XXIX.—*The Action of Methylene Diiodide on Aryl- and Naphthyl-amines: Diarylmethylenediamines, Acridines, and Naphthacridines.*

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IN a recent paper (Trans., 1901, 79, 254), we described two ethylene-diaryldiamines which resulted from the interaction of ethylene dibromide and xylidine and ψ -cumidine respectively. At the same time, we mentioned that we had extended the reaction to the methylene series and had obtained well crystallisable compounds. Methylene diiodide was found to give better results than either the dibromide or dichloride. We now submit the results of further study of those compounds and of the reaction generally. It was expected that these derivatives would prove to be methylenediamines or, at least, to belong to one of the classes of compounds which are known to result from the action of ethylenedibromide on aniline. They might, for example, be methylenediamines, $\text{CH}_2(\text{NHR}')_2$, methyleneaniline homologues, $\text{CH}_2\cdot\text{NR}'$, methylenepiperazines, $\text{CH}_2\langle\begin{smallmatrix} \text{NR}' \\ \text{NR}' \end{smallmatrix}\rangle\text{CH}_2$, or higher polymerides, $\begin{smallmatrix} \text{CH}_2\cdot\text{NR}'\cdot\text{CH}_2 \\ \text{NR}'\cdot\text{CH}_2\cdot\text{NR}' \end{smallmatrix}$. This view is in agreement with that of previous inquirers (Lermontoff, *Ber.*, 1874, 7, 1252; Grünhagen, *Annalen*, 1890, 256, 219 and 285; Bischoff and Nastvogel, *Ber.*, 1890, 23, 2055).

Parallel with the reaction of arylamines and methylene diiodide is the corresponding reaction between arylamines and formaldehyde or methylene oxide, $\text{CH}_2\cdot\text{O}$. The experiments of Pratesi (*Gazzetta*, 1884, 14, 351), Tollens (*Ber.*, 1884, 17, 653), Wellington and Tollens (*Ber.*, 1885, 18, 3298), Eberhardt and Welter (*Ber.*, 1894, 27, 1804), and Grassi-Cristaldi and Schiavo-Leni (*Gazzetta*, 1900, 30, ii, 112) with this latter reaction led to the discovery of the diamines and isomeric methylenearylamines previously referred to. The diamines were also shown to give rise by metastatic change to a series of methylene benzidenes. Methylenediphenyldiamine, $\text{CH}_2(\text{NHPh})_2$, for example, giving diaminodiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_4\text{NH}_2)_2$.

The study of these reactions by the investigators mentioned, evidently conducted with the greatest care, has led to very contradictory results. The physical characters of the compounds described under the same name differ enormously, and the analytical data are far from satisfactory (compare Bischoff and Nastvogel). Working with aniline and the toluidines, our experience has been the same. This is due, no doubt, partly to the proved instability of the compounds

formed, and partly to their number and the difficulty of separating them. With the increase in the number of alkyl groups, as in the case of xyldine and ψ -cumidine, the reaction becomes more definite, and with methylene di-iodide assumes a new character. With ψ -cumidine, beautiful, yellow crystals are obtained, easily recrystallised or sublimed, and in this way readily obtained of a constant and definite melting point. Elementary analysis proved that it was not a member of any of the classes of compounds alluded to above. It gave C=86.8, H=8.41, N=5.42 per cent., whereas methylenedicumyldiamine or its isomerides would require C=80.85, H=9.22, N=9.93 per cent., and methylenecumidine or its isomerides would require C=81.63, H=8.84, N=9.52 per cent. The relative proportion of nitrogen found pointed to a condensation reaction whereby ammonia or a derivative was evolved. This view found confirmation in the fact that the odour of ammonia was observed during the course of the reaction, and also that a notable quantity of ammonium iodide collected in the tube of the reflux condenser employed in the experiment. The solutions of the compound exhibited a marked and very beautiful fluorescence, and this, together with the high melting point, 221—222°, also indicated condensation.

