LXXIII.—*Derivatives of 2-Pyridylhydrazine and 2-Quinolylhydrazine.*

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DURING the course of their experiments on harmine and harmaline Perkin and Robinson (T., 1913, **103**, 1974) prepared acetone-2-quinolylhydrazine with the object of converting it into 2-methyl-12-quinindole by Fischer's method.

It was found that the quinindole derivative was not produced by heating with hydrochloric acid, zinc chloride, or other condensing agents, because hydrolysis occurred in most of the experiments.

Since it is important to determine whether the process is generally inapplicable to the pyridine nucleus, we have carried out, at the suggestion of Professor Perkin, a further series of experiments with derivatives of 2-pyridylhydrazine and 2-quinolylhydrazine.

2-Pyridylhydrazine does not appear to have been previously described, but we have found that it can be readily prepared by the following series of reactions. Pyridine methosulphate is oxidised by potassium ferricyanide to 1-methyl-2-pyridone, which, when heated with phosphorus pentachloride and phosphoryl chloride, yields 2-chloropyridine, and this, on boiling with hydrazine hydrate, is converted into 2-pyridylhydrazine:

2-Pyridylhydrazine melts at 46°, distils at 140°/20 mm., and

combines with aldehydes and ketones in the same manner as phenylhydrazine.

Ethyl acetoacetate combines readily with 2-pyridylhydrazine with the formation of the hydrazone, and this, when distilled under diminished pressure, loses ethyl alcohol with the formation of 1-(2'-pyridyl)-3-methyl-5-pyrazolone (m. p. 110°).

When 2-pyridylhydrazine is heated with nitrous acid an interesting change takes place, and 1:2:3:9-benzoisotetrazole is formed according to the scheme:

It melts at 159°, and explodes when touched with a red-hot rod.

1:2:9-Benzisotriazole is obtained when 2-pyridylhydrazine is heated with anhydrous formic acid:

and is a crystalline mass, which yields a platinichloride,

and a characteristic explosive silver nitrate derivative,

2-Quinolylhydrazine was first obtained by Marckwald and Meyer (*Ber.*, 1900, **33**, 1885) from 2-chloroquinoline and hydrazine hydrate.

Perkin and Robinson (*T.*, 1913, **103**, 1978) have described a modification of the original method, which allows of considerable quantities of 2-quinolylhydrazine being prepared with comparatively little trouble. The hydrazine separates from water in orange crystals, and melts at 142—143°.

2-Quinolylhydrazine combines readily with ethyl acetoacetate, and the resulting hydrazone (m. p. 90°) when heated on the steam-bath loses ethyl alcohol with the formation of 1-(2'-quinolyl)-3-methyl-5-pyrazolone, a crystalline substance which melts at 140°.

Many attempts have been made to convert derivatives of 2-pyridylhydrazine and 2-quinolylhydrazine into pyridole and quinindole derivatives by the action of zinc chloride, hydrochloric acid, and other agents for the removal of ammonia, but always without success, so that it appears unlikely that such substances can be obtained in the pyridine series by reactions analogous to those which work so well in the benzene series.

One of the reasons which led us to undertake this investigation

and to prepare so many derivatives of 2-pyridylhydrazine and 2-quinolyldiazine was the prospect that these substances might exhibit interesting physiological properties. This matter is being investigated.

EXPERIMENTAL.

1-Methylpyridone.

1-Methylpyridone was first prepared by Decker (*J. pr. Chem.*, 1911, [ii], **84**, 436), and more recently by Fischer and Neundlinger (*Ber.*, 1913, **46**, 2554). In preparing considerable quantities of the substance we have employed the following modification of Decker's method.

