LV.—*On the Action of Ammonia and the Amines upon Naphthoquinone.*

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THE importance of a study of the ammonia- and amine-compounds of the quinones, as a means of throwing further light upon the question of the constitution of these latter bodies, has been pointed out by G. Schultz (*Ber.*, **10**, 1791), who commenced an investigation of the so-called *quinonamines*, and more recently by Zincke.

It has been supposed that the oxygen-atoms of a quinone determine its reaction with ammonia and the amines, even in cases in which water is not eliminated in the combination; and that the nitrogen-group becomes attached to the carbon-atoms of the quinone only indirectly by means of oxygen. Thus, Wichelhaus (*Ber.*, **4**, 851) has assigned to one of the best-known members of the class in question, the quinone anilide of Hofmann, the structural formula

$$\text{C}_{10}\text{H}_6 \begin{matrix} \text{O} - \text{NHC}_6\text{H}_5 \\ \text{O} - \text{NHC}_6\text{H}_5 \end{matrix}$$

The subject of the probable difference in constitution of the ammonia derivatives of the quinones, according as these latter possess the structure assigned to them by Graebe, or are double ketones as supposed by Fittig, has been discussed recently at length by Professor Zincke, of Marburg (*Ber.*, **11**, 1999).

The material at his disposal was, however, too scanty to allow of any positive conclusions being drawn in the matter. At the instance of Professor Zincke, I undertook a study of naphthoquinone in the direction indicated, the results of which I now beg to lay before the Society.

The naphthoquinone used was the variety *a*, melting at 125°. The results obtained show that this quinone differs materially in its behaviour to ammonia and the amines from phenanthraquinone and anthraquinone; also from the quinone $\text{C}_{16}\text{H}_{10}\text{O}_2$, of Zincke and Breuer. Moreover, it does not react in quite the same way as common quinone, which in other respects it so closely resembles.

I find, namely, that by the action of primary monamines upon naphthoquinone in alcoholic solution, compounds are formed which consist of 1 mol. of quinone, plus 1 mol. of amine, minus 2 atoms of hydrogen. The methylamine, ethylamine, aniline, and paratoluidine derivatives may, therefore, all be represented by the general formula $\text{C}_{10}\text{H}_6\text{O}_2\text{NR}'$.

Secondary amines react necessarily in a somewhat different manner. Compounds were obtained with dimethylamine, and in presence of

hydrochloric acid, with diphenylamine. The dimethylamine compound on analysis gave numbers agreeing closely with those required by the formula $C_{10}H_5N(CH_3)_2O_2$.

Diphenylamine does not appear to react upon naphthoquinone in alcoholic solution, or even when the substances are melted together. In presence of hydrochloric acid, a dark purplish-blue compound is formed at once, either in presence of alcohol, or when the two substances are heated with dilute hydrochloric acid alone. The analysis of this substance, which was troublesome to purify, gave numbers which agree either with the formula $C_{10}H_5N(C_6H_5)_2O_2$ or with $C_{10}H_6O_2N(C_6H_5)_2$, which would have to be doubled. I have not been able to decide what part the hydrochloric acid plays in the formation of this compound. Experiments described later seemed to negative the hypothesis that a chloroquinone is first formed, which then reacts with the amine.

Tertiary amines do not appear to react on naphthoquinone even in presence of hydrochloric acid.

The whole of the compounds mentioned may be obtained from naphthoquinol instead of from the quinone; the reaction then proceeds more slowly, and oxidation is observed on the surface of the liquid.

It is worthy of remark that it is not necessary to use the amines in the free state; indeed, it is advantageous in the preparation of methyl-, ethyl-, and dimethyl-amine derivatives, to neutralise the amine solution with acetic acid before adding it to the naphthoquinone. In this way a purer product is obtained.

These compounds crystallise well in needles, which possess a brilliant lustre, and may be sublimed unaltered.

