CXXXVII.—*Dinaphthacridines*.

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It may in the first place be useful briefly to review the present position of the theory of the constitution of the dinaphthacridines. As was pointed out by one of us (*Brit. Assoc. Report*, 1903, 616; *Chem. News*, 1903, 88, 272), the existence of six isomeric compounds is to be expected, and of these, four are known.

Making use of the notation proposed in the communication referred to, it will be observed that one of these is an α -N- α compound, two are α -N- β compounds, and three are β -N- β , thus :

One α -N- α :

(Senier and Goodwin.)

Two α -N- β :

(Ullmann and Fetvadjan.)

(Unknown.)

Three β -N- β :

The behaviour of β -naphthylamine towards methylene di-iodide leads us to suppose that in the preparation of dinaphthacridines with the use of methylene compounds, the normal course of the reaction can be divided into four stages: first, condensation of the primary to a secondary amine; secondly, further condensation to a dihydro-dinaphthacridine; thirdly, oxidation to a "naphthacridine" of the type of Morgan's "isonaphthacridine," which we should prefer to designate as "bisdinaphthacridine dihydride," $[C_{21}H_{13}N]_2H_2$; lastly, oxidation to a dinaphthacridine. In our experiments with benzal chloride (phenylmethylene dichloride) and β -naphthylamine, we find that we can vary the conditions so as to obtain either the dinaphthacridine or the dinaphthylamine, and in the case of the corresponding reaction with ethylidene chloride (methylmethylene dichloride) we have not been able to get the reaction to go beyond the first stage.

That a secondary amine is first formed finds additional support in the well-known synthesis of diphenocridine and phenonaphthacridine from secondary amines.

α -N- α
 β -CH- β Dinaphthacridine (" α -naphthacridine," Senier and Goodwin)

has the structure represented by the graphic formula *A*. It is obtained by the condensation of two molecules of α -naphthylamine, forming in the first place $\alpha\alpha$ -dinaphthylamine. Hence the dinaphthacridine must be an α -N- α compound, for which only one formula is possible.

We find that α -naphthylamine gives with benzal chloride (phenylmethylene dichloride) the corresponding 7-phenyldinaphthacridine. The constitution of the latter compound receives independent proof from the fact that we have also prepared it by the action of benzaldehyde on a mixture of α -naphthylamine and α -naphthol.

That Reed's " β -naphthacridine" is a dinaphthacridine possessing the formula *D* is also now placed beyond much doubt. Its formation from two molecules of β -naphthylamine and methylene compounds, and also by condensation of the reaction product of β -naphthol and β -naphthylamine by means of trioxymethylene (Ullmann and Fetvad-jian, *Ber.*, 1903, 36, 1027), proves conclusively that the base is of the

type β -N- β . Another synthesis of the same compound by these investigators proves that one of the CH linkings is α ; for they obtain it from the reaction of 2:2-dihydroxy-1:1-dinaphthylmethane with β -naphthylamine. In this reaction one naphthol group is eliminated, which leaves the position of the C linking on that side still unproved. The nitrogen must, however, join the ring at the position of the β -hydroxyl.

That the base is symmetrical and has the formula *D*, not *E* (the only other $\begin{smallmatrix} \beta\text{-N} \\ | \\ \alpha\text{-CH} \end{smallmatrix}$ isomeride possible), may be assumed in view of, first, the analogy between its synthesis and that of the corresponding α -N- α compound; secondly, for the reasons given by Strohbach (*Ber.*, 1901, 34, 4146) in regard to the greater readiness with which substitution takes place in the α -position in the case of β -naphthylamine compounds (Möhlau and Strohbach, *Ber.*, 1900, 33, 804); thirdly, the laws put forward by Hinsberg (*Ber.*, 1902, 36, 4051), who, from a study of condensed six-membered ring compounds of carbon or of carbon and nitrogen, concludes that those which contain rings joined at an angle, *angular*, are more stable than those in which the rings are in a line, *linear*.

