Synthesis of 4-Amino[1]benzofuro[3,2-*g*]cinnolines

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The synthesis of the new heterocycles, 4-amino[1]benzofuro[3,2-*g*]cinnolines, was accomplished by the intramolecular cyclization of the *Z*-configuration of cyanoarylhydrazones. The latter compounds were obtained *via* interaction between the diazonium salt of 3-aminodibenzofuran and various active methylene compounds *via* the Japp-Klingemann reaction. The alkaline treatment of azo intermediates **4**, which may be isolated in the course of condensation, gave the corresponding cyanoarylhydrazones **5**. A study of the configuration and possible isomerisations is reported.

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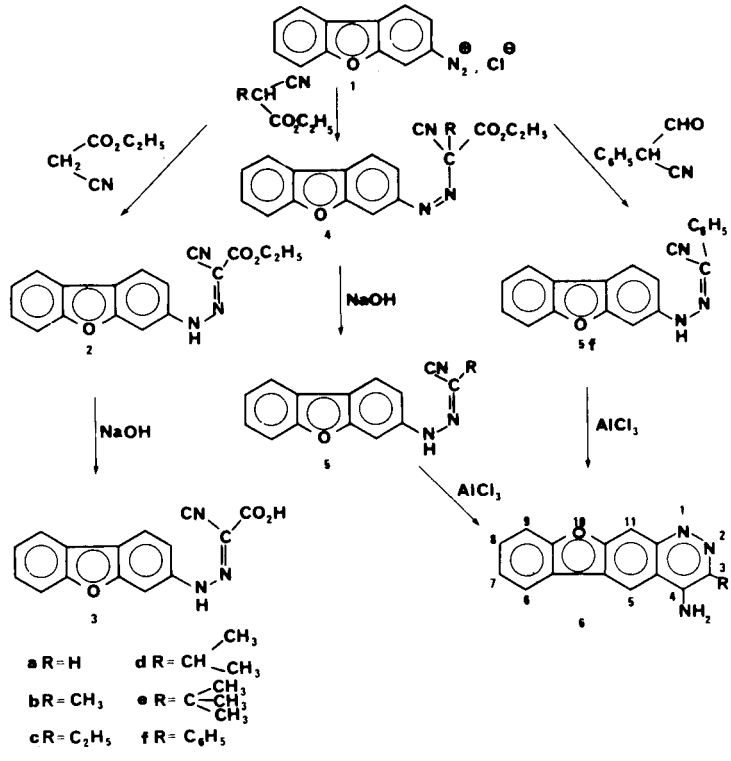
In continuation of our work on the synthesis of condensed polycyclic systems (1) (including evaluation of their biological properties, such as their antineoplastic activity) we now report a study on the synthesis of a new class of heterocycles. Thus, this article is devoted to the synthesis of 4-amino[1]benzofuro[3,2-*g*]cinnolines (6). A study on the configuration and possible isomerisation of some hydrazones is also presented.

As it is well known, the most important synthesis of the cinnoline ring involves the Friedel-Crafts intramolecular cyclization (2,3,4). In particular, cyclization of cyanoarylhydrazones gives 4-aminocinnolines (5). However, such a cyclization reaction proceeds only with the *Z*-stereoisomers of those hydrazones.

In our present study, the Japp-Klingemann synthesis (6) was selected for the preparation of the hydrazones **5**. Thus, the diazotized 3-aminodibenzofuran (**1**) was coupled with substituted ethyl cyanoacetates to give the azo-derivatives **4b-e**. These latter compounds, when treated with dilute aqueous sodium hydroxide solution at room temperature, suffered hydrolysis and decarboxylation to give the hydrazones **5b-e**. The two hydrazones **5a** and **5f**, on the other hand, were prepared using a somewhat different procedure. Starting with the diazonium salt **1**, the first hydrazone **5a** was prepared in three steps: the diazo compound was coupled with ethyl cyanoacetate to give the hydrazone **2** which was hydrolyzed to the corresponding acid **3** and finally decarboxylated by heat (a discussion of the configuration of both **5a** and **2** follows). The second hydrazone **5f** was prepared by the direct coupling of **1** with 2-formylphenylacetonitrile according to the Wislicenus method (7).

