Electrochemical Reactions. Part 24.[1] Reductive Cyclisation of *i*-(2-Halogenophenyl)-*j*-phenyl Compounds: A General Reaction

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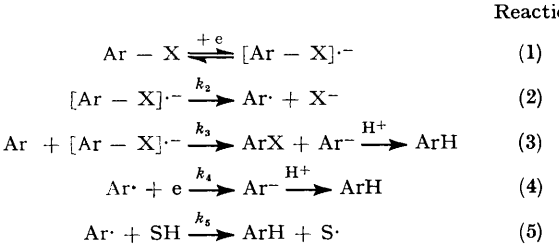
The phenyl σ-radical formed by reduction of aryl halides in an aprotic solvent undergoes efficient radical substitution on an adjacent benzene ring. Several examples of this cyclisation reaction are given. The reaction is appropriate for the synthesis of 6-membered aromatic rings where the two reacting phenyl groups are held in a *cis*-configuration by an olefin bond or another aromatic ring.

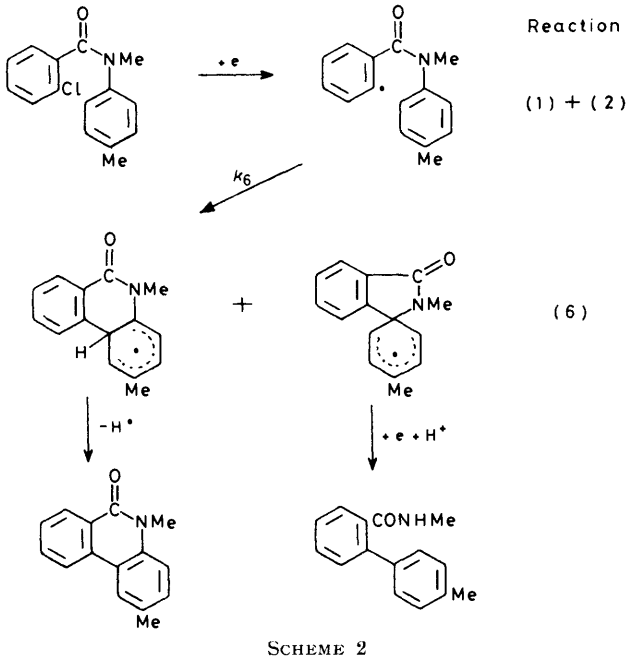
THE electrochemical reduction of aryl halides in aprotic solvents proceeds by stepwise additions of one electron and the sequence of reactions shown in Scheme 1. The



SCHEME 1 X = Cl, Br or I; SH = solvent

rate of reaction (2) varies widely with the aryl residue, the halogen, solvent, and temperature. Examples [2-4] are known where the radical-anion can be detected by e.s.r. spectroscopy and its decomposition readily followed by cyclic voltammetry and also where the radical-anion is too short lived for direct observation. Termination step (5) has been demonstrated during the reduction of 2-, 3- and 4-iodonitrobenzenes by incorporation of deuterium into the product from [$^2H_3$]acetonitrile.[4] The operation of either step (5) or a combination of termination steps (3) and (4) depending on the aryl halide substrate has been demonstrated by reduction in dimethylformamide–deuterium oxide (1%) when reactions involving carbanionic intermediates incorporate deuterium into the product.[5]

The Cyclisation Reaction.—Benzene readily undergoes radical substitution so that, for suitable substrates, a reaction sequence like that shown in Scheme 2 is possible. A final stage in this scheme involves the formal elimination of a hydrogen atom and the mechanism by which this result is achieved has not been elucidated. In previous papers of this series we have demonstrated that reaction (6) can occur in competition with the termination reactions (3), (4), and (5).[6-8] A quantitative study[7] of the reduction products from 2-halogeno-*N*-methylbenzanilides indicated that $k_6 \gg k_5$ and that k_4 becomes important only under certain predictable reaction conditions. We offered a qualitative explanation for the relative importance of termination steps (4) and (5) as due to the concentration profiles about the electrode surface of the radical-anion and σ-radical formed in steps (1) and (2). Thus depending on the value of k_2 relative to the diffusion rate for species from the electrode surface, if k_2 is larger a high concentration of σ-radical will form close to the electrode surface making reaction (4) important so that $k_4 \gg k_5$, whereas if k_2 is small then a high concentration of σ-radical will form outside the diffusion layer and $k_5 \gg k_4$. Savéant[9] has given a