Strohbach's dinaphthacridine is prepared from $\beta\beta$ -dinaphthylamine-2:3-monocarboxylic acid, which shows that the condensation product derived from it must be of the type $\begin{smallmatrix} \beta\text{-N-}\beta \\ | \\ \text{CH-}\beta \end{smallmatrix}$. Its formula must therefore be *E* or *F*. *E* is chosen for the reasons stated above.

When equal weights of α -naphthylamine and β -naphthylamine are melted together and brought into reaction with methylene dichloride or methylene di-iodide the resulting base is the same as the dinaphthacridine first obtained by Ullmann and Fetvadjan by the action of trioxymethylene on a mixture of α -naphthylamine and β -naphthol. That this compound has the formula *B* as stated by these chemists is settled beyond doubt, though from both the above methods of synthesis the formula *C* might also be inferred. The fact, however, that it can be obtained by the action of α -naphthylamine on 2:2-dihydroxy-1:1-dinaphthylmethane by replacement of one β -naphthol group shows that the CH group is linked on one side in the α -position and on the other side in the β -position. This excludes formula *C* and establishes formula *B*.

A fuller investigation of the $\begin{smallmatrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CH-}\beta \end{smallmatrix}$ dinaphthacridine was the object in the first instance of the experiments still to be described. It had been obtained from α -naphthylamine (2 mols.) condensed by means of methylene di-iodide. This method does not give a good yield, but we are now able to suggest important improvements.

Our attempts to replace methylene di-iodide by formaldehyde have

been without success, but we have found that methylene dichloride may be used to great advantage, a good yield of the base being easily obtained.

Further, using the analogous ethylidene chloride (methylmethylene dichloride) and benzal chloride (phenylmethylene dichloride), we have synthesised two new derivatives, namely, methyl dinaphthacridine $\alpha\text{-N-}\beta$ $\beta\text{-CMe-}\beta$ and phenyl dinaphthacridine $\alpha\text{-N-}\beta$ $\beta\text{-CPh-}\beta$. To these derivatives and those described previously (Senier and Goodwin) should be added the dinaphthacridine disulphonic acid discovered by Möhlau and Haase (*Ber.*, 1902, **35**, 4175).

The generality of the methylene dichloride method is also shown by its application to the synthesis of the already known $\alpha\text{-N-}\beta$ $\beta\text{-CH-}\alpha$ and $\beta\text{-N-}\beta$ $\alpha\text{-CH-}\alpha$ dinaphthacridines and $\beta\text{-N-}\beta$ $\alpha\text{-CPh-}\alpha$ phenyl dinaphthacridine. In the case at least of α -compounds it is by far the best method on account of the good yield and freedom from by-products. The application of the use of methylene di-iodide is extended to the synthesis of $\alpha\text{-N-}\beta$ $\beta\text{-CH-}\alpha$ dinaphthacridine and to Morgan's "isonaphthacridine."

I. *Synthesis of Dinaphthacridines by the Interaction of Methylene Dichloride or its Analogues and Naphthylamines.*

1. *Methylene Dichloride and α -Naphthylamine.* $\alpha\text{-N-}\beta$ $\beta\text{-CH-}\beta$ *Dinaphthacridine* (" α -Naphthacridine," Senier and Goodwin),

Owing to the low boiling point of methylene dichloride (42°), the reaction cannot be carried out in an open vessel, as is the case when the di-iodide (b. p. 180°) is used. The experiments were made therefore in a closed tube heated to 220—230° for one or two hours. It was noticed that pale yellow crystals began to collect at the cooler end of the tube when the temperature of the furnace was about 210°. It was not found necessary to use pure methylene dichloride; the commercial product (Kahlbaum's "refined") was employed.

Theoretical proportions were taken, namely, α -naphthylamine (2 mols.) and methylene dichloride (1 mol.). On opening the tube a mixture of methylated spirit and a small proportion of concentrated aqueous potassium hydroxide was added and the whole heated on the water-bath for a few minutes.

The liquid was then separated from the viscous residue which contained the base and the latter was washed with cold acetone, which left the base undissolved in a crystalline form. The crystals were washed on a filter with more acetone and then with water, to remove any potassium chloride, and finally dried at 100° and recrystallised once or twice from benzene. It was rarely necessary to recrystallise further.