An nmr study of the hydrazones **5c-f** reveals that these compounds exist only in one configuration, since the spectra show a single signal for the NH proton and a non-split signal for the alkyl or for the phenyl groups (see Experimental). In contrast, the hydrazones **5a, 5b** and **2** exist in both the *Z*- and *E*-configurations.



In the synthesis of **2**, the coupling of **1** with ethyl cyanoacetate gave a yellow compound (m.p. 160°) which was found to possess the *E*-configuration. However, the *Z*-isomer was obtained as a brown compound (m.p. 214°) by boiling the former compound in acetone. This assignment of both *E*- and *Z*-configurations is based on the study of their ir spectral patterns in the solid state. The spectrum of the yellow compound shows a carbonyl absorption band at 1710 cm^{-1} while the same band appears at 1675 cm^{-1} in the spectrum of the brown compound. Therefore, the brown compound should possess the *Z*-configuration which permits an intramo-

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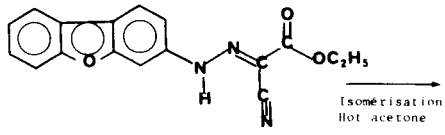
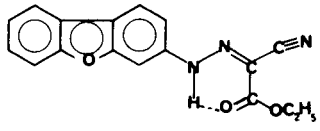
lecular hydrogen bonding (NH---O=C-) responsible for the lower carbonyl absorption frequency compared with that of the yellow compound (*E*-isomer). However, when the spectrum of the *Z*-form was recorded in tetrachloroethane no band shift was observed upon dilution. This indicates that this form contains intramolecular H bonding, *i.e.*, *Z*-form.

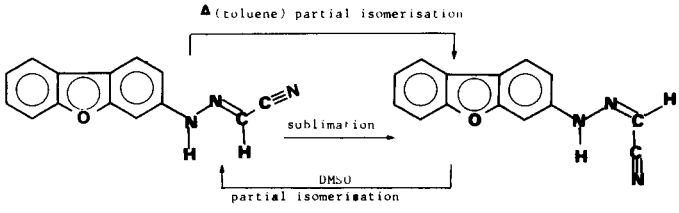
On the other hand, when the nmr spectrum of the *E*-form of **2** was recorded in DMSO-d_6, an equilibrium between the *E*- and *Z*-forms took place, where both forms were detected in this solvent. However, when this *E*-form was hydrolyzed by an alkaline solution, it gave the hydrazone carboxylic acid **3**, which is highly unstable and did not give a good elemental analysis. It is easily decarboxylated by heating at 180° at atmospheric pressure to give the hydrazone **5a**. This latter hydrazone exists in a single form (*E*-form) as concluded from ir and nmr spectral studies.



2 E mp 140



2 Z mp 214°



5a E 5a Z

The ir spectrum showed a ν C≡N at 2210 cm^{-1} while the nmr spectrum showed the signal of the methylenic proton at δ 7.06 ppm. The *Z*-form of **5a** can be obtained in a 50% yield by sublimation the *E*-form at 190° under 7.10^{-2} torr. However, heating the *E*-form at reflux in toluene afforded a mixture of both the *Z*- and *E*-forms, as shown by nmr spectra.

The chemical shifts of the methylene and NH protons are the main differences in the spectra of the two forms (DMSO-d_6). The CH signal in the spectrum of the *Z*-form is shifted upfield and appears at δ 6.66 ppm, meanwhile another CH signal, corresponding to the *E*-form appears at δ 7.06 ppm. The assignment of both *E*- and *Z*-configurations is based on the rules of Karabatsos (8) and on effect of the solvent on the chemical shift. The difference in the chemical shift observed when DMSO-d_6 was substituted by benzene-d_6 Δ (δ DMSO-d_6-δ C_6D_6) is equal to 2 ppm for the *E*-form and 1.2 ppm for the *Z*-form. Similar results were found by other investigators in their studies on cyanoformylhydrazones (9).

