VI.—*Attempted Synthesis of β -N- β -
 β -CH β -Dinaphthacridines:*
Condensation of Methylene Dichloride and 1-Sub-
stituted-2-naphthylamines.

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Two of the six theoretically possible dinaphthacridines (Senier and Austin, Trans., 1906, **89**, 1387) are still unknown, and our attempts to synthesise derivatives of one of these by using β -naphthylamines

in which the neighbouring α -position is substituted have led only to the formation of dinaphthacridines of the $\beta\text{-N-}\beta\text{-}\alpha\text{-CH}\alpha$ type. But, although we have not succeeded in obtaining the desired compounds, the results in themselves possess sufficient interest to be recorded.

In view of the experiments described in a former paper on halogen addition compounds (Senier and Austin, *Trans.*, 1904, **85**, 1196) and of recent work by A. E. Dunstan and Hilditch (*Trans.*, 1907, **91**, 1659) on the substitution of halogens in acridines by working with hot solutions, the bromo-substitution derivative of $\beta\text{-N-}\beta\text{-}\alpha\text{-CH}\alpha$ -dinaphth-acridine described is worthy of note. It undoubtedly contains the halogen in the meso-carbon position, for the linking of the naphthylene groups by means of the meso-carbon must take place at the position previously occupied by the bromine. Further, it is important to observe that this synthesis effectually removes any doubt that remained as to the constitution of Reed's dinaphthacridine, the proof of which until now was incomplete, since it depended in part on the assumption of Strohbach (*Ber.*, 1901, **34**, 4146) that the α -position in β -naphthylamine is more readily substituted than the other β -position :

Taking into consideration the general fact that a linear arrangement of the rings in the synthesis of cyclic compounds is only obtained with difficulty (Senier and Austin, *loc. cit.*), it was expected that it would not be easy to prepare the $\beta\text{-N-}\beta\text{-}\beta\text{-CH}\beta$ base, for this contains a linear arrangement of rings on either side of the acridine nucleus, the only known dinaphthacridine containing a linear arrangement, and that only on one side, being Strohbach's $\beta\text{-N-}\beta\text{-}\alpha\text{-CH}\beta$ isomeride. Again, in view of the fact that when β -naphthylamine condenses with methylene dihalides or with formaldehyde the neighbouring α -position enters into the reaction, it was hoped that by fixing the α -position before the experiment by substitution the condensation might then affect the other β -position and give the type of acridine desired. Methylene dichloride was selected as a condensing reagent, because, unlike formaldehyde, it reacts with both β - and α -naphthylamines and because the behaviour of formaldehyde

with 1-substituted-2-naphthylamines has already been the subject of an investigation by Morgan (*Trans.*, 1900, **77**, 814), in which no indication of the condensation we wished to bring about was observed.

The results of our experiments show that when the α -position next to that occupied by the amino-group in β -naphthylamine is taken by an easily replaceable element, such as chlorine or bromine, such substituents are eliminated and condensation takes place at the α -position with the formation either of Reed's base or, in the case of bromine, of a bromo-derivative of that base; but that when the α -position is taken by such a substituent as the nitro-group, which is not easily replaced, no condensation takes place.

1. *Interaction of Methylene Dichloride and 1-Chloro-2-naphthylamine.*

Five grams of 1-chloro-2-naphthylamine were heated in a closed tube with $2\frac{1}{2}$ c.c. (excess) of methylene dichloride for a short time to 200° , when an orange sublimate was noticed at the end of the tube. After the first appearance of this sublimate, the heating was only continued for about fifteen minutes. More prolonged heating or higher temperatures led to unsatisfactory results. When the tube was opened, the contents were first washed with a little cold acetone, then boiled with methylated spirit to which a little aqueous ammonium hydroxide was added, and poured into cold water. After decanting the liquid and recrystallising the dried residue from benzene, large triboluminescent crystals containing no halogen and melting at 216° were obtained. They were identified with β -N- β - α -CH α -dinaphthacridine (Reed).

2. *Preparation of 1-Bromo-2-naphthylamine.*

In preparing 1-bromo-2-naphthylamine by the method given by Morgan (*loc. cit.*), it was found to be of advantage to warm the solution of aceto- β -naphthalide in glacial acetic acid to about 60° and to add more of the solvent whenever the mass became too thick to stir, otherwise an intimate mixture of the reagents was not obtained. Moreover, the brown precipitate thus formed was purified before hydrolysis. This was done by boiling it with methylated spirit until no more dissolved, and filtering, when it was found that the alcoholic filtrate contained bromoacetonaphthalide in a fairly pure condition. This solution was then hydrolysed by boiling with hydrochloric acid, and the hydrochloride thus obtained was treated with alkali to liberate the base. One crystallisation from light petroleum was generally sufficient to yield crystals of pure 1-bromo-2-naphthylamine.

