One-pot Synthesis of 2-Aryloxymethyl-1-cyanomethyl-5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinoline *via* Rearrangement of the *N*-Oxide from 1-Aryloxy-4-tetrahydro-1-quinolylbut-2-yne[1]

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1-Aryloxy-4-tetrahydro-1-quinoylbut-2-yne (**1**), on treatment with *m*-chloroperbenzoic acid in dichloromethane at room temperature for 12 h, rearranged to give the bispyrroloquinoline derivative (**3**) in 30—45% yield. Addition of aqueous potassium cyanide to the intermediate (not isolated) gave the title compound (**5**) in 55—75% yield.

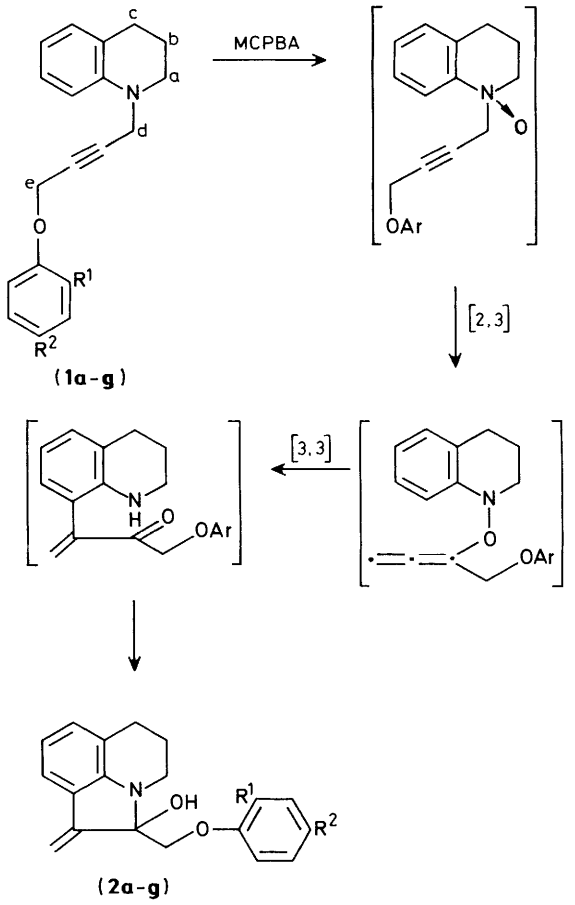
Tricyclic heteroaromatic systems with a bridgehead nitrogen atom of which pyrrolo[3,2,1-*ij*]quinoline is an important example occur in a number of alkaloids.[2] Some derivatives of the latter show interesting pharmacological properties and, as a result, their synthesis has been attempted.[3–7]

Usually this has involved application of the Fischer indole synthesis[8–13] to 1-aminotetrahydroquinoline or Friedel–Crafts-type substitution[14–16] on the aromatic ring of 1,2,3,4-tetrahydroquinoline. Since it is difficult to synthesize systems containing electron-withdrawing groups by these reactions, the [2,3]-sigmatropic rearrangement of azasulphenium ylides[17] at low temperatures (−78 °C) has been used.

The construction of the five-membered heterocyclic ring in indoles and benzothiophenes through rearrangements of aryl propynyl amine oxides[18–20] and aryl propynyl sulphoxides[21–24] respectively was shown by Thyagarajan and Majumdar to be an excellent, high yield one-step process. Later, Makisumi *et al.* synthesized naphthothiophenes[25] from allyl naphthyl sulphoxides though extension of the method to selenium analogues proceeded with different results.[26] Whilst the sulphoxides rearranged in refluxing carbon tetrachloride, the corresponding rearrangement of the amine oxides occurs more readily, and the nitrogen heterocycles are obtained in almost quantitative yield by simply stirring a solution of *N*-aryl propynamine with 1 equiv. of *m*-chloroperbenzoic acid (MCPBA) at room temperature. The intermediacy of [2,3]-and [3,3]-sigmatropic rearrangements in this process results in negligible charge build up in the aromatic ring and the reaction proceeds with extreme facility even in the presence of electron-withdrawing groups.[20,22,24] It was of interest to investigate whether the five-membered ring in the pyrrolo[3,2,1-*ij*]quinoline system could be constructed *via* the aforesaid amine oxide rearrangement.

