Pyrazolo[1,5-*f*]phenanthridine and Derivatives: Electrochemical and Photochemical Synthesis

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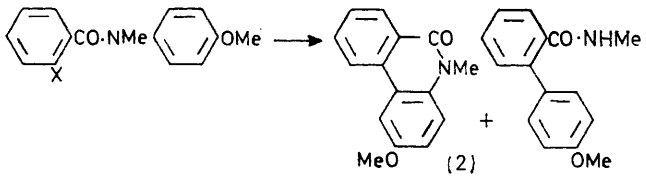
5-(2-Chlorophenyl)-1-phenylpyrazole affords a good yield of pyrazolo[1.5-*f*]phenanthridine on electroreduction in dimethylformamide and on irradiation in cyclohexane at 254 nm. 2-Methyl-, 2-phenyl-, and 5,6-methylenedioxy-2-phenyl-pyrazolo[1,5-*f*]phenanthridine were also prepared from the appropriately substituted pyrazoles. 5-(2-Bromophenyl)-1,3-diphenylpyrazole also undergoes these reactions. Pyrazolo[1,5-*f*]phenanthridine and its derivatives form charge-transfer complexes with 1,3,5-trinitrobenzene and with picric acid.

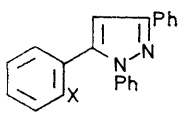
In many cases the reduction of aryl halides involves initial addition of an electron to the lowest unfilled molecular orbital to give a radical anion, which decomposes with fragmentation of the carbon–halogen bond to a σ-radical and halide ion. The σ-radical can then abstract a hydrogen atom from the solvent.[1] Alternatively, with suitable substrates, this σ-radical can undergo intramolecular cyclisation involving a neighbouring phenyl group, as in the reduction of 2-bromo- and 2-iodo-*N*-methylbenzanilides (1) to give the *N*-methylphenanthridone (2) (and other products).[2] This reaction is particularly appropriate for synthesis of aromatic nitrogen heterocycles because the heteroatom lowers the energy of the first unoccupied π-orbital. Large negative reduction potentials are therefore not necessary and in the cases examined here the initially formed radical ion is still sufficiently energetic to cause fragmentation of a carbon–chlorine bond.

The pyrazoles (3; X = Cl or Br) are readily prepared by treating the appropriate halogeno-chalcones with phenylhydrazine and oxidising the resulting pyrazoline with lead(IV) acetate.[3] Electroreduction of either pyrazole in dimethylformamide afforded

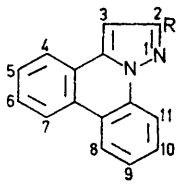


(1) X = Br or I (2)

+ (1; X = H)

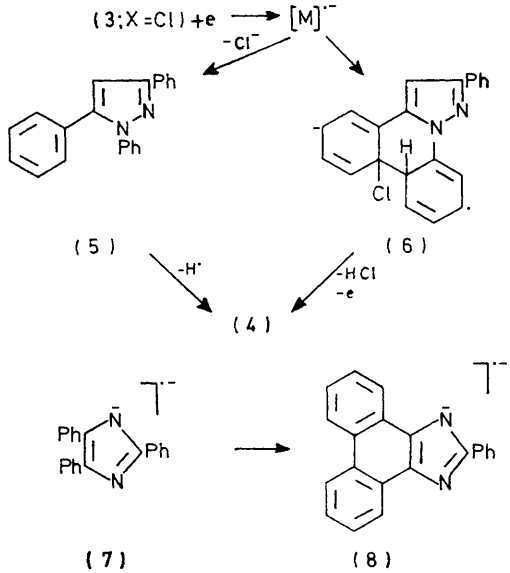


(3)



(4)

2-phenylpyrazolo[1,5-*f*]phenanthridine (4; R = Ph) in high yield. N.m.r. analysis of the total reaction mixture showed the presence of 1,3,5-triphenylpyrazole (3; X = H), which results from the intermediate σ-radical abstracting a hydrogen atom from the solvent.