SCHEME 2

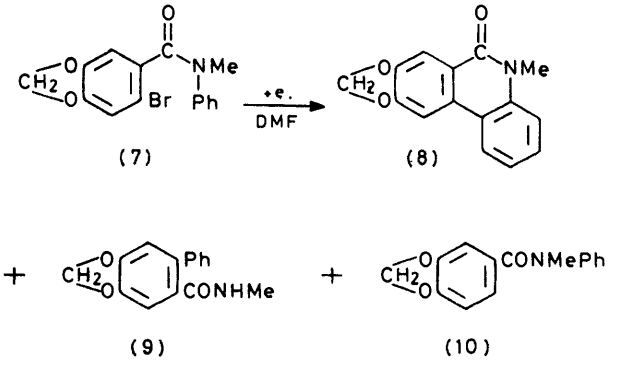
general quantitative treatment of such electrochemically initiated competitive reactions and also introduced the disproportionation reaction (3) into the scheme. In his treatment reaction (2) is considered as an equilibrium with equilibrium constant $K = k_{-2}/k_2$. The general treatment can be applied to the aryl halide case discussed here by allowing K to approach zero when this quantitative treatment of the aryl halide reaction sequence agrees with our qualitative explanation.

Electrochemical cyclisation according to the specific example given in Scheme 2 is, in general, a desirable preparative goal in the achievement of which a variable at one's disposal is the choice of halogen atom in the substrate for reduction. For a given reaction according to Schemes 1 and 2, the value of k_2 depends upon the redox potential for step (1) and the carbon–halogen bond

strength. In reactions of any preparative value the choice of halogen is limited to chlorine, bromine, or iodine by the ease of formation of the substrate. A semiquantitative examination we [3] made on the influence of redox potential and bond strength on k_2 gives sufficient information for a choice of halogen to be made. The ideal condition is that the lowest molecular weight halogen derivative consistent with rapid fragmentation of the radical-anion should be chosen as substrate. Under conditions where k_2 is small so that the radical-anion has a longer life, a competing reaction becomes capture of the radical-anion by extraneous moisture. Chloro-substituted radical-anions are expected to fragment at a satisfactory rate when the E_0 value for the parent system is more negative than −1.6 V *vs.* s.c.e. and bromo-derivatives when E_0 is more negative than −1.2 V.

The purpose of this paper is to demonstrate that the electrochemical cyclisation of aryl halides can be a high yield reaction of value in the synthesis of condensed aromatic ring systems. Our examples of the reaction are restricted to nitrogen heterocycles but the possible range of substrates is more varied than this. This electrochemical reaction is related to the Pschorr reaction in that both involve aryl radicals as reaction intermediates. In the classical Pschorr reaction [10] the radical is formed by reduction of a diazonium salt with copper powder and then elimination of nitrogen. The substrates for the electrochemical process are more easily prepared than diazonium salts, the process gives good yields, and on these counts is preferred to the Pschorr reaction. Aryl halides can also be cyclised in a photochemical process.[11] The photochemical reaction has a disadvantage in that the product absorbs light which at best screens the substrate and which may give rise to further photochemical decomposition processes.

Examples.—Reduction of the 2-bromo-*N*-methylbenzanilide (7) proceeded according to previous examples [7,8] to give a mixture of the phenanthridone (8) and the diphenyl derivative (9). A large proportion (54%) of the product (10) resulting from simple replacement of bromine by hydrogen was formed in this reaction and a better yield of the desired products would undoubtedly be obtained from reduction of the 2-chloro-compound as noted previously for a series of 2-halogeno-*N*-methylbenzanilides.[7] Formation of both a phenanthridone by 1→6 cyclisation and a diphenyl by 1→5 cyclisation are the characteristic reactions of a radical derived from a 2-halogeno-*N*-methylbenzanilide. So far, for other cyclisations we have only observed reactions by 1→6 cyclisation.