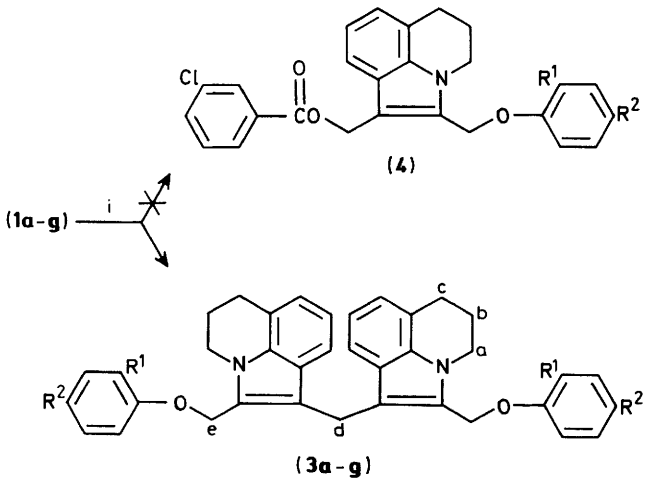
The starting materials chosen for this study, 1-aryloxy-4-tetrahydroquinol-1-ylbut-2-ynes (**1a**—**g**), were prepared by treatment of 1-aryloxy-4-chlorobut-2-yne with tetrahydroquinoline in refluxing acetone or butan-1-ol in the presence of anhydrous potassium carbonate in good yields, either as crystalline solids or viscous liquids. Since attempted purification of the latter by distillation under reduced pressure resulted in decomposition they were chromatographed over silica gel and characterized on the basis of elemental analyses and u.v., i.r., and ^{1}H n.m.r. spectral results.

The corresponding *N*-oxides were prepared *in situ* by slow addition of 1 equiv. of MCPBA in dichloromethane to a solution of the tertiary amine (**1a**—**g**) in the same solvent during 1 h at 0—5 °C. Although the peracid was consumed within 30—45 min of completion of addition, the *N*-oxides were too labile to be isolated. Instead, they spontaneously underwent a [2,3]-followed by a [3,3]-sigmatropic rearrangement; favourable positioning of the relevant functional groups then resulted in cyclization to form the intermediate (**2**) (Scheme 1) which, despite repeated attempts, could not be isolated. However, its presence was demonstrated spectroscopically[1] and it was successfully trapped with stronger nucleophiles (CN^-, PhS^-), on the basis of which the title one-pot procedure was developed.

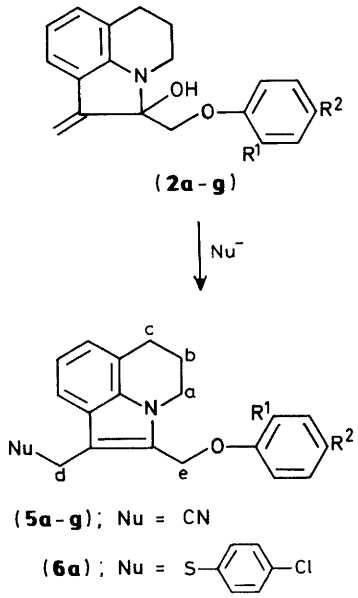


(**a**); R^1 = H, R^2 = H
(**b**); R^1 = H, R^2 = Me
(**c**); R^1 = Me, R^2 = H
(**d**); R^1 = Me, R^2 = Me
(**e**); R^1 = Cl, R^2 = H
(**f**); R^1 = H, R^2 = Cl
(**g**); R^1 = Cl, R^2 = Cl

Scheme 1.



Scheme 2. i MCPBA, CH_2Cl_2, r.t., 12 h



Scheme 3.

The nucleophilic addition of *m*-chlorobenzoic acid present in the reaction medium having been described earlier, an excess of nucleophile was avoided in order to allow the reaction to follow its normal course. Accordingly the butynes (**1a**—**g**) were stirred with 1 equiv. of MCPBA at room temperature for 12 h, when instead of the expected product (**4**) the bispyrroloquinolines (**3a**—**g**) were obtained (Scheme 2).

