therefore identified as the 9,10-dimethyl-anthracene hydride of Anschutz.¹ No dibenzyl could be found.

The question then arose as to whether this anthracene was formed from 2 molecules of styrene, or from one of diphenyl-ethane and one of acetylene. The latter method was tried. It yielded the anthracene derivative which indicates the probability that this is the main reaction. This conclusion is further borne out by the results of the condensation with toluene described below.

At present, we are unable to account for the large percentage of styrene in the product reported by Varet and Vienne. A variation of the conditions as to temperature, amount and condition of the aluminum chloride, rate of flow of acetylene, and length of run changed the proportions of the diphenyl-ethane and the anthracene to some extent, but in no case was more than an indication of styrene obtained, which seems to indicate that it reacted further as soon as it was formed.

From the average run (200 g. of benzene, 15 to 20 g. of acetylene and 50 g. of aluminum chloride) 10 to 15 g. of diphenylethane and 10 g. of dimethyl anthracene hydride were obtained, together with some tar.

The consideration of a large number of runs made under various conditions shows that (a) the fresher the aluminum chloride, the greater the proportion of dimethyl-anthracene hydride formed; (b) the rate of flow of the acetylene has little effect on the proportions of the products formed; (c) dilution of the benzene with a neutral solvent has no appre-

¹ *Ber.*, 17, 165 (1884); *Ann.*, 235–305 (1886).

cial effect. Lavaux¹ found that, in a typical Friedel-Craft reaction, the smaller the proportion of aluminum chloride to benzene, the larger the proportion of low boiling products formed. This conclusion was verified in our case also.

II. Condensation with Toluene.

At the conclusion of the previous experiments, toluene was substituted for benzene. The reaction was of the same nature and intensity; the material distilled as before, except that only one fraction was obtained with steam! The volatile fraction was found to be unchanged toluene, together with xylene, mesitylene and pseudocumene. The xylene was obtained by the action of aluminum chloride on the toluene alone.² The formation of the other 2 compounds is discussed later.

The residue from the steam distillation was dried and fractionated. One fraction was obtained which, after several redistillations, boiled between 290° and 300°. This material refused to crystallize and was oxidized in acetic acid-chromic acid solution. The oxidation product was also dark and viscous, and yielded an oxime with difficulty. This oxime on purification melted at 163°, which showed the oxidation product to be *p,p*-ditolyl-ketone and indicated that the original material was *unsym. p,p*-ditolyl-ethane, b. p. 294–295°.

The second fraction, above 360°, solidified completely and was obtained from benzene as yellow feathery crystals, m. p. 243.5°, which matted together on the filter and showed a greenish fluorescence. Oxidation of the impure material yielded an anthraquinone, brown needles, m. p. 235.5°, from alcohol; another, somewhat like the first, melting at 177°; and a third, in very small quantity, m. p. 163°.

The 235.5° anthraquinone is the derivative of the 243.5° product, which is identified as the 2,7-dimethyl-anthracene of Lavaux.³ By analogy, one would expect to obtain 2,7,9,10-tetramethyl-anthracene hydride. It is well known, however, that aluminum chloride produces molecular rearrangements and elimination of groups.⁴ Our explanation is that the 9,10-methyl groups were eliminated with the formation of the mesitylene and pseudocumene previously mentioned.

The product, small in quantity, with a melting point of 177° showed the characteristics of an anthraquinone and was identified as β -methyl-anthraquinone. The corresponding anthracene, m. p. 205°, could not be isolated, because it was present in so small an amount. It is probably formed by the elimination of a methyl side chain from the dimethyl-anthracene, although there is the possibility that it may be formed by the combination of a toluene and a benzene molecule with 2 molecules of acetylene. The benzene needed could be produced by the demethylation of toluene.⁵

¹ *Compt. rend.*, **139**, 976 (1905).

² Anschütz and Immendorf, *Ber.*, **18**, 657 (1885).

³ *Compt. rend.*, **143**, 687 (1907).

⁴ Friedel and Craft, *ibid.*, **100**, 692 (1885); and Jacobsen, *Ber.*, **18**, 338 (1885).

⁵ Anschütz and Immendorf, *ibid.*, **18**, 657 (1885).