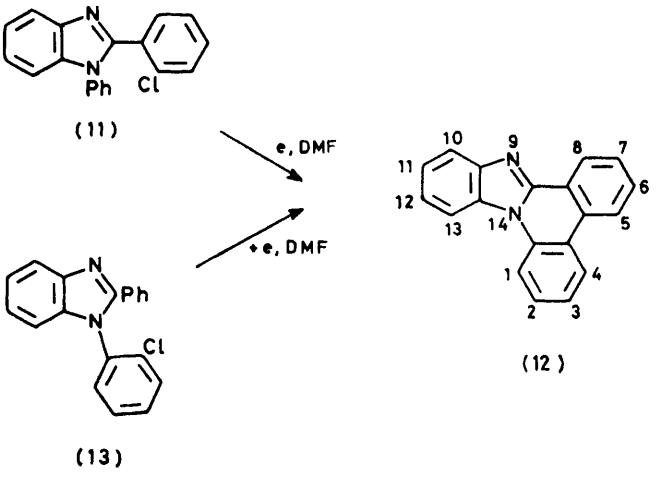


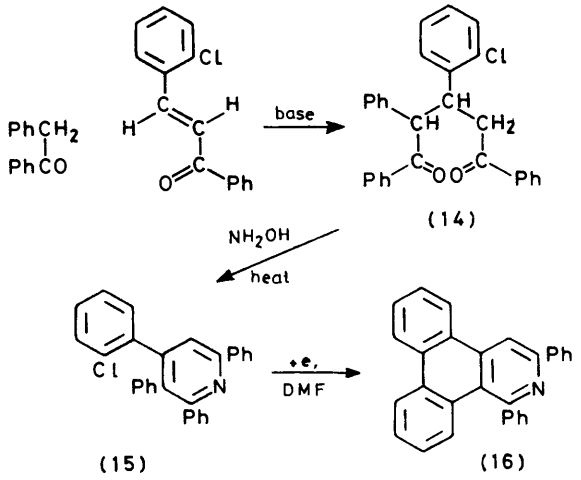
The phenanthridone (8) has also been obtained in a photochemical ring-closure reaction [12] of (7) and by the Pschorr reaction.[12,13]

Reductive cyclisation of the benzimidazole (11) to form (12) proceeded in excellent yield.[14] This reaction was followed by h.p.l.c. and the total product shown to contain 2% of 1,2-diphenylbenzimidazole formed by replacement of chlorine by hydrogen. Cyclic voltammetry of 1,2-diphenylbenzimidazole indicated no reduction wave at a potential less negative than −2.4 V *vs.* s.c.e. and choice of the chloro-compound, according to the rules for cyclisation of halogeno-compounds, gives very high yields of the desired product. The reaction follows a route equivalent to the 1→6 cyclisation only and not the 1→5 cyclisation of Scheme 2.

This condensed-cyclic product (12) was also obtained in equally good yield by reduction of the alternative benzimidazole (13).

Next, the conversion of (15) into (16) was examined as being typical for the formation of a carbocyclic 6-membered ring. The starting material is readily obtained by the route shown which proceeded analogously to the formation of 2,3,4,6-tetraphenylpyridine.[15] Cyclic voltammetry of 2,3,4,6-tetraphenylpyridine shows a reduction wave with $E_{\frac{1}{2}pc}$ −2.0 V *vs.* s.c.e. just prior to decomposition of the solvent. The background decomposition is probably due to hydrogen evolution from extraneous water catalysed at the mercury cathode by the pyridine basic centre.[16] Reduction of compound (15) at a mercury cathode in dimethylformamide consumed considerably more than 2 F mol^{-1} because of this hydrogen evolution reaction, without a decrease in current. Conversion of compound (15) into (16) was followed by h.p.l.c. and proceeded to at least 95% conversion on a small scale but it was impossible to determine the extent of conversion by integration of the