To potassium ferricyanide (195 grams) dissolved in water (400 c.c.) and well cooled in ice, are added, drop by drop from separate funnels, potassium hydroxide (50 grams) in water (60 c.c.), and pyridine methosulphate (53 grams), diluted to 60 c.c. with water. The mixture is mechanically stirred during the addition and for about half-an-hour afterwards; the potassium ferrocyanide, which crystallises, is filtered off, the filtrate is saturated with potassium hydroxide, and the oil which separates is extracted with ether, dried, and distilled, when 1-methylpyridone is obtained as a bright yellow oil boiling at 259°. The yield varies between 90 and 95 per cent. of that theoretically possible.

2-Chloropyridine.

2-Chloropyridine was obtained by O. Fischer (*Ber.*, 1898, **31**, 611; 1899, **32**, 1298; compare Pechmann and Baltzer, *Ber.*, 1891, **24**, 3150) by the action of a mixture of phosphorus pentachloride and phosphoryl chloride on 1-methylpyridone. We have found, however, that if more of the phosphoryl chloride and less of the pentachloride are used than Fischer recommends, the yield is much better.

1-Methylpyridone (26 grams) is heated in a Geissler flask with a mixture of phosphoryl chloride (40 grams) and phosphorus pentachloride (60 grams) for nine hours at 150–160°. The excess of phosphoryl chloride is distilled off under diminished pressure, and the residue is carefully decomposed with water, made strongly alkaline with sodium hydroxide, and distilled with steam. 2-Chloropyridine, extracted from the distillate with ether, dried over potassium hydroxide, and distilled, boils at 170° (uncorr.), and the yield is almost theoretical.

2-Pyridylhydrazine, $C_5H_4N \cdot NH \cdot NH_2$.

2-Pyridylhydrazine is readily obtained when 2-chloropyridine is heated to boiling with an excess of hydrazine hydrate, and when the following conditions are observed no hydrazopyridine appears to be produced.

2-Chloropyridine (34 grams) is boiled with hydrazine hydrate (140 grams) for four hours on a sand-bath, and, after cooling, the whole is extracted with ether (*A*), which dissolves a considerable part of the 2-pyridylhydrazine and some unchanged 2-chloropyridine. Hydrazine hydrate, hydrazine hydrochloride, and 2-pyridylhydrazine hydrochloride remain in the residue. The excess of hydrazine hydrate is distilled under diminished pressure, and the residue is treated with concentrated potassium hydroxide and extracted with ether (*B*). The extracts *A* and *B* are united, dried over potassium hydroxide, and evaporated, and the residue is fractionated under diminished pressure, when 21 grams of 2-pyridylhydrazine and 12 grams of unchanged 2-chloropyridine are obtained:

0.0892 gave 0.1805 CO_2 and 0.0529 H_2O . $C=55.2$; $H=6.6$.

0.0520 „ 17.1 c.c. N_2 at 16° and 764 mm. $N=38.5$.

$C_5H_7N_3$ requires $C=55.05$; $H=6.4$; $N=38.5$ per cent.

2-Pyridylhydrazine boils at $185^\circ/140$ mm., $170^\circ/55$ mm., $145^\circ/25$ mm., and $140^\circ/20$ mm., and when pure readily solidifies to a white, crystalline mass, melting at about 46° , which may be recrystallised from light petroleum. It decomposes rapidly on exposure to the air, and an intense odour of pyridine is noticeable; it can be kept indefinitely in sealed tubes. Towards picric acid and platinic chloride it behaves as a monacid base; it reduces Fehling's solution.

The *picrate*, which is insoluble in water, separates from alcohol in slender needles, and melts and decomposes at $160-161^\circ$:

0.0962 gave 20.5 c.c. N_2 at 18° and 772 mm. $N=25.0$.

$C_5H_7N_3 \cdot C_6H_3O_7N_3$ requires $N=24.9$ per cent.

A pale yellow precipitate of the *platinichloride* is obtained when platinic chloride is added to the aqueous solution of the hydrochloride of the base. It blackens at 160° , and melts and decomposes at 256° :

0.1046 gave 0.0326 Pt. $Pt=31.16$.

$(C_5H_7N_3)_2 \cdot H_2PtCl_6$ requires $Pt=31.05$ per cent.

