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THE PHOTO BROMINATION OF P-NITRO TOLUENE

BY

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THESIS SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE

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THE PHOTO-BROMINATION OF p-NITRO TOLUENE

Theoretical Considerations

The halogenation of benzene and its homologues in general results in addition, nuclear substitution and side chain substitution. With the exception of dichlorotoluenehexachloride addition compounds are known only in the case of benzene. Side chain halogen reacts with alcoholic silver nitrate, while nuclear halogen does not. Benzenehexachloride, the only addition compound the behaviour of which has been studied, does not react with alcoholic silver nitrate, but upon treatment with alcoholic soda it decomposes to form a trisubstitution product, thereby liberating half of the added halogen. Estimation of the three types of compounds depends on these reactions.

In general, rise of temperature, light and the absence of moisture favour side chain substitution, while catalysts, among which may be mentioned iodine and the halides of iron, aluminium, etc., favour nuclear substitutions. Concerning addition reactions little appears to be known beyond the fact that they are catalysed by light.

Several theories of the mechanism of side chain and nuclear substitution reactions have been put forward. Most workers agree in attributing side chain substitution to molecular halogen. In support of this theory is the fact that side chain substitution is catalysed by light. Moreover in the case of the bromination of toluene it has been shown that the most effective wave lengths are those corresponding to the absorption bands of molecular bromine.

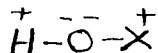
Bancroft, however, attributes side chain substitution to an excess of positive halogen ions.

Holleman (Rec. des Trav. chim. des Pays-Bas, 22, 435, 1908), supposes that nuclear substitution is brought about by perhalides such as HBr_3 ; Cohen (J. O. S., 22, 1623, 1910) also favors this explanation. This would account for the action of halogen carriers and for the negative effect of increase of temperature. Moreover when the reaction is carried out in nitrobenzene a distinct decrease in the amount of side chain substitution has frequently been noticed. According to the investigations of Cohen (Loc. cit.) polyiodides are formed to a far greater extent in this solvent than in other so-called neutral solvents such as carbon tetrachloride. He therefore explains the decrease in the side chain substitution by supposing that nuclear substitution takes place to an appreciable extent due to the great increase in perhalides molecules present.

Bancroft (J. Physical Chem., 1908, 12, 420), on the other hand believes that nuclear substitution is brought about by an excess of negative ions which excess results from the addition of positions ions to halogen molecules thus:

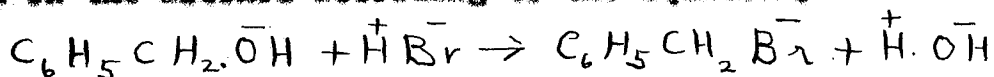
This view is directly opposed to that of Fry, (J.A.C.S., 36, 1035, 1914). Fry considers that in benzene the hydrogen atoms in the positions 1, 3, 5 are negative, while those in positions 2, 4, 6 are positive. He points out that the conditions promoting nuclear substitution, i.e., moisture, low temperature and absence of light, also promote the formation and stability of hypochlorous and of

hypobromous acid in each of which the halogen functions positively according to the valence formula

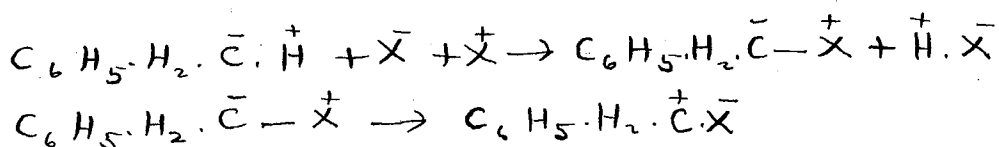


He considers that nuclear substituted halogen is always positive, since it fails to react with silver nitrate to form silver halide, in which it would of necessity be negative, and since it enters in the ortho and para positions to the negative methyl radicle. He therefore supposes that nuclear substitution is brought about by hypochlorous and hypobromous acids which effect the interchange of positive halogen atoms with positive hydrogen atoms of the nucleus. If water is regarded as a typical halogen carrier this explanation of its action throws light on the role played by carriers in general. These may be considered as catalysing the reaction through the formation of halogen addition compounds which dissociate to give a negative radicle and a positive halogen ion, which latter causes substitution in the nucleus.