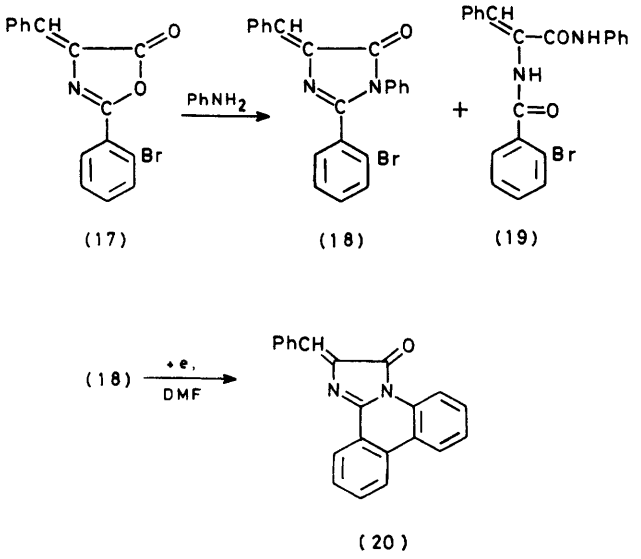




current flow. On a larger scale, prolonged reduction caused the formation of an insoluble by-product, presumably by further reduction of (16).

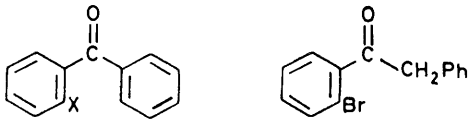
The electrochemical cyclisation to give compound (16) proceeds in a very satisfactory manner in spite of the current-consuming side reaction.

The conversion of compound (18) into (20) offers an



example of the application of this route to an unsaturated system where other electrochemical reactions could be expected.[14] In general, we are choosing reaction conditions where the most rapid reaction of the substrate radical-anion is cleavage of the carbon–halogen bond. Thus reactions of the σ-radical so formed can be expected to be dominant. Formation of the substrate by reaction of the oxazolone (17) with aniline according to the literature procedure [17] proved difficult and in our hands the principal product was the open-chain amide (19).

Since cyclisation of 2-halogeno-*N*-methylbenzanilides gives products from both 1→6 and 1→5 cyclisation processes we examined the reduction of 2-halogenobenzophenones in the hope of obtaining cyclisation to fluorenone. The major product from reduction of the chloro- and bromo-compounds (21; X = Cl or Br) proved to be benzophenone. Fluorenone could not be detected in the



(21) (22)

crude reaction mixture by v.p.c. and so amounted to less than 2% of the product. The equivalent Pschorr reaction of (21; X = N_2^+ BF_4^-) in the presence of copper powder also fails to yield any fluorenone.[18] Thermal decomposition of the diazonium salt in aqueous sulphuric acid does give rise to fluorenone by a carbonium ion mechanism.[19]

Conformational factors can be expected to be of considerable importance where the two aromatic rings involved in cyclisation are joined by a sequence of single bonds about which free rotation is possible. Such factors will probably limit the scope of the cyclisation process, thus reduction of the deoxybenzoin (22) yielded deoxybenzoin as the only product.

This cyclisation reaction is appropriate for the synthesis of 6-membered aromatic rings where the two reacting aromatic groups are held in a *cis*-configuration by an olefin bond or another aromatic ring. It has been used by other workers in a synthesis of the aporphine ring system.[20]

EXPERIMENTAL

Dimethylformamide was kept over anhydrous copper sulphate and then distilled under nitrogen, b.p. 42 °C at 12 mmHg.

Conditions for Electrochemical Reduction.—Preliminary cyclic voltammetry was conducted at a 2 mm diam. Pt sphere electrode coated with mercury and fused into a glass support tube with a platinum counter electrode and reference electrode of aqueous saturated calomel. The solution contained 10^{-3}M-substrate with 0.1M-tetrapropylammonium fluoroborate in dimethylformamide and was purged with nitrogen. Preparative-scale reductions were

TABLE 1

Cyclic voltammetry in dimethylformamide, 0.1M Pr_4NBF_4 at 0.2 V s^{-1}. Peak potential for first reduction wave.

