v-Triazolines. Part 34.[1] Thermal Behaviour of 1-(2-Aminophenyl)-4,5-dihydro-5-morpholino-1,2,3-triazoles: New Synthesis of 2-Alkylquinoxalines

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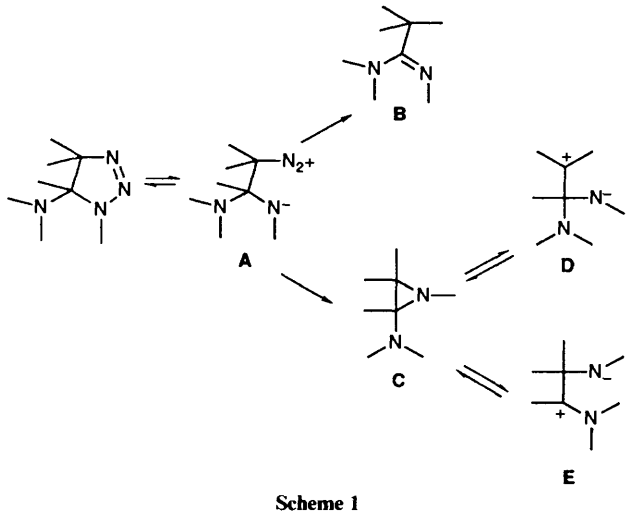
4,5-Dihydro-5-morpholino-1-(2-nitrophenyl)-1,2,3-triazoles **4** are prepared by reaction of an aldehyde with morpholine and the appropriate aryl azide. On reduction 1-(2-aminophenyl)-4,5-dihydro-5-morpholino-1,2,3-triazoles **5** are formed. Thermal rearrangement of compounds **5** affords unstable 2-alkyl-3-amino-1,2,3,4-tetrahydroquinoxalines **7**, which undergo deamination to 2-alkyl-1,2-dihydroquinoxalines **8**. Oxidation of these affords 2-alkylquinoxalines **10**. The mechanism of the thermal rearrangement of triazoles **5** is investigated and discussed.

Substituted 5-amino-1-aryl-4,5-dihydro-1,2,3-triazoles are thermally labile compounds which on heating undergo elimination of nitrogen and several transformations. The most frequently encountered outcome of the thermal decomposition is the formation of amidines **B** (Scheme 1); their formation is



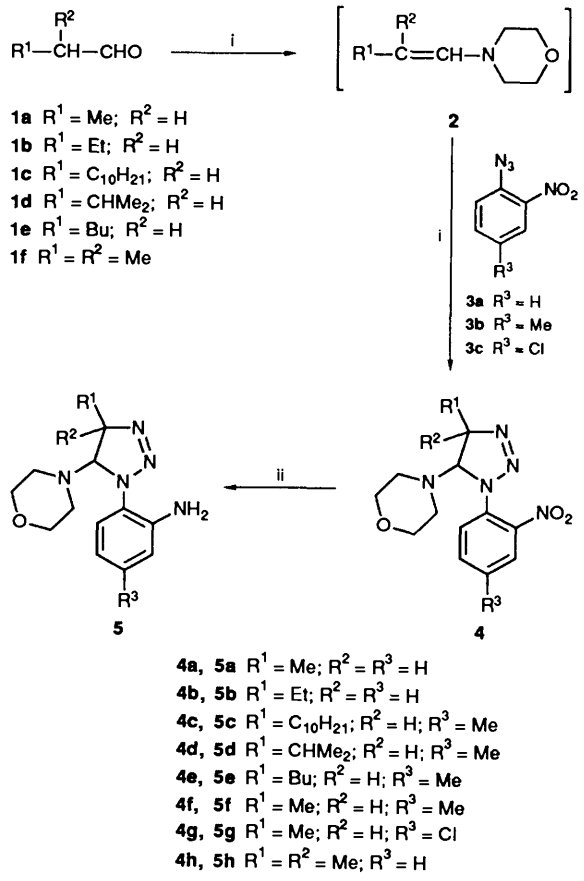
Scheme 1

best described by intramolecular anionotropic migration of the substituent on C-5—other than the amino group—on the neighbouring carbon atom in the dipolar intermediate **A** produced by ring-chain tautomerism of the triazoline ring.[2] Alternatively, the loss of nitrogen can produce a labile 2-aminoaziridine intermediate **C** which, possibly through open chain dipolar forms **D** and **E**, can react with nucleophilic species to afford final products. Some examples of the reaction of external nucleophiles have been occasionally observed[3] but appear to be of scarce practical relevance. However, nucleophilic atoms linked to the dihydrotriazole substituents are expected to take part efficiently in intramolecular cyclization processes which would eventually lead to the transformation of dihydrotriazoles in other heterocycles. In line with this idea we studied the thermal behaviour of dihydrotriazoles bearing a 2-aminophenyl group on N-1 and found a new route to the synthesis of quinoxalines.