These reductions required slightly more than 1 Faraday mol^{-1}. If one allows for some replacement of halogen by hydrogen (which requires 1·6—2·0 Faraday mol^{-1}),[4] the cyclisation process thus requires 1 Faraday mol^{-1} with the stoicheiometry (3; X = Cl or Br) + e ⟶ (4) + X$^-$ + ½H$_2$.

As an alternative mechanism to cyclisation *via* a σ-radical (5) we can consider that the radical anion undergoes an intramolecular reaction to give a non-aromatic intermediate of which (6) is one canonical form and which loses the elements of hydrogen chloride and one electron to give the aromatic product. Reactions somewhat analogous to this are known. The radical dianion of lophine (7), for example, cyclises with loss of hydrogen to give the radical dianion (8).[5] We have no firm evidence for cyclisation at either the σ-radical or the radical anion stage. However the cyclisation cannot involve a carbanion obtained by further reduction of the σ-radical (5) since attack by an anionic species on an unactivated benzene ring

[1] J. G. Lawless and M. D. Hawley, *J. Electroanalyt. Chem.*, 1969, **21**, 365; L. Nadjo and J. M. Saveant, *ibid.*, 1971 **30**, 41; R. P. van Duyne and C. N. Reilley, *Analyt. Chem.*, 1972, **44**,158; D. E. Bartak, D. J. Houser, B. C. Rudy, and M. D. Hawley, *J. Amer. Chem. Soc.*, 1972, **94**, 7526; K. Alwair and J. Grimshaw, *J.C.S. Perkin II*, 1973, 1150, 1811.

[2] J. Grimshaw and J. Trocha-Grimshaw, *Tetrahedron Letters*, 1974, 993.

[3] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1966, 1536.

[4] J. Grimshaw and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1974, 1383.

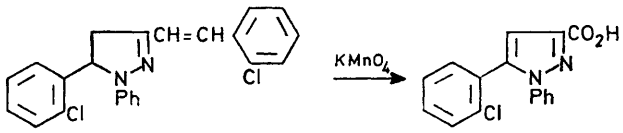
[5] K. Volkamer, H. Kiesele, and H. Zimmermann, *Tetrahedron*, 1972, **28**, 5667; H. Kiesele, K. Volkamer, and H. Zimmermann, *Ber. Bunsengesellschaft Phys. Chem.*, 1973, **77**, 108.

and the subsequent loss of hydride ion, which would be necessary to arrive at the product, is unlikely to proceed faster than protonation of the anion by extraneous water.

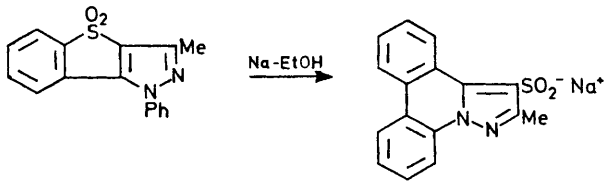
Photochemical intramolecular cyclisation of suitable aryl halides is well known.[6,7] The pyrazoles (3; X = Cl or Br) show a long-wavelength u.v. absorption band around 260 nm (see Table) and they were readily converted into (4; R = Ph) by irradiation in cyclohexane at 254 nm (low-pressure mercury lamp). Since the orbital which holds the unpaired electron in the electrochemically generated radical anion also participates in one of the photoexcited states of the molecule, both the electrochemical and the photochemical reaction would be expected to give the same products. In iodobenzenes a transition associated with the iodine atom is superimposed on the long-wavelength transition of the aromatic system.[6] The photoexcited state of our pyrazole may decompose with carbon–halogen bond fragmentation to give the σ-radical (5), which cyclises. Alternatively the excited state may cyclise to a non-aromatic intermediate which then loses hydrogen halide to give the final product (4). Evidence against the second alternative is the fact that 1,3,5-triphenylpyrazole gave no 2-phenylpyrazolo[1,5-*f*]phenanthridine on irradiation under the same conditions as the chloro-compound or in the presence of iodine.