According to Fry, side chain halogen is negative since, for example, benzyl bromide is formed by the direct action of hydrobromic acid on the alcohol according to the equation:



and since benzyl bromide is easily hydrolyzed. But the hydrogen which is replaced is ^{positive} ~~negative~~ and Fry therefore conceives the reaction to be one of oxidation and reduction according to the equations:



In this connection it is interesting to note that recently

Esines (J.C.S., 121, 2810, 1922), investigated the bromination of phenol and came to the conclusion that nuclear substitution is preceded by the formation of addition compounds of hypobromous acid. This assumption is supported by the fact that he was able to prepare tribromophenol by the direct action of hypobromous acid.

We come now to some of the more specific problems presented by the photo-bromination of toluene. In the absence of catalysts the main product is always benzyl bromide, though the presence of moisture may bring about considerable nuclear substitution also. In studying the rate of the reaction Bruner and Czarnecki (Bull. Ac. Cr., 1910, 516) found that traces of oxygen effected the rate so greatly that reproducible results could be not obtained. They attributed the action of oxygen to the formation of unstable oxides of bromine which act as catalysts. They were able to eliminate this disturbing influence by the addition of a small quantity of iodine to the reaction mixture. They suggested that the iodine unites to form a more stable oxide, in this way eliminating the effect of oxygen on the reaction. They found that in the presence of a trace of oxygen the reaction proceeds regularly, and is monomolecular when the concentration of the bromine is small. They also found that the temperature coefficient was unusually high for a photo-chemical reaction, namely, 1.8, a fact which is held by Andrich and Le Blanc (Zeitsch Wiss, Photo-Chem., 1916, 15, 217) to result from the increasing decomposition of perhalide molecules with increasing temperature.

Bruner and Lahocinski (Bull. Ac. Cr. 1910, 560) investigated a peculiar after effect which occurs when the reaction has been

carried out in the presence of oxygen. This after effect causes further quantities of bromine to react with the mixture in the dark. It lasts for six hours or more but is destroyed by heating to 100° C. for two hours, or by the addition of oxidisable substances, such as hydrobromic acid or iodine. Hydrochloric acid does not have this effect. It does not occur when the reaction is carried out in the presence of carbon dioxide, nitrogen or hydrogen. They attribute it to an oxide of bromine which catalyses substitution in the side chain. In agreement with this view they observed that oxygen is strongly absorbed during the reaction and the reaction mixture is colored yellow.

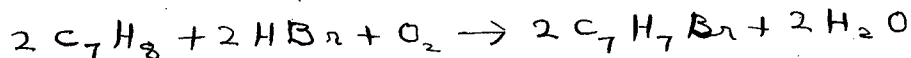
In this connection it is interesting to note that Cohen (Loc. cit.) refers to a similar yellow solution obtained in the chlorination of toluene. He states that it is discharged by the addition of iodine or hydrochloric acid or by washing with water.

Andrich and Le Blanc (Loc. cit.) studied the photo-bromination of toluene at 15° and 25° C. They measured the amount of hydrobromic acid evolved and also the amount of bromine removed by alcoholic silver nitrate. They found the relation between these quantities very variable and that the latter quantity often exceeded the former. On carrying out the reaction in the presence of excess of oxygen they found that the quantity of bromine removed by the alcoholic silver nitrate was greatly increased, being in some cases 40% greater than that evolved as hydrobromic acid. Bruner had previously noticed a similar discrepancy in the photo-bromination of propylbenzol, of which he said "die Reaktionsprodukte halten den Bromwasserstoff hartnäckig auf". Andrich and Le Blanc noticed that these reaction mixtures had a yellow colour which was

destroyed by washing with water. Working with dry solutions they found that the presence of oxygen greatly increased the yield of side chain bromine but also greatly decreased the rate of the reaction. In the presence of excess of oxygen they found that a moist solution and one covered by a layer of water react differently. In the first, the speed of the reaction is increased and the yield of side chain bromine decreased by the moisture. Similar results had been obtained by Cohen in the chlorination of toluene. When the reaction mixture is covered by a layer of water, on the other hand, the rate of the reaction is slightly decreased and the yield of side chain bromine greatly decreased. In air, however, the presence of moisture or of excess of water has little effect upon the ~~MIXTURE~~ reaction. These results they attribute to the formation of catalysts and they consider it not unlikely that in the presence of excess and of deficiency of oxygen the catalysts are different, in which case their results would seem to indicate that the first is decomposed by water while the latter is not.

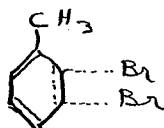
They suspected that the deficiency in hydrobromic acid evolved was due to oxidation. They therefore passed a mixture of hydrobromic acid and oxygen through illuminated toluene. They were able to effect considerable bromination by this means. The resulting mixture was yellow and possessed oxidising and phenolic properties. Finally they carried out the reaction in a gas burette and measured the amount of oxygen absorbed and the amount of hydrobromic acid decomposed. On the assumption that the

decomposition takes place according to the equation

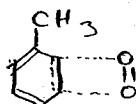


the amount of oxygen absorbed was more than double the calculated quantity.