The role of acid catalysis in the formation of (**3**) could not be tested by further addition of acid since the latter might protonate the oxygen atom of the *N*-oxide group, thereby suppressing the rearrangement. The formation of the products could be followed by t.l.c. since all of the products (**3a**—**g**) developed a pink colour after absorption of iodine. The process can, therefore, be regarded as general for the synthesis of bispyrroloquinolines of type (**3**), although yields are low.

The intermediates (**2**) could be converted into the pyrroloquinolines (**5**) by addition of a stronger nucleophile such as CN^-, through either S_N2' displacement of the allylic hydroxy group or elimination of the hydroxy group and conjugate addition of the nucleophile. The selection of cyanide ion as nucleophile was based on the following: (i) it is a stronger nucleophile than *m*-chlorobenzoic acid, (ii) as its aqueous solution is alkaline, it can accelerate the amine oxide rearrangement, and (iii) it can easily be transformed to functional groups such as CH_2NH_2 and CO_2H that are known to attribute interesting and valuable biological effects upon indoles, *e.g.* indomethacin.[27,28]

It was found that a solution of the intermediate (**2**) in dimethylformamide and aqueous potassium cyanide undergoes reaction in the desired direction during 1.5—2.0 h at 50—60 °C. All seven butynes studied underwent facile transformation and gave well-defined products (**5a**—**g**), the formation of which was readily followed by t.l.c. since each developed a characteristic light green colour on absorption of iodine. The i.r. spectra of the products (**5a**—**g**) showed an absorption at *ca.* 2 260 cm^{-1} (CN) and the mass spectrum contained a peak at $M^+ - CN$.

In a similar fashion, nucleophilic addition of ArS^- to the intermediate (**2a**) gave the product (**6**) in 50% yield and was fully characterized.

This method therefore provides a general and straightforward one-pot synthesis of substituted pyrroloquinolines (**5a**—**g** and **6**). The advantage of the method resides in the predetermined direction of ring closure and the variety of substituents that can be incorporated into both the starting compounds as well as into the newly formed heterocyclic ring.

Experimental

M.p.s were determined in a sulphuric acid bath and are uncorrected. I.r. spectra were run on a Perkin–Elmer 1330 apparatus using KBr discs and u.v. absorptions were recorded on a Hitachi 200-20 spectrometer for solutions in chloroform. ^1H N.m.r. spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on Bruker WH-400, Zeol F_x-100, or Hitachi R-600 instruments. *m*-Chloroperbenzoic acid was obtained from E. Merck (Germany). Silica gel (60—120 mesh), neutral alumina, and basic alumina were obtained from B.D.H. Extracts were dried over anhydrous sodium sulphate. Ether refers to diethyl ether. Light petroleum and petroleum refer to the fractions of b.p. 40—60 °C and 60—80 °C respectively.

Preparation of 1-*Aryloxy*-4-*chlorobut*-2-*yne*.—These compounds were prepared according to published procedure.[23]

Preparation of 1-*Aryloxy*-4-*tetrahydro*-1-*quinolylbut*-2-*yne* (**1a**—**g**).—A mixture of 1-aryloxy-4-chlorobut-2-yne (0.1 mol), tetrahydroquinoline (16.0 g, 0.12 mol), and anhydrous potassium carbonate (10.0 g, excess) was refluxed in dry acetone (200 ml) for 12 h. A slight variation of the reaction procedure was followed for compounds (**1d**—**g**); 1-aryloxy-4-chlorobut-2-yne (0.1 mol) and tetrahydroquinoline (16.0 g, 0.12 mol) were refluxed in butan-1-ol (150 ml) in the presence of K_2CO_3 (10.0 g, excess). The solvent was removed *in vacuo* and the residue was extracted with chloroform, and the extract washed with brine, dried, and concentrated to give a highly viscous pale yellow liquid. In the case of products (**1a,e**—**g**) the viscous liquid was triturated with ethanol–light petroleum (1:5) and cooled to give a solid. Recrystallization from dichloromethane–petroleum gave crystalline white solids. In the case of products (**1b**—**d**) the viscous liquid obtained was purified by chromatography on silica gel using petroleum as eluant.