A number of quinoxaline preparations are known, but the one most widely used rests on the condensation reaction of *o*-phenylenediamines with 1,2-dicarbonyl compounds. A well known disadvantage is that unsymmetrically substituted reactants give rise to mixtures of isomers which are generally difficult to separate.[4] The synthesis described in this paper has the merit of affording a single product.

Results and Discussion

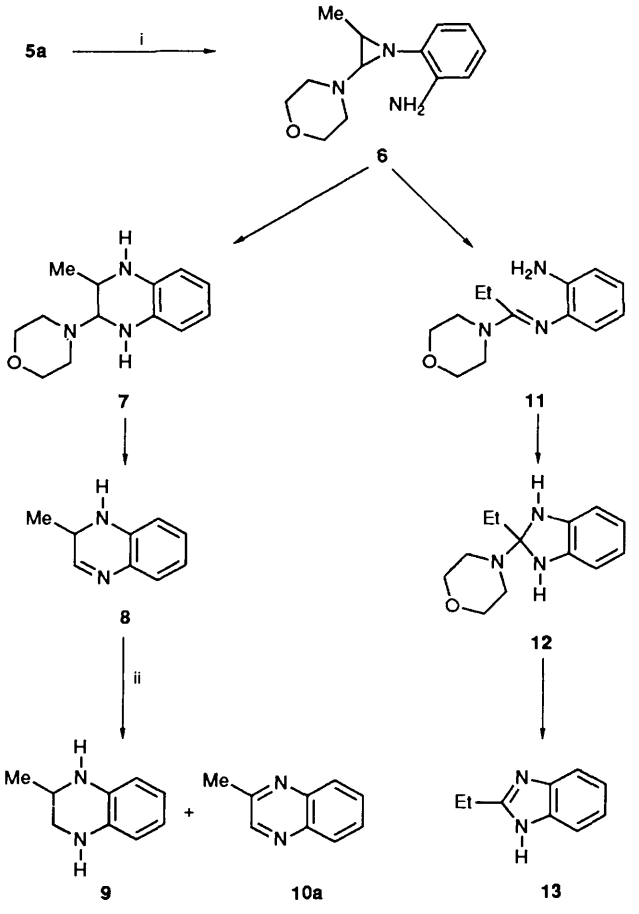
1-Aryl-4,5-dihydro-5-morpholinotriazoles **4a–h**, which are mostly new compounds, were straightforwardly prepared according to a one-pot procedure[5] by reaction of the appropriate aldehyde **1a–f** with morpholine and aromatic azide **3a–c** in benzene solution at room temperature. The formation of compounds **4a–h** occurs through cycloaddition of the azide to the enamine **2** produced *in situ*. Reduction of compounds **4** to the corresponding amines **5a–h** is an easy task since the triazoline ring is rather stable to reducing agents.[6] The classical reduction by hydrogen on palladium was used for all compounds but **4g**, which was allowed to react with sodium borohydride and copper acetylacetonate. Amines **5a–h** were relatively unstable substances. Most of them could be isolated in analytically pure form, but further reaction immediately after preparation was found advisable in all cases (Scheme 2).



Scheme 2 *Reagents and conditions:* i, PhH, room temp.; ii, H_2, 10% Pd/C, room temp.

The thermal behaviour of compounds **5** was fully examined and clarified for compounds **5a**, **5f** and **5h**.

Refluxing of a toluene solution of the triazoline **5a** resulted in evolution of nitrogen and formation of an intractable reaction mixture. However, evaporation, dissolution in ethanol, and prolonged refluxing in the presence of palladium on charcoal resulted in a mixture of products **9**, **10a** and **13** which could be isolated and which were identified by ^{1}H NMR spectroscopy and, for products **10a** and **13**, by comparison with authentic samples. This result is rationalized as shown in Scheme 3. Two

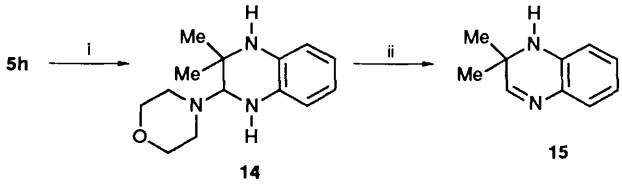


Scheme 3 *Reagents and conditions:* i, toluene, reflux; ii, ethanol, Pd/C 10%, reflux

reaction pathways are open for intermediate **6**, *i.e.* (i) 'normal' rearrangement to amidine **11** or (ii) intramolecular nucleophilic attack of the NH_2 group on the aziridine with ring enlargement. Amidine **11** could not be isolated under the reaction conditions since benzimidazole **13** was rapidly produced by addition of the NH_2 group to the amidine carbon, followed by elimination of morpholine.

