Electrochemical Cyclization of 1-Phenyl-2(-1′chlorophenyl)-substituted Five-membered Nitrogen Heterocycles. Application to the Synthesis of Phenanthridines

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Pyrrolo[1,2-*f*]phenanthridine (compound **4**), 3-phenylimidazo[1,2-*f*]phenanthridine **8**, tetrazolo[1,5-*f*]phenanthridine **11** and benzo[*c*]tetrazolo[1,5-*f*]phenanthridine **12** have been prepared using an electrochemical cyclization procedure. Treatment of the imidazophenanthridine with singlet oxygen yields a phenanthridone by degradation of the heterocyclic system. Lithium aluminium hydride reduction of the tetrazolophenanthridines yields the phenanthridine.

The electrochemical reduction, in aprotic solvents, of both open chain and heterocyclic compounds bearing adjacent substituents of phenyl and 2-halogenophenyl leads to a cyclization reaction.[1,2] Examples of 5-membered ring nitrogen heterocycles which undergo the reaction are given here. The process involves generation of a phenyl radical by carbon–halogen bond cleavage of the electrochemically generated radical-anion

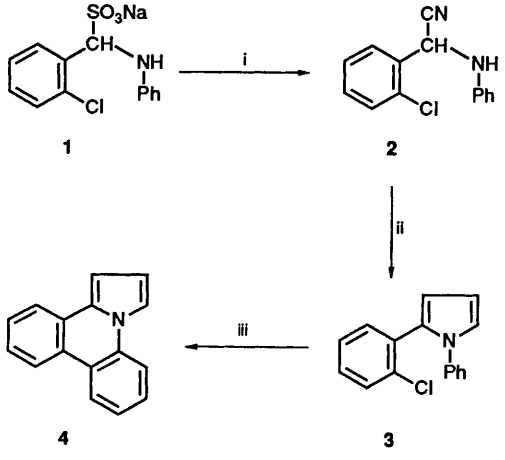
$$Ar\text{–}X + e \rightleftharpoons [Ar\text{–}X]\cdot^- \quad (1)$$

$$[Ar\text{–}X]\cdot^- \longrightarrow Ar\cdot + X^- \quad (2)$$

[eqns. (1) and (2)]. The σ-radical can either undergo cyclization or be reduced further and then protonated to give Ar–H.[3] The radical can also abstract a hydrogen atom from the solvent.[4] Cyclization of the σ-radical is usually accompanied by formation of Ar–H through one of these processes. The usefulness of this electrochemical cyclization is demonstrated by its application to a series of pyrrole, imidazole and tetrazole derivatives.

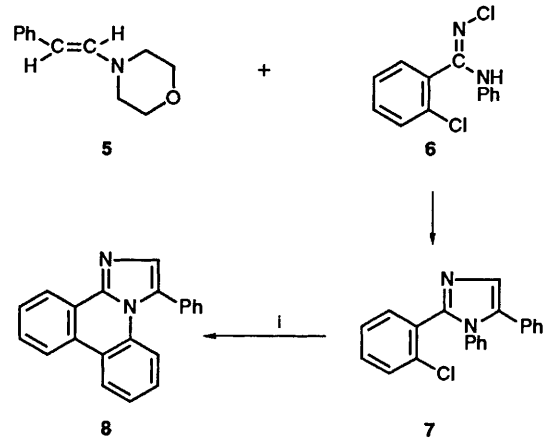
Results and Discussion

Pyrroles.—The anilinonitrile **2** was prepared by the general procedure[5] due to Bucherer, and condensed with acrolein according to the general method,[6] to yield the pyrrole **3**. Cathodic reuction of pyrrole **3** in dimethylformamide gave pyrrolo[1,2-*f*]phenanthridine **4** along with 1,2-diphenylpyrrole (Scheme 1). Photochemical reaction is often an alternative cyclization process for compounds with adjacent phenyl rings and the mechanism of such reactions has been discussed.[7] Photolysis of **3** yielded **4** as the only isolated product. Pyrrolo[1,2-*f*]phenanthridine was first prepared by Acheson[8] during an investigation of the reaction between 6-methylphenanthridine *N*-oxide and dimethyl acetylenedicarboxylate.



Scheme 1. *Reagents and conditions:* i, KCN; ii, CH_2=CHCHO; iii, cathodic reduction.