They point out that, according to Suida (Wien Monatsch 33, 1255, 1912) and others, aromatic hydrocarbons containing methyl groups react with oxygen in the presence of light to form peroxides, and that the formation of such compounds would explain the excess of oxygen absorbed by the mixture and also its oxidising and phenolic properties. A portion of the peroxides formed would oxidise some of the hydrobromic acid, being in the process decomposed, thereby forming bodies which on the addition of water react to give phenols. Since the oxidation is catalysed by light of the visible region of the spectrum, i.e., by wave lengths which correspond to the absorption bands neither of toluene nor of oxygen, and since they found that the oxidation mainly takes place only during the reaction, they argue that the catalytic action of light on the formation of such peroxides must depend on the presence of bromine, a connection which is moreover known to exist between bromine and other photochemical reactions. They therefore suggest that an addition compound of bromine is first formed, thus:



the bromine of which is then replaced by oxygen, giving



It is abundantly clear from this summary of the work already carried out that the exact mechanism of the photo-bromination

of toluene is still unknown. Cohen says: "It must be confessed that nothing definite is known about the mechanism of the process." (Org. Chem. for Advanced Students, 2, 397, 1913). Holliman, referring to his theory of the action of complex perhalide molecules, says (loc. cit.) "Cependant un nombre de difficultés ^{devraient} ~~deveint~~ encore ^{être} levées avant qu'elle puisse servir à expliquer les phénomènes observés". While Andrich and Le Blanc in reviewing the results of their exhaustive research say: "Die bei der Untersuchung der Photobromierung des Toluols erhaltenen Ergebnisse sind so mannigfaltig, dass es bis jetzt nicht möglich ist, eine Theorie über den Verlauf der Reaktion aufzustellen."

Preliminary Experiments.

It was thought that a study of the photo-bromination of p. nitro toluene might throw some light on the general problem. In 1918 Brewster (J.A.C.S. 40, 406, 407) described a method for preparing p. nitro benzyl bromide using boiling carbon tetrachloride as the solvent. Since it appeared highly probable from the work of Andrich and Le Blanc that the reaction would proceed normally when carried out in this solvent a detailed study of the reaction as carried out by Brewster was decided upon.

A series of preliminary experiments were carried out. 10 gr. of p. nitro toluene was dissolved in 100 c.c. of carbon tetrachloride and the theoretical quantity of bromine, namely 11.7 gr. was dissolved in 50 c.c. of carbon tetrachloride. The nitro toluene solution was boiled and the bromine solution added through

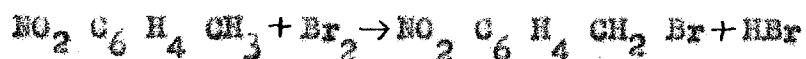
the top of a reflux condenser. In experiments 1 - 5 the bromine was added slowly as the reaction proceeded, following the directions of Brewster. In No. 6 it was all added before the reaction began. In experiments 1 - 3 .01 gr. of iodine was added as advocated by Brewster, but in experiments 4 - 6 none was added and it will be noticed that these reactions appeared to proceed more rapidly and to greater completion. The carbon arc light was used as an artificial source of light.

| No. of Exp. | Source of light | Catalyser | Time | Yield | |
|-------------|-------------------|------------------------|---------|-------|-------|
| 1 | Arc Light | .01 gr. I ₂ | 50 min. | 64.57 | 64.63 |
| 2 | Diffused Daylight | " | " | 2.79 | |
| 3 | Arc Light | " | " | 49.91 | 49.62 |
| 4 | Arc Light | - | " | 93.40 | 93.60 |
| 5 | Sunlight | - | 25 min. | 95.92 | 95.21 |
| 6 | Arc Light | - | 20 min. | 95.28 | |

In No. 3 the reaction was carried out in a quartz flask. Since the yield in this experiment was distinctly lower than that in experiment No. 1, ultra-violet light has apparently little effect on the reaction. This was to be expected from the results obtained in the bromination of toluene by other workers.