The first reaction product **7** was not isolated, very likely because its aminal structure greatly favoured elimination of morpholine. The ^{1}H NMR spectrum of the crude reaction mixture suggested that both compound **8** and isomers having a different location of the double bond were present at this point. In the presence of the hydrogenation–dehydrogenation catalyst compound **8** disproportionated to form products **9** and **10a**. Confirmation was obtained by performing the reaction with Pd/C in the presence of excess of cyclohexene. In this case only the aromatic quinoxaline **10a** was obtained besides the benzimidazole **13**.

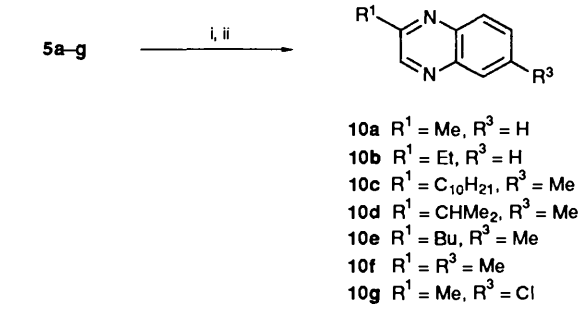
In good agreement with the above picture, heating of the triazoline **5h** in toluene solution resulted in the formation of a crystalline product which crystallized out on cooling of the reaction mixture (Scheme 4). This compound, which gave



Scheme 4 *Reagents and conditions:* i, toluene, reflux; ii, methylene chloride, H_2O washing, room temp.

erratic analytical results, was identified by its mass spectrum (m/z = 247, M^+) as the tetrahydroquinoxaline **14**. However, in the mass spectrum strong peaks at m/z = 160 and m/z = 87 are present, which correspond to the dihydroquinoxaline **15** and morpholine, respectively. This confirmed the instability of 2-amino-1,2,3,4-tetrahydroquinoxalines toward elimination of amine. The ^{1}H NMR spectrum of a solution of compound **14**, though evidencing small signals corresponding to this product, can be better read as the superimposition of the spectra of compound **15** and morpholine. As expected, thorough washing of a methylene dichloride solution of compound **14** with water left pure compound **15** in the organic phase.

To complete the mechanistic picture we had to establish which carbon atom of the aziridine ring becomes linked to the amino nitrogen in the formation of the quinoxaline ring. Starting from compound **5f** both 2,6-dimethylquinoxaline and/or 2,7-dimethylquinoxaline could be expected in principle. The starting compound was refluxed in toluene solution and the crude reaction product was oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Only 2,6-dimethylquinoxaline **10f** was found and was unequivocally identified by its physical and spectral data which are known with great accuracy.[7] This result confirms the greater reactivity (toward nucleophiles) of the aziridine carbon bearing the morpholino group, which is expected to assist its electrophilic behaviour. From a preparative point of view the experimental conditions applied to the thermal rearrangement of substrate **5f** represent a general entry to 2-alkylquinoxalines. Also, starting from compounds **5a–e**, **g** a satisfactory yield of the corresponding quinoxalines was obtained (Scheme 5). In agreement with the proposed reaction



10a R^1 = Me, R^3 = H
10b R^1 = Et, R^3 = H
10c R^1 = $C_{10}H_{21}$, R^3 = Me
10d R^1 = $CHMe_2$, R^3 = Me
10e R^1 = Bu, R^3 = Me
10f R^1 = R^3 = Me
10g R^1 = Me, R^3 = Cl

Scheme 5 *Reagents and conditions:* i, toluene, reflux; ii, DDQ, THF, room temp.

mechanism a single isomer was produced in the case of compounds **10** bearing a further substituent on the benzo ring, *i.e.* products **10c–g**.

Experimental

M.p.s were determined using a Büchi 510 (capillary) apparatus. IR spectra were measured using a JASCO IR Report 100 instrument. NMR spectra were obtained with Bruker AC 200

and EM-390 Varian instruments at 200 MHz. *J*-Values are given in Hz. Mass spectra data were obtained on a Varian MAT 1H COS 50 instrument using electron-impact ionization techniques. Column chromatography was performed on silica gel [Kieselgel 60–70 230 ASTM (Merck)] and on neutral alumina 100–125 (Fluka).