The nmr spectrum of the cyanopropionylhydrazone **5b**, obtained by the hydrolysis of the azo compound **4b**, shows signals of two methyl groups indicating the presence of both *Z*- and *E*-configurations. These two forms could be separated from one another by sublimation or fractional crystallization. The assignment of the two forms depends on the same bases mentioned before. Thus, the value Δ (δ DMSO-d_6 - δ C_6D_6) which equals 0.97 ppm accounts for the *E*-form, and that which equals 0.56 ppm refers to the *Z*-one.

The cyanohydrazones **5a-d** and **5f** were cyclized in good yield to the corresponding aminobenzofurocinnolines **6a-d** and **6f** when they were refluxed in toluene using an excess of aluminium chloride following the Lamant Procedure (5). Attempts to extend this synthesis to the cyclization of tertiary butyl cyanohydrazone **5e** were unsuccessful due to the transformation of this substance to 3-aminodibenzofuran hydrochloride. The failure of this reaction can be attributed to the steric hinderance of the bulky tertiary butyl group which hinders the aluminium chloride molecule from approaching the cyano group.

The cyclization of the *E*-form **5a** to **6a** is postulated to proceed *via* the formation of the *Z*-isomer that may be formed in the course of the reaction. This postulation is most likely since the *E*-form isomerises easily to the *Z*-isomer in boiling toluene. Likewise, the cyclization of the hydrazone **5b** to the cinnoline **6b** is performed using a mixture of the two *E*- and *Z*-forms, implying a concomitant isomerization.

The easy thermal isomerization of the *E*- to the *Z*-forms of **5a** and **5b** makes it difficult to ascertain the configuration of the other hydrazones **5**. However, the facile intramolecular cyclizations of the hydrazones **5a-d** and **5f** to the corresponding cinnolines **6** lead us to presume that the hydrazones exist in the *Z*-configurations, taking in consideration that no isomerization was observed by heating these hydrazones.

Apparently the intramolecular cyclization of the cyanohydrazones **5** may occur at the 2- or at the 4-positions of the dibenzofuran leading to a linear or angular structure, respectively. In fact, the reaction results always in a single cyclized product, the linear one.

This latter structure was elucidated by ^1H nmr spectral study. The signals of the two protons H-5 and H-11, situated down field, do not show an *ortho* coupling. Furthermore, the presence of these two protons are

confirmed using the Overhauser effect: the signal of the H-5 proton, which is the more deshielded one, is enlarged by 25% upon the irradiation of the NH_2 protons. The assignment of the signals of the other H-6, H-7, H-8 and H-9 homocyclic protons is achieved by the double resonance decoupling technique.

EXPERIMENTAL

All melting points were determined on a Kofler block, or on a Maquenne block apparatus and are uncorrected; ir spectra were recorded (potassium bromide) on a Perkin-Elmer model 157 G spectrometer. The ir spectra (tetrachloroethane) were recorded on a Perkin-Elmer model 225 spectrometer. The nmr spectra were obtained with Varian EM 360 and EM 390, using TMS (tetramethylsilane) as an internal standard and chemical shifts were expressed as δ, parts per million.

The nmr spectra of 4-amino[1]benzofuro[3,2-*g*]cinnolines were recorded on a Brucker spectrospin 270 MHz using TMS as internal standard. Completely satisfactory elemental analysis (±0.04%) were obtained for all compounds.

Preparation of Materials.

3-Aminodibenzofuran was obtained by reduction of 3-nitrodibenzofuran (10) under pressure (30 atm) at 80° over Raney nickel in a steel bomb.

The various substituted ethyl cyanoacetates and the 2-formylphenylacetonitrile were prepared according to the known procedures (11,12,13).