Substrate	E_{pc}/V *vs.* s.c.e.
(7)	−2.34
1,2-Diphenylbenzimidazole	below −2.4
(11)	−2.2
(13)	−2.2
2,3,4,6-Tetraphenylpyridine	−2.1
(15)	−2.0
(17)	−1.35
2-Chlorobenzophenone	−1.76
2-Bromobenzophenone	−1.70
(22)	−1.85

carried out at a potential close to E_{pc} from cyclic voltammetry in an H-type cell with 0.1M-tetrapropylammonium fluoroborate in dimethylformamide 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. At the end of an experiment when the current had fallen to a low value the catholyte was evaporated to a small volume, diluted with water, and the product isolated either by filtration or by extraction with dichloromethane.

2-Bromo-4,5-methylenedioxybenzoic Acid.—3-Bromo-4,5-methylenedioxybenzaldehyde (4.6 g) was suspended in aqueous 2M-sodium hydroxide (40 ml) with stirring and silver nitrate (6.8 g) in a little water was added. After 24 h at room temperature the black suspension was filtered. Acidification of the filtrate with concentrated hydrochloric acid precipitated the required acid (4.8 g) m.p. 203—204 °C (lit.,[21] m.p. 204—205 °C). Oxidation of the aldehyde with potassium permanganate gave very poor yields.

2-Bromo-N-methyl-4,5-methylenedioxybenzanilide (7).—The above acid (5 g) was refluxed with an excess of thionyl chloride to give the acid chloride which with an excess of *N*-methylaniline gave 2-bromo-*N*-methyl-4,5-methylenedioxybenzanilide (4.6 g), crystallised from ethanol as needles, m.p. 131—132 °C (lit.,[12] m.p. 118—119 °C) (Found: C, 53.8; H, 3.7; Br, 24.1; N, 4.2. Calc. for $C_{15}H_{12}BrNO_3$: C, 53.9; H, 3.7; Br, 23.9; N, 4.2%); n.m.r., NMe signal at δ 3.47 at 30 °C where rapid equilibration of rotamers is expected, OCH_2O signal at δ 5.90.

Reduction of 2-Bromo-N-methyl-4,5-methylenedioxybenzanilide.—A solution of the above anilide (1.0 g) in the electrolyte (10 ml) was reduced at a mercury cathode at −2.3 V *vs.* s.c.e. After 24 h the current became negligible. The catholyte was poured into water, acidified with a little hydrochloric acid, and the product extracted with dichloromethane and dried ($MgSO_4$). Evaporation of the solvent left a residue (0.67 g) shown by n.m.r. analysis (N-Me signals) to contain compounds (8) : (10) : (9) in the ratio 13 : 54 : 33. The total reaction mixture was separated by preparative t.l.c. on silica with chloroform–methanol (5%) as eluant. The first fraction crystallised from ethanol to give 5-methyl-8,9-methylenedioxyphenanthridone (8) (0.03 g), m.p. 239—240 °C (lit.,[12, 13, 22] m.p. 238 °C) (Found: C, 71.2; H, 4.3; N, 5.7. Calc. for $C_{15}H_{11}NO_3$: C, 71.1; H, 4.4; N, 5.5%); n.m.r. ($CDCl_3$) δ 3.80 (NCH_3), 6.12 (OCH_2O), and 7.0—8.0 (ArH); M^+ 253.

The second fraction crystallised from ethanol to give *N-methyl-3,5-methylenedioxybiphenyl-2-carboxamide* (9) (0.20 g), m.p. 191—192 °C (Found: C, 70.3; H, 5.5; N, 5.3. $C_{15}H_{13}NO_3$ requires C, 70.6; H, 5.1; N, 5.5%); n.m.r. ($CDCl_3$) δ 2.61 (d, *J* 5 Hz, NHMe), 6.03 (OCH_2O), and 6.8—7.4 (ArH).

A sample of *N-methyl-3,4-methylenedioxybenzanilide* (10) prepared from the acid chloride and *N*-methylaniline had m.p. 63—64 °C (Found: C, 70.3; H, 5.1; N, 5.5. $C_{15}H_{13}NO_3$ requires C, 70.6; H, 5.1; N, 5.5%); n.m.r. ($CDCl_3$) δ 3.47 (NMe), 5.88 (OCH_2O), 6.5—7.4 (ArH); it was not isolated from the electrochemical reaction in a pure form.

