119. *New Syntheses of Heterocyclic Compounds. Part XII. The Condensation of Ethyl β-Aminocrotonate with Some Cyclic Amidines.*

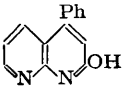
By H. Antaki and V. Petrow.

The base, m. p. 123°, obtained from 2-aminopyridine and ethyl acetoacetate and believed to be 2 : 10-dihydro-2-keto-4-methyl-1 : 10-diazanaphthalene (II) is now shown to be the 4-keto-2-methyl isomer (III) by its alternative synthesis from 2-bromopyridine and ethyl β-aminocrotonate.

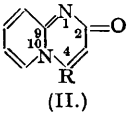
Reaction of 2-aminopyridine with ethyl β-aminocrotonate represents a novel and improved route to compounds of type (III). The reaction may be extended by employing other cyclic amidines in place of 2-aminopyridine, the ring systems (V)—(XV) being thus obtained.

By reaction between 2-aminopyridine and benzoylacetic ester, Palazzo and Tamburini (*Atti R. Accad. Lincei*, 1911, **20**, I, 37) obtained 2-benzoylacetamidopyridine, which underwent ring closure under the action of concentrated sulphuric acid at 100° to give a compound they regarded as a 2-hydroxy-4-phenyl-1 : 8-naphthyridine (I). Acetoacetic ester likewise gave 2-acetoacetamidopyridine, m. p. 113°, but experiments on its ring closure were not reported. The reaction was subsequently re-examined by Seide (*Ber.*, 1925, **58**, 352), who obtained 4-hydroxy-6-phenylpyrimidine by oxidation of the so-called naphthyridine. Accordingly, he reformulated the latter product as a 2 : 10-dihydro-2-keto-4-phenyl-1 : 10-diazanaphthalene (II; R = Ph).

The corresponding condensation employing ethyl acetoacetate was effected by Crippa and Scevola (*Gazzetta*, 1937, **67**, 327), who heated the components in the presence of a small quantity of hydrochloric acid, obtaining a base, m. p. 123°, which they regarded as a 2 : 10-dihydro-2-keto-4-methyl-1 : 10-diazanaphthalene (II; R = Me). They postulated the initial formation



(I.)



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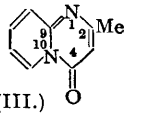

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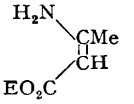
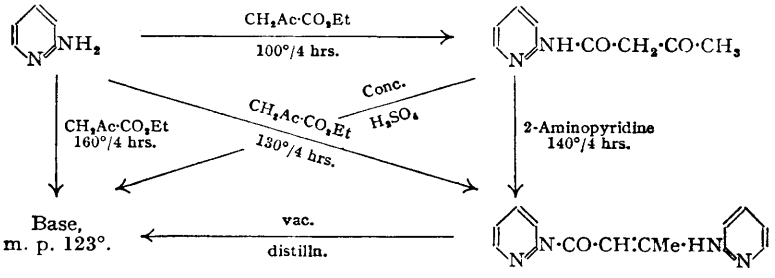


(IV.)

of a 1 : 2 : 3 : 4-tetrahydro-2-keto-4-methyl 1 : 10-diazanaphthalene, m. p. 84°, which underwent facile dehydration on crystallisation to give the base, m. p. 123°, a result in marked contrast to the earlier observation of Palazzo and Tamburini (*loc. cit.*) (*vide supra*). The work was carried a stage further by Khitrik (*J. Gen. Chem. Russia*, 1939, **9**, 1109), who isolated a 2-acetoacetamidopyridine, m. p. 113°, by reaction of the components for 4 hours at 100°. The formulation

assigned to this compound followed from its conversion into a methiodide, a reaction which excluded the alternative 1-acetoacetylpyridone-2-imine structure from consideration. 2-Acetoacetamidopyridine passed into the pyrimidine base, m. p. 123°, in low yield on treatment with concentrated sulphuric acid. The last compound readily formed a monohydrate, m. p. 107°, in air, and a hydrate, m. p. 84°, containing $1{\cdot}25H_2O$ on crystallisation from water. β-2′-Pyridylaminocrotono-2-pyridylamide, on vacuum distillation, gave the pyrimidine base the structure of which (II; R = Me) was apparently confirmed by nitration, followed by treatment with alkali, whereupon ammonia was liberated. These preparative changes are summarised in the reaction scheme below :