General Procedure for the Preparation of 4,5-*Dihydro*-5-*morpholino*-1-(2-*nitrophenyl*)-1,2,3-*triazoles* **4a–h**.—An aldehyde **1** (0.05 mol) was added to a solution of an azide **3** (0.05 mol) in benzene (100 cm^3). To this mixture was added dropwise a solution of morpholine (4.35 g, 0.05 mol) in benzene (10 cm^3). The mixture was stirred at room temperature for several (2–6) hours until complete reaction of the aldehyde (TLC). The solution was dried over sodium sulfate and evaporated. The residue was recrystallized from diisopropyl ether to afford triazoles **4a**, **b**, **d**, **f**, **g**. For complete purification of products **4c**, **e**, **h** column chromatography over alumina with cyclohexane–ethyl acetate (3:2) was necessary. Products **4a** and **4b** are known compounds.[8] The following new compounds **4c–h** were obtained:

4-*Decyl*-4,5-*dihydro*-1-(4-*methyl*-2-*nitrophenyl*)-5-*morpholino*-1,2,3-*triazole* **4c**. This compound was obtained as a non-distillable oil in 87% yield; $\delta_H(CDCl_3)$ 0.87 (3 H, t, *J* 5.8, Me), 1.17–1.69 (18 H, m, CH_2), 2.18–2.28 (4 H, m, CH_2NCH_2), 2.40 (3 H, s, MeC_6H_3), 3.41–3.47 (4 H, m, CH_2OCH_2), 4.40–4.52 (2 H, m, 4- and 5-H) and 7.36–7.87 (3 H, m, ArH).

4,5-*Dihydro*-4-*isopropyl*-1-(4-*methyl*-2-*nitrophenyl*)-5-*morpholino*-1,2,3-*triazole* **4d**. This compound was obtained as a *solid* in 70% yield, m.p. 118 °C (Found: C, 57.4; H, 6.7; N, 20.7. $C_{16}H_{23}N_5O_3$ requires C, 57.65; H, 6.95; N, 21.0%); $\delta_H(CDCl_3)$ 0.97 (3 H, d, *J* 6.8, Me), 1.04 (3 H, d, *J* 6.8, Me), 1.98–2.28 (5 H, m, CH_2NCH_2 and CH), 2.39 (3 H, s, MeC_6H_3), 3.30–3.50 (4 H, m, CH_2OCH_2), 4.34 (1 H, dd, *J* 3.4 and 5.7, 4-H), 4.50 (1 H, d, *J* 3.4, 5-H) and 7.34–7.89 (3 H, m, ArH).

4-*Butyl*-4,5-*dihydro*-1-(4-*methyl*-2-*nitrophenyl*)-5-*morpholino*-1,2,3-*triazole* **4e**. This compound was obtained as a *solid* in 61% yield, m.p. 80 °C (Found; C, 58.9; H, 7.35; N, 20.0. $C_{17}H_{25}N_5O_3$ requires C, 58.75; H, 7.25; N, 20.15%); $\delta_H(CDCl_3)$ 0.95 (3 H, t, *J* 6.7, Me), 1.36–1.79 (6 H, m, CH_2), 2.15–2.28 (4 H, m, CH_2NCH_2), 2.41 (3 H, s, MeC_6H_3), 3.37–3.50 (4 H, m, CH_2OCH_2), 4.41–4.48 (2 H, m, 4- and 5-H) and 7.37–7.88 (3 H, m, ArH).

4,5-*Dihydro*-4-*methyl*-1-(4-*methyl*-2-*nitrophenyl*)-5-*morpholino*-1,2,3-*triazole* **4f**. This compound was obtained as a *solid* in 88% yield, m.p. 97 °C (Found: C, 54.9; H, 6.25; N, 22.7. $C_{14}H_{19}N_5O_3$ requires C, 55.05; H, 6.25; N, 22.95%); $\delta_H(CDCl_3)$ 1.33 (3 H, d, *J* 6.9, Me), 2.23–2.25 (4 H, m, CH_2NCH_2), 2.41 (3 H, s, MeC_6H_3), 3.44–3.46 (4 H, m, CH_2OCH_2), 4.41–4.51 (2 H, m, 5- and 4-H) and 7.38–7.85 (3 H, m, ArH).