Imidazoles.—Reaction between *N*-chloro-*N*′-arylamidines and enamines derived from aldehydes yields 1,2,5-trisubstituted imidazoles. The regiospecificity of this reaction has been established.[9] 2-(2′-Chlorophenyl)-1,5-diphenylimidazole **7** was prepared from **5** and **6**. Cathodic reduction of the imidazole **7** gave the cyclization product **8** together with some 1,2,5-triphenylimidazole (Scheme 2).

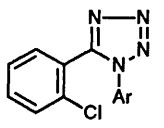


Scheme 2. *Reagent and conditions:* i, cathodic reduction.

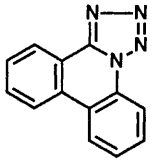
Tetrazoles.—Tetrazoles are easily obtained by the action of hydrazoic acid or sodium azide on the appropriate imino chloride.[10] The most convenient preparation involves carrying out the reaction in dry dimethylformamide with solid sodium azide. The reactivity of the azide ion is enhanced by its poor solvation in a dipolar aprotic solvent, with the result that only mild conditions and short reaction periods are necessary. The *N*-phenyl and *N*-(1-naphthyl) compounds, **9** and **10** respectively, were prepared. Cathodic reduction of these compounds resulted in the formation of the cyclized product uncontaminated by products arising from the hydrogen atom abstraction process.

We have shown thast it is necessary for the two reacting aromatic rings to be held in close proximity for cyclization to

proceed in good yield, otherwise the intermediate σ-radical is diverted towards the hydrogen abstraction reaction.[2] The formation of phenanthridine derivatives in good yield by cyclization of open chain compounds where the reacting groups are not held rigidly adjacent therefore presents difficulties. A way round this problem is to cyclize one of the five-membered heterocyclic compounds above and in a second reaction to degrade the heterocycle leaving a phenanthridine derivative.



9; Ar = Ph
10; Ar = 1 – naphthyl



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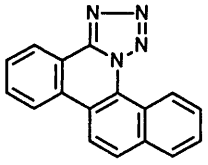

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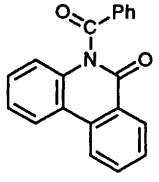

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A number of five-membered heterocyclic bases undergo cleavage when allowed to react with singlet oxygen, for example pyrroles,[11] oxazoles,[12] thiazoles[13] and imidazoles.[14,15] In such systems, singlet oxygen appears to behave as a dienophile adding to a *cis*-diene. Wasserman *et al.* have proposed the formation of a transannular peroxide in the photosensitized reaction of 1,2,4,5-tetraphenylimidazole with oxygen.[14] The magnitude of the resonance energy associated with the aromatic substrate determines the ability to form such *endo*-peroxides. Phenanthrene, for example, would lose 40 kcal* in resonance energy if it formed a peroxide, and experimentally it does not appear to react with singlet oxygen. However, anthracene reacts rapidly with singlet oxygen where in this case the loss of resonance energy is only about 28 kcal.

3-Phenylimidazo[1,2-*f*]phenanthridine in methanol reacted with singlet oxygen generated by irradiation from oxygen and Methylene Blue as sensitiser. Slow loss of starting material and generation of products was demonstrated by TLC analysis of aliquots. Removal of the solvent afforded a colourless solid that was identified as *N*-benzoylphenanthridone **13** from its m.p. and mass spectrum. The mass spectrum shows two principal fragments formed by cleavage of the benzoyl–nitrogen bond.

The known cleavage[16] of 1,5-disubstituted tetrazoles when treated with lithium aluminium hydride affords another route to the formation of phenazines. Reduction of 1,5-diphenyltetrazole gave *N*-benzylaniline. Under similar conditions, the tetrazole **11** afforded phenanthridine. Similarly, reduction of **12** gave the benzophenanthridine. The dihydrophenanthridine may be first formed in the last two reactions and then oxidized by air during the work-up procedure to give the phenanthridine.

Electrochemical reduction of vicinal phenyl and chlorophenyl substituted five-membered-ring nitrogen heterocycles is a convenient ring closure reaction yielding the condensed phenanthridine. Oxidative degradation of imidazophenanthridines will yield the phenanthridone while reductive degradation of tetrazolophenanthridines is a convenient route to the phenanthridine by loss of three nitrogen atoms.