By condensing ethyl acetoacetate with 2-aminopyridine, as described by Khitrik (*loc. cit.*), we readily obtained 2-acetoacetamidopyridine. The constitution assigned to this compound followed from the purple colour produced with ferric chloride. All attempts to cyclise this compound to the pyrimidine base, m. p. 123°, except by the sulphuric acid procedure described by Khitrik (*loc. cit.*), proved unsuccessful. We were thus led to question structure (II; R = Me) assigned to the base by earlier workers, and to consider its alternative formulation as 4 : 10-dihydro-4-keto-2-methyl-1 : 10-diazanaphthalene (III). The 1 : 10-diazanaphthalene structure, it should be noted, had previously been assigned by Lappin (*J. Amer. Chem. Soc.*, 1948, **70**, 3348) to the condensation products of some 2-aminopyridines with ethyl ethoxymethylenemalonate.

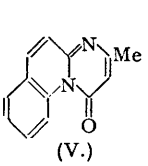
Oxidation, *per se*, cannot distinguish between structures (II) and (III) (cf. Seide, *loc. cit.*). We thus developed an unambiguous synthesis of (III), which was ultimately achieved by direct condensation of 2-bromopyridine with ethyl β-aminocrotonate (IV). The substance so obtained proved identical in every way with the pyrimidine base, m. p. 123°, prepared by Crippa and Scevola's method (*loc. cit.*) or by the pyrolytic distillation of β-2′-pyridylaminocrotono-2-pyridylamide (Khitrik, *loc. cit.*). Our failure to obtain it from 2-acetoacetamidopyridine thus receives a rational explanation. Its production by the action of concentrated sulphuric acid on the latter compound, however, is less readily interpreted unless some sort of rearrangement or formation of a pyridylaminocroton-2-pyridylamide is postulated. It is perhaps relevant to add, in this connection, that the yield of (III) obtained in this way has never exceeded 10% in our hands, and that reaction is always accompanied by evolution of gaseous products which were not identified.

Attempts to extend the chemistry of the 4 : 10-dihydro-4-keto-1 : 10-diazanaphthalene ring system have hitherto been handicapped by lack of a suitable preparative method. We now find that (III) is readily obtained in good yield by direct condensation of 2-aminopyridine with ethyl β-aminocrotonate (cf. Petrow, Rewald, and Sturgeon, *J.*, 1947, 1407). The latter reagent is indeed markedly superior to ethyl acetoacetate in reactions of this type, and its use has enabled a series of related compounds to become available for the first time.

Although 2-amino-3- and -4-methylpyridine gave 1 : 4-dihydro-4-keto-2 : 8- and -2 : 7-dimethyl-1 : 4-diazanaphthalene, reaction of 2-amino-6-methylpyridine with (IV) gave only the corresponding *s*-di-(6-methyl-2-pyridyl)urea. This result is paralleled by the observations of Lappin (*loc. cit.*) that, whereas 2-amino-3- and -4-methylpyridine yield quinolizines on condensation with ethyl ethoxymethylenemalonate, the 6-methyl isomer passes smoothly into the corresponding ethyl 4-hydroxy-7-methyl-1 : 8-naphthyridine-3-carboxylate. This difference in behaviour may no doubt be attributed to steric hindrance by the 6-substituent, coupled with a shift in the tautomeric equilibrium of the cyclic amidine residue present in the 2-aminopyridine ring system. 2-Aminoquinoline likewise gave *s*-di-2-quinolylurea with ethyl 2-aminocrotonate, 4 : 12-dihydro-4-keto-2-methyl-1 : 12-diazaphenanthrene (V) being ultimately obtained by reaction of 2-chloroquinoline with (IV). 9-Aminophenanthridine, in contrast,

gave a new base which appeared to be 9 : 9′-diphenanthridylamine, but the reason for this anomalous reaction is not evident.