The parent pyrazolo[1,5-*f*]phenanthridine (4; R = H) and its 2-methyl derivative were obtained from 5-(2-chlorophenyl)-1-phenylpyrazole and its 3-methyl derivative, respectively, in high yields by both the electrochemical and the photochemical technique. In the n.m.r. spectrum the proton at position 3 resonates further downfield than the corresponding 4-proton in the related 1,5-diphenylpyrazole and this distinction was used for the analysis of crude reaction mixtures which were suspected of containing both products. This downfield shift is caused by the magnetic anisotropy of the aromatic systems. The pyrazolophenanthridine, being rigidly planar, causes a more pronounced downfield shift than the diphenylpyrazole where rotation about the phenyl–pyrazole bond is possible. The derivatives of pyrazolo[1,5-*f*]phenanthridine formed charge-transfer complexes with 1,3,5-trinitrobenzene and with picric acid.

Preparation of 5-(2-chlorophenyl)-1-phenylpyrazole presented some problems. 3-(2-Chlorophenyl)propenal phenylhydrazone did not form the pyrazoline on treatment with acid or on distillation. Treatment of 3-methyl-1-phenyl-5-(2-chlorophenyl)pyrazole with permanganate failed to convert the methyl substituent into carboxy in good yield. However oxidation of the pyrazoline (9) with permanganate gave 2-chlorobenzoic acid and the 1,5-diphenylpyrazole-3-carboxylic acid (10), which were readily separated by fractional precipitation with acid from their solution in base. This process is successful probably because 2-chlorobenzoic acid (pK_a 2·94 in water [8]) is a relatively strong carboxylic acid. A pK_a value of 3·60 in water [9] has been recorded for 1-phenylpyrazole-3-carboxylic acid which suggests that (10) is not an exceptionally weak acid. Decarboxylation of (10) gave 5-(2-chlorophenyl)-1-phenylpyrazole.



(9) (10)



(11) (12)

2-Methylpyrazolo[1,5-*f*]phenanthridine is the only derivative of this ring system described in the literature.[10,11] It was obtained by reduction of the sulphone (11) with sodium–ethanol to give a precipitate of the sodium sulphinate (12). Reaction probably proceeds by addition of one electron and cleavage of a carbon–sulphur bond to give sulphinate and a σ-radical which cyclises on to the adjacent phenyl ring. The free sulphinic acid loses sulphur dioxide to yield the methyl heterocycle (4; R = Me).[10] This product was identical with a sample prepared by the Pschorr cyclisation of 1-(2-aminophenyl)-3-methyl-5-phenylpyrazole. Our material was identical with a sample prepared from (11). The Pschorr cyclisation of 5-(2-aminophenyl)-1-phenylpyrazoles does not occur since the intermediate diazonium salt reacts rapidly at the 4-position of the pyrazole ring to yield a cinnoline derivative.[11]

The foregoing results make possible a comparison of the electrochemical and photochemical routes for the synthesis of the same heterocyclic ring system. The product can be isolated from the photochemical reaction mixture by simple evaporation of the solvent. A longer work-up procedure is necessary with the electrochemical reaction in order to remove the supporting electrolyte, and this involves some loss of material. Material can also be lost by diffusion from the cathode

[6] R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Edn.*, 1968, **7**, 36.

[7] A. Fozard and C. K. Bradsher, *J. Org. Chem.*, 1967, **32**, 2966; P. W. Jeffs and J. F. Hansen, *J. Amer. Chem. Soc.*, 1967, **89**, 2798; W. A. Henderson, R. Lopresti, and A. Zweig, *ibid.*, 1969, **91**, 6049; Z. Horii, Y. Nakashita, and C. Iwata, *Tetrahedron Letters*, 1971, 1167; H. Hara, O Hoshino, and B. Umezawa, *ibid.*, 1972, 5031; T. Kametani and K. Fukumota, *Accounts Chem. Res.*, 1972, **5**, 212; N. E. Brightwell and G. W. Griffin, *J.C.S. Chem. Comm.*, 1973, 37.

[8] J. F. J. Dippy, F. R. Williams, and R. H. Lewis, *J. Chem. Soc.*, 1935, 343.

[9] S. Tobak, I. I. Grandberg, and A. N. Kost, *Tetrahedron*, 1966, **22**, 2703.

[10] W. J. Barry and E. W. McClelland, *J. Chem. Soc.*, 1935, 471; W. J. Barry, I. L. Finar, and A. B. Simmonds, *ibid.*, 1956, 4974.