The diazonium salt solution of **1** was prepared by adding drop wise 1.4 g. (0.02 mole) of sodium nitrite in 20 ml. of water to a suspension of 4.4 g. (0.02 mole) of 3-aminodibenzofuran hydrochloride in 100 ml. of 1 *N* hydrochloric acid. The reaction mixture was stirred for 1 hour at room temperature and filtered.

Azo Compounds **4b-e** and Compound **2**-*E*. General Procedure.

The solution of 0.02 mole of the diazonium salt solution of **1** was added at 0° to a well stirred mixture of 0.02 mole of ethylcyanoacetate or substituted ethyl cyanoacetates, ethanol (30 ml.) and water (400 ml.). Sodium acetate was added in small portions to keep the mixture alkaline to litmus. After 3 hours of stirring at 0°, the crude precipitates of the azo compounds **4b-e** were collected by suction, thoroughly washed with water and air dried. Recrystallization from ethanol gave yellow compounds.

Ethyl (2-Dibenzofuranyl)azomethylcyanoacetate (**4b**).

The general procedure was employed using (2.54 g., 0.02 mole) of ethyl methylcyanoacetate, yield, 4.36 g. (68%), m.p. 137°; ir (potassium bromide): ν cm^{-1} 1740 (C=O); ^1H nmr (deuteriochloroform): δ ppm 1.3 (t, 3H), 2.06 (s, 3H), 4.4 (q, 2H), 7.2-8.4 (m, 7H).

Anal. Calcd. for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found: C, 66.84; H, 4.54; N, 13.24.

Ethyl (2-Dibenzofuranyl)azoethylcyanoacetate (**4c**).

The general procedure was employed using (2.81 g, 0.02 mole) of ethyl ethylcyanoacetate, yield, 5.02 (75%), m.p. 108°; ir (potassium bromide): ν cm^{-1} 1735 (C=O); ^1H nmr (deuteriochloroform): δ ppm 1.16 (t, 3H), 1.33 (t, 3H), 2.5 (q, 2H), 4.36 (q, 2H), 7.06-8.13 (m, 7H).

Anal. Calcd. for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found: C, 68.28; H, 5.06; N, 12.66.

Ethyl (2-Dibenzofuranyl)azoisopropylcyanoacetate (**4d**).

The general procedure was employed using (3.10 g., 0.02 mole) of ethyl isopropylcyanoacetate, yield, 4.18 g. (60%), m.p. 108°; ir (potassium bromide) ν cm^{-1} 1635 (C=O); ^1H nmr (deuteriochloroform): δ ppm 1.06 (s, 3H), 1.2 (s, 3H), 1.3 (t, 3H), 3.08 (m, 1H), 4.36 (q, 2H), 7.23-8.5 (m, 7H).

Anal. Calcd. for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03. Found: C, 68.60; H, 5.51; N, 12.31.

Ethyl (2-Dibenzofuranyl)azo-*t*-butylcyanoacetate (**4e**).

The general procedure was employed using (3.38 g., 0.02 mole) of ethyl *t*-butyl cyanoacetate, yield, 6.24 g. (86%), m.p. 101°; ir (potassium bromide) ν cm^{-1} 1740 (C=O); ^1H nmr (deuteriochloroform): δ ppm 1.26 (s, 9H), 1.26 (t, 3H), 4.33 (q, 2H), 7.26-8.5 (m, 7H).

Anal. Calcd. for $C_{21}H_{21}N_3O_3$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.45; H, 6.02; N, 11.69.

Ethyl *E*-2-Cyano(2-dibenzofuranylhydrazono)acetate (**2**).

The general procedure was employed using (2.26 g., 0.02 mole) of ethyl cyanoacetate. Therefore, the crude product was not recrystallized in ethanol, yield, 5.9 g. (96%), m.p. 160°; ir (potassium bromide) ν cm^{-1} 1710 (C=O), 2212 (C≡N), 3205 (N-H); ^1H nmr (DMSO-d_6): δ ppm 1.33 (t, 3H), 4.36 (q, 2H), 7.26-8.26 (m, 7H), 12.43 (NH), 13.09 (NH).