Only hydrogenated derivatives of 7 : 9-diazathionaphthen have hitherto been described in the literature (Bogert and Masters, *J. Amer. Chem. Soc.*, 1942, **64**, 2709; Whitmore, *ibid.*, 1943, **65**, 2472). By condensing 2-aminothiazole with (IV), however, we have now obtained 4 : 9-dihydro-4-keto-6-methyl-7 : 9-diazathianaphthen (VI) in excellent yield. 2-Amino-4-methylthiazole likwise gave the 3-methyl analogue (VI*a*) but the yield obtained in this instance was less favourable. Reaction of (VI) with methanolic methyl iodide led to the formation of 4 : 9-dihydro-4-keto-6-methyl-7 : 9-diazathianaphthen methiodide, but attempts to convert this into the methochloride, which was required for biological study, were only partly successful as the product gave somewhat low analytical figures for halogen. Nitration of (VI) gave a mononitro-derivative, although in somewhat poor yield. In contrast to earlier work employing ethyl acetoacetate (G.P. 603,623), condensation of 2-aminobenzthiazole with (IV) led to 4 : 11-dihydro-4-keto-2-methyl-1 : 11-diaza-9-thiafluorene (VII; R = H). The 6-chloro-, 6-amino-, 6-carbethoxy-, and 6-ethoxy-derivatives of this novel ring system were obtained in the same way. 2-Aminonaphtho(2′ : 1′-4 : 5)thiazole gave 4 : 11-dihydro-4-keto-2-methyl-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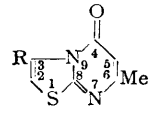
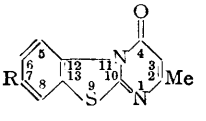

(VI.) (R = H.)
(VI*a*.) (R = Me.)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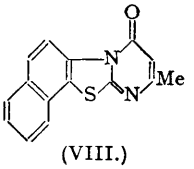
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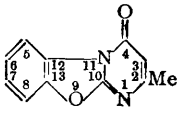
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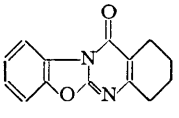
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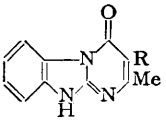
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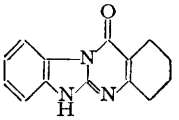
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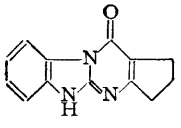
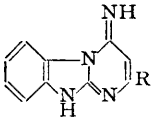
(XIII.)





(XIV; R = Me.)
(XV; R = Ph.)

7 : 8-benzo-1 : 11-diaza-9-thiafluorene (VIII). The oxygen analogue (IX) was prepared from 2-aminobenzoxazole and (IV), whilst reaction of the base with ethyl 2-keto*cyclo*hexanecarboxylate led to 4 : 11-dihydro-4-keto-2 : 3-*cyclo*hexeno-1 : 11-diaza-9-oxafluorene (X).

The formation of 4 : 11-dihydro-4-keto-2-methyl-1 : 9 : 11-triazafluorene (XI; R = H) from 2-aminobenziminazole and ethyl acetoacetate (Crippa and Perroncito, *Gazzetta*, 1935, **65**, 38) or β-aminocrotonate (Henecka, G.P. 641,598) has previously been reported. In addition to confirming this claim, we have also extended the reaction to include the 3-alkyl derivatives of this ring system, and, by employing ethyl 2-keto-*cyclo*hexanecarboxylate and -*cyclo*pentanecarboxylate as the non-basic reactants, have prepared the corresponding 2 : 3-*cyclo*hexeno- (XII) and the 2 : 3-*cyclo*penteno-analogue (XIII). When β-aminocrotononitrile and β-aminocinnamonitrile were condensed with 2-aminobenziminazole, the imino-triaza-compounds (XIV) and (XV) were obtained.

Experimental.

Microanalyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.