Acetaldehyde-2-pyridylhydrazone, $C_5H_4N \cdot NH \cdot N : CHMe$.

In the preparation of this substance freshly distilled acetaldehyde (1 gram) is added drop by drop to a solution of 2-pyridylhydrazine (2 grams) in ether, when a vigorous reaction ensues. After evaporation of the ether the solid residue is drained on porous porcelain, and then recrystallised from aqueous alcohol or light petroleum, from which it separates in needles, melting at 70° :

0.1074 gave 29.6 c.c. N_2 at 17° and 740 mm. $N = 31.1$.

$C_7H_9N_3$ requires $N = 31.1$ per cent.

The addition of a trace of potassium hydroxide to the alcoholic solution of the hydrazone causes the development of a pink colour, which is discharged by acids and regenerated by excess of the alkali. Crystallisation from water or aqueous alcohol containing a trace of potassium hydroxide does not appreciably affect the melting point.

Benzaldehyde-2-pyridylhydrazone, $C_5H_4N \cdot NH \cdot N : CH \cdot C_6H_5$.

This derivative is obtained when 2-pyridylhydrazine (2 grams), dissolved in dilute acetic acid, is mixed with benzaldehyde (2 grams); the condensation product separates immediately. It is recrystallised from alcohol, from which it separates in long, glistening, colourless needles, melting at 148° :

0.1596 gave 29.5 c.c. N_2 at 18° and 760 mm. $N = 21.3$.

$C_{12}H_{11}N_3$ requires $N = 21.3$ per cent.

Acetone-2-pyridylhydrazone, $C_5H_4N \cdot NH \cdot N : CMe_2$.

2-Pyridylhydrazine (8 grams) is dissolved in acetone and kept for some time; the excess of solvent is removed, water added, and the product extracted with ether, dried over calcium chloride, and fractionated under diminished pressure.

Acetone-2-pyridylhydrazone crystallises from light petroleum in rhombic prisms melting at 73° ; it boils at $145^\circ/25$ mm., $160^\circ/35$ mm., and $180^\circ/70$ mm. It dissolves readily in alcohol, chloroform, benzene, or toluene, and in cold dilute acids, from which it is precipitated by the addition of alkali:

0.1404 gave 33.8 c.c. N_2 at 14° and 750 mm. $N = 28.0$.

$C_8H_{11}N_3$ requires $N = 28.2$ per cent.

Many attempts were made to prepare a pyrindole derivative, but without success. The finely divided hydrazone, intimately mixed with a large excess of zinc chloride, was heated at temperatures varying between 170° and 300° ; on dissolving the fusion in water,

adding sodium hydroxide, and extracting with ether, much unchanged hydrazone was obtained, and it was evident that no pyridole formation had taken place. Similar results were obtained when dilute or concentrated acids were used, under pressure, in the place of zinc chloride.

Acetophenone-2-pyridylhydrazone, $C_6H_4N \cdot NH \cdot N : CMe \cdot C_6H_5$.

This derivative is prepared by keeping molecular quantities of acetophenone and 2-pyridylhydrazine for some time in alcoholic solution. Water is then added, and the product is collected and recrystallised from dilute alcohol, from which it separates in colourless crystals melting at 90° :

0.1467 gave 26.0 c.c. N_2 at 18° and 743 mm. $N = 20.0$.

$C_{13}H_{13}N_3$ requires $N = 19.9$ per cent.

The 2-Pyridylhydrazone of Pyruvic Acid,

The reaction between 2-pyridylhydrazine and pyruvic acid proceeds with almost explosive violence. Pyridylhydrazine (2 grams) dissolved in ether is gradually added to pyruvic acid (1.7 grams), when an extremely vigorous reaction ensues, and the condensation product separates immediately. It is triturated with ether, collected, and crystallised from aqueous alcohol, from which it separates in long needles, containing $1\frac{1}{2}$ molecules of water of crystallisation. It melts at 188° with evolution of carbon dioxide, and dissolves in both acids and alkalis. It is fairly soluble in hot water, and sparingly so in benzene or chloroform. Using the conditions described in the case of acetone-2-pyridylhydrazone, we were unable to induce pyridole formation:

0.1165 lost 0.0153 at 100° . $H_2O = 13.1$.