The analyses were carried out as follows. The reaction mixture was washed with a solution of sodium carbonate and with water and was made up to a known volume. A 20 c.c. portion was then removed and evacuated for not less than 15 minutes at 50° C. at a pressure not greater than 30 m.m. The residue was boiled with alcoholic silver nitrate for 20 minutes and the precipitated silver bromide weighed. The quantity of the bromine in the total product

was then calculated as a percentage of that theoretically possible according to the equation:



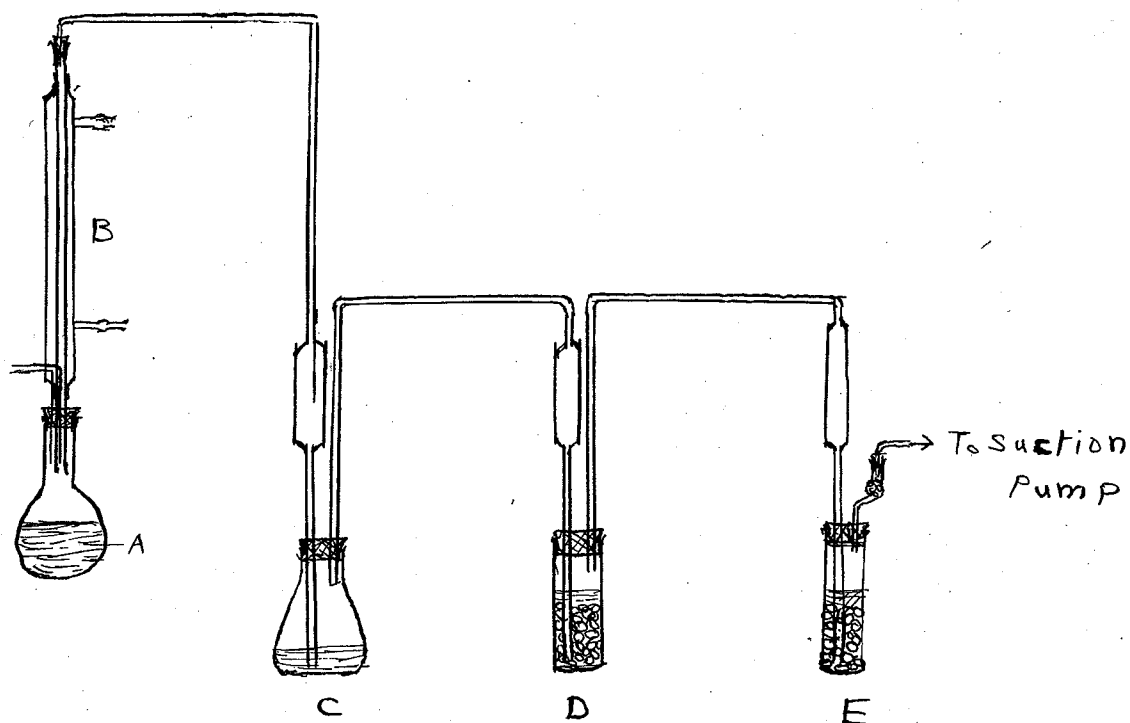
That the removal of the carbon tetrachloride was complete is evident from the concordant results obtained in the analysis of each mixture.

From each reaction mixture the main product, p. nitro benzyl bromide, was isolated and purified by recrystallisation from alcohol and its melting point taken. To definitely identify the product two derivatives, nitro benzyl acetate and nitro benzyl benzoate, were formed from the product obtained from experiment No. 5, according to the directions given by Reid (J.A.C.S. 39, 130- 132)

More exact experiments were then undertaken with a view to determining the amount of side chain substitution, nuclear substitution and addition taking place.

Apparatus and Method.

The apparatus consisted of a flask A in which the reaction



took place. To it was attached a reflux condenser B, which in turn was connected with the hydrobromic acid absorption flasks, C, D and E. C and D contained potassium iodide solution while E was filled with a known volume of standard N/2 NaOH solution. D and E were filled with glass beads. E was connected to a suction pump by means of which air was continually drawn through the apparatus during the experiment.

The quantities of nitro toluene and bromine were reduced to 6 gr. and 7 gr. respectively, owing to the limited solubility of the product in cold carbon tetrachloride. The nitro toluene and bromine together with 150 c.c. of carbon tetrachloride were placed in A. The solution was then heated to boiling and the 400 Watt Tungsten Lamp, which had been substituted for the arc light used in the preliminary experiments, was turned on. When all the bromine had been used up the light was turned off, air was drawn through the apparatus, and the reaction mixture was allowed to boil for another twenty minutes by which time all the hydrobromic acid had been swept into the absorption flasks. The reaction mixture was shaken up with sodium carbonate solution and then washed twice with water. It was made up to 200 c.c. and known volumes were used for analysing the product.

Analysis of the Product.