4 : 10-*Dihydro*-4-*keto*-2-*methyl*-1 : 10-*diazanaphthalene* (III).—(*a*) 2-Aminopyridine (9·4 g.) and ethyl β-aminocrotonate were heated for 6—8 hours at 160—180°, and then for a further hour at 200—220°. Distillation of the solid reaction product at 18 mm., followed by crystallisation from benzene–light petroleum (b. p. 100—120°), gave the *diazanaphthalene* as a hydrate, needles, m. p. 104—105°, converted into the anhydrous base, m. p. 124—125° (Found: C, 67·3; H, 5·0; N, 17·5. $C_9H_8ON_2$ requires C, 67·5; H, 5·0; N, 17·5%), after 24 hours in a vacuum-desiccator. The *picrate* formed yellow crystals (from acetone–alcohol), m. p. 184° (Found: C, 45·9; H, 2·6; N, 18·8. $C_9H_8ON_2,C_6H_3O_7N_3$ requires C, 46·2; H, 2·8; N, 18·0%). Neither the base nor the picrate gave m. p. depressions on admixture with material prepared from 2-aminopyridine and ethyl acetoacetate by Khitrik's method (*loc. cit.*).

(*b*) 2-Bromopyridine (6 g.), ethyl β-aminocrotonate (5 g.), anhydrous potassium carbonate (5 g.), and copper bronze (100—200 mg.) were heated together at 180—200° for 5—6 hours. After cooling, the

reaction product was extracted with benzene (charcoal) and treated with light petroleum (b. p. 100—120°). The yellow crystalline solid which separated was purified from benzene–light petroleum and finally from light petroleum, giving hygroscopic crystals of the anhydrous base, m. p. 124—125° (Found : C, 66·9; H, 4·9; N, 17·2%), not depressed on admixture with the product obtained by method (*a*). Its picrate, m. p. 184°, likewise gave no depression on admixture with the foregoing picrate.

(*c*) 2-Acetoacetamidopyridine was prepared by heating 2-aminopyridine (9·4 g.) and ethyl acetoacetate (26 g.) at 100° for 4 hours. Excess of the reactants was removed by distillation under reduced pressure and the solid residue crystallised from benzene–light petroleum and finally alcohol. It formed plates, m. p. 112—113° (Found : C, 60·3; H, 5·5; N, 15·9. Calc. for $C_9H_{10}O_2N_2$: C, 60·6; H, 5·6; N, 15·7%). The product so obtained was carefully added to concentrated sulphuric acid at room temperature, an exothermic reaction occurring with evolution of gas. After 24 hours the solution was poured on ice, basified with aqueous ammonia, and extracted with chloroform, evaporation of which gave (III) as needles, m. p. 123°, from benzene–light petroleum, not depressed on admixture with an authentic specimen.

1 : 4-*Dihydro*-4-*keto*-2 : 7-*dimethyl*-1 : 10-*diazanaphthalene*.—Prepared by heating 2-amino-4-methylpyridine (7 g.) and ethyl 2-aminocrotonate (8·5 g.) for 8 hours at 180—200°, this *base* formed needles from benzene–light petroleum (b. p. 60—80°), m. p. 137° (Found : C, 69·2; H, 5·6; N, 16·0. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·7; N, 16·0%). The *picrate* separated from acetone–ethanol in a felted mass of yellow needles, m. p. 198° (Found : C, 47·4; H, 3·1; N, 17·9. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires C, 47·6; H, 3·2; N, 17·3%).

4 : 10-*Dihydro*-4-*keto*-2 : 8-*dimethyl*-1 : 10-*diazanaphthalene* formed needles from benzene–light petroleum (b. p. 60—80°), m. p. 130° (Found : C, 69·2; H, 5·7; N, 15·9. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·7; N, 16·0%). The *picrate* formed yellow crystals, m. p. 154° (Found : N, 17·8. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires N, 17·3%).