Finally the vanishingly small amount of the 163° anthraquinone indicates the presence of 1,6-dimethyl-anthracene,¹ m. p. 240°. The occurrence of this hydrocarbon is evidently due to a molecular transposition.²

The formation of the 2,7-dimethyl-anthracene substantiates the idea that, as previously stated, the diphenylethanes are the intermediate products in the formation of the anthracenes, since, by the combination of 2 molecules of *p*-methyl-styrene, a 3,7-dimethyl-anthracene would be formed. Neither methyl-styrene, nor *sym.* ditolyl-ethane could be isolated.

Even under the most favorable conditions, the yields in this case did not exceed 5 g. of *unsym.* ditolyl-ethane and a like quantity of the combined anthracenes.

III. Condensation with Chlorobenzene.

At 90°–95° acetylene and chlorobenzene reacted to give a material resembling that obtained in previous runs. Since the reaction in this case was not quite so vigorous heat was necessary to start it. Although the residue after steam distillation was dark red and thick, it had less of the nature of tar, and on distillation it gave a fraction which boiled from 300–360°, accompanied by a considerable amount of tarry residue.

The fraction volatile with steam was unchanged chlorobenzene, slightly contaminated with the higher boiling products.

The 300° to 360° fraction obtained from the residue was yellow with a bluish fluorescence. By analogy, we expected to obtain *unsym. p,p*-dichloro-diphenyl-ethane from this fraction. Since no mention of this material can be found in the literature, a portion of the crude product was oxidized with chromic acid. The pink crystals extracted by carbon disulfide were recrystallized from alcohol until pure white pearly leaflets, melting at 146°, were obtained. This is the melting point of *p,p*-dichloro-benzophenone. The benzophenone oxime, melting at 134°, was also formed.³ After successive refractions, the original material showed a constant boiling point of 210° to 212° at 30 mm. pressure; and 319° to 321° at 760 mm. This evidently is the boiling point of *unsym. p,p*-dichloro-diphenyl-ethane.

The tarry residue could not be distilled further even under diminished pressure. Therefore it was extracted with hot acetic acid and the extracted material precipitated by the addition of water. This substance, of resinous nature, has refused to crystallize from any solvent, and is quite inert in the presence of most reagents. When it is boiled with chromic acetic acid solution for a long time, it is oxidized to give small quantities of a white waxy compound which melted, with preliminary softening, at 72°. Enough of this material has not yet been obtained in a pure state to identify it.

With 200 g. of chlorobenzene and 50 g. of aluminum chloride, the average yield was 25 g. of the dichloro-diphenyl-ethane fraction and 10 to 15 g. of tar. When the amount of aluminum chloride was increased to 120 g., only 8 to 10 g. was obtained between 300 and 360°, while the tar increased to 35 or 40 g.

IV. Condensation with Nitrobenzene.

Since nitrobenzene cannot be used in a typical Friedel-Craft's reaction,⁴ no con-

¹ Lavaux, *Compt. rend.*, **143**, 687 (1907).

² Lavaux, *ibid.*, **152**, 1400 (1911).

³ Dittrich, *Ann.*, **264**, 174 (1891).

⁴ Stockhausen and Gatterman, *Ber.*, **25**, 3521 (1893); and Perrier, *Compt. rend.*, **120**, 930 (1895).

denation with acetylene was to be expected. None was obtained. Several trials gave only a large amount of carbonized material.¹

V. Condensation with Methyl Benzoate.

When methyl benzoate was added to aluminum chloride a violent reaction occurred; the mixture became hot and evolved large quantities of hydrogen chloride, and at the same time, the aluminum chloride disappeared. Crystals separated after the reaction mixture cooled; these proved to be a molecular combination of the ester with the aluminum chloride. If acetylene is passed through the warm solution no apparent action takes place, for the addition of water caused a separation of material from which all of the methyl benzoate may be recovered unchanged. No other benzoic acid derivative was tried.

VI. Condensations with Aniline and with Dimethylaniline.

Aniline reacts violently with aluminum chloride with the evolution of much heat. A hard gray mass, probably of the formula $C_6H_5NH_2 \cdot Al_2Cl_6$, is produced which is practically insoluble in the available neutral solvents. No heat was evolved when dimethylaniline was mixed with aluminum chloride, but the temperature rose somewhat as the acetylene was passed into the mixture. On 2 occasions the temperature, after reaching 80° , rose almost instantly to 160° to 170° with the appearance of dense white fumes.