Compound (**1a**), yield 70%, m.p. 58 °C; $\lambda_{max.}$ 258 and 298 nm; $\nu_{max.}$ 1 595, 1 490, and 1 240 cm^{-1}; δ_H 1.8—2.1 (quintet, 2 H, CH^b_2, *J* 6 Hz), 2.6—2.85 (t, 2 H, CH^c_2, *J* 5.5 Hz), 3.15—3.3 (t, 2 H, CH^a_2, *J* 5.5 Hz), 4.05 (s, 2 H, CH^d_2), 4.7 (s, 2 H, CH^e_2), and 6.65—7.35 (m, 9 H, ArH); *m/z* 277 (M^+) (Found: C, 82.15; H, 6.75; N, 5.0. $C_{19}H_{19}NO$ requires C, 82.27; H, 6.91; N, 5.05%).

Compound (**1b**), yield 65%, viscous liquid; $\lambda_{max.}$ 259 and 296

nm; $\nu_{max.}$ 1 605, 1 500, and 1 230 cm^{-1}; δ_H 1.75—2.05 (quintet, 2 H, CH_2^b), 2.25 (s, 3 H, Ar*Me*), 2.6—2.9 (t, 2 H, CH_2^c), 3.2—3.4 (t, 2 H, CH_2^a), 4.1 (s, 2 H, CH_2^d), 4.65 (s, 2 H, CH_2^e), and 6.6—7.3 (m, 8 H, ArH); *m/z* 291 (M^+) (Found: C, 82.5; H, 7.05; N, 4.9. $C_{20}H_{21}NO$ requires C, 82.43; H, 7.27; N, 4.81%).

Compound (**1c**), yield 55%, viscous liquids; $\lambda_{max.}$ 260 and 295 nm, $\nu_{max.}$ 1 605, 1 495, and 1 240 cm^{-1}; δ_H 1.8—2.15 (quintet, 2 H, CH_2^b), 2.25 (s, 3 H, Ar*Me*), 2.7—3.0 (t, 2 H, CH_2^c), 3.2—3.5 (t, 2 H, CH_2^a), 4.1 (s, 2 H, CH_2^d), 4.85 (s, 2 H, CH_2^e), and 6.7—7.6 (m, 8 H, ArH) (Found: C, 81.2; H, 7.4; N, 4.65. $C_{20}H_{21}NO$ requires C, 82.43; H, 7.27; N, 4.81%).

Compound (**1d**), yield 60%, viscous liquid; $\lambda_{max.}$ 260 and 295 nm; $\nu_{max.}$ 1 605, 1 500, and 1 245 cm^{-1}; δ_H 1.6—2.0 (quintet, 2 H, CH_2^b), 2.2 (s, 6 H, Ar*Me*), 2.4—2.8 (t, 2 H, CH_2^c), 2.81—3.2 (t, 2 H, CH_2^a), 3.8 (s, 2 H, CH_2^d), 4.45 (s, 2 H, CH_2^e), and 6.4—7.3 (m, 7 H, ArH); *m/z* 305 (M^+) (Found: C, 82.3; H, 7.38; N, 4.37. $C_{21}H_{23}NO$ requires C, 82.57; H, 7.59; N, 4.59%).

Compound (**1e**), yield 60%; m.p. 91 °C; $\lambda_{max.}$ 260 and 295 nm; $\nu_{max.}$ 1 600, 1 495, and 1 235 cm^{-1}; δ_H 1.8—2.2 (quintet, 2 H, CH_2^b), 2.6—2.9 (t, 2 H, CH_2^c), 3.1—3.4 (t, 2 H, CH_2^a), 4.05 (s, 2 H, CH_2^d), 4.85 (s, 2 H, CH_2^e), and 6.8—7.6 (m, 8 H, ArH); *m/z* 311 (M^+) (Found: C, 73.35; H, 5.66; N, 4.30. $C_{19}H_{18}ClNO$ requires C, 73.17; H, 5.82; N, 4.49%).