s-*Di*-(6-*methyl*-2-*pyridyl*)*urea*.—Prepared by heating 2-amino-6-methylpyridine (10 g.) and ethyl β-aminocrotonate (12 g.) for 7—8 hours at 190°, followed by a further 2 hours at 210—220°, this *compound* formed plates [from benzene–light petroleum (b. p. 60—80°)], m. p. 194° (Found : C, 64·4; H, 5·7; N, 22·4. $C_{13}H_{14}ON_4$ requires C, 64·4; H, 5·7; N, 23·1%). The *picrate* formed yellow crystals (from acetone–ethanol), m. p. 190° (decomp.) (Found : N, 20·2. $C_{13}H_{14}ON_4,C_6H_3O_7N_3$ requires N, 20·8%).

s-*Di*-2-*quinolylurea*.—2-Aminoquinoline (5 g.) and ethyl β-aminocrotonate (5 g.) were heated at 180—200° for 6 hours. After cooling, the reaction mass was extracted with light petroleum (b. p. 100—120°) which removed unchanged 2-aminoquinoline. The residue was digested with hot alcohol, filtered, and finally crystallised from nitromethane giving the *urea* as needles, m. p. 286° (decomp.) (Found : C, 71·9; H, 4·5; N, 18·0. $C_{19}H_{10}ON_4$ requires C, 72·6; H, 4·4; N, 17·8%).

4 : 12-*Dihydro*-4-*keto*-2-*methyl*-1 : 12-*diazaphenanthrene* (V).—This *base*, forming pale yellow needles [from benzene–light petroleum (b. p. 60—80°)], m. p. 131° (Found : C, 73·8; H, 5·0; N, 13·0. $C_{13}H_{10}ON_2$ requires C, 74·4; H, 4·7; N, 13·3%), was made by heating 2-chloroquinoline (5 g.), ethyl β-aminocrotonate (4 g.), anhydrous potassium carbonate (5 g.), and a trace of copper bronze for 3 hours at 190° and for a further hour at 200—220°. The *picrate* formed yellow needles, m. p. 207° (Found : N, 15·6. $C_{13}H_{10}ON_2,C_6H_3O_7N_3$ requires N, 15·9%), from acetone–ethanol.

9 : 9′-*Diphenanthridylamine* formed yellow plates, m. p. >310° (Found : C, 83·9; H, 4·4; N, 11·2. $C_{26}H_{17}N_3$ requires C, 84·1; H, 4·5; N, 11·3%), from chlorobenzene.

4 : 9-*Dihydro*-4-*keto*-6-*methyl*-7 : 9-*diazathianaphthen* (VI) formed pale yellow needles (from benzene–light petroleum), m. p. 130° (Found : C, 50·7; H, 3·5; N, 17·3; S, 19·6. $C_7H_6ON_2S$ requires C, 50·6; H, 3·6; N, 16·8; S, 19·2%). It did not form a picrate, but gave a crystalline water-soluble sulphate and hydrochloride. The *methiodide*, prepared by heating the base (1 g.) in methanol (10 ml.) with methyl iodide (2 g.) in a sealed tube at 125° for 3 hours, formed needles, m. p. 304° (decomp.), from aqueous methanol (Found : I, 40·4. $C_8H_9ON_2SI$ requires I, 41·2%). The *nitrate*, pale yellow plates (from ethanol), m. p. 148° (decomp.) (Found : C, 36·6; H, 3·3; N, 17·7; S, 13·8. $C_7H_6ON_2S,HNO_3$ requires C, 36·4; H, 3·1; N, 18·3; S, 13·9%), separated on dilution of a solution of the base (3 g.) in nitric acid (5 ml. ; *d* 1·42) with ice-water (40 ml.).

Nitration. The foregoing base (1 g.), suspended in concentrated sulphuric acid (5 ml.), was treated at 0° with an ice-cold mixture of nitric acid (1·5 ml. ; *d* 1·42) and concentrated sulphuric acid (1·5 ml.), added dropwise with shaking. After 10 minutes at 0° the mixture was allowed to warm to room temperature and treated with ice-water (30 ml.), and the precipitate collected and crystallised from ethanol, yielding the x-*nitro*-derivative as yellow-brown plates, m. p. 165° (Found : C, 40·2; H, 2·4; N, 19·9; S, 14·5. $C_7H_5O_3N_3S$ requires C, 39·8; H, 2·3; N, 19·9; S, 15·1%).