Experimental

Dimethylformamide (DMF) was kept over anhydrous calcium chloride and then anhydrous copper sulphate and distilled under nitrogen, b.p. 42 °C at 12 mmHg. Tetrahydrofuran (THF) was refluxed over lithium aluminium hydride ($LiAlH_4$) and distilled.

Conditions for Electrochemical Reduction.—Preparative scale reductions were carried out in an H-type cell with 0.1M tetrapropylammonium fluoroborate in DMF as electrolyte, a Pt anode, a Hg pool cathode (area 20 cm^2) and saturated calomel reference electrode. The anolyte consisted of the electrolyte solution, the catholyte was kept under nitrogen and the composition is stated for each experiment. The cathode potential was selected to give a satisfactory initial current and maintained there using a potentiostat. Reactions were performed until the current fell to a very low value. Some of the current passed will generate hydrogen at the cathode so the number of Faradays† passed is not a reliable indicator of the number consumed by the organic reaction only.

2-(2-*Chlorophenyl*)*anilinoacetonitrile* **2**.—2-Chlorobenzaldehyde (15.3 g), aniline (9.6 g) and aqueous sodium bisulphite (90 ml, 40%) were mixed and stirred for 3 h. The colourless addition product **1** which separated was filtered off, washed with a little water and dried under vacuum. Finely powdered potassium cyanide (7.5 g) was added to a solution of this addition product (15 g) in ethanol (100 ml) and the suspension refluxed on a water bath for 2 h. The hot suspension was filtered and the residue of sulphite salts washed with boiling ethanol (100 ml). Evaporation of the combined ethanol extracts under reduced pressure left an orange residue which was dissolved in dichloromethane, washed with water and the dichloromethane layer dried (Na_2SO_4) and evaporated to dryness. The yellow-orange residue (10.2 g, 89%) crystallized to give colourless needles of the *title compound*, m.p. 75–78 °C (Found: C, 69.8; H, 4.7; N, 11.6. $C_{14}H_{11}ClN_2$ requires C, 69.3; H, 4.6; N, 11.5%); δ($CDCl_3$) 4.07 (1 H, d, *J* 0.6 Hz, NH), 5.67 (1 H, d, *J* 0.6 Hz, C–H), 6.57–7.50 (9 H, m, aromatic), on shaking with D_2O the doublet at δ 5.67 became a singlet and the peak at 4.07 disappeared; *m/z* (% abundance) 244 (20%), 242 (60, M^+), 215 (28), 152 (20, C_8H_5ClN), 150 (60, C_8H_5ClN), 92 (100, C_6H_6N).

2-(2′-*Chlorophenyl*)-1-*phenylpyrrole* **3**.—The above anilinoacetonitrile **2** (15.4 g) and freshly distilled acrolein (3.6 g) were dissolved in methanol (50 ml) and the mixture adjusted to pH 9 (indicator paper) by the addition of 1M potassium hydroxide in methanol. The mixture was allowed to stand at room temperature overnight when the colour changed from yellow to brown. Unchanged acrolein and methanol were removed under reduced pressure to leave a dark brown oil. This was heated at 160 °C for 2 h to convert the intermediate pyrrolidine into the pyrrole. The product was chromatographed over silica gel (100 g) with chloroform as eluent. Evaporation of the eluent under reduced pressure afforded a yellow solid which crystallised from ethanol to yield colourless needles (5 g, 31%) of the *title compound*, m.p. 119–122 °C (Found: C, 75.6; H, 4.7; N, 5.5. $C_{16}H_{12}ClN$ requires C, 75.7; H, 4.8; N, 5.5%); M^+ at *m/z* 255 (33%) and 253 (100%). The product gave a strong violet colouration in the Ehrlich test.

* 1 cal = 4.184 J.

† 1 Faraday ≈ 9.648 × 10^4 C mol^{-1}.