Compound (**1f**), yield 75%, m.p. 105 °C; $\lambda_{max.}$ 255 and 295 nm; $\nu_{max.}$ 1 605, 1 490, and 1 230 cm^{-1}; δ_H 1.8—2.2 (quintet, 2 H, CH_2^b), 2.6—3.0 (t, 2 H, CH_2^c), 3.1—3.4 (t, 2 H, CH_2^a), 4.0 (s, 2 H, CH_2^d), 4.6 (s, 2 H, CH_2^e), and 6.6—7.5 (m, 8 H, ArH); *m/z* 311 (M^+) (Found: C, 73.0, H, 5.7; N, 4.4. $C_{19}H_{18}ClNO$ requires C, 73.17; H, 5.82; N, 4.49%).

Compound (**1g**), yield 70%, m.p. 80 °C; $\lambda_{max.}$ 260 and 292 nm; $\nu_{max.}$ 1 600, 1 485, and 1 245 cm^{-1}; δ_H 1.8—2.2 (quintet, 2 H, CH_2^b), 2.6—2.9 (t, 2 H, CH_2^c), 3.1—3.4 (t, 2 H, CH_2^a), 4.1 (s, 2 H, CH_2^d), 4.8 (s, 2 H, CH_2^e), and 6.6—7.5 (m, 7 H, ArH); *m/z* 346 (M^+) (Found: C, 65.7; H, 4.81; N, 4.2. $C_{19}H_{17}Cl_2NO$ requires C, 65.89; N, 4.95; N, 4.05%).

General Procedure for the Synthesis of Bispyrroloquinolines (**3a**—**g**).—A solution of *m*-chloroperbenzoic acid (80%; 2.15 g, 10 mmol) in dichloromethane (50 ml) was added dropwise to a well-stirred solution of (**1a**—**g**) (10 mmol) in dichloromethane (75 ml) at 0—5 °C during 1 h. The mixture was stirred for an additional 12 h at room temperature and then successively washed with 10% aqueous sodium carbonate and saturated brine, and dried. The solvent was removed to give a crude residue which was purified by chromatography over neutral alumina. Compounds (**3a**—**f**) were eluted with petroleum while compound (**3g**) was eluted with petroleum–benzene (1:1). All the products (**3a**—**g**) were recrystallized from dichloromethane–petroleum.

Compound (**3a**), yield 30%, m.p. 158 °C; $\lambda_{max.}$ 240 and 280 nm; $\nu_{max.}$ 1 490, 1 230, and 990 cm^{-1}; δ_H 2.1—2.2 (quintet, 4 H, CH_2^b, *J* 6 Hz), 2.9—3.0 (t, 4 H, CH_2^c, *J* 6.5 Hz), 4.0—4.08 (t, 4 H, CH_2^a, *J* 7 Hz), 4.4 (s, 2 H, CH_2^d), 5.0 (s, 4 H, CH_2^e), and 6.8—7.45 (m, 16 H, ArH); *m/z* 538 (M^+), 445 (M^+ − OPh), and 352 *etc.* (Found: C, 82.2; H, 6.3; N, 5.14. $C_{37}H_{34}N_2O_2$ requires C, 82.49; H, 6.37; N, 5.2%).

Compound (**3b**), yield 35%, m.p. 152 °C; $\lambda_{max.}$ 240 and 280 nm; $\nu_{max.}$ 1 495, 1 235, and 990 cm^{-1}; δ_H 2.1—2.2 (quintet, 4 H, CH_2^b, *J* 6 Hz), 2.25 (s, 6 H, Ar*Me*), 2.9—3.0 (t, 4 H, CH_2^c, *J* 6.5 Hz), 4.0—4.08 (t, 4 H, CH_2^a, *J* 7 Hz), 4.38 (s, 2 H, CH_2^d), 4.98 (s, 4 H, CH_2^e), and 6.7—7.4 (m, 14 H, ArH); *m/z* 566 (M^+), 459 (M^+ − $OPhCH_3$), and 352 *etc.* (Found: C, 82.45; H, 6.54; N, 4.89. $C_{39}H_{38}N_2O_2$ requires C, 82.65; H, 6.76; N, 4.95%).