Consideration of the paper by Friedel and Crafts (*Ann. Chim. Phys.*, 1887, [vi], 11, 263) led to the hypothesis that the compound was an anthramine from which an amino-group had split off. These investigators found that benzene and methylene dichloride condensed to anthracene in presence of aluminium chloride thus :

The hydrogen formed, acting on an excess of methylene dichloride, gave, by a secondary reaction, methyl chloride. To make certain of the right conditions, we repeated this experiment and obtained anthracene. Cumidine was substituted for benzene and the experiment repeated, but no reaction appeared to take place, and when methylene diiodide replaced the dichloride in the last experiment, the yellow, crystalline compound was obtained, but only to the same extent as in the absence of the aluminium chloride. We next modified the hypothesis by supposing condensation to take place at the position of the liberated nitrogen group. In this way, an acridine might be formed, thus :

The odour of methyl iodide was always noticed, which would explain what becomes of the hydrogen written as free in the equation as in the reaction of Friedel and Crafts. Such a hexamethylacridine would

require C = 86.61, H = 8.06, N = 5.33 per cent., which is in agreement with the experimental numbers. A vapour density determination, using boiling sulphur, was found to be possible by Victor Meyer's method:

0.1303 gave 11.8 c.c. at 18° and 767.5 mm. Density = 130.

$C_{19}H_{21}N$ requires density = 131.5.

Further evidence in favour of this view was found in the experiments of Bernthsen and Bender (*Ber.*, 1883, 16, 1802), who prepared acridine from diphenylamine and formic acid, for dicumylamine might well result from cumidine and hydriodic acid, and formic acid is hydroxymethylene oxide. Similar analogies were found in the work of Möhlau (*Ber.*, 1886, 19, 2451).

Any doubt, however, that might remain as to the ψ -cumidine compound being hexamethylacridine was set at rest by the extension of the reaction to the α - and β -naphthylamines. These bases were found to react with methylene diiodide in precisely the same manner as ψ -cumidine. The same odour of ammonia and of methyl iodide was noticed, and the same condensation of ammonium iodide in the reflux condenser tube. From each of the naphthylamines we obtained yellow crystals with well-defined melting points, and their solutions exhibited the characteristic, well-marked fluorescence. On analysis, the numbers obtained agreed with those of naphthacridine. Finally, the β -compound was identified by its melting point and other characters with β -naphthacridine discovered by Reed (*J. pr. Chem.*, [ii], 1886, 34, 160; 1887, 35, 298) as a result of the action of methylal or of formaldehyde on β -naphthylamine. This base has also been studied in an interesting paper by Morgan (*Trans.*, 1898, 73, 536). In a preliminary communication (*Proc.*, 1898, 14, 132), Morgan announced that the result of experiments on α -naphthylamine would be published later. Meanwhile, we have obtained α -naphthacridine by the methylene diiodide reaction.

We find, then, that methylene diiodide yields methylene diamines with aniline, as originally stated by Lermontoff, also with xylydine and probably with the three toluidines. With ψ -cumidine, however, and with both α - and β -naphthylamines, condensation takes place with the formation of acridines. The acridines do not react with phenyl carbimide forming ureas, but the methylenediamines do so in the same manner as their ethylene homologues (*Trans.*, 1901, 79, 258), at least so far as we have been able to complete their investigation.

The further study of α -naphthacridine and of hexamethylacridine we desire to reserve for another communication.

*Diarylmethylenediamines.**Diphenylmethylenediamine*, $\text{CH}_2(\text{NHPh})_2$.