[11] I. L. Finar and A. B. Simmonds, *J. Chem. Soc.*, 1958, 200.

to the anode chamber during reaction. Such factors have an important bearing on the isolated yield from small-scale reactions and favour the photochemical route. For reactions on a larger scale choice of method will depend on the availability of the specialised apparatus required for either route.

The Pschorr synthesis *via* diazonium salts [12] is an alternative route and the choice between these reactions for a given preparation will depend on the relative availability of the starting amino- or halogeno-compound. Some Pschorr-like reactions appear to proceed by a homolytic and others by a heterolytic pathway. Recently [13] good yields in the latter reaction have been obtained under reducing conditions which allow the generation of phenyl σ-radicals from the diazonium salt so that the reaction passes through the same intermediate as that proposed for the electrochemical and photochemical reactions.

EXPERIMENTAL

Dimethylformamide was kept over anhydrous copper sulphate and then distilled under nitrogen (b.p. 42° at 12 mmHg). Nitrogen was purified over the BTS catalyst [14] and dried over a molecular sieve. The potentiostat for electrochemical reductions was constructed in this department; all potentials are measured *vs.* s.c.e.–1·0M-$NaNO_3$–0·1M-Pr_4NClO_4 in dimethylformamide (salt bridge). An H-type cell was used for reduction with a mercury cathode, a platinum anode, and anode compartment containing 0·1M-Pr_4NClO_4 in dimethylformamide.[15] For small-scale use the anode and cathode chambers had diameter 2·5 cm and contained up to 25 ml of solution. A hydrazine sulphate coulometer [16] was placed in series.

5-(2-*Chlorophenyl*)-1,3-*diphenylpyrazole* (3; X = Cl).—A solution of 3-(2-chlorophenyl)-1-phenylprop-2-en-1-one [17] (5 g) in acetic acid (20 ml) and phenylhydrazine (4 ml) was heated on a water-bath for 2 h. Dilution with ethanol (20 ml) and cooling precipitated 5-(2-chlorophenyl)-1,3-diphenyl-Δ²-pyrazoline (5·8 g), m.p. 136—137° (lit.,[18] 137°). The pyrazoline (5·0 g) was dissolved in dichloromethane (25 ml), mixed with lead(IV) acetate (10 g) in dichloromethane (20 ml), and left at room temperature for 24 h; aqueous acetic acid was then added, followed by hydrazine hydrate to destroy the lead(IV) oxide. The organic phase was washed with water, dried (K_2CO_3), and filtered through a short column of alumina. Evaporation afforded 5-(2-*chlorophenyl*)-1,3-*diphenylpyrazole*, as pale yellow needles (4·1 g), m.p. 148—149° (from ethanol) (Found: C, 76·0; H, 4·7; Cl, 10·5; N, 8·6. $C_{21}H_{15}ClN_2$ requires C, 76·2; H, 4·6; Cl, 10·7; N, 8·5%).

5-(2-*Bromophenyl*)-1,3-*diphenylpyrazole* (3; X = Br).—3-(2-Bromophenyl)-1-phenylprop-2-en-1-one [19] and phenylhydrazine, treated as above, afforded 5-(2-*bromophenyl*)-1,3-*diphenyl*-Δ²-*pyrazoline* as yellow needles, m.p. 147—148° (from ethanol) (Found: C, 67·1; H, 4·6; Br, 21·3; N, 7·7. $C_{21}H_{17}BrN_2$ requires C, 66·9; H, 4·5; Br, 21·3; N, 7·4%).

Oxidation of the pyrazoline with lead(IV) acetate gave 5-(2-*bromophenyl*)-1,3-*diphenylpyrazole*, as pale yellow rhombs, m.p. 135—136° (from ethanol) (Found: C, 67·1; H, 4·1; Br, 21·4; N, 7·8. $C_{21}H_{15}BrN_2$ requires C, 67·2; H, 4·0; Br, 21·3; N, 7·5%).