After dehydration, 0.1010 gave 21.0 c.c. N_2 at 19° and 750 mm. $N = 23.6$.

$C_8H_9O_2N_3$ requires $N = 23.5$ per cent.

$C_8H_9O_2N_3 \cdot 1\frac{1}{2}H_2O$ requires $H_2O = 13.1$ per cent.

The 2-Pyridylhydrazone of Ethyl Pyruvate,

This ester is obtained when the acid is esterified by boiling with alcohol and sulphuric acid, but is best prepared by mixing 2-pyridylhydrazine (2.2 grams) with ethyl pyruvate (2.3 grams) in alcoholic solution. After a short time the product is precipitated by the addition of water, and recrystallised from aqueous alcohol, from

which it separates in slender needles, containing one molecule of water of crystallisation, and melting at 53°. From light petroleum it crystallises in the anhydrous condition; it then melts at 74°.

I. Crystals from dilute alcohol:

0.1053 gave 17.3 c.c. N_2 at 17° and 744 mm. $N = 18.7$.

$C_{10}H_{13}O_2N_3 \cdot H_2O$ requires $N = 18.7$ per cent.

The same specimen after drying over phosphoric oxide:

0.1076 gave 19 c.c. N_2 at 18° and 760 mm. $N = 20.4$.

II. Crystals from light petroleum:

0.1333 gave 24.5 c.c. N_2 at 17° and 750 mm. $N = 20.7$.

$C_{10}H_{13}O_2N_3$ requires $N = 20.3$ per cent.

Acetyl-2-pyridylhydrazine, $C_5H_4N \cdot NH \cdot NH \cdot COMe$.

In the preparation of this substance, acetic anhydride (1 gram) is carefully added to 2-pyridylhydrazine (2.2 grams). Much heat is developed, and, after cooling, the hard mass is triturated with ether to remove the excess of either component, when a white solid is obtained, which is soluble in cold water, alcohol, or chloroform, but dissolves very sparingly in benzene. It separates from the latter solvent in twin prisms, which melt at 150°:

0.1164 gave 28.1 c.c. N_2 at 15° and 750 mm. $N = 27.9$.

$C_7H_9ON_3$ requires $N = 27.8$ per cent.

Phthalyl-2-pyridylhydrazide, $\begin{matrix} C_6H_4 \\ \diagup \quad \diagdown \\ CO-O \end{matrix} > C:N \cdot NH \cdot C_5H_4N$.

The hydrazide is obtained when molecular quantities of 2-pyridylhydrazine and phthalic anhydride are heated together in alcoholic solution for two hours, and the product cooled. It crystallises from alcohol in colourless, rhombic prisms, which melt at 208°:

0.1028 gave 15.7 c.c. N_2 at 19° and 764 mm. $N = 17.7$.

$C_{13}H_9O_2N_3$ requires $N = 17.6$ per cent.

2-Pyridylsemicarbazide, $C_5H_4N \cdot NH \cdot NH \cdot CO \cdot NH_2$.

2-Pyridylsemicarbazide is readily obtained when 2-pyridylhydrazine, dissolved in sufficient dilute hydrochloric acid to form the monohydrochloride, is treated with an equivalent quantity of potassium cyanate in aqueous solution and the mixture is warmed on the water-bath for half-an-hour. On cooling, the semicarbazide separates in granular form; it melts, after recrystallisation from hot water, at 186°. It dissolves readily in alcohol, hot water, and acids:

0.0634 gave 20.1 c.c. N_2 at 18° and 762 mm. $N=36.7$.