Methylene diiodide and aniline, in equal molecular proportions, were brought together with an excess of dry potassium carbonate in a flask fitted with a reflux condenser. The flask was placed in a paraffin-bath which was heated gradually to about 150° , when a violent reaction soon took place. The flask was then removed from the bath until this moderated, when it was replaced and the heating continued for 4 hours. After cooling, the residue in the flask was treated with hot water to remove potassium salts. The dark red, semi-solid mass remaining was freed from aniline by distillation with steam. The resulting mass solidified on cooling, and, when reduced to powder, was of a dark yellow colour. It melted at $65\text{--}67^\circ$. After boiling with alcohol, the melting point rose to 140° . Diphenylmethylenediamine, described by Eberhardt and Welter, melted at $64\text{--}65^\circ$, and by boiling with alcohol it was changed into methyleneaniline which melts at 139° . On analysis:

0.2502 gave 0.7148 CO_2 and 0.1590 H_2O . $\text{C} = 77.92$; $\text{H} = 7.06$.

$\text{C}_{13}\text{H}_{14}\text{N}_2$ requires $\text{C} = 78.75$; $\text{H} = 7.07$ per cent.

Diphenylmethylenediamine Platinichloride, $\text{CH}_2(\text{NHPh})_2, \text{H}_2\text{PtCl}_6$, separated as an olive-green precipitate on the addition of a solution of platinic chloride to the base dissolved in dilute hydrochloric acid. The salt was washed with water and dried in a vacuum over sulphuric acid. On analysis:

0.2318 gave 0.0736 Pt. $\text{Pt} = 31.75$.

$\text{C}_{13}\text{H}_{14}\text{N}_2, \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 32.06$ per cent.

Dicarbanilidodiphenylmethylenediamine, $\text{CH}_2(\text{NPh}\cdot\text{CO}\cdot\text{NHPh})_2$, was obtained by treating the base with phenylcarbimide in the manner described by us (Trans., 1901, 79, 258). The closed tube was heated at $120\text{--}124^\circ$ for 3 to 4 hours. The residue was washed with dry ether and recrystallised from glacial acetic acid. The melting point is not definite. On analysis:

0.2750 gave 0.7397 CO_2 and 0.1668 H_2O . $\text{C} = 73.35$; $\text{H} = 6.74$.

$\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_2$ requires $\text{C} = 74.31$; $\text{H} = 5.50$ per cent.

*Di-*tolyl*methylenediamines*, $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$.

Methylene diiodide (1 mol.) with toluidine (2 mols.), together with potassium carbonate, were heated in the manner described for the phenyl-homologue and the subsequent procedure was the same, except that the distillation with steam was omitted. The *o*-tolyl derivative,

probably di-*o*-tolylmethylenediamine, crystallised from alcohol in large, colourless, foliate crystals. After repeated recrystallisation, these melted at 156–157°. On analysis:

0.2888 gave 0.8374 CO₂ and 0.2124 H₂O. C = 79.08; H = 8.17.

0.3550 „ 38 c.c. moist nitrogen at 16° and 756.5 mm. N = 12.41.

C₁₅H₁₈N₂ requires C = 79.64; H = 7.96; N = 12.39 per cent.

From *o*-toluidine and methylene chloride, Grünhagen obtained two bases; one was a liquid and the other melted at 135°. Using formaldehyde, Eberhardt and Welter prepared a base which melted at 52°. The *p*-tolyl derivative, probably di-*p*-tolylmethylenediamine, was obtained in small, pale yellow crystals from solution in a mixture of alcohol and chloroform. After several recrystallisations, it melted at 149–150°. On analysis:

0.2562 gave 0.7456 CO₂ and 0.1800 H₂O. C = 79.37; H = 7.8.

0.1630 „ 0.4776 CO₂ „ 0.1168 H₂O. C = 79.91; H = 7.96.

C₁₅H₁₈N₂ requires C = 79.64; H = 7.96 per cent.

We were not successful in isolating a *m*-tolyl derivative in a definite form. Yellow, amorphous compounds were obtained in two experiments. The one melted at 78°, the other at 160°.

Dixylylmethylenediamine, CH₂(NH·C₆H₃Me₂)₂.