Dinaphthacridines are remarkable generally for their stability. They may be distilled in a partial vacuum without difficulty and, when pure, without decomposition. This process is, however, not necessary as a means of purification. In this instance the crystals melted constantly at 185.5° (189° corr.) whether distillation was employed or not. This melting point should be substituted for that previously given (Senier and Goodwin, *Trans.*, 1902, **81**, 288). The crystals are triboluminescent. Reed's base is known to possess this property (Morgan, *Chem. News*, 1905, **92**, 219; compare *Ber.*, 1904, **37**, 3697, foot-note).

0.1730 gave 0.5725 CO₂ and 0.0758 H₂O. C = 90.25; H = 4.86.

0.4117 gave 17.2 c.c. N at 10.5° and 773 mm. N = 5.08.

C₂₁H₁₃N requires C = 90.32; H = 4.66; N = 5.02 per cent.

In addition to the derivatives previously described we have prepared the

Aurichloride, C₁₀H₆ $\begin{smallmatrix} \diagup N \diagdown \\ | \\ CH \end{smallmatrix}$ C₁₀H₆.HAuCl₄.—This is obtained by adding a few drops of a concentrated solution of gold chloride to a solution of the base in a mixture of glacial acetic acid with a small proportion of concentrated hydrochloric acid.

The orange precipitate is washed first with a little warm glacial acetic acid and then with dry ether. It was dried at 105° and analysed:

0.1509 gave 0.0477 Au. Au = 31.61.

C₂₁H₁₄NCl₄Au requires Au = 31.82 per cent.

2. Methylene Dichloride and a Mixture of α - and β -Naphthylamines.

$\begin{smallmatrix} \alpha-N-\beta \\ \beta-CH-\alpha \end{smallmatrix}$ Dinaphthacridine (Ullmann and Fetvadjan),

When methylene dichloride (1 mol.) is heated in a closed tube with α -naphthylamine (1 mol.) and β -naphthylamine (1 mol.) at 240° for one hour, and the contents treated as in (1), yellow crystals are obtained which melt at 223° (corr. 228°). There can be no doubt that

this compound is identical with the dinaphthacridine of Ullmann and Fetvadjan (*Ber.*, 1903, **36**, 1027). For the sake of comparison, however, we prepared that base according to the directions given in their paper. The two preparations were found to be identical. These chemists used α -naphthylamine and β -naphthol, but having some difficulty at first in finding the requisite temperature to bring about the reaction, we tried α -naphthol and β -naphthylamine, with the interesting result that the base was produced more readily.

This also, after frequent recrystallisation, melted constantly at the same temperature. It does not exhibit triboluminescence.

0.1916 gave 0.6329 CO_2 and 0.0837 H_2O . $\text{C} = 90.08$; $\text{H} = 4.85$.

0.3526 gave 15.5 c.c. N at 15° and 761.5 mm. $\text{N} = 5.15$.

$\text{C}_{21}\text{H}_{13}\text{N}$ requires $\text{C} = 90.32$; $\text{H} = 4.66$; $\text{N} = 5.02$ per cent.

We have prepared the following new derivatives:

Platinichloride, $[\text{C}_{10}\text{H}_6\langle\text{N}\rangle\text{CH}\rangle\text{C}_{10}\text{H}_6]_2\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$.—A mixture of glacial acetic acid and hydrochloric acid is generally a most convenient solvent for dinaphthacridines. This one, however, is only very slightly soluble in solvents suitable for the preparation of salts. A dilute solution was prepared in alcohol acidified with hydrochloric acid, and from this, on adding platinic chloride, a bright yellow precipitate was obtained, which, on drying in the desiccator, gave the following numbers on analysis:

0.1098 gave 0.0210 Pt . $\text{Pt} = 19.12$.

$\text{C}_{42}\text{H}_{32}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires $\text{Pt} = 19.42$ per cent.