The naphthoquinone used for the following experiments was obtained by the oxidation of naphthalene dissolved in glacial acetic acid by chromic acid (Groves, this Journal [2], 11, 209). It was found advantageous to proceed as follows:—Naphthalene in portions of 5 grams was dissolved in glacial acetic acid (30 grams for each portion of naphthalene), 15 grams of chromic acid was then added little by little to each flask, and a brisk action kept up by means of gentle heating, until the whole of the chromic acid had been added. The mixture was then boiled for a few minutes and precipitated with water, the precipitate filtered off, distilled with steam, and crystallised from light petroleum, according to the directions of Groves. The yield is about 15–20 per cent. of the naphthalene employed.

I attempted to prepare naphthoquinone in a manner analogous to that given by Nietzki (*Ber.*, 11, 1102) for the preparation of common quinone, and oxidised naphthylamine in the cold, and at the temperature of a water-bath, with potassium bichromate and sulphuric acid,

but without success. In the cold a small quantity was formed, but at 100° the product was a purple-red amorphous body, which contained no trace of the substance sought. Some naphthoquinone was also obtained by oxidation of amidonaphthol with a dilute solution of chromic acid (Liebermann, *Liebig's Annalen*, **183**, 248); the separation of the isomeric α - and β -nitronaphthols by boiling water, a stage in the preparation of amidonaphthol from acetamidonaphthalide is, however, very tedious.

Naphthoquinol.

This body, which Groves obtained by reducing the quinone with strong hydriodic acid, may be readily obtained by throwing powdered naphthoquinone in small portions into a boiling mixture of tin and hydrochloric acid. The substance becomes dark, and after some minutes dissolves, and on leaving the filtrate to cool, the quinol crystallises out in white needles, melting at 173°. Sulphurous acid also reduces the quinone at 140—150°. On boiling the product with water, some naphthoquinol is dissolved out, but a large quantity of an amorphous insoluble body remains.

Compound formed from Naphthoquinone and Aniline.

I have been able to study this compound more fully than the others, on account of the ease with which it can be prepared. I therefore describe it first.

Preparation.—If an excess of aniline be added to an alcoholic solution of naphthoquinone, the liquid immediately becomes red, and after some minutes' heating on the water-bath, the reaction is ended. Water is then added, together with some acetic acid, the liquid well shaken and filtered. The precipitate is dissolved in alcohol, boiled with some animal charcoal to free it from small quantities of dark substances which are generally formed (especially if the mixture has been heated too long), and crystallised once or twice, from dilute alcohol. Thus prepared, it forms beautiful red needles of great brilliancy, which melt at 190—191°, and at a higher temperature sublime undecomposed.

The aqueous filtrate containing acetic acid deposits, on standing in the air, considerable quantities of the red compound.

It is best to use a considerable excess of aniline, about double the weight of the naphthoquinone employed. With smaller quantities of aniline, the precipitate is apt to be light in colour, and to contain undecomposed quinone.

The aniline compound dissolves easily in hot alcohol, benzene, and

ether, less so in cold alcohol. In light petroleum it is almost insoluble.

Concentrated sulphuric acid dissolves it, with production of a splendid crimson colour; water precipitates the compound apparently unaltered.

Alcoholic potash dissolves it with a purple colour: the solution can be evaporated to dryness without decomposition, and the remaining brown mass on becoming moist rapidly absorbs oxygen, and regains its purple colour.

The aniline compound, and indeed all the amine derivatives of naphthoquinone, burn with great difficulty, and combustion with oxide of copper generally gave results much too low. Of the following analyses, Nos. I and II were made with this material, the second, however, in a stream of oxygen. III and IV were made with chromate of lead.