5-(2-*Chloro*-4,5-*methylenedioxyphenyl*)-1,3-*diphenylpyrazole*.— 3-(2-Chloro-4,5-methylenedioxyphenyl)-1-phenylpropenone [20] and phenylhydrazine afforded 5-(2-*chloro*-4,5-*methylenedioxyphenyl*)-1,3-*diphenyl*-Δ²-*pyrazoline*, as pale yellow needles, m.p. 159—160° (from ethyl acetate) (Found: C, 69·9; H, 4·6; Cl, 9·2; N, 7·4. $C_{22}H_{17}ClN_2O_2$ requires C, 70·1; H, 4·6; Cl, 9·4; N, 7·4%). Oxidation with lead(IV) acetate gave the corresponding pyrazole as plates, m.p. 134—135° (from ethanol) (lit.,[20] 149—150°) (Found: C, 70·6; H, 4·1; Cl, 9·2; N, 7·5. Calc. for $C_{22}H_{15}ClN_2O_2$: C, 70·5; H, 4·0; Cl, 9·5; N, 7·5%).

5-(2-*Chlorophenyl*)-3-*methyl*-1-*phenylpyrazole*.—The corresponding Δ²-pyrazoline, prepared as described by v. Auwers,[21] had m.p. 99—100° (lit.,[21] 87°), τ 4·65 (q, H_a), 6·46 (q, H_b), and 7·43 (q, H_c) (pyrazoline ring protons) (J_{ab} 12, J_{ac} 8, J_{bc} 17 Hz), and 7·98 (s, Me). Oxidation with lead(IV) acetate afforded 5-(2-*chlorophenyl*)-3-*methyl*-1-*phenylpyrazole* as needles, m.p. 74—75° (from aqueous ethanol) (Found: C, 71·8; H, 5·0; Cl, 13·3; N, 10·6. $C_{16}H_{13}ClN_2$ requires C, 71·5; H, 4·9; Cl, 13·2; N, 10·4%).

5-(2-*Chlorophenyl*)-1-*phenylpyrazole*-3-*carboxylic Acid*.—1,5-Bis-(2-chlorophenyl)penta-1,4-dien-3-one [22] (20 g), phenylhydrazine (8 g), and acetic acid (6 ml) were refluxed in ethanol (1 l) for 3 h. The solution was then concentrated to 300 ml and cooled. 5-(2-Chlorophenyl)-3-(2-chlorostyryl)-1-phenyl-Δ²-pyrazoline separated and crystallised from ethanol as yellow needles (12·7 g), m.p. 143—145° (lit.,[22] 145°), τ ($CDCl_3$) 2·20—3·40 (15H, aromatic and olefinic) and 4·36 (q, H_a), 6·18 (q, H_b), and 7·08 (q, H_c) (J_{ab} 12·2, J_{ac} 6·8, J_{bc} 17·0 Hz).

The pyrazoline (12 g) and powdered potassium permanganate (24 g) were vigorously stirred with water (720 ml) at room temperature for 3 h. More potassium permanganate (24 g) was then added and the mixture heated on a water-bath with stirring for 3 h. Finally potassium permanganate (10 g) was added and heating continued for 5 h. The precipitated manganese dioxide was filtered off and washed with hot water, and sodium hydrogen sulphite solution was added to decolourise the filtrate. The filtrate was adjusted to pH 4·5 with 2N-hydrochloric acid and the precipitated *carboxylic acid* (4·0 g, 44%) was filtered off. The acid crystallised from light petroleum (b.p. 100—220°) as needles, m.p. 137—140°, with resolidification and remelting at 146—149° (Found: C, 64·1; H, 3·8; Cl, 11·7; N, 9·5. $C_{16}H_{11}ClN_2O_2$ requires C, 64·3; H, 3·7; Cl, 11·9; N, 9·4%), *m/e* 300 and 298 (M^+).

5-(2-*Chlorophenyl*)-1-*phenylpyrazole*.—The above acid (4·0 g) in quinoline (10 ml) was refluxed for 3 h with copper chromite (0·4 g). The solution was cooled, diluted with ether (50 ml), filtered, and washed with 2N-hydrochloric acid. The ethereal layer was dried ($MgSO_4$) and chromatographed in ether over a column of alumina. Evaporation left 5-(2-*chlorophenyl*)-1-*phenylpyrazole* (2·0 g, 59%), which crystallised from 50% ethanol as needles, m.p.