Anal. Calcd. for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.63. Found: C, 66.43; H, 4.36; N, 13.68.

Ethyl *Z*-(2-Dibenzofuranylhydrazono)cyanoacetate (**2**).

The hydrazone **2-E** (1 g., 3.25 mmoles) was dissolved in acetone. The hot solution was filtered and allowed to cool. The brown precipitate was collected by suction, yield, quantitative, m.p. 214°; ir (potassium bromide): ν cm^{-1} 1665 (C=O), 2225 (C≡N), 3400 (NH); ir (tetrachloroethane): ν cm^{-1} 1676 (C=O), 2212 (C≡N), after dilution no band shift was observed; ^1H nmr (DMSO-d_6) was the same as **2-E**.

Anal. Calcd. for $C_{17}H_{33}N_3O_3$: C, 66.44; H, 4.26; N, 13.63. Found: C, 66.20; H, 4.26; N, 13.65.

Hydrazones **5c-e**.

Five ml. of sodium hydroxide (40%) was added to a solution of azo compound (**4**) (0.01 mole) in a 100 ml. dioxan-water mixture (1/1). The mixture was stirred for 1 hour at room temperature. The solvent was evaporated *in vacuo* at room temperature. The crude product (**5**) was collected by suction, washed with water and air dried.

2-(2-Dibenzofuranylhydrazono)-*n*-butyronitrile (**5c**).

This compound was obtained in a yield of 1.57 g. (60%), m.p. 240°; ir (potassium bromide): ν cm^{-1} 2200 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 1.2 (t, 3H), 2.53 (q, 2H), 7-8.06 (m, 7H), 10.7 (s, NH).

Anal. Calcd. for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.98; N, 15.96. Found: C, 73.06; H, 4.60; N, 16.07.

2-(2-Dibenzofuranylhydrazono)-isovaleronitrile (**5d**).

This compound was obtained in a yield of 1.66 g. (60%), m.p. 114°; ir (potassium bromide): ν cm^{-1} 2200 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 1.23 (d, 6H), 2.73 (sept, 1H), 7.06-8.06 (m, 7H), 10.7 (s, NH).

Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 72.93; H, 5.53; N, 15.20.

2-(2-Dibenzofuranylhydrazono)-3,3-dimethyl-*n*-butyronitrile (**5e**).

This compound was obtained in a yield of 2.03 g. (70%), m.p. 181°; ir (potassium bromide): ν cm^{-1} 2200 (C≡N); ^1H nmr

(DMSO-d_6): δ ppm 1.33 (s, 9H), 7.1-8.06 (m, 7H), 10.9 (s, NH).

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.41; H, 5.84; N, 14.11.

Phenylglyoxylonitrile-2-dibenzofuranylhydrazone (**5f**).

A diazonium salt solution (**1**) (0.02 mole) is added dropwise at 0° to a well stirred mixture of 2-formylphenylacetonitrile (2.9 g., 0.02 mole) in 2 *N* aqueous sodium solution (500 ml.). After 3 hours of stirring at 0° the yellow precipitate was filtered off, washed with water, cold ethanol and air dried, yield, 2.58 g. (83%), m.p. 205°; ir (potassium bromide): ν cm^{-1} 2200 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 7.16-8.5 (m, 12H), 12.66 (s, NH).

Anal. Calcd. for $C_{20}H_{13}N_3O$: C, 77.15; H, 4.21; N, 13.50. Found: C, 77.05; H, 4.28; N, 13.10.

(2-Dibenzofuranylhydrazono)cyanoacetic Acid (**3**).

One g. (3.25 mmoles) of **2-E** was refluxed in 20% aqueous sodium hydroxide solution until complete dissolution. After being cooled the mixture was poured with stirring into 2 *N* hydrochloric acid at 0°. The orange solid was filtered off, washed with water, triturated with ether and dried, yield, 0.8 g. (90%), m.p. 220° dec.; ir (potassium bromide): ν cm^{-1} 1665 (C=O), 2200 (C≡N).