Bisdinaphthacridine hexabromide, $[\text{C}_{10}\text{H}_6\langle\text{N}\rangle\text{CH}\rangle\text{C}_{10}\text{H}_6]_2\text{Br}_6$, was precipitated as an orange-yellow powder when solutions of bromine and the base in chloroform were mixed. The precipitate was collected on a filter, washed with dry ether, and dried in the oven at $105\text{--}106^\circ$.

0.1014 gave 0.1090 AgBr . $\text{Br} = 45.73$.

$\text{C}_{42}\text{H}_{26}\text{N}_2\text{Br}_6$ requires $\text{Br} = 46.2$ per cent.

It is an isomeride of the two compounds previously described by us (*Trans.*, 1904, **85**, 1204, 1205).

3. *Methylene Dichloride and β -Naphthylamine.* $\begin{array}{c} \beta\text{-N-}\beta \\ \alpha\text{-CH-}\alpha \end{array}$ *Dinaphth-*
acridine (" *β -Naphthacridine*," Reed), $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{CH} \end{array} \text{C}_{10}\text{H}_6$.

Methylene dichloride (1 mol.) and β -naphthylamine (2 mols.) were heated in a closed tube at 200° for two hours and treated as above. Reed's dinaphthacridine was obtained in good yield.

4. *Ethylidene Chloride and α -Naphthylamine.* $\begin{array}{c} \alpha\text{-N-}\alpha \\ \beta\text{-CMe-}\beta \end{array}$ *Methylidi-*
naphthacridine (7-Methyl derivative of Senier and Goodwin's base),
 $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{CMe} \end{array} \text{C}_{10}\text{H}_6$.

Ethylidene chloride (1 mol.) and α -naphthylamine (2 mols.), heated in a closed tube at $220\text{--}230^\circ$ for two hours and treated as previously described, gave a base crystallising in distinct greenish-yellow octahedra. The action appeared to commence at 215° . The crystals melt at 219° (224° corr.) and do not exhibit triboluminescence.

0.2138 gave 0.7080 CO_2 and 0.1030 H_2O . C = 90.31; H = 5.35.

0.2668 „ 11 c.c. N at 13° and 758 mm. N = 4.86.

$\text{C}_{22}\text{H}_{15}\text{N}$ requires C = 90.10; H = 5.12; N = 4.77 per cent.

The following derivatives were prepared :

Hydrochloride, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{CMe} \end{array} \text{C}_{10}\text{H}_6 \cdot \text{HCl}$.—A solution of the base in a mixture of glacial acetic acid and concentrated hydrochloric acid deposited, on cooling, yellow needles. These were recrystallised from the same solvent, washed with dry ether, and dried in the desiccator. This salt is easily decomposed by water.

0.2285 gave 0.0941 AgCl. Cl = 10.17.

$\text{C}_{22}\text{H}_{16}\text{NCl}$ requires Cl = 10.77 per cent.

Aurichloride, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \text{CMe} \end{array} \text{C}_{10}\text{H}_6 \cdot \text{HAuCl}_4$.—To a hot solution of the base, as described above for the hydrochloride, a concentrated solution of gold chloride was added. A yellow precipitate separated on cooling. It was washed with glacial acetic acid and dry ether and finally dried at 105° . It is easily decomposed by water.

0.1012 gave 0.0311 Au. Au = 30.73.

$\text{C}_{22}\text{H}_{16}\text{NCl}_4\text{Au}$ requires Au = 31.12 per cent.

Platinichloride, $\left[\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C}_{\text{Me}} \end{array} \right]_2 \text{C}_{10}\text{H}_6 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O} \cdot \text{A}$ solution of platinic chloride was added to a solution of the base in alcohol, acidified with hydrochloric acid. A yellow powder was precipitated, which was washed with dry ether and dried in a desiccator. It is easily decomposed by water.

0.2085 gave 0.0396 Pt. Pt = 18.99.

$\text{C}_{44}\text{H}_{36}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires Pt = 18.89 per cent.