1-(4-*Chloro*-2-*nitrophenyl*)-4,5-*dihydro*-4-*methyl*-5-*morpholino*-1,2,3-*triazole* **4g**. This compound was obtained as a *solid* in 92% yield, m.p. 110 °C (Found: C, 47.8; H, 4.6; N, 21.55. $C_{13}H_{16}ClN_5O_3$ requires C, 48.1; H, 4.65; N, 21.55%); $\delta_H(CDCl_3)$ 1.34 (3 H, d, *J* 7, Me), 2.15–2.26 (4 H, m, CH_2NCH_2), 3.37–3.50 (4 H, m, CH_2OCH_2), 3.38 (1 H, d, *J* 1, 5-H), 4.56 (1 H, dq, *J* 7 and 1, 4-H) and 7.51–7.98 (3 H, m, ArH).

4,5-*Dihydro*-4,4-*dimethyl*-5-*morpholino*-1-(2-*nitrophenyl*)-1,2,3-*triazole* **4h**. This compound was obtained as a *solid* in 67% yield, m.p. 94 °C (Found: C, 54.9; H, 6.25; N, 23.05. $C_{14}H_{19}N_5O_3$ requires C, 55.05; H, 6.25; N, 22.95%); $\delta_H(CDCl_3)$ 1.25 (3 H, s, Me), 1.51 (3 H, s, Me), 2.27–2.36 (4 H, m, CH_2NCH_2), 3.38–3.48 (4 H, m, CH_2OCH_2), 4.29 (1 H, s, 5-H), 7.32 (1 H, t, *J* 8.1, Ar 5-H), 7.62 (1 H, t, *J* 8.2, Ar 4-H), 7.86 (1 H, d, *J* 8.1, Ar 6-H) and 8.1 (1 H, d, *J* 8.2, Ar 3-H).

General Procedure for the Preparation of 1-(2-*Aminophenyl*)-4,5-*dihydro*-5-*morpholino*-1,2,3-*triazoles* **5a–f**, **h**.—To a suspension of a nitrotriazole **4** (0.02 mol) in ethanol (30 cm^3) was added 10% Pd on charcoal (2 g). The mixture was hydrogenated at room pressure and temperature. The reaction mixture was filtered through a bed of Celite, washed twice with methylene dichloride (2 × 10 cm^3). The filtrate was combined with the washings and evaporated to dryness. If possible the residue was recrystallized from ethanol. Otherwise it was used as such for the next reaction. Yields, analytical and spectroscopic data are given below.

1-(2-*Aminophenyl*)-4,5-*dihydro*-4-*methyl*-5-*morpholino*-1,2,3-*triazole* **5a**. This compound was obtained as a *solid* in 70% yield, m.p. 124 °C (Found: C, 59.95; H, 7.2; N, 26.85. $C_{13}H_{19}N_5O$ requires C, 59.75; H, 7.3; N, 26.8%); ν_{max}(Nujol)/cm^{-1} 3400 and 3350 (NH_2); $\delta_H(CDCl_3)$ 1.29 (3 H, d, *J* 7, Me), 2.17–2.55 (4 H, m, CH_2NCH_2), 3.55–3.60 (4 H, m, CH_2OCH_2), 4.37 (1 H, dq, *J* 3 and 7, 4-H), 4.51 (1 H, d, *J* 3, 5-H), 4.43 (2 H, br s, NH_2) and 7.03–7.26 (4 H, m, ArH).

1-(2-*Aminophenyl*)-4-*ethyl*-4,5-*dihydro*-5-*morpholino*-1,2,3-*triazole* **5b**. This compound was obtained as a *solid* in 80% yield, m.p. 139 °C (Found: C, 60.9; H, 7.45; N, 25.5. $C_{14}H_{21}N_5O$ requires C, 61.05; H, 7.7; N, 25.45%); ν_{max}(Nujol)/cm^{-1} 3350 and 3300 (NH_2); $\delta_H(CDCl_3)$ 1.03 (3 H, t, *J* 7.3, Me), 1.50–1.75 (2 H, m, CH_2), 2.28–2.55 (4 H, m, CH_2NCH_2), 3.57–3.63 (4 H, m, CH_2OCH_2), 4.27 (1 H, 2t, *J* 3 and 7.3, 4-H), 4.52 (3 H, d, *J* 3, 5-H and NH_2) and 6.70–7.16 (4 H, m, ArH).

