

EXPERIMENTS ON THE INFLUENCE OF *s*-TRINITROBENZENE ON REACTIONS IN WHICH ARYLAMINES ARE INVOLVED.

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The part which catalysts play in various chemical reactions is still not clearly understood. It is highly probable that different catalysts behave in different ways, e.g. it is quite possible that finely divided nickel or colloidal palladium, which are used as catalysts in processes of reduction with hydrogen, act more or less physically by bringing about a high concentration of the reacting materials on the surface of the metal. In other reactions it has been proved that the catalyst enters into chemical union with one or more of the reacting substances, e.g. the aluminium chloride used in the Friedel-Crafts reaction, or the catalysts commonly used in halogenations.

It has not yet been determined how far a substance C which enters into chemical reaction with either A or B or both can act catalytically in facilitating the reaction between A and B.

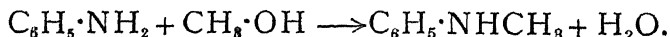
It is well known that polynitro aromatic compounds form additive compounds with most of the simple arylamines and it appeared to us to be worth while ascertaining whether a substance like *s*-trinitrobenzene could act as a catalyst in condensations in which at least one of the reacting substances is an arylamine.

E. Knoevenagel¹ has shown the catalytic activity of small amounts of iodine on many condensations of this type and we have selected some of the reactions studied by Knoevenagel and in each case carried out three sets of experiments, viz. :—

- (a) Condensation without a catalyst.
- (b) Condensation in the presence of small amounts of iodine.
- (c) Condensations in the presence of *s*-trinitrobenzene.

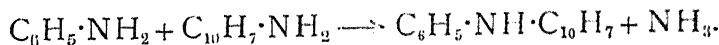
The types of reactions studied were the following :—

- I. Alkylation of an arylamine by the condensation of the arylamine with an alcohol. The substances selected were aniline and methyl alcohol.



¹ *J. Pr. Chem.*, 1914, [ii], 89, 1.

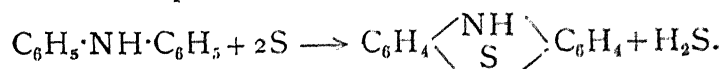
2. Condensation of two primary arylamines to a secondary arylamine, e.g. phenyl- α naphthylamine from aniline and α -naphthylamine.



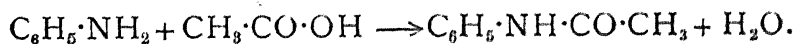
3. Formation of keto-anils by the condensation of a primary arylamine with a ketone, e.g. diphenyl-keto-anil from aniline and benzophenone.



4. Ring formation by the action of sulphur on a secondary arylamine, e.g. thiodiphenylamine from diphenylamine and sulphur.



5. Acylation of a primary arylamine by means of the free acid, e.g. acetanilide from aniline and acetic acid.



EXPERIMENTAL

1. FORMATION OF MONOMETHYLANILINE FROM ANILINE AND METHYL ALCOHOL

Knoevenagel's experiments have proved that small amounts of iodine have a pronounced positive catalytic action on this condensation. In the absence of a catalyst very little secondary amine is formed, whereas with 0.72 per cent. of iodine (calculated on the weight of the aniline) a 97 per-cent. yield of methylaniline can be obtained.

Three sets of experiments were carried out. In (a) 27.9 grams of aniline and 6.4 grams of pure methyl alcohol were used. In (b) the same quantities were used with the addition of 0.2 gram of iodine and in (c) 0.2 gram of trinitrobenzene was used in the place of iodine. In all three experiments the mixtures were sealed in hard glass tubes and heated during nine hours at 230°. An examination of the contents of the tubes was then made as follows. The major portion of the unaltered aniline was precipitated by pouring dilute sulphuric acid onto the mixture, stirring and cooling to 5°. The precipitated aniline sulphate was removed, washed with a little dilute acid, dried at 50° and weighed and from the filtrate the free amines were liberated by

the addition of caustic soda and then extracted with ether. After drying the solution with anhydrous sodium sulphate the ether was removed and the oil distilled.

Table I gives the results obtained in the three experiments.

TABLE I

No. of Experiment	Weight of aniline sulphate	Weight of aniline corresponding with sulphate	Weight of amine from filtrate	B.P. of amine at 682 mm.	M.P. of acetyl derivative
<i>a</i>	33.0	21.5	4.4	173°	113°
<i>b</i>	12.9	9.0	21.0	183-184°	101°
<i>c</i>	32.2	21.0	5.2	174°	112.8°

The boiling point of aniline is 177° and that of monomethylaniline 185° at 682 mm. (corr.) The melting point of acetanilide is 113° and of acetylmonomethylaniline is 102°.

It is clear from these experiments that the results with trinitrobenzene are similar to those obtained in the absence of a catalyst and quite different from those obtained when a little iodine is used.

2. FORMATION OF PHENYL- α -NAPHTHYLAMINE FROM ANILINE AND α -NAPHTHYLAMINE

The quantities of materials used were as follows :—

Experiment (a).—5.0 grams of aniline and 7.5 grams of α -naphthylamine.

Experiment (b).—7.2 grams of aniline, 11.0 grams of α -naphthylamine and 0.08 gram of iodine.

Experiment (c).—5.0 grams of aniline, 7.5 grams of α -naphthylamine and 0.08 gram of trinitrobenzene.

The reactions were carried out in small round bottom flasks provided with air condensers and heated in an oil bath at 230° for six hours and then at 250° for two hours.