It was required to determine the amount of side chain substitution, nuclear substitution and addition taking place. Since in view of the conditions under which the reaction was carried out it seemed unlikely that any large percentage of the hydrobromic acid would be oxidised, the following method was employed:

1st. The total bromine present in the mixture was estimated by Stepanow's method.

2nd. The amount of bromine which reacts with alcoholic silver nitrate was measured.

3rd. The hydrobromic acid evolved was measured.

These three measurements give what may be briefly termed "Silver Nitrate Br_2 " and "Hydrobromic acid Br_2 " "Total Br_2 ". Representing side chain, nuclear and added bromine by A, B and C, respectively, we get:

$$\text{"Total Br}_2\text{"} = A + B + C$$

$$\text{"Silver nitrate Br}_2\text{"} = A + B$$

$$\text{"Hydrobromic acid Br}_2\text{"} = A \text{ or } = A + C$$

A consideration of the actual results obtained is necessary before the ambiguity of the last equation can be discussed.

Estimation of "Total Br_2 ".

Stepanow's method was used. The residue obtained after removing the carbon tetrachloride from 5 c.c. of the solution was dissolved in 25 c.c. of absolute alcohol, and boiled on a water bath while 3 gr. of sodium was slowly added over a period of thirty minutes. The mixture was then boiled for one hour longer, 30 c.c. of water, and the mixture acidified with nitric acid. Owing to the nitro group present in the substance a dark brown precipitate was formed which made filtration necessary. The solution was then titrated with N/10 AgNO_3 and KSCN solutions using ferric salt as an indicator. Owing to the orange colour of the solution, considerable practice was necessary before the end point could be determined with accuracy. For ~~this~~ this reason gravimetric

methods were tried but the precipitate could not be washed free from the organic matter carried down with it and the results obtained were too high.

| Substance | Theoretical % of Br | Observed % of Br | |
|-------------------------|---------------------|------------------|----------------|
| | | Gravimetrically | Volumetrically |
| p. nitro benzyl bromide | 37.07 | 38.66 | 36.87, 36.33 |
| p. chloronitro benzene | 22.51 | | 22.65 |

Estimation of "Silver nitrate Br₂".

Although it is known that benzenehexachloride does not react with alcoholic silver nitrate yet it does not seem justifiable to conclude that, therefore, bromine addition compounds, of nitro toluene, should they be formed, would also fail to react with this reagent, especially in view of the far reaching changes known to be produced by the introduction of a nitro group into the benzene ring. Since no halogen addition compounds of nitro toluene have ever been isolated, it was, therefore, impossible to decide beforehand whether the silver bromide formed by treating the product of the reaction with alcoholic silver nitrate was or was not partly due to added bromine.

The product obtained by nitrating ortho bromo toluene was boiled with alcoholic silver nitrate in order to make certain that this reagent would not remove bromine from the 2 bromo 4 nitro toluene which would result from nuclear substitution. No silver bromide was formed.

H Br Acid Determination.

The hydrobromic acid together with a considerable quantity of free bromine was absorbed in the absorption flasks already described. The iodine set free by the bromine was carefully discharged with thiosulphate and the solution titrated ~~was~~ using methyl orange as an indicator. In order to determine whether the iodine thus discharged interferes with the titration of the acid, iodine in potassium iodide solution was added to a known volume of standard hydrochloric acid. Upon discharging the iodine with thiosulphate and titrating the solution no change in the end point was observed.

Results of Experiments

Eleven experiments have been carried out and a complete analysis of the product has been made in each case. In experiments 11-16 ordinary pieces of coloured glass were used to obtain light of the different colours. This was done in order to obtain a general idea of which regions of the spectrum would repay detailed study with accurate light filters. In experiments 17 oxygen was drawn through the solution during the reaction. The abnormally slow rate of reaction of experiments 7 and 10 was probably due to an accidental formation of a partial vacuum in the apparatus which lowered the temperature of the boiling solution and in that way decreased the speed of the reaction. The results are given in the table on the following page. The fifth column gives the amount of nuclear substitution, while the fourth and sixth added together give the amount of side chain plus added bromine. If no added bromine is formed then the sixth ~~also~~ column gives the amount of hydrobromic acid decomposed. If no hydrobromic acid is decomposed