[12] D. F. Detar, *Org. Reactions*, 1957, **9**, 409.
[13] R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 1971, **36**, 1769; F. F. Gadallah, A. A. Cantu, and R. M. Elofson, *ibid.*, 1973, **39**, 2386.
[14] M. Schutze, *Angew. Chem.*, 1958, **70**, 697; Badische Anilin und Soda Fabrik AG, Technical Buletin ' BTS Catalyst.'
[15] ' Organic Electrochemistry,' ed. M. M. Baizer, Marcel Dekker, New York, 1973, ch. IV.
[16] J. A. Page and J. J. Lingane, *Analyt. Chim. Acta*, 1957, **16**, 175.
[17] C. L. Bickel, *J. Amer. Chem. Soc.*, 1946, **68**, 865.
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[19] W. Davey and J. R. Gwilt, *J. Chem. Soc.*, 1957, 1008.
[20] S. G. Dev and T. S. Wheeler, *J. Univ. Bombay*, 1938, **7**, 205.
[21] K. v. Auwers and A. Kreuder, *Ber.*, 1925, **58**, 1974.
[22] F. Straus, *Ber.*, 1918, **51**, 1457.

90—91° (Found: C, 71·0; H, 4·2; Cl, 13·8; N, 10·8. $C_{15}H_{11}ClN_2$ requires C, 70·7; H, 4·4; Cl, 13·9; N, 11·0%), *m/e* 256 and 254 (M^+), τ ($CDCl_3$) 2·28 (1H, d, *J* 1·6 Hz), 2·6—2·9 (11H, aromatic), and 2·91 (1H, d, *J* 1·6 Hz).

Polarography.—A dropping mercury electrode, a platinum wire anode, and a s.c.e. reference electrode–1·0M-$NaNO_3$–0·1M-Pr_4NClO_4 in dimethylformamide (salt bridge) were used. The cell solution contained the substrate ($1·0 \times 10^{-3}$M) and Pr_4NClO_4 (0·1M) in dimethylformamide. The results are given in the Table.

Polarographic data (solvent dimethylformamide; 0·1M-Pr_4NClO_4) and u.v. spectra (cyclohexane) of 1,5-diphenylpyrazole and pyrazolo[1,5-*f*]phenanthridine derivatives

	$-E_{\frac{1}{2}}$/V *vs.* s.c.e.[a]	$\lambda_{max.}$/nm (ε)
Pyrazoles		
5-(2-Chlorophenyl)-1-phenyl	2·17, 2·33	235(12,400), 252(13,400)
5-(2-Chlorophenyl)-3-methyl-1-phenyl	2·19, 2·35	239(14,800), 256(15,400)
5-(2-Chlorophenyl)-1,3-diphenyl	2·12, 2·29	259(27,100)
5-(2-Bromophenyl)-1,3-diphenyl	2·07, 2·29	261(24,400)
Pyrazolo[1,5-*f*]-phenanthridines	2·31 [b]	255(35,900), 267(2,300), 276(26,700), 308(5400), 317(6600), 332(6200)
Unsubst.		
2-Methyl	2·34 [b]	244(31,400), 253(36,600), 271(20,100), 282(20,300), 309(4800), 321(6100), 337(5670)
2-Phenyl	2·28 [b]	259(46,000), 265(45,800), 283(40,400), 326(7540), 341(5150)

[a] All waves had height 3·0—3·4 μA. Dropping mercury electrode with the following characteristics in 0·1M-KCl: drop time 6·3 s, flow rate $1·20 \times 10^{-3}$ g s^{-1}. [b] Reversible behaviour shown on cyclic voltammetry, sweep rate 0·04 V s^{-1}. The wave is due to formation of a radical anion.