4 : 9-*Dihydro*-4-*keto*-3 : 6-*dimethyl*-7 : 9-*diazathianaphthen* (VI*a*) separated from light petroleum in pale yellow needles, m. p. 136° (Found : C, 53·4; H, 4·4; N, 15·8; S, 17·4. $C_8H_8ON_2S$ requires C, 53·3; H, 4·4; N, 15·5; S, 17·7%).

4 : 11-*Dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*thiafluorene* (VII ; R = H) formed needles, m. p. 199° from light petroleum (Found : C, 61·0; H, 4·1; N, 13·2; S, 14·1. $C_{11}H_{10}ON_2S$ requires C, 61·1; H, 3·7; N, 12·9; S, 14·8%).

7-*Acetamido*-4 : 11-*dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*thiafluorene* (VII ; R = NHAc) separated from amyl alcohol in plates, m. p. 290° (Found : C, 57·2; H, 4·2; N, 15·4; S, 11·4. $C_{13}H_{11}O_2N_3S$ requires C, 57·1; H, 4·0; N, 15·4; S, 11·7%). The free base gave a *dihydrochloride monohydrate* as yellow-brown needles, m. p. >266° (decomp.), from aqueous-alcoholic hydrochloric acid (Found : C, 41·8; H, 3·8; Cl, 21·8. $C_{11}H_9ON_3S,2HCl,H_2O$ requires C, 41·0; H, 4·0; Cl, 22·0%), after hydrolysis

of the forgoing acetamido-compound (6 g.) in water (100 ml.), glacial acetic acid (20 ml.), and concentrated sulphuric acid (6 ml.) for 1 hour under reflux, basification of the resulting solution with potassium hydroxide, and precipitation of the base from hydrochloric acid with aqueous ammonia.

Ethyl 4 : 11-*Dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*thiafluorene*-7-*carboxylate* (VII; R = CO_2Et) separated from benzene–ethanol in needles, m. p. 204—205° (Found : C, 58·1; H, 4·1; N, 9·5; S, 11·0. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·4; N, 9·6; S, 11·1%).

7-*Chloro*-4 : 11-*dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*thiafluorene* (VII; R = Cl) formed pale yellow crystals, m. p. 220°, from benzene–ethanol (Found : C, 52·5; H, 2·9; N, 10·6; S, 12·4; Cl, 14·1. $C_{11}H_7ON_2SCl$ requires C, 52·6; H, 2·7; N, 11·1; S, 12·7; Cl, 14·1%).

7-*Ethoxy*-4 : 11-*dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*thiafluorene* (VII; R = OEt) separated from ethanol in crystals, m. p. 198° (Found : C, 59·8; H, 4·6; N, 10·8; S, 10·6. $C_{13}H_{12}O_2N_2S$ requires C, 60·0; H, 4·6; N, 10·7; S, 12·0%).

4 : 11-*Dihydro*-4-*keto*-2-*methyl*-7 : 8-*benzo*-1 : 11-*diaza*-9-*thiafluorene* (VIII) formed crystals, m. p. 207°, from benzene (Found : C, 67·2; H, 3·3; N, 10·9; S, 10·5. $C_{15}H_{10}ON_2S$ requires C, 67·6; H, 3·7; N, 10·5; S, 12·0%).

4 : 11-*Dihydro*-4-*keto*-2-*methyl*-1 : 11-*diaza*-9-*oxafluorene* (IX) separated from benzene–light petroleum (b. p. 60—80°) in needles, m. p. 146° (Found : C, 65·7; H, 3·9; N, 14·4. $C_{11}H_8O_2N_2$ requires C, 66·0; H, 4·0; N, 14·0%).

4 : 11-*Dihydro*-4-*keto*-2 : 3-cyclo*hexeno*-1 : 11-*diaza*-9-*oxafluorene* (X), prepared by heating 2-aminobenzoxazole (2 g.) with ethyl 2-keto*cyclo*hexanecarboxylate (2·6 g.) at 180—200° for 1 hour, formed needles (from ethanol), m. p. 198° (Found : C, 69·7; H, 4·9; N, 11·8. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0; N, 11·6%).