	I.	II.	III.	IV.	Calculated for $C_{16}H_{11}NO_2$.
C	68.01	76.75	76.35	77.44	77.10
H	4.68	4.38	4.71	5.09	4.41
N	—	—	—	5.75	5.62

The nitrogen was estimated by Dumas' method. These numbers agree with the formula, $C_{16}H_{11}NO_2$, which may be resolved into—

A body of the composition II, and perhaps III also, should give an acetyl-derivative with acetic anhydride; the substance was therefore heated for several hours in a sealed tube with acetic anhydride to $150-160^\circ$, and in a second experiment to 170° , but it remained unaltered. Benzoic anhydride did not attack the substance when heated with it in a test-tube.

A compound of formula II might also be expected to split into oxynaphthoquinone and aniline when heated with hydrochloric acid. Some of the red crystals heated to $160-170^\circ$ with hydrochloric acid were completely decomposed, with formation of a black substance. The filtrate from this substance was evaporated and found to contain aniline, but the black substance which was similar to that obtained by heating naphthoquinone with strong hydrochloric acid, did not contain any oxynaphthoquinone.

In a second experiment the substance was boiled with hydrochloric acid and alcohol, till the colour had quite disappeared, then evaporated

down, and after addition of a little water, shaken with ether. The residue left by the ether on evaporation was yellowish, and no oxynaphthoquinone was found in it. On standing, the red compound was gradually reproduced. The aqueous solution on evaporation was found to contain aniline.

There remain the formulæ, $C_{10}H_5\overset{O}{\underset{O}{>}}NC_6H_5$ and $C_{10}H_5(NHC_6H_5)O_2$.

It was thought probable that if the former were correct, the compound could be reduced to naphthoquinol and aniline. Experiments were made with zinc and hydrochloric acid and with sulphurous acid in aqueous and alcoholic solution.

The red crystals were heated to 125–130° with aqueous sulphurous acid for some hours, and the resulting yellowish solution filtered from an undecomposed residue. On evaporating the filtrate and allowing it to stand, red needles melting at 190–192° soon appeared on the surface.

To compare the action of naphthoquinol and aniline, solutions of each in water were mixed and allowed to stand in the air. Red needles soon formed on the surface, which possessed all the properties of the anilide. Some of the anilide was then heated to 130° with sulphurous acid, the liquid quickly filtered and made acid with hydrochloric acid. Ether dissolved from this solution a substance which remained after evaporation of the ether in blackish needles, which melted at 165°. The aqueous solution contained aniline. The needles did not appear to be the quinol, as no naphthoquinone could be obtained from this by oxidation.

At 150° to 155°, the reaction with sulphurous acid is more complicated, a quantity of black substance is found mixed with melted globules of sulphur and white needles, which oxidise at once in the air.

Zinc and hydrochloric acid boiled with naphthoquinone anilide decolorise it, and on addition of water a reddish-white precipitate falls, which rapidly oxidises in the air to the original compound. In a second experiment the liquid was shaken out with ether as soon as decolorisation had taken place. On evaporating the ether, a reddish mass was left which soon gave again the red compound (m. p. 188°). The liquid contained aniline.

Whether the reddish substance is a single reduction-product or a mixture could not be decided, on account of the small quantity at disposal.

A white reduction-product is also obtained by reducing the anilide in alcoholic solution with ammonium sulphide. The reagent is added in large quantities, and after some time white crystals are formed, not, however, needles (naphthoquinol). The substance may be washed

with dilute ammonium sulphide, but oxidises too rapidly for analysis. The red compound appears to be reproduced.

The ease with which the aniline compound is decomposed, with separation of aniline, by sulphurous acid and hydrochloric acid, appeared to favour the adoption of the formula $C_{10}H_5<\overset{O}{\underset{O}{\text{O}}}>NC_6H_5$. The analysis of the dimethylamine compound subsequently obtained agrees, however, with the formula $C_{10}H_5N(CH_3)_2O_2$, according to which the nitrogen must be supposed directly combined with carbon. The aniline body, probably similarly constituted, must then be represented by the formula $C_{10}H_5(NC_6H_5H)O_2$. The facts obtained do not allow of a decisive conclusion on this point.