2-*Phenylpyrazolo*[1,5-f]*phenanthridine* (4; R = Ph).—(*a*) 5-(2-Chlorophenyl)-1,3-diphenylpyrazole (1·0 g) in anhydrous dimethylformamide (15 ml) containing 0·1M-tetrapropylammonium perchlorate was reduced at a mercury pool electrode, potential −2·1 V, until the current had fallen to a negligible value. (A run with 0·20 g of pyrazole required 1·15 Faraday mol^{-1}.) Addition of water precipitated a solid (0·77 g) which was chromatographed in light petroleum (b.p. 40—60°) on alumina. Elution with light petroleum afforded a trace of gum. Elution with light petroleum–ether (1 : 1) gave a solid (0·61 g), m.p. 144—146°, which differed [t.l.c. on alumina plates eluted with light petroleum–ether (1 : 1)] from 1,3,5-triphenylpyrazole and from starting material. Recrystallisation of the product from ethanol afforded 2-*phenylpyrazolo*[1,5-f]*phenanthridine* as needles (0·52 g, 59%), m.p. 151—153° (Found: C, 85·8; H, 4·8; N, 9·7. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8; N, 9·5%), *m/e* 295 (24%), 294 (100, M^+), 293 (24), and 190 (19), τ ($CDCl_3$) 1·35 (1H), 1·70 (2H), 1·95 (3H), and 2·5 (7H) (aromatic multiplets) and 2·84 (1H, s, pyrazole ring). A mixture m.p. with 1,3,5-triphenylpyrazole was strongly depressed. 1,3,5-Triphenylpyrazole shows τ ($CDCl_3$) 2·1 (*ca.* 2H), 2·65 (*ca.* 13H), and 3·18 (1H, s, pyrazole ring).

Reactions were conducted with 0·2—1·0 g of starting material in the same volume of solvent. N.m.r. analysis of the crude product showed the presence of 1,3,5-triphenylpyrazole (20%).

In separate experiments, 5-(2-bromophenyl)-1,3-diphenylpyrazole (0·5 g) was reduced at −2·1 V to yield 2-phenylpyrazolo[1,5-*f*]phenanthridine (0·20 g, 44%), m.p. 151—153°. The total crude product contained 35% of 1,3,5-triphenylpyrazole (by n.m.r. analysis).

(*b*) In the photochemical reaction a 90 W low-pressure mercury resonance lamp was arranged around a cylindrical quartz of 200 ml capacity. 5-(2-Chlorophenyl)-1,3-diphenylpyrazole (0·3 g) in cyclohexane (100 ml) was kept under nitrogen and irradiated for 10 h after which the solution was evaporated to dryness. The product crystallised from ethanol to yield 2-phenylpyrazolo[1,5-*f*]phenanthridine, m.p. and mixed m.p. 151—154°.

In separate experiments, 5-(2-bromophenyl)-1,3-diphenylpyrazole gave (4; R = Ph), m.p. 151—153° (81%).

Treatment of 2-phenylpyrazolo[1,5-*f*]phenanthridine in ethanol with cold saturated ethanolic picric acid afforded the picric acid *adduct*, which crystallised from ethanol containing some picric acid as orange needles, m.p. 164—165° (Found: C, 61·7; H, 3·3; N, 13·3. $C_{27}H_{17}N_5O_7$ requires C, 62·0; H, 3·3; N, 13·4%). The 1,3,5-trinitrobenzene *adduct*, prepared similarly, crystallised from ethanol as orange needles, m.p. 186—188° (Found: C, 64·1; H, 3·3; N, 13·7. $C_{27}H_{17}N_5O_6$ requires C, 63·9; H, 3·4; N, 13·8%).

5,6-*Methylenedioxy*-2-*phenylpyrazolo*[1,5-f]*phenanthridine*.— 5-(2-Chloro-4,5-methylenedioxyphenyl)-1,3-diphenylpyrazole (0·50 g) was reduced electrochemically at −2·2 V as described above to give the *pyrazolophenanthridine* as needles (0·30 g, 60%), m.p. 234—235° (from dioxan), subliming at 180° and 0·1 mmHg (Found: C, 78·3; H, 4·5; N, 8·1. $C_{22}H_{14}N_2O_2$ requires C, 78·1; H, 4·2; N, 8·3%), *m/e* 338 (M^+).