Dibromide, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NBr} \\ \diagup \quad \diagdown \\ \text{C}_{\text{Me}}\text{Br} \end{array} \text{C}_{10}\text{H}_6 \cdot \text{A}$ solution of the base was prepared in glacial acetic acid mixed with a small proportion of toluene. To this a solution of bromine in glacial acetic acid was added. A yellow precipitate appeared, which was separated at once, washed with glacial acetic acid, then with dry ether, and dried at 105°. The compound is decomposed by water, but is somewhat soluble in glacial acetic acid or chloroform. Its solutions do not fluoresce.

0.1888 gave 0.1570 AgBr. Br = 35.38.

$\text{C}_{22}\text{H}_{15}\text{NBr}_2$ requires Br = 35.32 per cent.

5. *Ethylidene Chloride and a Mixture of α - and β -Naphthylamines.*

Ethylidene chloride (1 mol.), α -naphthylamine (1 mol.), and β -naphthylamine (1 mol.) were heated in a closed tube at 270° for half an hour. The contents of the tube were treated in the manner previously described, when crystals were obtained identical with the base just mentioned, $\begin{array}{c} \alpha\text{-N-}\alpha \\ \beta\text{-C}_{\text{Me}}\text{-}\beta \end{array}$ methylidinaphthacridine. No trace of the desired compound, $\begin{array}{c} \alpha\text{-N-}\beta \\ \beta\text{-C}_{\text{Me}}\text{-}\alpha \end{array}$ dinaphthacridine, nor of any intermediate product, could be detected.

6. *Ethylidene Chloride and β -Naphthylamine.*

Ethylidene chloride (1 mol.) and β -naphthylamine (2 mols.) were heated in a closed tube at 250° for one hour. The contents of the tube were examined as before and gave crystals of $\beta\beta$ -dinaphthylamine. Heating to a higher temperature caused decomposition unless a solvent was used. We therefore added naphthalene to a fresh portion and heated it to 300°. Even in this case we only obtained $\beta\beta$ -dinaphthylamine.

7. *Benzal Chloride and α -Naphthylamine.* $\begin{matrix} \alpha\text{-N-}\alpha \\ \beta\text{-CPh-}\beta \end{matrix}$ *Phenyldinaphth-acridine* (7-Phenyl derivative of Senier and Goodwin's base),

When benzal chloride and α -naphthylamine are heated together, a solid is readily formed which contains no acridine. If, however, such a solvent as naphthalene is present, the acridine is readily obtained on prolonged heating. Benzal chloride (1 mol.) is mixed with about twice its weight of naphthalene and heated to its boiling point. α -Naphthylamine (2 mols.) is then added in small portions at a time, the mixture being kept agitated and in ebullition. It is best to work with small quantities at a time in large test-tubes, when the heating can be conveniently done in the flame. The product is worked up as before and yields a yellow, crystalline powder. This on recrystallisation twice from toluene or benzene assumes the form of hexagonal plates which melt at 224° (229° corr.) and can be distilled. The crystals do not exhibit triboluminescence.

0.1750 gave 0.5853 CO_2 and 0.0776 H_2O . $\text{C} = 91.21$; $\text{H} = 4.92$.

0.2815 „ 9.8 c.c. N at 19.5° and 767 mm. $\text{N} = 4.02$.

$\text{C}_{27}\text{H}_{17}\text{N}$ requires $\text{C} = 91.26$; $\text{H} = 4.79$; $\text{N} = 3.94$ per cent.

We have also obtained the same compound by the application of Ullmann and Fetvadjian's method.

α -Naphthylamine (2.5 grams) was mixed with α -naphthol (3 grams) and heated to boiling. Excess of benzaldehyde was used, only a few drops at a time being added. Heating was continued for some time. On cooling, the mass was boiled with a little toluene, filtered, and the residue recrystallised from more toluene. The resulting substance was identical with that just described.

The following derivatives were prepared:

Hydrochloride, $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} \end{matrix} \text{C}_{10}\text{H}_6, \text{HCl}$.—Yellow crystals of this salt were obtained by dissolving the base in a hot mixture of glacial acetic acid and concentrated hydrochloric acid and allowing the solution to cool. These were recrystallised from the same solvent, washed with dry ether, and dried in a desiccator.

0.3415 gave 0.1312 AgCl . $\text{Cl} = 9.49$.