Pyrrolo[1,2-f]*phenanthridine* **4**.—A solution of compound **3** (0.5 g) in the electrolyte (10 ml) was reduced at a cathode potential of −2.3 V when 1.69 Faraday mol^{-1} was consumed, and the colour of the solution changed from orange to lime green. The catholyte was evaporated to a small volume under reduced pressure, dissolved in dichloromethane (50 ml), washed with water to remove the electrolyte, dried (Na_2SO_4) and evaporated to dryness. The reaction products were then dissolved in light petroleum (b.p. 40–60 °C) and chromatographed on silica gel preparative TLC plates, eluting with light petroleum containing 5% ether. This effected a separation of the two components. 1,2-Diphenylpyrrole was obtained as a brown solid which sublimed at 80 °C/0.1 mmHg and crystallised from methanol as needles (0.13 g, 30%), m.p. 91–92 °C (lit.,[6] 91 °C); M^+ at *m/z* 219. Pyrrolo[1,2-*f*]phenanthridine sublimed at 80 °C/0.1 mmHg and crystallised from methanol as colourless needles (0.18 g, 42%), m.p. 153–156 °C (lit.,[8] m.p. 151 °C) (Found: C, 88.2; 5.2; N, 6.4. Calc. for $C_{16}H_{11}N$: C, 88.4; H, 5.1; N, 6.5%); M^+ at *m/z* 217.

Photolysis of 2-(2′-chlorophenyl)-1-phenylpyrrole in methanol using a medium pressure mercury lamp in a quartz immersion well afforded, after chromatography, pyrrolo[1,2-*f*]-phenanthridine (55%), m.p. 154–156 °C.

β-*Morpholinostyrene* **5**.—Phenylacetaldehyde (11 g) and morpholine (15.5 g) were heated for 5 h at 110–120 °C under nitrogen. Distillation of the product gave a fraction b.p. 175–183 °C which solidified on cooling and crystallised from ether to give the title compound **5** (9.2 g, 52%), m.p. 77–78 °C (lit.,[17] m.p. 77–78 °C) (Found: C, 76.6; H, 8.2; N, 7.4. Calc. for $C_{12}H_{15}NO$: C, 76.2; H, 8.2; N, 7.4%); δ($CDCl_3$) 2.9–3.2 (4 H, m, morpholine), 3.6–4.0 (4 H, m, morpholine), 5.44 (1 H, d, *J* 15 Hz, olefinic), 6.63 (1 H, d *J* 15 Hz, olefinic), 6.63 (1 H, d *J* 15 Hz, olefinic) and 7.0–7.4 (5 H, m, aromatic).

2,N-*Dichloro*-N′-*phenylbenzamidine* **6**.—Finely powdered aluminium trichloride (29.6 g) was added in portions over a period of 20 min to a stirred mixture of aniline (20.3 ml) and 2-chlorobenzonitrile (30.4 g) cooled in an ice-bath. The mixture was kept at 200 °C for 30 min, cooled and while still molten added carefully to a stirred solution of concentrated hydrochloric acid (10 ml) in water (600 ml). Activated charcoal (15 g) was added and the mixture stirred and cooled to 0 °C. The mixture was filtered through Celite and the filtrate added to a stirred solution of sodium hydroxide (80 g) in water (400 ml). The colourless precipitate of 2-chloro-*N*-phenylbenzamidine (45 g, 82%) was collected, washed with water and dried. A sample recrystallised from benzene as needles, m.p. 102–104 °C (lit.,[18] m.p. 102 °C) (Found: C, 67.7; H, 4.8; N, 12.1. Calc. for $C_{13}H_{11}ClN_2$: C, 67.8; H, 4.8; N, 12.1%).

N-Chlorosuccinimide (3.4 g) dissolved in dichloromethane (50 ml) was added dropwise to a solution of 2-chloro-*N*-phenylbenzamidine (5.7 g) in dichloromethane (50 ml). The mixture was stirred at room temperature for 2 h, filtered, washed with water, dried (Na_2SO_4) and the solvent removed. The product crystallised from benzene as colourless needles of the *title compound* (5.8 g, 87%), m.p. 125–128 °C (Found: C, 59.1; H, 3.8; N, 10.6. $C_{13}H_{10}Cl_2N_2$ requires C, 58.9; H, 3.8; N, 10.6%).

2-(2′-*Chlorophenyl*)-1,5-*diphenylimidazole* **7**.—β-Morpholinostyrene (2.9 g) and dry pyridine (0.92 g) were dissolved in dry chloroform (50 ml) and a solution of compound **6** (2.63 g) in chloroform (50 ml) added dropwise. The reaction mixture was refluxed for 20 h until no dichlorophenylbenzamidine was detected by TLC on silica gel using benzene–ether (4:1) as eluent. The solution was cooled, washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4) and the solvent evaporated. The residue was dissolved in benzene and chromatographed on silica gel (120 g), eluting with benzene–ether (4:1). The product (R_f 0.25) was collected and the solvent removed leaving an orange oil. Crystallisation from ether–light petroleum afforded colourless crystals (2.6 g, 79%) of the *title compound*, m.p. 126–128 °C (Found: C, 76.1; H, 4.7; N, 8.5. $C_{21}H_{15}ClN_2$ requires C, 76.2; H, 4.6; N, 8.5%); M^+ at *m/z* 332 (33%) and 330 (100%).