Compound (**3c**), yield 30%, m.p. 141 °C; $\lambda_{max.}$ 240 and 280 nm; $\nu_{max.}$ 1 495, 1 235, and 1 000 cm^{-1}; δ_H 2.1—2.3 (m, 10 H, CH_2^b + Ar*Me*), 2.9—3.0 (t, 4 H, CH_2^c), 4.0—4.2 (t, 4 H, CH_2^a), 4.4 (s, 2 H, CH_2^d), 4.95 (s, 4 H, CH_2^e), and 6.75—7.45 (m, 14 H, ArH); *m/z* 566 (M^+) (Found: C, 82.40; H, 6.49; N, 4.8. $C_{39}H_{38}N_2O_2$ requires C, 82.64; H, 6.76; N, 4.95%).

Compound (**3d**), yield 40%, m.p. 175 °C; $\lambda_{max.}$ 242 and 282 nm; $\nu_{max.}$ 1 495, 1 220, and 995 cm^{-1}; δ_H 2.0—2.48 (m, 16 H, CH_2^b + Ar*Me*), 2.84—3.16 (t, 4 H, CH_2^c), 3.92—4.2 (t, 4 H, CH_2^a), 4.36 (s, 2 H, CH_2^d), 5.0 (s, 4 H, CH_2^d), and 6.58—7.44 (m, 12 H, ArH); *m/z* 594 (M^+) (Found: C, 82.59; H, 7.20; N, 4.80. $C_{41}H_{42}N_2O_2$ requires C, 82.78; H, 7.12; N, 4.71%).

Compound (**3e**), yield 30%. m.p. 155 °C; $\lambda_{max.}$ 240 and 276 nm; $\nu_{max.}$ 1 490, 1 235, and 990 cm^{-1}; δ_H 2.1—2.2 (quintet, 4 H, CH_2^b), 2.9—3.04 (t, 4 H, CH_2^c), 4.0—4.1 (t, 4 H, CH_2^a), 4.4 (s, 2 H, CH_2^d), 5.0 (s, 4 H, CH_2^e), and 6.5—7.6 (m, 14 H, ArH); *m/z* 607 (M^+) (Found: C, 73.25; H, 5.2; N, 4.7. $C_{37}H_{32}Cl_2N_2O_2$ requires C, 73.13; H, 5.31; N, 4.61%).

Compound (**3f**), yield 40%, m.p. 207 °C; $\lambda_{max.}$ 240 and 282 nm; $\nu_{max.}$ 1 495, 1 230, and 995 cm^{-1}; δ_H 2.04—2.48 (quintet, 4 H, CH_2^b), 2.88—3.2 (t, 4 H, CH_2^c), 3.88—4.16 (t, 4 H, CH_2^a), 4.4 (s, 2 H, CH_2^d), 4.92 (s, 4 H, CH_2^e), and 6.6—7.6 (m, 14 H, ArH); *m/z* 607 (M^+) (Found: C, 73.43; H, 5.15; N, 4.5. $C_{37}H_{32}Cl_2N_2O_2$ requires C, 73.13; H, 5.31; N, 4.61%).

Compound (**3g**), yield 45%, m.p. 197 °C; $\lambda_{max.}$ 240 and 285 nm; $\nu_{max.}$ 1 490, 1 235, and 990 cm^{-1}; δ_H 2.0—2.48 (quintet, 4 H, CH_2^b), 2.84—3.2 (t, 4 H, CH_2^c), 3.96—4.2 (t, 4 H, CH_2^a), 4.4 (s, 2 H, CH_2^d), 5.0 (s, 4 H, CH_2^e), and 6.52—7.6 (m, 12 H, ArH); *m/z* 676 (M^+) (Found: C, 65.45; H, 4.40; N, 4.05. $C_{37}H_{30}Cl_4N_2O_2$ requires C, 65.68; H, 4.47; N, 4.14%).