2-Aminodiphenylamine.—Hydrazine hydrate (1.5 ml) and 5%-palladium charcoal (0.2 g) were added to a refluxing solution of 2-nitrodiphenylamine (2.0 g) in ethanol (10 ml). The yellow solution became colourless after 2 h and was filtered and the filtrate diluted with water to precipitate 2-aminodiphenylamine (1.6 g), m.p. 78—79 °C, which was used immediately as it rapidly darkened in air.

2-Chloro-2′-phenylaminobenzanilide.—2-Chlorobenzoyl chloride (3.0 g) was added to a solution of 2-aminodiphenylamine (1.6 g) in pyridine (15 ml). After 3 h at room temperature the mixture was poured into dilute hydrochloric acid to precipitate *2-chloro-2′-phenylaminobenzanilide* (2.7 g) which crystallised from ethanol as needles, m.p. 126—127 °C (Found: C, 70.6; H, 4.9; N, 8.8. $C_{18}H_{15}ClN_2O$ requires C, 70.7; H, 4.7; N, 8.7%).

2-(2-Chlorophenyl)-1-phenylbenzimidazole (11).—A solution of the above benzanilide (1.0 g) in 2-chlorobenzoyl chloride (5 ml) was heated at 200 °C for 3 h, cooled, and diluted with benzene. The hydrochloride which separated was collected and shaken with aqueous ethanol and ammonia to yield *2-(2-chlorophenyl)-1-phenylbenzimidazole* (0.8 g) which crystallised from aqueous ethanol as needles, m.p. 162—163 °C (Found: C, 75.0; H, 4.4; Cl, 11.8; N, 9.0. $C_{19}H_{13}ClN_2$ requires C, 74.9; H, 4.3; Cl, 11.6; N, 9.2%); M^+ 306 and 304.

2-Chloro-2′-nitrodiphenylamine.—A solution of 1,2-dinitrobenzene (5 g) in 2-chloroaniline (7 ml) was heated at 180 °C for 3 days, cooled, and poured into an excess of dilute hydrochloric acid. The precipitate was extracted with benzene and chromatographed on benzene on a short column of alumina; solvent was evaporated to yield an orange solid, m.p. 111—112 °C. Crystallisation from benzene afforded orange needles (3.4 g) of *2-chloro-2′-nitrodiphenylamine*, m.p. 112—113 °C (Found: C, 57.8; H, 3.7; N, 11.3. $C_{12}H_9ClN_2O_2$ requires C, 58.0; H, 3.6; N, 11.3%).

1-(2-Chlorophenyl)-2-phenylbenzimidazole.—Hydrazine hydrate (2 ml) and 5% palladium-charcoal (0.2 g) were added to a refluxing solution of 2-chloro-2′-nitrodiphenylamine (2.0 g) in ethanol (25 ml). After a few minutes the solution became colourless. The mixture was then filtered and the filtrate cooled and diluted with water; the product was extracted with dichloromethane and dried ($MgSO_4$). Evaporation of the solvent left an oil which was heated at 200 °C for 8 h with benzoyl chloride (5 ml). Cooling and addition of benzene precipitated a colourless solid which was collected and basified with aqueous ethanolic ammonia. The colourless product crystallised from aqueous ethanol as needles of *1-(2-chlorophenyl)-2-phenylbenzimidazole*, m.p. 67—69 °C raised to m.p. 104—105 °C after drying at 60 °C/0.1 mmHg (Found: C, 75.1; H, 4.3; Cl, 11.7; N, 9.2. $C_{19}H_{13}NCl$ requires C, 74.9; H, 4.3; Cl, 11.6; N, 9.2%). Prolonged reaction with hydrazine and palladium–charcoal caused hydrogenolysis of the carbon–chlorine bond.