1-(2-*Amino*-4-*methylphenyl*)-4-*decyl*-4,5-*dihydro*-5-*morpholino*-1,2,3-*triazole* **5c**. This compound was obtained in 77% yield, m.p. 55 °C (Found: C, 68.9; H, 9.55; N, 17.75. $C_{23}H_{33}N_5O$ requires C, 68.8; H, 9.8; N, 17.45%); ν_{max}(Nujol)/cm^{-1} 3400 and 3300 (NH_2); $\delta_H(CDCl_3)$ 0.88 (3 H, t, *J* 5.8, Me), 1.10–1.80 (18 H, m, CH_2), 2.10–2.50 (4 H, m, CH_2NCH_2), 2.76 (3 H, s, MeC_6H_3), 3.00–3.60 (2 H, m, NH_2), 3.40–3.60 (4 H, m, CH_2OCH_2), 4.20–4.50 (2 H, m, 4- and 5-H) and 6.50–7.00 (3 H, m, ArH).

1-(2-*Amino*-4-*methylphenyl*)-4,5-*dihydro*-4-*isopropyl*-5-*morpholino*-1,2,3-*triazole* **5d**. This compound was obtained as a *solid* in 83% yield, m.p. 116 °C (Found: C, 63.0; H 8.1; N, 22.9. $C_{16}H_{25}N_5O$ requires C, 63.55; H, 8.3; N, 23.1%); ν_{max}(Nujol)/cm^{-1} 3460 and 3340 (NH_2); $\delta_H(CDCl_3)$ 0.95 (3 H, d, *J* 6.7, Me), 1.03 (3 H, d, *J* 6.7, Me), 2.00 (1 H, sept, *J* 3, CH), 2.27 (3 H, s, *Me*Ar), 2.21–2.55 (4 H, m, CH_2NCH_2), 3.54–3.65 (4 H, m, CH_2OCH_2), 4.18 (1 H, dd, *J* 3.7 and 6.7, 4-H), 4.50 (2 H, br s, NH_2), 4.51 (1 H, d, *J* 3, 5-H) and 6.52–7.02 (3 H, m, ArH).

1-(2-*Amino*-4-*methylphenyl*)-4-*butyl*-4,5-*dihydro*-5-*morpholino*-1,2,3-*triazole* **5e**. This compound was obtained as a labile oil in 73% yield, ν_{max}(neat)/cm^{-1} 3450 and 3550 (NH_2); $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 6.6, Me), 1.26–1.73 (6 H, m, CH_2), 2.27 (3 H, s, Ar*Me*), 2.21–2.58 (4 H, m, CH_2NCH_2), 3.57–3.65 (4 H, m, CH_2OCH_2), 4.26–4.36 (1 H, m, 4-H), 4.36–4.46 (2 H, m, NH_2), 4.47 (1 H, d, *J* 3.2, 5-H) and 6.53–7.10 (3 H, m, ArH).

1-(2-*Amino*-4-*methylphenyl*)-4,5-*dihydro*-4-*methyl*-5-*morpholino*-1,2,3-*triazole* **5f**. This compound was obtained as a labile oil, ν_{max}(neat)/cm^{-1} 3350 and 3200 (NH_2); $\delta_H(CDCl_3)$ 1.28 (3 H, d, *J* 7, Me), 2.27 (3 H, s, Ar*Me*), 2.28–2.60 (4 H, m, CH_2NCH_2), 3.53–3.64 (4 H, m, CH_2OCH_2), 4.23–4.40 (3 H, m, 4-H and NH_2), 4.45 (1 H, d, *J* 3, 5-H) and 6.50–7.10 (3 H, m, ArH).

1-(2-*Aminophenyl*)-4,5-*dihydro*-4,4-*dimethyl*-5-*morpholino*-1,2,3-*triazole* **5h**. This compound was obtained as a *solid* in 42% yield, m.p. 101 °C (Found: C, 60.85; H, 7.55; N, 25.25. $C_{14}H_{21}N_5O$ requires C, 61.05; H, 7.7; N, 25.45%); ν_{max}(Nujol)/cm^{-1} 3340 and 3475 (NH_2); $\delta_H(CDCl_3)$ 1.22 (3 H, s, Me), 1.50 (3 H, s, Me), 2.27–2.61 (4 H, m, CH_2NCH_2), 3.43–3.51 (4 H, m, CH_2OCH_2), 4.21 (2 H, br s, NH_2), 4.56 (1 H, s, 5-H) and 6.74–7.28 (4 H, m, ArH).