General Procedure for the Synthesis of the Pyrroloquinolines (**5a**—**g**).—*m*-Chloroperbenzoic acid (80%; 1.1 g, 5 mmol) dissolved in dichloromethane (25 ml) was slowly added to a well-stirred solution of 1-aryloxy-4-tetrahydroquinol-1-ylbut-2-yne (**1a**—**g**) (5 mmol) in dichloromethane (40 ml) at 0—5 °C during 1 h. The mixture was stirred for a further 45 min at the same temperature and then evaporated under reduced pressure at 0—5 °C. The residue was dissolved in cold dimethylformamide (15 ml) and a solution of potassium cyanide (1 g, excess) in water (3 ml) was added to it; the mixture was then warmed at 50—60 °C for 2 h. After this it was poured into water and extracted with ether. The combined organic extracts were washed thrice with saturated brine, dried, and evaporated to give a crude mass which was purified by chromatography over basic alumina. Compounds (**5a**—**d**) were eluted with petroleum while compounds (**5e**—**g**) were eluted with petroleum–benzene (1:1). All the products (**5a**—**g**) were recrystallized from chloroform–petroleum.

Compound (**5a**), yield 60%, m.p. 144 °C; $\lambda_{max.}$ 240 and 278 nm; $\nu_{max.}$ 2 250, 1 590, 1 490, and 1 230 cm^{-1}; δ_H 2.0—2.4 (quintet, 2 H, CH_2^b, *J* 6 Hz), 2.8—3.2 (t, 2 H, CH_2^c, *J* 5.5 Hz), 3.85 (s, 2 H, CH_2^d), 4.0—4.3 (t, 2 H, CH_2^a, *J* 5.5 Hz), 5.25 (s, 2 H, CH_2^e), and 6.9—7.7 (m, 8 H, ArH); *m/z* 302, 276 (M^+ − CN), and 209 (M^+ − OPh) *etc.* (Found: C, 79.8; H, 6.2; N, 9.0. $C_{20}H_{18}N_2O$ requires C, 79.44; H, 6.0; N, 9.27%).

Compound (**5b**), yield 60%, m.p. 95 °C; $\lambda_{max.}$ 245 and 278 nm; $\nu_{max.}$ 2 280, 1 590, 1 485, and 1 240 cm^{-1}; δ_H 2.3 (br s, 5 H, CH_2^b + Ar*Me*), 2.9—3.2 (t, 2 H, CH_2^c), 3.85 (s, 2 H, CH_2^d), 4.1—4.3 (t, 2 H, CH_2^a), 5.2 (s, 2 H, CH_2^e), and 6.9—7.7 (m, 7 H, ArH); *m/z* 316 (M^+) (Found: C, 80.05; H, 6.25; N, 8.6. $C_{21}H_{20}N_2O$ requires C, 79.7; H, 6.37; N, 8.86%).

Compound (**5c**), yield 55%, m.p. 186 °C; $\lambda_{max.}$ 245 and 280 nm; $\nu_{max.}$ 2 250, 1 590, 1 485, and 1 240 cm^{-1}; δ_H 2.0—2.4 (m, 5 H, CH_2^b + Ar*Me*), 2.8—3.2 (t, 2 H, CH_2^c), 3.9 (s, 2 H, CH_2^d), 4.1—4.4 (t, 2 H, CH_2^a), 5.3 (s, 2 H, CH_2^e), and 6.9—7.9 (m, 7 H, ArH); *m/z* 316 (M^+) (Found: C, 80.0; H, 6.7; N, 9.15. $C_{21}H_{20}N_2O$ requires C, 79.70; H, 6.37; N, 8.86%).

Compound (**5d**), yield 65%, m.p. 118 °C; $\lambda_{max.}$ 240 and 278 nm; $\nu_{max.}$ 2 260, 1 595, 1 505, and 1 240 cm^{-1}; δ_H 2.0—2.4 (m, 8 H, CH_2^b + Ar*Me*), 2.8—3.2 (t, 2 H, CH_2^c), 3.9 (s, 2 H, CH_2^d), 4.1—4.3 (t, 2 H, CH_2^a), 5.3 (s, 2 H, CH_2^e) and 6.8—7.6 (m, 6 H, ArH);

m/z 330 (M^+) (Found: C, 80.15; H, 6.55; N, 8.4. $C_{22}H_{22}N_2O$ requires C, 79.95; H, 6.71; N, 8.48%).