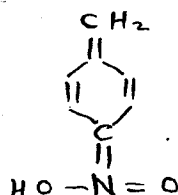
| Exp. No. | Conditions | Time | Total Br ₂ | "AgNO ₃ Br ₂ " | "HBr, Br ₂ " | %A | %B | %C |
|----------|--------------------------------|----------|-----------------------|--------------------------------------|-------------------------|-------|-------|-------|
| 7 | Carbon arc | 100 min. | 3.33 gr. | 3.25 gr. | 2.63 gr. | 76.82 | 2.25 | 20.93 |
| 8 | 400 Watt D.C. - 10 in. distant | 28 " | 3.55 " | 3.45 " | 2.75 " | 74.65 | 2.87 | 22.53 |
| 9 | " " A.C. - " " " | 25 " | 2.99 " | 3.02 " | 2.34 " | 79.65 | .90 | 21.85 |
| 10 | " " " - " " " | 85 " | 3.41 " | 3.39 " | 2.68 " | 76.87 | .67 | 22.46 |
| 11 | Red Light - 6 " " | - " | 2.77 " | 2.48 " | 1.80 " | 54.71 | 10.36 | 34.93 |
| 12 | " " - " " " | 30 " | 3.29 " | 3.26 " | 2.54 " | 76.54 | .88 | 22.58 |
| 13 | Yellow & Green light - " " " | 100 " | 2.69 " | 2.67 " | 1.99 " | 73.10 | .78 | 26.12 |
| 14 | " " - " " " | 116 " | 2.61 " | 2.38 " | 1.77 " | 58.43 | 9.10 | 32.47 |
| 15 | Blue Light - " " " | 180 " | 2.12 " | 1.60 " | 1.11 " | 23.29 | 24.52 | 52.19 |
| 16 | " " - " " " | 150 " | 2.64 " | 2.20 " | 1.59 " | 43.74 | 16.61 | 39.65 |
| 17 | 400 Watt A.C. - " " " | 33 " | 3.17 " | 3.19 " | 2.26 " | 64.11 | 9.28 | 26.61 |
| | In presence of Oxygen | | | | | | | |

the fourth column gives the amount of side chain bromine and the sixth represents added bromine.

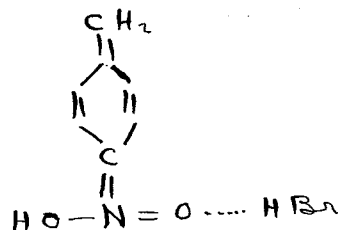
Although the work of previous investigators would lead one to suppose there might be some slight oxidation of the hydrobromic acid by the oxygen of the air, yet, in view of the fact that the reaction is carried out in boiling carbon tetrachloride thereby eliminating all but traces of oxygen in the reaction mixture and rapidly removing the hydrobromic acid as it is evolved, it seems hardly probable that the very considerable values which are given in the sixth column can be due solely to the oxidation of the hydrobromic acid by the oxygen of the air. In support of this view it will be noticed that the passage of a stream of oxygen through the reaction mixture as in experiment 17 has comparatively little effect on the amount of added bromine. Finally the results of all former investigations go to show that the oxidation of the hydrobromic acid by traces of oxygen in the reaction mixture is characterised by the greatest irregularity. This is in marked contrast to the surprisingly uniform results obtained in the present case.

Though it seems improbable, therefore, that the oxidation of the hydrobromic acid, which takes place in the photo-bromination of toluene and which has been so carefully investigated by previous workers can be sufficient to account for the deficiency of the hydrobromic^{acid} in the present case, yet there is one other explanation that should be investigated before one makes the radical assumption that large quantities of addition compounds must, therefore, be formed. This is the possibility of the reduction of the nitro group. Since nitro toluene is a light yellow substance it is not unreasonable to

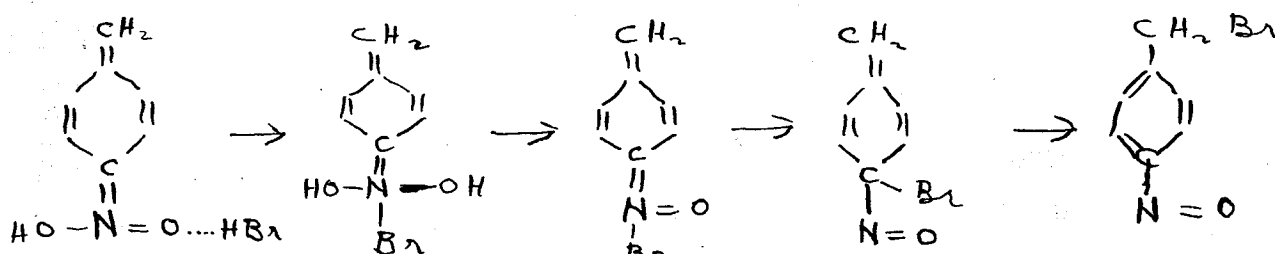
suppose that it exists partly in the quinoidal form:



Now it is well known that nitro groups in common with other unsaturated groups exhibit the phenomenon of halochromism. It is highly probable that a molecular compound consisting of one molecule of nitro toluene and one molecule of hydrobromic acid might be formed. Such a compound would be formulated according to Pfeiffer's theory thus:



Molecular compounds of this type have been studied by Fiedlitz (Jour prakt Chemie, 91, 213, 1915). Such compounds show a tendency to undergo chemical rearrangements resulting in the saturation of the double bond. It is therefore not unreasonable to suppose that the above molecular compound might undergo the following transformations which would result in a side chain substituted compound.