2-*Methylpyrazolo*[1,5-f]*phenanthridine* (4; R = Me).—(*a*) In electrochemical reduction of 5-(2-chlorophenyl)-3-methyl-1-phenylpyrazole (0·20 g) at −2·2 V, 1·1 Faraday mol^{-1} was consumed. When the current fell to a low value, the solution became brown and a fine white precipitate began to form. The mixture was worked up as before and n.m.r. analysis of the total product (0·17 g) showed 5% of 3-methyl-1,5-diphenylpyrazole. Crystallisation of the product from ethanol afforded 2-methylpyrazolo[1,5-*f*]phenanthridine as needles (0·08 g), m.p. 110—114° (lit.,[10] 122—124°) (Found: C, 82·9; H, 5·4; N, 12·2. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·2; N, 12·1%), *m/e* 232 (100%, M^+), 231 (29), and 190 (17). There was no depression in m.p. on admixture with ' compound-A '[10] prepared from (11), or with material prepared in (*b*). The products showed identical n.m.r. spectra: τ ($CDCl_3$) 1·35—2·85 (8H, m), 3·37 (1H, s, H-3), 7·49 (3H, s, Me) (a high resolution spectrum showed $J_{H,Me}$ 0·55 Hz).

(*b*) 5-(2-Chlorophenyl)-3-methyl-1-phenylpyrazole (0·2 g) in cyclohexane (100 ml) was irradiated as previously described for 10 h. Evaporation of the solvent and crystallisation of the residue from ethanol afforded 2-methyl pyrazolo[1,5-*f*]phenanthridine as needles, m.p. 111—115° (0·16 g, 94%).

The compound in ethanol, treated with cold saturated ethanolic picric acid, afforded the picric acid *adduct*, which crystallised from ethanol containing a little picric acid as bright yellow needles, m.p. 172—175° (Found: C, 57·1; H, 3·4; N, 15·1. $C_{22}H_{15}N_2O_7$ requires C, 57·3; H, 3·3; N, 15·2%). The 1,3,5-trinitrobenzene *adduct*, prepared similarly, crystallised from ethanol as yellow needles, m.p. 184—186° (Found: C, 59·1; H, 3·4; N, 16·0. $C_{22}H_{15}N_5O_6$ requires C, 59·3; H, 3·4; N, 15·7%).

Pyrazolo[1,5-f]*phenanthridine* (4; R = H).—(*a*) 5-(2-Chlorophenyl)-1-phenylpyrazole (0·18 g) was reduced electrochemically at −2·1 V as previously described. The current decreased after passage of 1·0 Faraday mol^{-1} but did not cease. After 1·5 Faraday mol^{-1} had been consumed the reaction was stopped and the product isolated (yield 0·13 g; m.p. 117—119°). Crystallisation from aqueous ethanol afforded needles of *pyrazolo*[1,5-*f*]-*phenanthridine*, m.p. 120—121°, undepressed on admixture with material described in (*b*) (Found: C, 82·8; H, 4·7; N, 12·7. $C_{15}H_{10}N_2$ requires C, 82·5; H, 4·6; N, 12·8%), *m/e* 218 (100%, M^+), 217 (12), and 190 (37), τ ($CDCl_3$) 2·08 (d) and 3·14 (d) (pyrazole ring, *J* 2·0 Hz) and 1·3—2·9 (other protons).

(*b*) Irradiation of 5-(2-chlorophenyl)-1-phenylpyrazole (0·3 g) in cyclohexane (125 ml) for 24 h afforded pyrazolo-[1,5-*f*]phenanthridine (0·24 g, 92%) which crystallised from aqueous ethanol as needles, m.p. 114—118°. On one occasion crystals were obtained with m.p. 109—112°, resolidifying and remelting at 114—118°.

The picric acid *adduct* crystallised from ethanol containing a little picric acid as yellow needles, m.p. 164—165° (Found: C, 56·6; H, 2·9; N, 15·6. $C_{21}H_{13}N_5O_7$ requires C, 56·4; H, 2·9; N, 15·7%). The 1,3,5-trinitrobenzene *adduct* crystallised from ethanol containing an excess of reagent as yellow needles, m.p. 173—175° (Found: C, 58·4; H, 3·2; N, 16·2. $C_{21}H_{13}N_5O_6$ requires C, 58·5; H, 3·4; N, 16·2%).

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