E-(2-Dibenzofuranylhydrazono)acetonitrile (**5a**).

One g. (3.58 mmoles) of compound **3** was heated in a small flask in a oil bath at 170-190° until carbon dioxide emission ceased and then cooled at room temperature, a brown-yellow compound is obtained, yield, quantitative, m.p. 301-302°; ir (potassium bromide): ν cm^{-1} 2210 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 7.06 (s, 1H), 7.13-8.13 (m, 7H), 12.06 (s, NH); ^1H nmr (deuteriobenzene): δ ppm 5.06 (s, 1H).

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 71.91; H, 4.27; N, 16.60.

Z-(2-Dibenzofuranylhydrazono)acetonitrile (**5a**).

One half g. (2.13 mmoles) of compound **5a**-*E* was heated at 190° in a sublimation apparatus under vacuo (7 10^{-2} torr). Yellow crystals are obtained, yield, 0.25 g. (50%), m.p. 220°; ir (potassium bromide): ν cm^{-1} 2195 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 6.66 (s, 1H), 7.13-8.13 (m, 7H), 11.53 (s, NH); ^1H nmr (deuteriobenzene): δ ppm 5.06 (s, 1H).

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86. Found: C, 71.26; H, 3.79; N, 18.12.

When the ^1H nmr spectra were recorded after standing at room temperature for 12 hours, changes were observed. A new singlet appeared at 7.06 (s, 1H) and the singlet at 6.66 (s, 1H) decreased. After 36 hours, an equilibrium was reached and the new spectrum showed 88% of the *E*-isomer and 12% of the *Z*-isomer.

A suspension of 1 g. (3.58 mmoles) of **5a**-*E* was heated at reflux in 300 ml. of toluene. After 3 hours of stirring the hot toluene solution was filtered and the insoluble fraction collected was the pure hydrazone **5a**-*E* (0.5 g.). After evaporation of the toluene under *vacuo*, a second crop of yellow solid was obtained. The ^1H nmr (DMSO-d_6) showed a mixture of 60% and 40%, respectively, of **5a**-*Z* and **5a**-*E*.

(2-Dibenzofuranylhydrazono)propionitrile (**5b**).

Compound **4b** (3.21 g., 0.01 mole) was treated following the general procedure for the synthesis of compounds **5c-e**. An equimolecular mixture of two *Z*- and *E*-isomers was obtained, yield, 2.76 g. (94%).

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 71.91; H, 4.27; N, 16.60.

E-(2-Dibenzofuranylhydrazono)-2-propionitrile (**5b**).

The separation was realized as follows: the mixture of the two isomers was refluxed in ethanol, the insoluble crude isomer **5b**-*E* was collected by suction, m.p. 264°; ir (potassium bromide): ν cm^{-1} 2216 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 2.16 (s, 3H), 7.13-8.01 (m, 7H), 10.55 (s, NH); ^1H nmr (deuteriobenzene): δ ppm 1.19 (s, 3H).

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 72.41; H, 4.59; N, 16.75.

Z-(2-Dibenzofuranylhydrazono)-2-propionitrile (**5b**).

Sublimation of 1 g. (4 mmoles) of the mixture of two isomers under *vacuo* (7.10^{-2} torr) at 180° gave yellow a crystalline compound, yield, 0.5 g. (50%), m.p. 204°; ir (potassium bromide): ν cm^{-1} 2195 (C≡N); ^1H nmr (DMSO-d_6): δ ppm 2.21 (s, 3H), 7.23-8.06 (m, 7H), 10.9 (s, NH); ^1H nmr (deuteriobenzene): δ ppm 1.54 (s, 3H).

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 72.01; H, 4.44; N, 16.97.

4-Amino[1]benzofuro[2,3-*g*]cinnolines (**6**).