This series of possible transformations has been sketched only to demonstrate the intrinsic probability of such a reaction. The whole problem undoubtedly needs further investigation.

THE EFFECT OF A MAGNETIC FIELD ON ORGANIC SYNTHESSES

BY

HELEN D. CHATAWAY

THESIS SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE

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THE EFFECT OF A MAGNETIC FIELD ON ORGANIC SYNTHESIS

In view of the growing recognition of the electronic theories of chemical change, it seemed of interest to investigate the effect of a magnetic field on organic reactions. The first reaction chosen was the chlorination of toluene, since its course is known to be easily altered by external conditions. Toluene was chlorinated by the action of dry chlorine gas on excess of toluene and the product was analysed by the method described by Cohen. Preliminary experiments were carried out to determine whether a magnetic field influences either the rate of the reaction or the relative proportion of the isomers formed. Each experiment was carried out in duplicate, the one reaction taking place inside a magnetic field, the other outside it but under otherwise identical conditions.

The Magnetic Field. The magnet employed was a circular one similar to that used by Lowery for the measurement of magnetic rotations being built according to the directions given in his paper (J.C.S., T II, p. 1322). The magnetic field is formed within the magnet and according to measurements made by Perkin on his own magnet the field strength was 865 and 520 gauss, when the current was 1.7 and 1 amperes respectively. In the present experiments a current of 1.3 amperes was used since at higher amperages the magnet became overheated when run for any length of time.

Method of Analysis. Analysis of the product was carried out according to the method described by Cohen, Dawson, Blockey and Woodmansey (J.C.S., 1910 T p. 1625). The benzyl chloride was determined by boiling a portion of the product with alcoholic silver

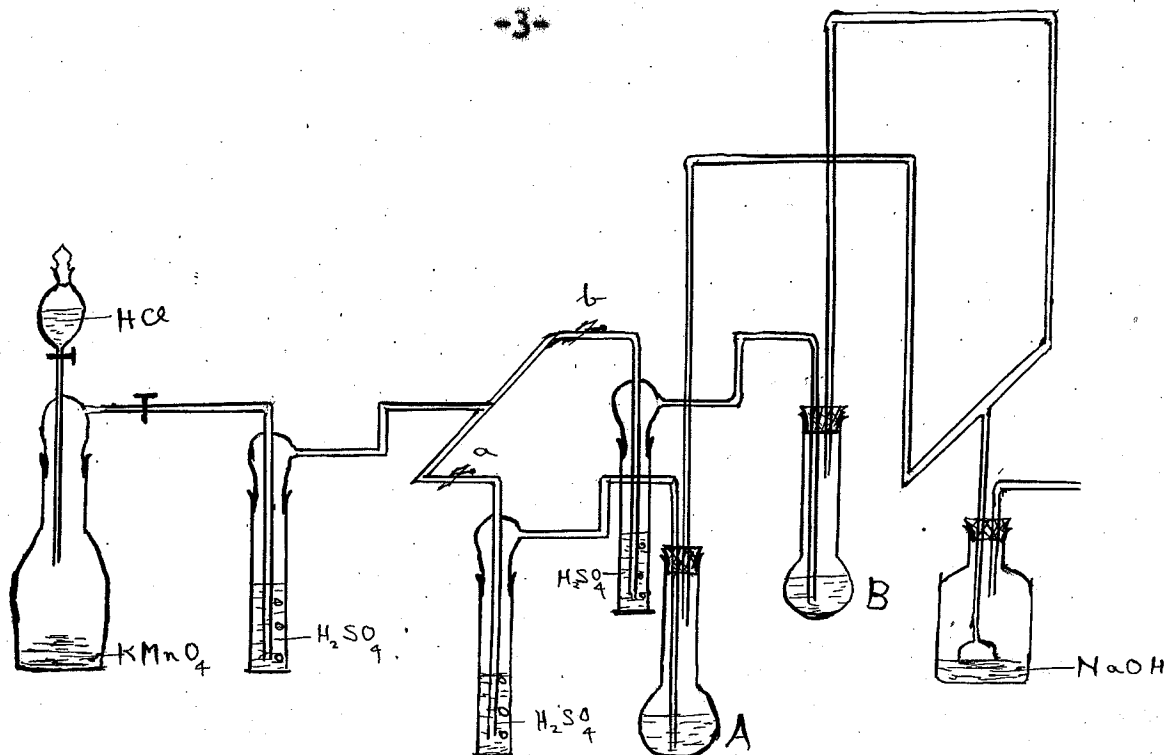
nitrate, and weighing the precipitated silver chloride. To determine the amount of para chlorotoluene a weighed portion was oxidised with nitric acid (1 part HNO_3 ; 2 parts H_2O) in a sealed tube at 115° to 120°C . for five or six hours. The mixture of acids thus produced was washed and boiled with 200cc. of water. This dissolved all the benzoic acid, ortho chlore benzoic acid, and about .2 gr. of para chlore benzoic acid. The para compound was then filtered, dried at 100°C ., weighed, and a correction made for the amount of acid lost during purification. The density of the crude mixture was then determined and its composition calculated from the following equations:

$$\alpha + \beta = 100 - \gamma - \delta$$

$$\text{and } \frac{\alpha}{d_1} + \frac{\beta}{d_2} = \frac{100}{d} - \frac{\gamma}{d_3} - \frac{\delta}{d_4}$$

where α, β, γ , and δ equal the percentages of toluene, ortho chlore toluene, para chlore toluene, and benzyl chloride present in the mixture, respectively, and where d_1, d_2, d_3 , and d_4 equal the corresponding densities of the pure substances and d the density of the mixture.

Effect on the Rate of Reaction. The apparatus was set up as shown in the diagram. The flask A was placed in the magnetic field within the magnet while the flask B was surrounded by a shade made of heavy paper the same size and shape as the interior of the magnet. This was done in order that each reaction should proceed under the influence of the same amount of light. Equal quantities of toluene containing iodine as a catalyst were placed in the flasks and the chlorine generated in c was passed through each flask simultaneously.



By adjusting the screw clips, a, and b, it was possible to maintain the rate of flow through each approximately equal. The flasks were removed every hour and the gain in weight noted. At the end of three hours the flasks together with their respective sulphuric acid bottles were interchanged.

| Time | Approx. rate of flow of bubbles of Cl. | Gain of weight of A | Gain of weight of B |
|-------------------------|-------------------------------------------|------------------------|------------------------|
| 1st hour | 60 per minute | .5 gr. | .4 gr. |
| 2nd " | 120 " " | 1.8 " | 1.7 " |
| 3rd " | 100 " " | 1.4 " | 1.2 " |
| A and B interchanged | | | |
| 4th " | 50 " " | .7 gr. | .45 gr. |
| 5th " | 240 " " | 8.6 " | 6.1 " |
| 6th " | 200 " " | 7.8 " | 6.6 " |

Since even after interchanging the positions of the flasks, A still continued to gain faster than B this difference was attributed to a possible difference in the size of bubbles of chlorine from the sulphuric acid bottles and not to the effect of the magnetic field.

Effect on the Proportion of the Isomers Formed. Four experiments were carried out each consisting of two simultaneous chlorinations, one inside and one outside the magnetic field. In the first experiment no provision was made for keeping the temperature of both reaction mixtures the same. In the other experiments the reactions were carried out in large test tubes placed in outer jackets through which tap water circulated. In the first three experiments iron was used as a catalyst and in the fourth iodine. The results are given below.

| Position of flask | % of Toluene | % of o. chloro toluene | % of p. chloro toluene | % of benzyl chloride |
|-----------------------|--------------|------------------------|------------------------|----------------------|
| Inside magnetic field | 54.27 | 23.21 | 22.52 | 0.00 |
| Outside " " | 54.31 | 24.21 | 20.48 | 0.00 |
| Inside " " | 7.74 | 60.43 | 30.67 | 1.16 |
| Outside " " | 7.73 | 60.28 | 31.01 | .98 |
| Inside " " | 45.10 | 33.61 | 20.42 | .87 |
| Outside " " | 43.63 | 30.94 | 23.09 | 1.34 |
| Inside " " | 13.85 | 55.21 | 28.71 | 2.13 |
| Outside " " | 20.25 | 51.01 | 26.58 | 2.16 |

As will be noticed the differences lie within the limits of experimental error. Moreover it had become apparent that the magnet employed was not suitable for the production of intense fields. The problem was therefore abandoned for the present.