3. *Interaction of Methylene Dichloride and 1-Bromo-2-naphthylamine.*

After several partially successful attempts to determine the proper conditions, we found that a temperature of 230—240° was most suitable for bringing about the acridine condensation. In our first experiment, we heated the closed tube to 200° and obtained as the chief product a black, non-crystallisable substance, insoluble in benzene, but soluble in alcohol. Distillation of this black substance under reduced pressure gave rise to a yellow substance, which could not be crystallised and was not further examined. The latter compound is possibly dinaphthacridone.

Satisfactory results were, however, obtained by heating 5 grams of 1-bromo-2-naphthylamine with 2 c.c. of methylene dichloride in a closed tube to 230—240° for three-quarters of an hour. It was not found advisable to work with larger quantities. The contents of the opened tube were easily removed by boiling with methylated spirit containing some potassium hydroxide in solution.

A heavy, black, oily substance was obtained, which, when washed by decantation with cold water, solidified. This was rubbed with a little cold acetone, drained on a filter, and dried in a desiccator. It was then boiled with benzene, and the highly fluorescent, but dark, solution filtered from an insoluble residue, mixed with animal charcoal, boiled for two hours under a reflux condenser, and again filtered and allowed to stand. The solution was thereby rendered much clearer, and slowly deposited well-formed, pale brown crystals. One or two further recrystallisations from benzene sufficed to purify them. When pure they are of a very pale yellow colour and melt at 215.5° (corr.) They contain bromine, but are not triboluminescent. On analysis:

0.1564 gave 0.4011 CO₂ and 0.0500 H₂O. C = 69.94; H = 3.54.

0.1920 „ 6.7 c.c. nitrogen at 14° and 756 mm. N = 4.08.

0.0853 „ 0.0452 AgBr. Br = 22.54.

C₂₁H₁₂NBr requires C = 70.39; H = 3.35; N = 3.91; Br = 22.34 per cent. The substance is evidently a *monobromodinaphthacridine*. It is essentially different from a dinaphthacridine bromide (compare Senier and Austin, *Trans.*, 1904, **85**, 1196), since it may be boiled with alcoholic potassium hydroxide and may even be distilled in a partial vacuum without decomposition.

According to the method of formation, it might be a derivative either of Reed's or of Strohbach's base, that is, either 7-bromo-

It is readily soluble in chloroform or carbon disulphide, less so in benzene or toluene, and very sparingly so in alcohol. It dissolves easily in hot glacial acetic acid, depositing yellow crystals on cooling. The latter melt at 273° and have not yet been investigated. The *hydrochloride* of the base is yellow, and is precipitated from an alcoholic solution by means of hydrochloric acid. No method was found for purifying it. The preparation of double salts with metals was difficult, owing to the fact that no very suitable solvent could be found.

The *aurichloride*, $[C_{21}H_{12}NBr]_3[HAuCl_4]_2$, was obtained as a yellow, flocculent precipitate when a few drops of auric chloride solution were added to a solution of the base in a mixture of alcohol and acetic acid. The yellow precipitate was washed with dry ether and dried at 105° . On analysis :

0.0694 gave 0.0156 Au. $Au = 22.47$.

$C_{63}H_{38}N_3Cl_8Br_3Au_2$ requires $Au = 22.46$ per cent.

The *platinichloride*, $[C_{21}H_{12}NBr]_2H_2PtCl_6$, was obtained in a similar way by using platinic chloride. It is a yellow powder, which was washed with dry ether and dried at 105° . The specimen was evidently not quite pure :

0.0603 gave 0.0108 Pt. $Pt = 17.91$.

$C_{42}H_{26}N_2Cl_6Br_2Pt$ requires $Pt = 17.31$ per cent.

4. Replacement of the Bromine in Monobromodinaphthacridine by Hydrogen.

In order to prove the constitution of monobromodinaphthacridine, it was necessary to replace the bromine by hydrogen. The reduction took place readily by the action of an alcoholic solution of stannous chloride on the base partly dissolved and partly suspended in alcohol. Some tin and free hydrochloric acid were added, and the mixture was boiled for several hours under a reflux condenser, when a green substance gradually formed. When cold, the liquid was removed by filtration, and the green substance was separated mechanically from the residual tin. This green substance was boiled with methylated spirit, in which it was moderately soluble, then treated with potassium hydroxide, boiled, mixed with water, and the yellow, flocculent precipitate obtained was dissolved in aqueous pyridine. The filtered solution deposited orange crystals melting at 243° . They were identified as bis- β -N- β - α -CH α -dinaphthacridine dihydride (Senier and Austin, Trans., 1906, 89, 1398), which is known to give a green hydrochloride.

The bromodinaphthacridine is evidently therefore a derivative of β -N- β - α -CH α -dinaphthacridine (Reed).

5. *Interaction of Methylene Dichloride and 1-Nitro-2-naphthylamine.*

When 1-nitro-2-naphthylamine was heated to 210° in a closed tube with methylene dichloride for one hour, it was found that no reaction had taken place, for the original substance was recovered unchanged. Another attempt was made by heating the tube to 250—260° for two hours, when the contents of the tube were completely charred, although acridines are stable at this temperature.

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