General Procedure.

In a 500 ml. round bottomed flask with a reflux condenser carrying a calcium chloride tube, 0.04 mole of anhydrous aluminium chloride was added to a suspension of 0.01 mole of compound **5** in 200 ml. of toluene. The mixture was stirred and refluxed for 3 hours. After cooling at room temperature the mixture was poured into crushed ice (300 g.). A brown-yellow solid was removed by suction and washed with water, then with petroleum-ether. The product was stirred vigorously in a hot sodium hydroxide aqueous solution (100 ml.) and the mixture was cooled at room temperature. The compound was filtered and washed with water and dried. Sublimation under *vacuo* gave yellow crystals.

Compound **6a**.

The reaction of cyclisation was realized with **5a**-*E* (2.35 g., 0.01 mole) following the general procedure, yield, 0.94 g. (40%), m.p. 320°; ir (potassium bromide): ν cm^{-1} 1645, 3310 (NH); ^1H nmr (DMSO-d_6): δ ppm 8.77 (s, 1H), 7.5 (s, NH_2) arom-protons, 7.60 H-7, 7.75 H-8, 7.86 H-9, 8.22 H-6, 8.3 H-11, 9.1 H-5.

Anal. Calcd. for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86. Found: C, 71.27; H, 4.02; N, 17.90.

Compound **6b**.

The general procedure was employed using the mixture of the two *Z*- and *E*-**5b** isomers (2.5 g., 0.01 mole), yield, 2 g. (80%), m.p. 346°; ir (potassium bromide): ν cm^{-1} 1640, 3305, 3370 (NH); ^1H nmr (DMSO-d_6): δ ppm 2.61 (s, 3H), 7 (s, NH_2), arom-protons, 7.45 H-7, 7.57 H-8, 7.68 H-9, 8.04 H-6, 8.08 H-11, 9.0 H-5.

Anal. Calcd. for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 72.86; H, 4.74; N, 16.99.

Compound **6c**.

The general procedure was employed using 2.63 g. (0.01 mole) of compound **5c**, yield, 1.7 g. (65%), m.p. 323°; ir (potassium bromide): ν cm^{-1} 1655, 3140, 3320 (NH); ^1H nmr (DMSO-d_6): δ ppm 1.33 (t, 3H), 3.06 (q, 2H), 7.05 (s, NH_2), arom-protons, 7.5 H-7, 7.65 H-8, 7.76 H-9, 8.1 H-6, 8.16 H-11, 9.07 H-5.

Anal. Calcd. for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.98; N, 15.96. Found: C, 73.02; H, 5.04; N, 15.83.

Compound **6d**.

The general procedure was employed using 2.77 g. (0.01 mole) of compound **5d**, yield, 1.66 g. (60%), m.p. 276-277°; ir (potassium bromide): ν cm^{-1} 1650, 3320, 3450 (NH); ^1H nmr (DMSO-d_6): δ ppm 1.37 (d, 6H), 3.5 (sept, 1H), 7.2 (s, NH_2); arom-protons, 7.42 H-7, 7.57 H-8, 7.68 H-9, 8.03 H-6, 8.08 H-11, 9.06 H-5.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.75; H, 5.12; N, 15.01.

Compound **6f**.

The general procedure was employed using 3.11 (0.01 mole) of compound **5f**, yield, 2.49 g. (80%), m.p. 342°; ir (potassium bromide); ν cm^{-1} 1625, 3280, 3450 (NH_2); ^1H nmr (DMSO-d_6): δ ppm 7.53 (3H), 7.71 (2H), 6.90 (s, NH_2), arom-protons, 7.46 H-7, 7.60 H-8, 7.7 H-9, 8.05 H-6, 8.21 H-11, 9.18 H-5.

Anal. Calcd. for $C_{20}H_{13}N_3O$: C, 77.15; H, 4.21; N, 13.50. Found: C, 77.07; H, 4.34; N, 13.00.

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