3-*Phenylimidazo*[1,2-f]*phenanthridine* **8**.—A solution of compound **7** (0.43 g) in the electrolyte (10 ml) was reduced at a cathode potential of −2.2 V when 1.4 Faraday mol^{-1} was consumed. The colour of the solution was initially red, finally changing to green. The catholyte was evaporated under reduced pressure to a small volume, diluted with water and extracted with dichloromethane. The organic layer was washed with water, dried (Na_2SO_4) and the solvent removed. The residue was chromatographed on silica gel (100 g) eluting with ether, fractions from the column being monitored by TLC on silica (ether as eluent). Two products were isolated. Material (0.16 g, 42%) with R_f 0.49 crystallised from ether–light petroleum to give the *title compound*, m.p. 236–238 °C (Found: C, 85.4; H, 4.8; N, 9.3. $C_{21}H_{14}N_2$ requires C, 85.7; H, 4.8; N, 9.5%); M^+ at *m/z* 294.

Material (0.1 g, 26%) with R_f 0.38 crystallised from ethanol to yield, 1,2,5-triphenylimidazole, m.p. 245–247 °C (lit.,[9] m.p. 250 °C); M^+ at *m/z* 296.

Photooxygenation of 3-*Phenylimidazo*[1,2-f]*phenanthridine*.—A solution of 3-phenylimidazo[1,2-*f*]phenanthridine (81 mg) in methanol (100 ml) containing Methylene Blue (25 mg) was kept under oxygen and irradiated for 20 h with a medium pressure mercury lamp contained in a Pyrex immersion well. The resulting solution was evaporated to a small volume under reduced pressure and the residue chromatographed on silica gel, eluting with ethyl acetate. On removing the solvent under reduced pressure, the product crystallised from ethanol to give *N*-benzoylphenanthridone **13** (52 mg, 69%), m.p. 193–194 °C (lit.,[19] m.p. 189–193 °C), M^+ at *m/z* 194. Attempted photooxygenation of 3-phenyltriazolo[4,3-*f*]phenanthridine under the same conditions returned only starting material.

5-(2′-*Chlorophenyl*)-1-*phenyltetrazole* **9**.—An intimate mixture of 2-chlorobenzanilide (11.6 g) and phosphorus pentachloride (11.25 g) was heated gently for 1 h under a current of dry air so that hydrogen chloride and phosphorus oxychloride were removed. The residual imido chloride was dissolved in anhydrous DMF (75 ml) and added dropwise to a stirred suspension of sodium azide (6.5 g) in DMF (50 ml) kept at 26 °C over a period of 45 min. The reaction mixture was stirred for a further 30 min. Water was then added and the precipitate collected. Crystallisation from ethanol afforded colourless plates (11.5 g, 84%) of the *title compound*, m.p. 109–112 °C (Found: C, 60.8; H, 3.5; N, 21.7. $C_{13}H_9ClN_4$ requires C, 60.8; H, 3.5; N, 21.8%); *m/z* (% abundance) 258 (6), 256 (18, M^+), 230 (31), 228 (100, $M^+ - N_2$), 91 (40) and 77 (30).

Tetrazolo[1,5-f]*phenanthridine* **11**.—A solution of compound **9** (2.6 g) in electrolyte (40 ml) was reduced at a cathode potential of −1.9 V when 1.65 Faraday mol^{-1} were consumed. The solution became deep red and a white precipitate formed. The catholyte was evaporated under vacuum to a small volume and the residue dissolved in dichloromethane. This solution was washed with water, dried (Na_2SO_4) and the solvent removed. The product was chromatographed on silica gel, eluting with ethyl acetate–methanol (9:1), recovered and crystallised from propan-2-ol to yield colourless needles of the *title compound*, m.p. 234–236 °C (lit.,[20] m.p. 228–230 °C) (Found: C, 70.9; H, 3.8; N, 25.7. Calc. for $C_{13}H_8N_4$: C, 70.9; H, 3.7; N, 25.4%); *m/z*

(% abundance) 220 (10, M^+), 193 (19), 192 (100, $M^+ - N_2$), 165 (19), 164 (23) and 138 (10); λ_{max}/nm (ethanol) 238 (ε/dm^3 mol^{-1} cm^{-1}, 52 200), 246 (62 550), 271 (11 300), 281 (7300), 296 (1600), 309 (2900) and 322 (3850).