Methylene diiodide (1 mol.) and xylidine (2 mols.) were treated in the same manner as in the corresponding reaction with the toluidines. The base, recrystallised several times from rectified spirit, consisted of pale yellow, large, foliate crystals, and melted at 127–128°. On analysis:

0.2592 gave 0.7576 CO₂ and 0.2140 H₂O. C = 79.71; H = 9.17.

0.3743 „ 35.2 c.c. moist nitrogen at 13° and 767 mm. N = 11.21.

C₁₇H₂₂N₂ requires C = 80.31; H = 8.67; N = 11.02 per cent.

Dixylylmethylenediamine Platinichloride,

was precipitated when an alcoholic solution of platonic chloride was added to an alcoholic solution of the base acidified with hydrochloric acid. The precipitate, of a golden-yellow colour, was dried at 100°. On analysis:

0.2076 gave 0.0620 Pt. Pt = 29.86.

C₁₇H₂₂N₂ requires Pt = 29.36 per cent.

Nitro-derivatives of dixylylmethylenediamine are produced readily by direct nitration. Two experiments were made, but the products were evidently mixtures. One contained N = 11.5 and the other

N = 12·7 per cent. A mononitro-derivative requires N = 9·82 and a dinitro- N = 16·28 per cent.

Dicarbanilidocarbanilidodixylylmethylenediamine,

—When an excess of phenylcarbimide reacts with dixylylmethylenediamine, a urea derivative is formed from 4 molecules of the carbimide instead of 2 molecules, as in other cases. The reaction described (Trans., 1901, 79, 258) may be supposed to occur twice in each amino-group of the diamine. This reaction is, indeed, only an extension of Wöhler's urea synthesis, for it may be assumed that a methylenediammonium dicyanate is first formed, which metastasises to urea. An excess of phenyl carbimide was heated in a closed tube with the base at 150° for 6 hours; the contents of the tube, freed from excess of phenylcarbimide by evaporation, consisted of a yellowish-white substance resembling in appearance imperfectly bleached beeswax, this was washed with dry ether, which effected no apparent change. When rubbed in a mortar with successive small quantities of alcohol, there was left a hard, white residue, which was dissolved in more alcohol, and was recrystallised several times from that medium. Well-formed, colourless needles were thus obtained which melt at 203°. On analysis:

0·2766 gave 0·7438 CO₂ and 0·1470 H₂O. C = 73·33; H = 5·9.

0·2978 „ 28·1 e.c. moist nitrogen at 10° and 754 mm. N = 11·21.

C₄₅H₄₂N₆O₄ requires C = 73·97; H = 5·75; N = 11·5 per cent.

The constitution of this hexamethylacridine we reserve for further investigation. If, however, it be supposed that the positions of condensation are neighbouring to the amino-groups, the positions of the methyl groups are 1 : 2 : 4 and 5 : 6 : 8. ψ -Cumidine, which melted at 67° (2 mols.), with methylene diiodide (1 mol.), and an excess of potassium carbonate were taken. The cumidine and potassium carbonate were melted together and then brought into a flask fitted with a reflux condenser, to which the weighed amount of methylene diiodide was then added; the flask and its contents were heated in a paraffin bath until a temperature of about 160° was reached, when an energetic reaction took place; the flask was removed from the bath until the violence had subsided, when it was replaced and the temperature continued at 150—160° for about 6 hours. The formation of a sublimate in the tube of the condenser continued during the course of the reaction, and its ceasing to form was an indication that the heating had been sufficiently prolonged. This method was found to give better

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results than when the diiodide was added in small quantities at a time. No advantage, either, was found in omitting the alkali and treating the product afterwards with potassium hydroxide. The contents of the flask were then treated with hot water to remove potassium salts, when there remained a yellow, crystalline mass; after being washed with dilute alcohol, this assumed a greenish-yellow colour. It was next dissolved and recrystallised from alcohol or, in some cases, from acetone or light petroleum, when extremely fine, yellow crystals, usually needles, were obtained. These crystals are slightly soluble in alcohol or ether and more soluble in acetone, chloroform, benzene, or light petroleum. They are insoluble in water. All the solutions exhibit a beautiful, green fluorescence. Purified by repeated recrystallisation or sublimation, the compound melts at $221-222^{\circ}$, and sublimes easily without decomposition. On analysis:

0.2406 gave 0.7658 CO_2 and 0.1823 H_2O . $\text{C} = 86.80$; $\text{H} = 8.41$.