In the reaction between naphthoquinone and aniline, two atoms of hydrogen are eliminated for each molecule of the quinone; the same takes place with benzoquinone, if the formula given by Wichelhaus is correct.

Hofmann's formula contains two atoms of hydrogen less (*Watts's Dict.*, 4, 426), and he represents the reaction by the following equation:—

The four atoms of hydrogen eliminated, therefore, go to form quinol, which is found in the mother-liquid after the reaction.

As already mentioned, during the preparation of naphthoquinone-anilide, the mother-liquid deposits on standing considerable quantities of the substance; this may be explained if naphthoquinol be a product of the reaction, for it has been shown that the latter body reacts with aniline in aqueous solution. Attempts to separate naphthoquinol were, however, unsuccessful. Once only long white needles were observed, very soluble in alcohol. The dark substances formed in small quantity are probably reduction-products of naphthoquinone: common naphthoquinhydrone is not formed. Another explanation must be sought for to account for the disappearance of two atoms of hydrogen; possibly a simple addition-product of 1 mol. of quinone and 1 mol. of aniline is formed which then quickly oxidises in the air. I noticed, indeed, that the compound when first precipitated by water is lighter in colour.

The aniline compound remains unacted upon by aniline when heated with it in alcoholic solution to 200°.

Paratoluidine Compound.

The paratoluidine-compound, which is very similar to the preceding,

was obtained by heating 1 molecular proportion of naphthoquinone with rather more than 1 molecular proportion of paratoluidine in alcoholic solution for some minutes, and precipitating with water and acetic acid. The precipitate was purified by dissolving in alcohol, boiling with a small quantity of animal charcoal, and crystallising once or twice from dilute alcohol. It crystallises in red needles which melt at 200° .

A combustion with oxide of copper in a stream of oxygen gave the following numbers:—

	Found.	Calculated for $C_{10}H_6O_2NC_6H_4(CH_3)$.
C . . .	77.65	77.56
H ..	5.14	4.94

The colourless filtrate obtained in the preparation of this body gives, on standing, further quantities of red needles, just as in the case of the aniline derivative.

Concentrated sulphuric acid dissolves the toluidine-derivative with a fine purple colour.

With orthotoluidine, naphthoquinone also gives a compound very soluble in alcohol. I have not obtained it in a pure state.

Compound with Methylamine.

The methylamine and ethylamine-derivatives are not quite so easy to prepare as the preceding, for it was found difficult to prevent the formation of dark-coloured bye-products, the removal of which caused loss of time and material.

If a solution of methylamine (33 per cent.) is added drop by drop to a small quantity of naphthoquinone dissolved in alcohol, and the test-tube warmed for a minute or two very gently, the liquid becomes red, and on addition of water and acetic acid the compound separates out in small bright red needles. If, however, the experiment is made with larger quantities, the result is a brown or nearly black liquid, which gives on precipitation a brown and very impure precipitate. This is also the case when the warming is avoided.

In one experiment 5 grams of naphthoquinone were dissolved in 50 grams of alcohol, and, drop by drop, 10 grams of methylamine solution (33 per cent.) added; the mixture was heated gently for five minutes, and then precipitated with water and acetic acid. The precipitate was brown, and the filtrate appeared to contain quinol, for, when heated with more methylamine solution a further precipitate was obtained. As it was suspected that the precipitate also contained reduction-products of the quinone, it was dissolved in alcohol, filtered from an insoluble brown substance, and again heated with some methylamine solution and a few drops of acetic acid. By precipita-

tion with water a substance was obtained of a redder colour, and this precipitate was therefore again subjected to a similar treatment.

The substance partially purified by this means was boiled in alcoholic solution for a long time with charcoal; the filtrate then deposited small red needles.