1-(2-*Amino*-4-*chlorophenyl*)-4,5-*dihydro*-5-*morpholino*-1,2,3-*triazole* **5g**.—The literature procedure[9] was adapted as follows: to a suspension of copper(II) acetylacetonate (0.52 g, 0.002 mol)

in propan-2-ol (20 cm^3), a suspension of $NaBH_4$ (0.38 g, 0.01 mol) in ethanol (20 cm^3) was added under nitrogen at room temperature. A suspension of compound **4g** (0.01 mol) in propan-2-ol (20 cm^3) was added and finally a solution of $NaBH_4$ (0.75 g, 0.02 mol) in ethanol (10 cm^3) was slowly added to the reaction mixture. After being stirred at 30 °C for 6 h the mixture was evaporated as much as possible. After addition of water (50 cm^3) the organic layer was extracted with methylene dichloride (3 × 30 cm^3). The combined organic phase was dried over sodium sulfate and concentrated under reduced pressure to afford impure compound **5g**, which was used for the next step without further purification. Oil, ν_{max}(neat)/cm^{-1} 3450 and 3350 (NH_2); δ_H($CDCl_3$) 1.27 (3 H, d, *J* 7.2, Me), 2.25–2.52 (4 H, m, CH_2NCH_2), 3.52–3.63 (4 H, m, CH_2OCH_2), 4.31–4.47 (2 H, m, 4- and 5-H), 4.6 (2 H, br s, NH_2) and 6.65–7.15 (3 H, m, ArH).

Thermal Reactions of Compound **5a**.—(*a*) A solution of the aminotriazole **5a** (0.8 g, 0.003 mol) in toluene (10 cm^3) was heated under reflux (1 h). The progress of the reaction being followed by TLC. After disappearance of the starting material the solvent was removed and the residue was dissolved in ethanol, a catalytic amount of 10% Pd/C (0.1 g) was added, and the mixture was refluxed for 30 min. The reaction mixture was filtered through Celite and concentrated to give a residue, which was separated by column chromatography with cyclohexane–ethyl acetate (4:1). Three fractions were obtained corresponding to: 2-methyl-1,2,3,4-tetrahydroquinoxaline **9** as an oil in 9% yield; δ_H($CDCl_3$) 1.20 (3 H, d, *J* 6.3, Me), 3.00, 3.30 and 3.50 (3 H, ABX-system, *J* 10.7, 8.7 and 2.8, 2- and 3-H_2), 3.40–3.60 (2 H, m, NH_2) and 6.40–6.70 (4 H, m, ArH); 2-methylquinoxaline **10a** as an oil [7] in 27% yield; δ_H($CDCl_3$) 2.65 (3 H, s, Me), 7.57–7.99 (4 H, m, ArH) and 8.62 (1 H, s, 3-H); 2-ethylbenzimidazole **13** as a solid in 12% yield, m.p. 168 °C;[10] δ_H($CDCl_3$) 1.45 (3 H, t, *J* 7.7, Me), 3.00 (2 H, q, *J* 7.7, CH_2), 7.10–7.30 (2 H, m, ArH), 7.45–7.65 (2 H, m, ArH) and 9.60 (1 H, br s, NH).

(*b*) Aminotriazole **5a** (2 g, 7.6 mmol) (10 cm^3) was dissolved in toluene (50 cm^3) and the solution was heated at reflux for 1 h. Concentration of the solvent left a residue, which was dissolved in tetrahydrofuran (THF) (50 cm^3) and heated with 10% Pd/C (0.1 g) and cyclohexene (0.57 g, 7 mmol). The progress of the reaction was followed by TLC. Then, the mixture was filtered through a bed of Celite and the filtrate was concentrated to dryness affording a crude residue, which was purified by column chromatography with cyclohexane–ethyl acetate (3:2) to yield compound **10a** (0.48 g, 44%).

Thermal Reaction of Compound **5h**.—A solution of compound **5h** (1.35 g, 4.9 mmol) in toluene (30 cm^3) was heated under reflux (1 h). After removal of the solvent the crude residue was recrystallized from diisopropyl ether to give, as a crystalline solid, 1,2,3,4-tetrahydro-2,2-dimethyl-3-morpholinoquinoxaline **14** (0.87 g, 72%), m.p. 95–99 °C; δ_H($CDCl_3$) 1.45 (6 H, s, Me), 2.80–2.90 (4 H, m, CH_2NCH_2), 3.65–3.75 (4 H, m, CH_2OCH_2), 4.4 (1 H, br s, NH) and 6.45–7.35 (5 H, m, ArH and 3-H); *m/z* 247 (M^+, 5.2%), 178 (78), 160 (88), 145 (100), 118 (42) and 86 (34).