5-(2′-*Chlorophenyl*)-1-(1-*naphthyl*)*tetrazole* **10**.—The imino chloride was prepared from an intimate mixture of *N*-(2′-chlorobenzoyl)-1-naphthylamine (28 g) and phosphorus pentachloride (11.25 g), heated gently for 1 h in a current of air. The imino chloride in anhydrous dimethylformamide (75 ml) was added dropwise to a suspension of sodium azide (6.5 g) in DMF (50 ml) and the mixture stirred for 1 h at 26 °C. Water was then added and the precipitate collected. Crystallisation from ethanol afforded pale yellow plates (26 g, 85%) of the *title compound*, m.p. 141–143 °C (Found: C, 66.3; H, 3.5; N, 18.1. $C_{17}H_{11}ClN_4$ requires C, 66.5; H, 3.6; N, 18.2%).

Benzo[c]*tetrazolo*[1,5-f]*phenanthridine* **12**.—A solution of compound **10** (0.5 g) in the electrolyte (10 ml) was reduced at a cathode potential of −1.7 V when 1.75 Faraday mol^{-1} were consumed. The catholyte was worked up as described for tetrazolo[1,5-*f*](phenanthridine to yield only one product. Crystallisation from methyl acetate–methanol yielded colourless needles (0.35 g, 81%) of the *title compound*, m.p. 247–250 °C (Found: C, 75.4; H, 3.7; N, 20.5. $C_{17}H_{10}N_4$ requires C, 75.5; H, 3.7; N, 20.7%); *m*/*z* (% abundance) 270 (13, M^+), 243 (19) and 242 (100, $M^+ - N_2$); λ_{max}/nm (methanol) 226 (ε/dm^3 mol^{-1} cm^{-1} 18 600), 262 (41 400), 270 (49 700), 294 (7900), 306 (9220) and 334 (1500).

Action of Lithium Aluminium Hydride on Tetrazoles.—(*a*) 1,5-*Diphenyltetrazole*. The tetrazole (2.3 g) was dissolved in THF (20 ml) and added dropwise to a stirred suspension of $LiAlH_4$ (0.96 g) in THF (40 ml). The mixture was refluxed for 60 h under a nitrogen atmosphere, then cooled in ice during the cautious addition of water. The solution was extracted with ether and the extract washed with water, dried (Na_2SO_4) and evaporated. The residual brown oil was distilled at 180 °C/12 mmHg to yield a colourless oil (1.64 g, 78%) which crystallised as colourless needles of *N*-benzylaniline, m.p. 34–36 °C (lit.,[21] m.p. 37–38 °C) (Found: C, 85.2; H, 7.1; N, 7.7. Calc. for $C_{13}H_{13}N$: C. 85.2; H, 7.2; N, 7.6%); δ($CDCl_3$) 3.77 (1 H, s, NH); 4.23 (2 H, s, CH_2) and 6.5–7.3 (10 H, m, aromatic).

(*b*) *Tetrazolo*[1,5-f]*phenanthridine* **11**. The tetrazole (250 mg) was dissolved in THF (30 ml) and added dropwise to a stirred suspension of $LiAlH_4$ (155 mg) in THF (20 ml). The mixture was refluxed for 48 h under a nitrogen atmosphere and the product isolated in ether as above. The product was chromatographed on silica gel plates, eluting with ether. It crystallised from ethanol as needles (0.17 g, 82%) of phenanthridine, m.p. 104–105 °C (lit.,[22] m.p. 104 °C); M^+ at *m*/*z* 179.

(*c*) *Benzo*[c]*tetrazolo*[1,5-f]*phenanthridine*. The tetrazole (22 mg) was dissolved in THF (10 ml) and $LiAlH_4$ (200 mg) added with stirring. The mixture was stirred and refluxed for 48 h under an atmosphere of nitrogen and then cooled and worked up as above. Crystallization from ethanol afforded needles (10 mg, 53%) of benzo[*c*]phenanthridine, m.p. 136–137 °C (lit.,[23] m.p. 136 °C); M^+ at *m*/*z* 229.

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