$C_6H_8ON_4$ requires $N=36.8$ per cent.

In preparing this substance, the following method was found to give the best results. Ethyl acetoacetate (5.2 grams) is mixed with 2-pyridylhydrazine (4.4 grams), when water soon separates. The hydrazone is then dissolved in ether, dried, and distilled under diminished pressure, whereby ethyl alcohol is eliminated and the pyrazolone distils in almost quantitative yield.

0.0594 gave 12.3 c.c. N_2 at 18° and 760 mm. $N=23.9$.

0.1425 „ 0.3237 CO_2 and 0.0710 H_2O . $C=61.9$; $H=5.5$.

$C_9H_9ON_3$ requires $C=61.7$; $H=5.14$; $N=24.0$ per cent.

The compound is sparingly soluble in cold water, but dissolves readily in alcohol or toluene. After recrystallisation from dilute alcohol or light petroleum, it melts at 110° . Its aqueous solution gives a blue coloration with ferric chloride.

This substance is obtained when 2-pyridylhydrazine (1 gram), dissolved in dilute acetic acid (50 per cent.) and cooled in a freezing mixture, is treated with a solution of sodium nitrite (0.8 gram $NaNO_2$). After a short time crystals are deposited, which, after being collected and washed, are quite pure, and melt at 159° :

0.0668 gave 26.6 c.c. N_2 at 18° and 771 mm. $N=46.7$.

$C_5H_4N_4$ requires $N=46.7$ per cent.

The compound crystallises in colourless, elongated prisms, which are almost insoluble in cold water or ether, but soluble in warm water, alcohol, or acetone. When touched with a red-hot rod it decomposes explosively.

This substance was prepared by the condensation of 2-pyridylhydrazine and formic acid. 2-Pyridylhydrazine (1 gram) is boiled with an excess of formic acid (4 grams) during an hour, the excess of the acid is evaporated, and the residue is placed in a vacuum desiccator; it gradually solidifies to a white, crystalline mass, which

is extremely hygroscopic and retains water even when exposed over sulphuric acid for some hours. In order to characterise the substance, the compounds with platinic chloride and with silver nitrate were prepared, since, like naphthatriazole (Marckwald and Meyer, *Ber.*, 1900, **33**, 1885), it has the property of forming double compounds with many metallic salts.

The *platinichloride*, prepared in the usual way, is a light yellow, crystalline substance, which does not melt at 300°:

0.1421 gave 0.0430 Pt. Pt=30.2.

$(C_6H_5N_3)_2, H_2PtCl_6$ requires Pt=30.1 per cent.

The *silver nitrate* derivative is immediately precipitated when a solution of silver nitrate is added to the aqueous solution of the base. It crystallises from hot water in slender needles, which decompose at 228° when heated in a capillary tube, but explode when heated in larger quantity:

0.1343 gave 0.0497 Ag. Ag=37.0.

$C_6H_5N_3, AgNO_3$ requires Ag=37.2 per cent.

s-2-Pyridyl-2-quinolyldiazine, $C_9H_6N \cdot NH \cdot NH \cdot C_6H_4N$.

This substance is readily obtained by the interaction of 2-chloroquinoline and 2-pyridylhydrazine, either without a solvent or in the presence of a tertiary base, such as pyridine. Molecular proportions of the two substances, dissolved in an excess of pyridine, are warmed during about an hour, after which the pyridine and pyridine hydrochloride are removed from the mixture by treatment with water. The yellow residue is recrystallised from alcohol, from which it separates in colourless crystals melting at 177°.

2-Pyridyl-2-quinolyldiazine is very sparingly soluble in water or light petroleum, but fairly readily so in boiling alcohol. By oxidation with nitrous acid in acetic acid it yields the corresponding azo-compound:

0.0942 gave 19.7 c.c. N_2 at 16° and 746 mm. N=23.9.

$C_{14}H_{12}N_4$ requires N=23.7 per cent.