0.2622 „ 0.8290 CO_2 „ 0.1992 H_2O . $\text{C} = 86.23$; $\text{H} = 8.44$.

0.2454 „ 0.7756 CO_2 „ 0.1770 H_2O . $\text{C} = 86.20$; $\text{H} = 8.01$.

0.3430 „ 16 c.c. moist nitrogen at 15° and 755.5 mm. $\text{N} = 5.42$.

$\text{C}_{19}\text{H}_{21}\text{N}$ requires $\text{C} = 86.69$; $\text{H} = 7.98$; $\text{N} = 5.32$ per cent.

Using methylene dibromide instead of diiodide, the acridine was obtained, but the yield was much less. With methylene dichloride, no acridine was formed. In the latter experiment, a marked odour of an isonitrile was noticed.

Hexamethylacridine Picrate, $\text{C}_6\text{HMe}_3\langle\begin{smallmatrix}\text{CH} \\ \text{N} \end{smallmatrix}\rangle\text{C}_6\text{HMe}_3\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$, was prepared by adding an alcoholic solution of picric acid to an alcoholic solution of the base, heating to boiling, and allowing to stand. Very fine, brown, plume-like crystals separated. These were collected on a filter and washed with a small quantity of alcohol and again with dilute alcohol and dried at 110° . They melted, not very sharply, at $200-202^{\circ}$. On analysis:

0.3090 gave 30.5 c.c. moist nitrogen at 18° and 752.5 mm. $\text{N} = 11.27$.

$\text{C}_{19}\text{H}_{21}\text{N}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ requires $\text{N} = 11.38$ per cent.

Dinitrohexamethylacridine, $\text{C}_6(\text{NO}_2)\text{Me}_3\langle\begin{smallmatrix}\text{CH} \\ \text{N} \end{smallmatrix}\rangle\text{C}_6(\text{NO}_2)\text{Me}_3$, was produced by treating the base with concentrated nitric acid, boiling well, and pouring the solution into water; the yellow precipitate was collected on a filter, well washed with water and dried on a porous plate. It melted at $85-87^{\circ}$. It was dried in an exhausted desiccator over sulphuric acid, and on analysis:

0.2064 gave 20.3 c.c. moist nitrogen at 18° and 761 mm. $\text{N} = 11.37$.

$\text{C}_{19}\text{H}_{19}(\text{NO}_2)_2\text{N}$ requires $\text{N} = 11.89$ per cent.

Tribromohexamethylacridine, $\text{C}_6\text{BrMe}_3\langle\text{CBr}\rangle\text{C}_6\text{BrMe}_3$, was obtained by exposing the base to the action of bromine vapour for 3 days in a covered vessel. The product was heated on a water-bath to remove excess of bromine and then allowed to stand in a desiccator over solid potassium hydroxide for 2 days. Finally, the red compound was heated in an air-bath at 105° . On analysis by Carius's method :

0.3116 gave 0.3466 AgBr. Br = 47.33.

$\text{C}_{19}\text{H}_{18}\text{Br}_3\text{N}$ requires Br = 47.98 per cent.