The aqueous liquids, acid with acetic acid, obtained during the treatment of the precipitate with methylamine and acetic acid, gave on evaporation small quantities of a black substance soluble in alcohol, which, when oxidised with chromic acid and acetic acid, was converted into an orange-coloured body precipitated by water. This substance, which was not quinone, possibly belongs to the class of dinaphthoquinhydrones obtained by Stenhouse and Groves (*Liebig's Annalen*, 194, 202) by the action of acids on β -naphthoquinone. Further experiments showed that it is better to act upon naphthoquinone with a methylamine salt than with the free amine. The quinone is dissolved in alcohol, and then an excess of methylamine solution first neutralised with acetic acid, is added, and the mixture evaporated nearly to dryness. Water is added, and the precipitate filtered off, dissolved in alcohol, and boiled with animal charcoal until a small portion filtered off shows a red colour.

The needles which separate on cooling have a bright red colour and brilliant lustre. They melt at 232° (uncorr.), and are easily soluble in alcohol.

Analysis gave the following numbers:—

	I.	II.	Calculated for $C_{10}H_6O_2NCH_3$.
C....	69.98	70.72	70.59
H ..	5.03	Lost	4.81
N....	7.25	—	7.48

The combustions were made with chromate of lead, and the nitrogen was estimated by Dumas' method.

The methylamine derivative is also reduced by sulphurous acid in aqueous solution at 150° , with formation of white needles, sulphur, and dark substances. The white needles could not be obtained pure, as they oxidise rapidly in the air.

Compound with Ethylamine.

The ethylamine derivative is obtained in the same way as the preceding by using acetate of methylamine and naphthoquinone in alcoholic solution. As might be expected, if instead of working with a nearly neutral solution, much hydrochloric or acetic acid is present, neither the methyl- nor ethylamine derivative is formed, except in very small quantity.

The quinol may be used instead of naphthoquinone itself, and reacts easily with either methyl- or ethyl-amine and their acetates. A dark brown colour forms at first on the upper layer of the mixture, and gradually extends downwards.

The ethylamine compound may be purified by boiling in alcoholic solution with animal charcoal, and crystallises after evaporation of a portion of the alcohol in needles, which are not so red as the methyl-amine compound. Addition of water is not advisable. The needles melt at 139–140°, and sublime unaltered in long needles which have a very brilliant lustre. They are easily soluble in hot alcohol and benzene, but very slightly in light petroleum.

Combustions were made at first with oxide of copper, but the results obtained were much too low. No. III was made with chromate of lead.

	I.	II.	III.	Calculated for $C_{10}H_6O_2NC_2H_5$.
C....	67.12	64.1	71.96	71.64
H ..	5.55	5.57	6.44	5.47
N....	—	—	7.3	6.96

Action of Ammonia on Naphthoquinone.

If ammonia solution be added drop by drop to an alcoholic solution of naphthoquinone, the liquid at once becomes dark brown, and by precipitation by water a brown amorphous body is obtained. With the quinol ammonia reacts more slowly, and on addition of water a red-brown substance separates, which contains no nitrogen. Acetic acid produces a further precipitate, which also contains no nitrogen.

Ammonia apparently acts in the same way as the potassium and sodium hydrate or carbonates, which dissolve naphthoquinone to a brownish-red solution, from which acids precipitate a red substance, the nature of which has not been ascertained. It is, however, doubtless, the so-called "carminaphe" discovered by Laurent, and lately described by A. Guyard (*Bull. Soc. Chim.* [2], **31**, 64), who obtained it by oxidising naphthalene dissolved in acetic acid with chromic acid, and neutralising with sodium carbonate.