4 : 11-Dihydro-4-keto-2-methyl-1 : 9 : 11-triazafluorene (XI; R = H), prepared from 2-aminobenziminazole and ethyl β-aminocrotonate or acetoacetate, formed needles, m. p. 294° (decomp.), from ethanol (Found : C, 66·8; H, 4·4; N, 21·4. Calc. for $C_{11}H_9ON_3$: C, 66·3; H, 4·5; N, 21·1%). The N-*acetyl* derivative formed needles, m. p. 168°, from ethanol (Found : C, 64·5; H, 4·4; N, 16·7. $C_{13}H_{11}O_2N_3$ requires C, 64·7; H, 4·5; N, 17·3%).

3-*Ethyl*-4 : 11-*dihydro*-4-*keto*-2-*methyl*-1 : 9 : 11-*triazafluorene* (XI; R = Et), prepared from 2-aminobenziminazole (1·2 gm.) and ethyl ethylacetoacetate (1·4 g.) by heating them at 130—140° until the reaction mass had solidified, formed crystals (from benzene–ethanol), m. p. 284° (decomp.) (Found : C, 68·4; H, 6·1; N, 18·4. $C_{13}H_{13}ON_3$ requires C, 68·7; H, 5·7; N, 18·5%). The 3-n-*propyl* analogue formed silvery-white plates (from benzene–ethanol), m. p. 253° (Found : C, 69·6; H, 6·3; N, 16·5. $C_{14}H_{15}ON_3$ requires C, 69·7; H, 6·2; N, 17·4%). The 3-iso*propyl* analogue, crystallised from ethanol, had m. p. 294° (Found : C, 69·3; H, 6·7; N, 17·3%).

4 : 11-*Dihydro*-4-*keto*-2 : 3-cyclo*hexeno*-1 : 9 : 11-*triazafluorene* (XII), prepared by heating 2-aminobenziminazole (1·3 g.) and ethyl 2-keto*cyclo*hexanecarboxylate (1·7 g.) at 100° until the mixture liquefied, and then at 150—160° until the mass had solidified, and crystallised from benzene–ethanol, had m. p. 296° (Found : C, 70·2; H, 5·7; N, 17·1. $C_{14}H_{13}ON_3$ requires C, 70·2; H, 5·4; N, 17·5%). The *methiodide*, prepared by heating this base (2·2 g.) with excess of methyl iodide in methanol (15 ml.) at 125° for 3 hours, formed needles, from acetone–ethanol, which decomposed at *ca.* 228° (Found : I, 23·6. $C_{15}H_{16}ON_3I$ requires I, 24·2%).

4 : 11-*Dihydro*-4-*keto*-2 : 3-cyclo*penteno*-1 : 9 : 11-*triazafluorene* (XIII), crystallised from benzene, had m. p. 304° (Found : C, 69·2; H, 5·1; N, 18·5. $C_{13}H_{11}ON_3$ requires C, 69·3; H, 4·9; N, 18·6%).

4 : 11-*Dihydro*-4-*imino*-2-*methyl*-1 : 9 : 11-*triazafluorene* (XIV).—2-Aminobenziminazole (1·3 g.) and β-aminocrotononitrile (0·83 g.) were heated at 180°. The mass liquefied, ammonia was evolved, and the product gradually solidified. Extraction with hot alcohol, followed by crystallisation from acetic acid–ethanol, gave the 4-*imino*-2-*methyl* compound, m. p. >300° (Found : C, 65·9; H, 4·7; N, 29·1. $C_{11}H_{10}N_4$ requires C, 66·7; H, 5·0; N, 28·3%). The 2-*phenyl* analogue, similarly prepared from β-aminocinnamonitrile, formed yellow crystals, m. p. >300°, from acetic acid–ethanol (Found : C, 73·3; H, 4·7; N, 21·2. $C_{16}H_{12}N_4$ requires C, 73·8; H, 4·6; N, 21·5%).

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