Acetaldehyde-2-quinolyldiazine, $C_9H_6N \cdot NH \cdot N \cdot CHMe$.

Acetaldehyde and 2-quinolyldiazine combine readily at the ordinary temperature with the evolution of much heat, so that the reaction is best carried out in the presence of a diluent.

2-Quinolyldiazine (2 grams) is powdered very finely, and made into a paste with a little alcohol. Acetaldehyde (2 grams) is then added drop by drop, the mixture being cooled during the addition. After a few minutes the mass becomes homogeneous, and then begins to deposit well-defined crystals, which are collected and

recrystallised from alcohol, when they are obtained in slender, colourless, silky needles, melting at 151° :

0.1052 gave 20.7 c.c. N_2 at 18° and 762 mm. $N = 22.8$.

$C_{11}H_{11}N_3$ requires $N = 22.7$ per cent.

The addition of a trace of potassium hydroxide to the solvent used for the recrystallisation had no appreciable effect on the melting point (compare Laws and Sidgwick, T., 1911, 101, 2085). The presence of a trace of hydrochloric acid caused a slight lowering in the melting point, but this may have been due to the formation of a trace of the hydrochloride, although we could not detect chlorine in the product. It was noticed that when a drop of potassium hydroxide solution was added to the dilute alcoholic solution of the hydrazone an intense pink colour gradually developed, which was discharged on acidifying, and regenerated immediately on basifying.

Acetophenone-2-quinolylhydrazone,* $C_9H_6N \cdot NH \cdot N : CMe \cdot C_6H_5$.

When a solution of molecular proportions of acetophenone and 2-quinolylhydrazine in acetic acid is kept, yellow needles are deposited, which, after recrystallisation from alcohol, melt at 122° :

0.1213 gave 16.8 c.c. N_2 at 15° and 756 mm. $N = 16.2$.

$C_{17}H_{15}N_3$ requires $N = 16.0$ per cent.

The 2-Quinolylhydrazone of Pyruvic Acid,*

$C_9H_6N \cdot NH \cdot N : CMe \cdot CO_2H$.

When molecular quantities of pyruvic acid and quinolylhydrazine are mixed in ethereal solution the condensation product immediately separates as a yellow precipitate, which is very sparingly soluble in all the ordinary solvents. On heating, it darkens at 170° , and decomposes at 200° , with the evolution of carbon dioxide and ammonia:

0.1126 gave 17.8 c.c. N_2 at 17° and 760 mm. $N = 18.2$.

$C_{12}H_{11}O_2N_3$ requires $N = 18.3$ per cent.

The hydrazone was found to esterify readily when boiled with alcohol and sulphuric acid; the resulting ester melts at 134° :

0.1065 gave 15.0 c.c. N_2 at 14° and 760 mm. $N = 16.5$.

$C_{14}H_{15}O_2N_3$ requires $N = 16.3$ per cent.

Several attempts were made to induce quinindole formation, both by heating with zinc chloride at temperatures up to 300° , and with hydrochloric acid in sealed tubes. After heating with hydrochloric acid at 180 — 200° under pressure during four hours, and allowing

* This compound was prepared by Mr. Eric Robinson.

the tube to cool, long, silky needles separated, which, recrystallised from water, melted at 195° . The substance, which was insoluble in sodium carbonate, but soluble in sodium hydroxide, proved to be carbostyryl (Found, $C=74.2$; $H=4.9$; $N=10.3$. Calc., $C=74.5$; $H=4.8$; $N=9.7$ per cent.)

*The 2-Quinolyldiazone of Lævulic Acid,**

A yellow precipitate of this derivative is immediately obtained when alcoholic solutions of 2-quinolyldiazine and lævulic acid are mixed. After recrystallisation from boiling alcohol, in which it is only sparingly soluble, it melts and decomposes at 200° :

0.1419 gave 19.5 c.c. N_2 at 14° and 760 mm. $N=16.3$.

$C_{14}H_{15}O_2N_3$ requires $N=16.3$ per cent.