After hydrolysis of the mixture it was made alkaline and distilled with steam. The distillate was entirely unchanged material. The residue yielded a fraction which boiled between 300° to 360° . This deposited fine white needles, with a silvery sheen. At first these crystals melted at 58° , but on recrystallization the melting point became constant at 68° . A blue color, which fades on warming, was produced when the material was oxidized with lead dioxide in the presence of acetic acid.² These facts prove the material to be unsym. *p,p*-tetramethyl-diamino-diphenylethane. No other compounds were found to be present. The yield from a single run in no case exceeded half a gram.

VII. Condensation with Phenolic Derivatives.

Since phenol combines with aluminum chloride to form³ a compound of the formula $(C_6H_5O)_2Al_2Cl_4$, it was necessary to resort to derivatives of phenol. Both the phenyl ethers and the esters are hydrolyzed to some extent by aluminum chloride.⁴

When pure phenyl acetate was used, a vigorous action ensued; quantities of hydrogen chloride were liberated and the product became thick. Apparently the reaction does not follow the regular course. The material was hydrolyzed and the product which separated was dried and distilled directly. It yielded unchanged phenyl acetate, phenol, and a fraction boiling at 250° to 290° , which crystallized on standing to give bluish-purple stubby needles. During successive crystallizations from water, the color of the material passed through orange, and the material finally collects in aggregates of short colorless prismatic needles. In time these crystals turn white, somewhat like phthalic anhydride; they melt at 108.5° . The benzoyl derivative was formed easily by employing the Schotten-Baumann reaction. This product, recrystallized from alcohol, gave white needles melting at 133.5° . Since the action seemed irregular, a blank

¹ Roedtker, *Bull. soc. chim.*, [4] 3, 729 (1908).

² Trillait, *Compt. rend.*, 127, 1113 (1899).

³ Perrier, *ibid.*, 122, 195 (1896).

⁴ Hartmann and Gatterman, *Ber.*, 25, 3531 (1893).

was run in which no acetylene was used. This produced the same material in practically the same proportion. With this information, the material was readily identified as *p*-hydroxy-acetophenone. Its formation is to be explained by the rearrangement of phenyl acetate under the influence of aluminum chloride. The source of the purple color of the crude product has not been determined. When the crude material is melted, the color changes from purple to dull orange, but the purple tinge does not reappear when the solid cools. With anisol the reaction was not vigorous even with fresh aluminum chloride and at a temperature of 95°. With aluminum chloride 6 to 8 weeks old, a quantity representing about 25% of the original anisol appears in a fraction boiling at 175° to 180°. This product readily forms a benzoyl derivative which melts at 69°. The fraction is found to be phenol in solution in anisol. Evidence also points to a small amount of hydroxy-styrene, although its presence is not yet proved.

Accompanying this fraction is a portion which boils at 185° to 200° and a 5-g. residue of a high boiling liquid which does not crystallize.

With fresh aluminum chloride, a fraction boiling from 170° to 190° and containing phenol is obtained, and a high boiling residue left in the flask; the major portion, however, distills unchanged. The residue crystallized from alcohol gives micaceous scales which melt at 139.5°.

This account of our work represents the present state of our investigations. We expect to continue them along similar lines with variations in conditions and catalysts.

Summary.

Benzene, condensed with acetylene in the presence of aluminum chloride produces 9,10-dimethyl-anthracene hydride, in addition to *unsym.* diphenyl-ethane and traces of styrene.

Toluene gives xylene, mesitylene and pseudocumene (side reactions), *unsym.* *p,p*-ditolyl-ethane and 2,7-dimethyl-anthracene, together with some 2,6-dimethyl- and β -monomethyl-anthracenes.

Chlorobenzene produces *unsym.* *p,p*-dichloro- diphenyl-ethane, b. p. 210° to 212° at 30 mm., and 319° to 321° at 760 mm., and one higher compound as yet unidentified.

Nitrobenzene and phenyl acetate do not condense due to reaction with the aluminum chloride, but the latter rearranging to *p*-hydroxy-acetophenone.

Dimethyl aniline gives *unsym.* *p,p*-tetramethyl-diamino-diphenyl-ethane in small quantity.

Phenol, methyl benzoate, and aniline unite with the aluminum chloride in molecular proportions and do not act further.

The action of anisol is being investigated at the present time.

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