Compound (**5e**), yield 65%, m.p. 135 °C; $\lambda_{max.}$ 242 and 278 nm; $\nu_{max.}$ 2 260, 1 590, 1 490, and 1 240 cm^{-1}; δ_H 2.1—2.4 (quintet, 2 H, CH_2^b, *J* 6 Hz), 2.8—3.2 (t, 2 H, CH_2^c, *J* 5.5 Hz), 3.9 (s, 2 H, CH_2^d), 4.1—4.3 (t, 2 H, CH_2^a, *J* 5.5 Hz), 5.3 (s, 2 H, CH_2^e), and 6.9—7.8 (m, 7 H, ArH); *m/z* 336 (M^+) (Found: C, 71.2; H, 5.2; N, 8.05. $C_{20}H_{17}ClN_2O$ requires C, 71.3; H, 5.09; N, 8.32%).

Compound (**5f**), yield 75%, m.p. 133 °C; $\lambda_{max.}$ 245 and 278 nm; $\nu_{max.}$ 2 260, 1 590, 1 490, and 1 230 cm^{-1}; δ_H 2.1—2.3 (quintet, 2 H, CH_2^b), 2.8—3.1 (t, 2 H, CH_2^c), 3.85 (s, 2 H, CH_2^d), 4.0—4.3 (t, 2 H, CH_2^a), 5.2 (s, 2 H, CH_2^e), and 6.85—7.6 (m, 7 H, ArH); *m/z* 336 (M^+) (Found: C, 71.2; H, 5.25; N, 8.1. $C_{20}H_{17}ClN_2O$ requires C, 71.3; H, 5.09; N, 8.32%).

Compound (**5g**), yield 65%, m.p. 191 °C; $\lambda_{max.}$ 245 and 280 nm; $\nu_{max.}$ 2 265, 1 590, 1 490, and 1 245 cm^{-1}; δ_H 2.0—2.4 (quintet, 2 H, CH_2^b), 2.8—3.1 (t, 2 H, CH_2^c), 3.85 (s, 2 H, CH_2^d), 4.0—4.35 (t, 2 H, CH_2^a), 5.3 (s, 2 H, CH_2^e), and 6.9—7.8 (m, 6 H, ArH); *m/z* 371 and 373 (M^+) (Found: C, 64.65; H, 4.3; N, 7.25. $C_{20}H_{16}Cl_2N_2O$ requires C, 64.69; H, 4.35; N, 7.55%).

Synthesis of the Pyrroloquinoline Derivative (**6**).—*m*-Chloroperbenzoic acid (80%; 1.1 g, 5 mmol) dissolved in dichloromethane (25 ml) was slowly added to a well-stirred solution of (**1a**) (1.4 g, 5 mmol) in dichloromethane (25 ml) at 0 °C during 1 h. The mixture was stirred for an additional hour at the same temperature, after which the solvent was removed at 0 °C under reduced pressure and the residue dissolved in cold dimethylformamide (10 ml). To this was added a solution of *p*-chlorothiophenol (1.4 g, 10 mmol) and sodium hydroxide (0.4 g, 10 mmol) in water (5 ml), and the mixture was stirred at 80 °C for 2 h under argon. The reaction mixture was then poured into water and extracted with ether. The ether extract was washed successively with 10% aqueous sodium hydroxide and saturated brine, and then dried. Concentration of the solution gave a viscous mass which was chromatographed over basic alumina using benzene–petroleum (1:1) as eluant. The product was recrystallized from chloroform–methanol.

Compound (**6**), yield 1.0 g (50%), m.p. 135 °C; $\lambda_{max.}$ 242 and 270 nm; δ_H 2.0—2.45 (quintet, 2 H, CH_2^d), 2.8—3.2 (t, 2 H, CH_2^c), 3.9—4.25 (t, 2 H, CH_2^a), 4.4 (s, 2 H, CH_2^d), 5.0 (s, 2 H, CH_2^e), and 6.8—7.75 (m, 12 H, ArH) (Found: C, 71.3; H, 5.2; N, 3.3. $C_{25}H_{22}ClNOS$ requires C, 71.5; H, 5.3; N, 3.3%).

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