*Acetyl-2-quinolyldiazine,** $C_9H_6N \cdot NH \cdot NH \cdot CO \cdot CH_3$.

This derivative is obtained when acetic anhydride (1 mol.) is added to 2-quinolyldiazine (2 mols.), and the mixture stirred with a glass rod until it sets to a hard mass. This is triturated with ether to remove impurities, and recrystallised from alcohol, from which it separates in clusters of elongated, rhombic prisms, melting at 195° :

0.0630 gave 11.4 c.c. N_2 at 16° and 754 mm. $N=20.9$.

$C_{11}H_{11}ON_3$ requires $N=20.9$ per cent.

Benzoyl-2-quinolyldiazine, $C_9H_6N \cdot NH \cdot NH \cdot CO \cdot C_6H_5$.

This derivative may be prepared by the action of either benzoic anhydride or benzoyl chloride on 2-quinolyldiazine.

Molecular proportions of benzoic anhydride and 2-quinolyldiazine are dissolved in alcohol and heated to boiling during two hours. The sparingly soluble diazine separates almost completely on cooling, and is collected and recrystallised from hot acetone, from which it is obtained in clusters of colourless needles melting at 204° . It is sparingly soluble in water, alcohol, acetone, or benzene:

0.1161 gave 16.3 c.c. N_2 at 19° and 764 mm. $N=16.2$.

$C_{16}H_{13}ON_3$ requires $N=16.0$ per cent.

This derivative is obtained when equivalent quantities of 2-quinolyldiazine and succinic anhydride, dissolved in alcohol,

* This compound was prepared by Mr. Eric Robinson.

are mixed and warmed on the water-bath during two hours. The hydrazide separates on cooling, and after recrystallisation from alcohol is obtained in pale yellow rhombs, which melt at 160° and decompose at a slightly higher temperature:

0.1392 gave 21.0 c.c. N_2 at 18° and 764 mm. $N=17.5$.

$C_{13}H_{11}O_2N_3$ requires $N=17.4$ per cent.

Phthalyl-2-quinolyldiazide, $\begin{matrix} C_6H_4 \\ CO-O \end{matrix} > C:N \cdot NH \cdot C_9H_6N$.

The phthalylhydrazide of 2-quinolyldiazine is obtained by boiling together molecular quantities of phthalic anhydride and 2-quinolyldiazine in alcoholic solution during two hours. The hydrazide separates on cooling, and is collected and recrystallised from alcohol, from which it is deposited in pale orange plates melting at 236° :

0.1810 gave 22.9 c.c. N_2 at 17° and 744 mm. $N=14.3$.

$C_{17}H_{11}O_2N_3$ requires $N=14.5$ per cent.

The 2-Quinolyldiazone of Ethyl Acetoacetate,

$C_9H_6N \cdot NH \cdot N : CMe \cdot CH_2 \cdot CO_2Et$.

Equimolecular proportions of 2-quinolyldiazine and ethyl acetoacetate are mixed and kept overnight. The resulting solid mass is spread on porous porcelain, and recrystallised from light petroleum, from which it separates in colourless needles melting at 90° :

0.1456 gave 20.3 c.c. N_2 at 19° and 743 mm. $N=15.6$.

$C_{15}H_{17}O_2N_3$ requires $N=15.5$ per cent.

1-(2'-Quinoly)-3-methyl-5-pyrazolone, $\begin{matrix} CH_2 \cdot CO \\ CMe=N \end{matrix} > N \cdot C_9H_6N$.

In order to obtain this derivative, the ester just described is warmed on the water-bath until the liquid mass solidifies to a hard cake; this dissolves fairly readily in boiling alcohol, and, on cooling, a voluminous mass of fluffy needles, melting at 140° , is obtained:

0.1710 gave 28.2 c.c. N_2 at 18° and 750 mm. $N=18.8$.

$C_{13}H_{11}ON_3$ requires $N=18.7$ per cent.

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