I have prepared carminaphe according to the directions of Guyard, in order to ascertain whether, as seemed probable, this substance is the result of the action of the sodium carbonate upon the naphthoquinone formed by the oxidation. In the first experiment made, as soon as the oxidation was finished and the liquid had cooled, it was neutralised with sodium carbonate. Carminaphe was found neither in the precipitate nor in the filtrate, but on distilling the precipitate with steam, much naphthoquinone came over. In a second experiment the neutralisation was effected, on the contrary, in the hot liquid, and

the carminaphe obtained in abundance from the precipitate, and also from the filtrate on adding hydrochloric acid. It is soluble in benzene, and is precipitated on addition of light petroleum as a dark red powder.

Compound with Dimethylamine.

Dimethylamine solution added to alcoholic solution of naphthoquinone, produces a brownish-red coloration, and on addition of water a very small quantity of resinous substance is precipitated. The filtrate, on standing in an open dish, deposits needles of a bright red colour, which melt at 115° , and can be purified by recrystallisation from hot water.

A good method of preparation is to dissolve naphthoquinone in alcohol, add excess of dimethylamine solution (33 per cent.) neutralised with acetic acid, and allow the mixture to stand for a day or so in a large dish. The residue is extracted several times with boiling water, and the crystals obtained purified by one or two recrystallisations. The dimethylamine-derivative forms bright red needles, which melt at 118° .

Analysis gave the following numbers:—

	I.	II.	Calculated for $C_{10}H_5(N(CH_3)_2)O_2$.
C....	71.52	71.99	71.64
H ..	5.66	5.67	5.47
N....	—	7.6	6.96

The dimethylamine compound is easily reduced by tin and hydrochloric acid. If the colourless liquid be shaken out with ether, on evaporation of the latter a reddish-white substance is left, which is converted by ferric chloride into the original compound.

Action of Diphenylamine on Naphthoquinone in presence of Hydrochloric Acid.

Attempts to prepare a compound of diphenylamine and naphthoquinone in alcoholic solution, and by melting the substances together, gave no result. It was observed, however, that on adding hydrochloric acid, and heating to remove the diphenylamine from such a mixture, that a dark violet substance was formed, which on addition of water separated as a black oil, and solidified very slowly.

This substance was heated gently with solution of carbonate of sodium, and then extracted with boiling benzene. On filtering, a small quantity of a blue amorphous substance was separated. The solution was precipitated with light petroleum, and the precipitate, after numerous crystallisations from alcohol, finally obtained in beautiful violet-black needles, melting at 164° . The substance contained no chlorine.

A number of experiments showed that the precipitation with light petroleum was necessary. When the crude product is purified by precipitation from hot alcohol by strong hydrochloric acid, it is obtained solid, but even after the treatment had been repeated several times the substance often separates from alcohol in a pasty condition, and refuses to crystallise after repeated treatment with alcohol.

Finally the following method of preparation proved advantageous. Naphthoquinone and diphenylamine in the proportion of somewhat more than 1 molecular proportion of amine to 1 molecular proportion of quinone are dissolved in alcohol at a gentle heat, and strong hydrochloric acid (about 10 c.c. for 5 grams quinone) added. The mixture is heated on a water-bath for about 20 minutes, precipitated with water, and collected by decantation. On standing, the aqueous liquid deposits further quantities of the substance mixed with diphenylamine.

The semi-solid precipitate is dissolved in alcohol, and filtered from a small quantity of a blue substance, and the hot solution precipitated with hydrochloric acid with vigorous shaking. The now solid substance is warmed with sodium carbonate, and repeatedly precipitated by light petroleum from its solution in benzene, by which the remainder of the diphenylamine is separated. As soon as the substance becomes very crystalline it is recrystallised once or twice from alcohol. It also crystallises well from alcohol containing a little acetic acid, on addition of hot water.

It is not necessary to use alcohol for the preparation of the diphenylamine-compound, as the same black oil is formed by heating naphthoquinone and diphenylamine with hydrochloric acid.

The needles melting at 164° gave on analysis the following numbers:—

	I.	II.	III. CuO.	IV.
C.	78.83	81.64	80.269	80.87
H	5.63	5.18	5.053	5.11
N	—	—	—	4.55

Combustion III was made with oxide of copper, the others with chromate of lead.