Hexamethylacridine Nitrate, $\text{C}_6\text{HMe}_3\langle\text{CH}\rangle\text{C}_6\text{HMe}_3\cdot\text{HNO}_3$, was formed by adding dilute nitric acid to an alcoholic solution of the base, warming for a short time on a water-bath, and then setting aside to crystallise. On standing, the solution, which had a deep orange colour, deposited bright scarlet needles. An attempt was made to further purify the compound by recrystallisation from dilute alcohol, but this treatment was found to decompose the salt regenerating the original base. The needles were washed with a little alcohol only and partly dried by pressing between filter-paper. Finally, they were dried at 100° and left over sulphuric acid in a desiccator. They melted with decomposition at $163\text{--}164^\circ$. On analysis :

0.3356 gave 25.1 c.c. moist nitrogen at 14° and 770 mm. N = 8.92.

$\text{C}_{19}\text{H}_{21}\text{N}\cdot\text{HNO}_3$ requires N = 8.59 per cent.

Hexamethylacridine Platinichloride,

separated in the form of scarlet needles on the addition of a solution of platinic chloride to a solution of the base in dilute hydrochloric acid. Like acridine salts generally, it is decomposed by treatment with water or boiling with alcohol. On analysis :

0.0577 gave 0.0118 Pt. Pt = 20.45.

$(\text{C}_{19}\text{H}_{21}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$ requires Pt = 20.82 per cent.

Hexamethylacridine Aurichloride, $\text{C}_6\text{HMe}_3\langle\text{CH}\rangle\text{C}_6\text{HMe}_3\cdot\text{HAuCl}_4$,

was obtained in a similar manner to the platinichloride. It is yellow, and on analysis :

0.1110 gave 0.0358 Au. Au = 32.25.

$(\text{C}_{19}\text{H}_{21}\text{N})\text{HAuCl}_4$ requires Au = 32.70 per cent.

Hexamethylacridine Mercurichloride, $\text{C}_6\text{HMe}_3\langle\text{CH}\rangle\text{C}_6\text{HMe}_3\cdot\text{HgCl}_2$.

—An alcoholic solution of the base acidified with hydrochloric acid was

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mixed with an alcoholic solution of mercuric chloride and the mixture allowed to stand. Dark red, glistening needles with a characteristic yellow lustre separated. On analysis:

0.3076 gave 0.1272 HgS. Hg = 35.65.

$(C_{19}H_{21}N)HgCl_2$ requires Hg = 35.11 per cent.

Hexamethylacridine Dichromate, $C_6HMe_3 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} \text{C}_6HMe_3 \cdot H_2Cr_2O_7$, was formed on the addition of a solution of potassium dichromate to a solution of the base in hydrochloric acid. It consists of deep red crystals which were washed rapidly and dried at 100°. On analysis:

0.6536 gave 0.1378 Cr_2O_3 . Cr = 14.44.

$(C_{19}H_{21}N)H_2Cr_2O_7$ requires Cr = 14.00 per cent.

Other salts examined were the *sulphate*, forming dark red crystals, which do not melt below 285°; the *hydrochloride*, red crystals which decompose on heating, and the *nitrite*, a pale yellow powder obtained by adding potassium nitrite to a solution of the base in glacial acetic acid. The nitrite decomposes on heating.

An *ethylhexamethylacridinium iodide* was also prepared but not further examined. The base was heated with excess of ethyl iodide in a closed tube for 4 hours. It consists of bronze-coloured crystals which, after drying on a porous plate, melted at 214–215°.

α-Naphthacridine.

α-Naphthylamine (2 mols.), *methylene diiodide* (1 mol.), and an excess of potassium carbonate were treated exactly as in the case of the corresponding cumidine experiment. The contents of the flask were washed with water, then with a small proportion of alcohol, after which the residue was dissolved in and recrystallised from alcohol. More than one compound appeared to be formed, and the acridine was best separated by sublimation and subsequent recrystallisation from alcohol. It consists of pale yellow crystals which melt at 173°. The colour becomes darker on exposure to light. It is soluble in chloroform, ether, acetone, benzene, or light petroleum. The fluorescence exhibited by its solutions is very noticeable. In solution in benzene, it is red-green, in the other solvents it is violet or blue. On analysis:

0.1532 gave 0.5040 CO_2 and 0.0707 H_2O . C = 89.72; H = 5.12.