$\text{C}_{27}\text{H}_{18}\text{NCl}$ requires $\text{Cl} = 9.06$ per cent.

The specimen was evidently not quite pure.

Platinichloride, $\left[\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} \end{matrix} \text{C}_{10}\text{H}_6 \right]_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.—To the

last-mentioned solution of the base, platinic chloride was added, when an orange precipitate was obtained. This was washed successively with glacial acetic acid and dry ether and dried in a desiccator.

0.0944 gave 0.0160 Pt. Pt = 16.94.

$C_{54}H_{40}O_2N_2Cl_6Pt$ requires Pt = 16.86 per cent.

Aurichloride, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{Ph} > C_{10}H_6, HAuCl_4$.—This was prepared from gold chloride in a manner similar to that used for the platinichloride. It is a yellow, crystalline powder.

0.1445 gave 0.0406 Au. Au = 28.09.

$C_{27}H_{18}NCl_4Au$ requires Au = 28.34 per cent.

8. Benzal Chloride and a Mixture of α - and β -Naphthylamines.

It was hoped by this reaction to prepare the already known α -N- β -phenyldinaphthacridine (Ullmann and Fetvadjan, *Ber.*, 1903, **36**, 1029), but so far the experiment has not yielded a definite result.

9. *Benzal Chloride and β -Naphthylamine.* β -N- β - α -CPh-*Phenyldinaphthacridine* (7-Phenyl derivative of Reed's base), $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{Ph} > C_{10}H_6$.

This reaction requires special care, as secondary products are easily formed.

If the two reagents are heated alone, the resulting compound is $\beta\beta$ -dinaphthylamine. Generally the method followed for the preparation of the dinaphthacridine was the same as in the corresponding experiment with α -naphthylamine. The benzal chloride and naphthalene were first heated together to boiling, then the β -naphthylamine was added in small portions at a time in order to avoid loss by distillation. A solid separated which contained the acridine. On partial cooling, the liquid was decanted from the solid and again heated, when more of the solid separated. This process was repeated until no more solid could be obtained. The solid product was then worked up in the usual way. It was recrystallised from benzene or toluene, when it assumed the form of pale yellow needles melting at 293° (301.5° corr.). It is identical with the compound described as *meso*-phenyl- β -naphthacridine by Claus and Richter (*Ber.*, 1884, **17**, 1595). It has also been investigated by Ris (*Ber.*, 1884, **17**, 2030), Klopsch (*Ber.*, 1885, **18**, 1586), Haase (*Ber.*, 1903, **36**, 592), and Ullmann and

Fetvadjian (*loc. cit.*). It is more soluble in glacial acetic acid than in toluene, very soluble in chloroform or carbon disulphide, and insoluble in ethyl acetate. It is less soluble than the α -isomeride in benzene and toluene.

II. *Further Study of Dinaphthacridines. Synthesis by the Interaction of Methylene Di-iodide and Naphthylamines.*

1. *Methylene Di-iodide and α -Naphthylamine.* $\begin{matrix} \alpha\text{-N-}\alpha \\ \beta\text{-CH-}\beta \end{matrix}$ *Dinaphthacridine* (Senier and Goodwin).

The method by which this compound was originally prepared gives only a small yield. If the alkali be omitted the action is too energetic, even when small quantities are used, and loss by decomposition is the result. Solvents were then tried, including benzene, naphthalene, paraffin wax, and benzoic acid. The last mentioned gave very satisfactory results. The α -naphthylamine was mixed with about twice its weight of benzoic acid, the methylene di-iodide added, and heat applied in the usual way. Before recrystallising, the contents were heated to boiling with a mixture of methylated spirit and a small proportion of concentrated aqueous potassium hydroxide. This treatment removes hydrogen iodide and benzoic acid.

2. *Methylene Di-iodide and a Mixture of α - and β -Naphthylamines.* $\begin{matrix} \alpha\text{-N-}\beta \\ \beta\text{-CH-}\alpha \end{matrix}$ *Dinaphthacridine* (Ullmann and Fetvadjian).