In Experiment (*b*) the product was treated as recommended by Knoevenagel, viz. shaken with dilute hydrochloric and then with ether

which removes the secondary base. After removal of the ether the residue distilled under a pressure of 8 mm. at 220°.

The amounts of condensation product in Experiments (*a*) and (*c*) were so small that another method of analysis was adopted, viz. treatment of the product with excess of hot dilute hydrochloric acid and weighing the residual secondary base after washing with hot dilute hydrochloric acid and drying.

As the secondary base is very slightly soluble in hot water or hot dilute acid, two control experiments were made in order to ascertain the correction to be allowed for this solubility. By using 4.0 grams of *α*-naphthylamine, 0.2 gram of phenyl-*α*-naphthylamine and 270 c.c. of dilute hydrochloric (3 N.) acid at 70° and a further 70 c.c. for washing, a residue of 0.093 gram of secondary base was recovered. This corresponds with a loss of 0.031 gram of phenyl-*α*-naphthylamine for each 100 c.c. of dilute hydrochloric acid at a temperature of 70°. A similar experiment gave a value of 0.029, so that 0.030 gram has been taken for purposes of calculation in Table II.

The results of the experiments are given in Table II.

TABLE II

No. of Experiment	Weight of secondary base	Percentage yield
<i>a</i>	0.43 gram	3.8
<i>b</i>	12.5 grams	77.0
<i>c</i>	0.52 gram	4.6

The secondary base in experiments (*a*) and (*c*) was by no means pure and had a dark colour, but the results show that trinitrobenzene has no catalytic effect on the formation of phenyl-*α*-naphthylamine.

3. PREPARATION OF DIPHENYL-KETO-ANIL

The quantities of materials used in the three experiments were as follows :—

(*a*) 3.76 grams of aniline and 5.00 grams of benzophenone.

(*b*) 3.64 grams of aniline, 5.00 grams of benzophenone and 0.05 gram of iodine.

(c) 3.75 grams of aniline, 5.00 grams of benzophenone and 0.050 gram of trinitrobenzene.

The three experiments were carried out by heating the mixtures in short test tubes¹ for 0.5 hour in an oil bath at 165–170°. The mixture was cooled and poured into dilute acetic acid containing a little alcohol. The solid (keto-anil) was removed, washed with dilute acetic acid and crystallised from hot alcohol. The treatment with dilute acetic acid removed any unaltered aniline, any benzophenone remained in the alcoholic mother liquor as it dissolves readily in cold alcohol and the condensation product, which is only sparingly soluble in cold alcohol, is deposited as pale yellow, glistening plates when the solution cools.

The results are given in Table III.

TABLE III

Experiment	Weight of anil in grams	M.P.	Percentage yield
<i>a</i>	0	—	0
<i>b</i>	2.6	112°	37
<i>c</i>	0	—	0

4. FORMATION OF THIODIPHENYLAMINE FROM DIPHENYLAMINE AND SULPHUR

Knoevenagel studied the reaction by estimating the evolved hydrogen sulphide gasometrically in a Hempel burette with a three-way cock.

In our experiments the mixtures were placed in small flasks and heated in an oil bath for twenty minutes. The flask was provided with inlet and outlet tubes and at the end of the experiment a slow stream of carbon dioxide was passed through the flask in order to remove the hydrogen sulphide formed. The issuing gas was passed through two wash bottles containing known volumes of standard iodine solution and a third flask containing standard thiosulphate to catch iodine

¹ Earlier experiments were made in longer tubes but it was found that the water liberated in the reaction condensed on the upper part of the tube, dropped on to the reacting mass and diminished the yield of anil.

vapour, and at the end of the experiment the excess of iodine was titrated by means of standard sodium thiosulphate and a correction applied for the iodine absorbed by the thiosulphate.

The results are given in the appended table.

TABLE IV

No. of Experiment	Catalyst	Weight of diphenylamine in grams	Weight of sulphur in grams	Hydrogen sulphide in grams	Percentage yield
<i>a</i>	<i>Nil</i>	1.12	0.4	0.009	4.2
<i>b</i>	Iodine	1.12	0.4	0.208	98.0
<i>c</i>	Trinitrobenzene	1.12	0.4	0.0093	4.4

5. ACETANILIDE FROM ANILINE AND ACETIC ACID

The amounts of aniline and glacial acetic acid used in each experiment were respectively 5.15 grams and 6.3 grams and the mixture in each experiment was heated in tubes in an oil bath at 162° during two hours. The tubes were provided with air condensers. In Experiment (*a*) no catalyst was used, in Experiment (*b*) 0.08 gram of iodine and in Experiment (*c*) 0.08 gram of trinitrobenzene. To isolate the acetanilide formed the product was poured into 30 c.c. of dilute (5 N.) acetic acid, the precipitate well crushed with a glass pestle, then filtered, washed and dried. The filtrate was concentrated and two more crops of crystals obtained. The crystals obtained melted at 113°.

The results are given in Table V.

TABLE V

Experiment	Catalyst	Weight of acetanilide	Percentage yield of theoretical
<i>a</i>	<i>Nil</i>	5.07	67.8
<i>b</i>	Iodine	5.04	67.4
<i>c</i>	Trinitrobenzene	5.05	67.5

SUMMARY

In all five reactions studied, viz. :—

1. Alkylation of aniline,
2. Formation of phenyl- α -naphthylamine,
3. Preparation of benzophenoneanil,
4. Formation of thiodiphenylamine, and
5. Acetylation of aniline,

it is clear that *s*-trinitrobenzene has no catalysing effect, although in the first four reactions iodine acts as a strong positive catalyst.

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