0.1783 „ 7.6 c.c. moist nitrogen at 9° and 764 mm. N = 5.15.

$C_{21}H_{13}N$ requires C = 90.32; H = 4.66; N = 5.02 per cent.

The following are the only derivatives obtained so far, but the work is being continued.

Mononitro- α -naphthacridine, $C_{21}H_{12}(NO_2)N$, was precipitated when the base was warmed with concentrated nitric acid and the mixture thrown into water. After washing and drying, first on a porous plate and then in an exhausted desiccator over sulphuric acid, it melted at 105—107°. On analysis :

0.3248 gave 24.8 c.c. moist nitrogen at 16° and 767.5 mm. $N = 8.85$.

$C_{21}H_{12}(NO_2)N$ requires $N = 8.64$ per cent.

A second nitro-derivative was prepared which, after recrystallisation from alcohol and drying, melted at 185°, but was not further examined.

(α)-*Naphthacridine Platinichloride*, $C_{10}H_6 \begin{smallmatrix} <CH \\ N- \end{smallmatrix} > C_{10}H_6 \cdot H_2PtCl_6 \cdot 2H_2O$,

was obtained in the form of small, deep yellow crystals on allowing a mixture of alcoholic solutions of the base and platinic chloride, acidulated with hydrochloric acid, to stand. They could not be subjected to 100° without decomposition. Dried over sulphuric acid and analysed :

0.1676 gave 0.0322 Pt. $Pt = 19.2$.

$(C_{21}H_{13}N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ requires $Pt = 19.41$ per cent.

α -Naphthacridine Picrate, $C_{10}H_6 \begin{smallmatrix} <CH \\ N- \end{smallmatrix} > C_{10}H_6 \cdot C_6H_2(NO_2)_3 \cdot OH$, was

formed by mixing alcoholic solutions of the base and picric acid. It separated in the form of scarlet needles. These were washed with a little alcohol and dried by pressing between filter paper, and afterwards by leaving them in an exhausted desiccator over sulphuric acid. It melts at 176—178°. On analysis :

0.2312 gave 21 c.c. moist nitrogen at 10° and 771.5 mm. $N = 11.03$.

$C_{21}H_{13}N \cdot C_6H_2(NO_2)_3OH$ requires $N = 11.02$ per cent.

β -Naphthacridine.

The process adopted for the preparation of α -naphthacridine yields its β -isomeride with greater readiness and in better yield. After sublimation and recrystallisation from alcohol, it consists of pale yellow needles which darken on exposure to light. It melts at 215.5°. It is soluble in chloroform, ether, benzene, or light petroleum, and sparingly so in alcohol ; the solutions exhibit the characteristic blue fluorescence. On analysis :

0.1882 gave 0.6172 CO_2 and 0.0858 H_2O . $C = 89.44$; $H = 5.06$.

0.1990 „ 0.6540 CO_2 „ 0.0916 H_2O . $C = 89.63$; $H = 5.11$.

0.4260 „ 17.8 c.c. moist nitrogen at 13° and 776 mm. $N = 5.05$.

$C_{21}H_{13}N$ requires $C = 90.32$; $H = 4.66$; $N = 5.02$ per cent.

The compound is identical with the β -naphthacridine discovered by Reed, who gives its melting point as 216°. We obtained the following derivative, which has not been previously described.

β-Naphthacridine Platinichloride,

precipitated as a golden-yellow powder on the addition of alcoholic solution of platinic chloride to an alcoholic solution of the base acidified with hydrochloric acid. Dried over sulphuric acid and analysed :

0.1396 gave 0.027 Pt. Pt = 19.34.

$(\text{C}_{21}\text{H}_{18}\text{N})_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$ requires Pt = 19.41 per cent.

QUEEN'S COLLEGE.

GALWAY.