This method seems to be very satisfactory for the preparation of this base. It is, however, necessary to use alkali.

Methylene di-iodide (1 mol.) is mixed with α -naphthylamine (1 mol.), β -naphthylamine (1 mol.), and an excess of previously ignited potassium carbonate (3 mols.). The mixture is either heated in a closed tube at 200° for two to four hours, or heated to 200° in an open flask with a reflux condenser for the same length of time.

The product is boiled with a mixture of toluene and absolute alcohol and the hot solution filtered from potassium salts. On cooling, the solution deposits yellow crystals, which, on recrystallisation from toluene, melt at 223° (228° corr.). This compound is identical with

the $\begin{matrix} \alpha\text{-N-}\beta \\ \beta\text{-CH-}\alpha \end{matrix}$ dinaphthacridine described in this paper. In some experiments the alkali was omitted, but it was then found more difficult to prevent over-heating.

3. *Methylene Di-iodide and β -Naphthylamine.* $\beta\text{-N-}\beta$
 $\alpha\text{-CH-}\alpha$ *Dinaphth-*
acridine (Reed) and *Bisdinaphthacridine Dihydride* ["*isoNaphth-*
acridine," Morgan], $(\text{C}_{21}\text{H}_{13}\text{N})_2\text{H}_2$.

When methylene di-iodide (1 mol.) and β -naphthylamine (2 mols.) are mixed with excess of potassium carbonate in an open vessel and treated in the usual way, or when the alkali is omitted, Reed's dinaphthacridine is obtained and no trace of Morgan's base is formed. If, however, potassium hydroxide, previously fused and powdered, replaces the carbonate, only orange crystals are obtained, which are identical with bisdinaphthacridine dihydride ("*isoNaphthacridine*," Morgan, *Trans.*, 1898, 73, 536; "*Naphthacrihydridine*," Möhlau and Haase, *Ber.*, 1902; 35, 4169). In a closed tube with potassium carbonate, a mixture of the two bases is obtained, Morgan's predominating.

In the above investigation we repeated the experiments of Ullmann and Fetvadjan to obtain Reed's base from β -naphthylamine, β -naphthol, and trioxymethylene, and found that Morgan's base was first formed as an intermediate product. It was, indeed, the chief product of the reaction when the temperature did not exceed 225° , whereas at 250° Reed's base predominated. That the orange crystals obtained by the above methods are really crystals of the substance obtained by Morgan and reinvestigated by Möhlau there can be no doubt, although the melting point was found to be 243° (248° corr.), whereas Morgan gives 227° and Möhlau 236° . The compound is easily distinguished from Reed's dinaphthacridine by its higher melting point and characteristic colour, and the two substances may be easily separated by fractional crystallisation from toluene, when the less soluble orange compound is first deposited in long needles, the dinaphthacridine forming more compact greenish-yellow crystals when the mother liquor has been evaporated to a small bulk. To remove any possible doubt as to the identity of the orange crystals with Morgan's base, we first converted it into the characteristic green hydrochloride (by passing hydrochloric acid gas into a benzene solution of the base). The green salt of Morgan's base gradually changed to the yellow salt of Reed's base (compare Morgan, Möhlau and Haase, *ibid.*), and from the latter Reed's base was obtained; secondly, we oxidised the compound by well-known methods, with bromine, also with nitrous acid, and in both cases obtained Reed's base; thirdly, the latter was reduced by sodium amalgam to orange crystals melting at 243° (248° corr.); fourthly, we submitted the compound to analysis:

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0.2795 gave 0.9224 CO_2 and 0.1284 H_2O . $\text{C} = 90.00$; $\text{H} = 5.10$.

0.3093 „ 13.4 c.c. N at 19° and 765 mm. $\text{N} = 5.01$.

$\text{C}_{42}\text{H}_{28}\text{N}_2$ requires $\text{C} = 90.00$; $\text{H} = 5.00$; $\text{N} = 5.00$ per cent.

For the earliest experiments on the synthesis of the $\alpha\text{-N}\text{-}\beta$ di-naphthacridine by using methylene di-iodide we are indebted to Miss F. M. G. Micklethwait.

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