A solution of compound **14** (150 mg) in CH_2Cl_2 (10 cm^3) was stirred with water (10 cm^3) for one day. The organic layer was separated, and washed with water (3 × 10 cm^3). The organic phase was dried over sodium sulfate and evaporated to give a residue, which was recrystallized from diisopropyl ether to give 1,2-*dihydro*-2,2-*dimethylquinoxaline* **15** as a solid (90 mg, 93%), m.p. 107 °C (Found: C, 75.2; H, 6.6; N, 17.4. $C_{10}H_{12}N_2$ requires C, 75.43; H, 6.96; N, 17.60%); δ_H($CDCl_3$) 1.32 (6 H, s, Me_2), 3.70 (1 H, br s, NH), 6.49 (1 H, dd, *J* 7.6 and *ca.* 0.5, 8-H), 6.72 (1 H, dt, *J* 7.6 and *ca.* 0.5, 6-H), 7.02 (1 H, dt, *J* 7.6 and 1.7, 7-H), 7.22–7.29 (2 H, m, 3- and 5-H).

General Procedure for the Preparation of 2-*Alkylquinoxalines* **10a–g**.—A solution of an aminotriazole **5** (0.01 mmol) in toluene (30 cm^3) was refluxed for 1 h. The solvent was removed and the residue was dissolved in THF (20 cm^3). To the solution was added DDQ (0.009 mol). The mixture was stirred for 3–6 h at room temperature. The reaction mixture was filtered, the filtrate was evaporated to dryness, and the residue was chromatographed on silica gel with cyclohexane–ethyl acetate (3:2) to give the corresponding product **10**. Yields, analytical and spectroscopic data are given below:

2-*Methylquinoxaline* **10a**. This compound was obtained as an oil in 92% yield with the properties indicated above.

2-*Ethylquinoxaline* **10b**. This compound was obtained as an oil [11] in 89% yield; δ_H($CDCl_3$) 1.42 (3 H, t, *J* 7.6, Me), 3.03 (2 H, q, *J* 7.6, CH_2), 7.63–8.08 (4 H, m, ArH) and 8.74 (1 H, s, 3-H).

2-*Decyl*-6-*methylquinoxaline* **10c**. This compound was obtained as an oil in 76% yield; δ_H($CDCl_3$) 0.79 (3 H, t, *J* 6.6, CH_2*Me*), 1.17–1.79 (16 H, m, CH_2), 2.47 (3 H, s, 6-Me), 2.89 (2 H, t, CH_2-α), 7.43–7.86 (3 H, m, ArH) and 8.61 (1 H, s, 3-H).

2-*Isopropyl*-6-*methylquinoxaline* **10d**. This compound was obtained as an oil in 70% yield; δ_H($CDCl_3$) 1.43 (6 H, d, *J* 6.9, Me_2), 2.57 (3 H, s, 6-Me), 3.29 (1 H, sept, *J* 6.9, C*H*Me_2), 7.53–7.95 (3 H, m, ArH) and 8.73 (1 H, s, 3-H).

2-*Butyl*-6-*methylquinoxaline* **10e**. This compound was obtained as an oil in 70% yield; δ_H($CDCl_3$) 0.96 (3 H, t, *J* 6.1, CH_2*Me*), 1.39–1.89 (4 H, m, CH_2), 2.57 (3 H, s, 6-Me), 2.97 (2 H, t, *J* 5.8, CH_2-α), 7.53–7.93 (3 H, m, ArH) and 8.68 (1 H, s, 3-H).

2,6-*Dimethylquinoxaline* **10f**. This compound was obtained as a solid in 44% yield; m.p. 75 °C (lit.,[12] 74–75 °C); δ_H($CDCl_3$) 2.54 (3 H, s, 6-Me), 2.73 (3 H, s, 2-Me), 7.53–7.88 (3 H, m, ArH) and 8.64 (1 H, s, 3-H); δ_C($CDCl_3$) 21.49 (6-Me), 22.25 (2-Me), 127.87 (C-5), 128.00 (C-8), 131.90 (C-7), 138.88 (C-6), 140.28 (C-8a), 140.80 (C-4a), 145.65 (C-3) and 152.49 (C-2).

6-*Chloro*-2-*methylquinoxaline* **10g**. This compound was obtained as a solid (from Pr^i_2O; 57%); m.p. 131 °C (lit.,[13] 131 °C); δ_H($CDCl_3$) 2.76 (3 H, s, 2-Me), 7.65–8.06 (3 H, m, ArH) and 8.73 (1 H, s, 3-H); δ_C($CDCl_3$) 22.65 (2-Me), 128.18, 130.02 and 131.07 (C-5, -7 and -8), 134.69, 140.67 and 141.28 (C-6, -8a, -4a), 146.91 (C-3) and 154.14 (C-2).

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