The formula $C_{10}H_5N(C_6H_5)_2O_2$, for which the hydrogen results are somewhat too high, requires—

C	81.23
H	4.61
N	4.30

The formula $C_{22}H_{17}NO_2$, containing 2 atoms of hydrogen more, corresponds, however, with 5.19 per cent. H, and is therefore improbable.

The formula $C_{22}H_{16}NO_2$ agrees perhaps best (4.91 H), but would have to be doubled.

Formulae containing two or more nitrogen groups are inadmissible.

The analytical numbers do not allow of deciding with certainty upon the formula of this compound, which may possess a very complex constitution. It appeared probable that the hydrochloric acid necessary in the preparation of the substance must act by forming a chloroquinone, which then reacted further with the diphenylamine giving such a body as $C_{10}H_5N(C_6H_5)O_2$.

The results of some experiments in this direction did not, however, agree with this hypothesis, when, for example, naphthoquinone is heated in alcoholic solution for some minutes with hydrochloric acid and diphenylamine added to the mixture, no trace of the purple body is produced.

Further in presence of a good quantity of sulphuric acid the reaction also takes place. Hydrobromic acid acts like hydrochloric acid. With chloride of zinc the purple compound is also formed, but together with much insoluble matter.

It was also thought possible that the dye-stuff was merely an oxidation-product of diphenylamine; it should then be produced also by the action of common quinone.

Experiments were therefore made with benzoquinone. This substance was dissolved in alcohol together with a little more than the quantity of diphenylamine requisite to form a mono-derivative, hydrochloric acid added, and the liquid heated for some minutes. The flask was then closed, and left to stand for twelve hours. At the end of this time the contents become originally blue had assumed a brownish tint. By careful addition of ferric chloride the blue compound was reproduced, and on addition of water precipitated as a blue-black oil. The filtrate, on shaking out with ether, yielded a small quantity of quinol. The precipitate when treated with strong hydrochloric acid lost its colour, but this was restored on treating the mass with sodium carbonate. Benzene extracted a substance which was precipitated by light petroleum. Repeated treatment with benzene and light petroleum failed to purify it completely, and it remained resinous. This substance, however, has a totally different colour from that of the naphthoquinone-compound described.

Acetyl-derivative of the Diphenylamine-derivative of Naphthoquinone.

By heating the diphenylamine-compound with acetic anhydride to 120° a brown liquid is obtained, which on decomposing the excess of anhydride with sodium carbonate, yields a yellow crystalline body. This was purified by boiling with animal charcoal and alcohol, and on

evaporating the latter, small yellow crystals melting at 172—173° were obtained. A combustion was made of these crystals, and gave—

		Calculated for $C_{24}H_{19}NO_3$.
C.....	77.30	78.05
H	5.50	5.15

A diacetyl-derivative, $C_{20}H_{20}O_4N$, requires 76.09 per cent. C and 4.9 per cent. H.

If the acetic anhydride had merely eliminated water, an anhydride must have been produced, containing more than 80 per cent. of carbon. This capacity of forming an acetyl-derivative is not, however, easy to reconcile with the formula $C_{10}H_5(N(C_6H_5)_2)O_2$.

Sulphurous acid in alcoholic solution reduces the diphenylamine-compound at 150°. Water precipitates a brown mass, which in alcoholic solution gives the original compound when allowed to stand over hydrochloric acid.

Sulphide of ammonium at once destroys the colour of an alcoholic solution even in the cold. Water precipitates a white substance, which in the air rapidly changes into the original compound.

Tertiary Amines.

These do not appear to react with naphthoquinone alone, or in presence of hydrochloric acid.

I cannot conclude this paper without expressing my thanks to Professor Zincke for his kind assistance and counsel during the progress of this research, which was made in the University Laboratory of Marburg.