Benzimidazo[1,2-f]phenanthridine (12).—A solution of 2-(2-chlorophenyl)-1-phenylbenzimidazole (0.50 g) in the electrolyte (25 ml) was reduced at a mercury cathode potential −2.1 V *vs.* s.c.e. Reaction was complete in 4 h (1.3 F mol^{-1} consumed). The reaction mixture was poured into water, acidified with a few drops of acetic acid, and the precipitate collected (0.40 g), m.p. 142—144 °C. Chromatography in ether over neutral alumina and crystallisation from ethanol afforded needles of *benzimidazo[1,2-f]phenanthridine* (0.30 g), m.p. 151—152 °C (Found: C, 84.9; H, 4.7; N, 10.3. $C_{19}H_{12}N_2$ requires C, 85.1; H, 4.5; N, 10.4%); M^+ 268. For comparison, 1,2-diphenylbenzimidazole [23] has m.p. 110—111 °C. A sample of the total reaction mixture was monitored by h.p.l.c., column 25 cm of 5 μm Spherisorb, eluant hexane–ether (4 : 1), flow rate 3 ml min^{-1}, absorption detector wavelength 310 nm. It contained (12) and 1,2-diphenylbenzimidazole in ratio 98 : 2 with R_t 8.4 and 10.5 min respectively.

Reduction of 1-(2-chlorophenyl)-2-phenylbenzimidazole (50 mg) in dimethylformamide with a cathode potential of −2.1 V *vs.* s.c.e., as for the previous example, consumed 1.2 F mol^{-1}. The isolated product was examined by h.p.l.c. as

for the previous example and contained (12) and 1,2-diphenylbenzimidazole in the ratio 98 : 2.

3-(2-Chlorophenyl)-1,2,5-triphenylpentane-1,5-dione (14).—To a solution of sodium (1 g) in ethanol (30 ml) was added deoxybenzoin (10 g) and 2-chlorobenzylideneacetophenone (12 g) with vigorous shaking. The solution was refluxed for 30 min. *3-(2-Chlorophenyl)-1,2,5-triphenylpentane-1,5-dione* separated as the mixture cooled and was recrystallised from ethanol to give needles (20 g), m.p. 149—150 °C (Found: C, 79.1; H, 5.2. $C_{29}H_{23}ClO_2$ requires C, 79.4; H, 5.3%).

4-(2-Chlorophenyl)-2,3,6-triphenylpyridine (15).—The above diketone (5 g, 1 mol equiv.) was heated with hydroxylamine hydrochloride (2 g, 2.5 mol equiv.) in 80% ethanol in a sealed tube at 140 °C for 18 h. The product crystallised on concentration of the reaction solution and was recrystallised from ethanol to yield *4-(2-chlorophenyl)-2,3,6-triphenylpyridine* (4 g) as colourless needles, m.p. 148—150 °C (Found: C, 83.3; H, 4.8; Cl, 8.4; N, 3.3. $C_{29}H_{20}ClN$ requires C, 83.4; H, 5.0; Cl, 8.5; N, 3.4%).

1,3-Diphenyldibenz[f,h]*isoquinoline* (16).—Reduction of the above chlorophenylpyridine (1.0 g) in the electrolyte (17 ml) at a mercury cathode potential of —1.80 V and work-up in the usual way afforded a solid which was digested with hot ethanol to leave a residue (0.1 g); concentration of the solution followed by recrystallisation from ethanol afforded *1,3-diphenyldibenz*[f,h]*isoquinoline* (0.4 g), m.p. 223—225 °C (Found: C, 91.4; H, 5.2; N, 3.6. $C_{29}H_{19}N$ requires C, 91.3; H, 5.0; N, 3.7%), mass spectrum with M^+ 381 (100%), 380 (98), 301 (15), 190 (22), and 189 (26).

2-(2-Bromophenyl)-4-phenylmethylene-Δ²-oxazolin-5-one (17).—2-Bromobenzoylglycine [24] (18.9 g), benzaldehyde (7.8 g), fused sodium acetate (6.0 g), and acetic anhydride (23 ml) were heated under reflux on a water-bath, with protection from moisture. All dissolved and the solution then deposited a yellow solid. After 3 h the mixture was cautiously diluted with ethanol (45 ml) and cooled; the yellow product was filtered off and washed with ethanol and hot water. *2-(2-Bromophenyl)-4-phenylmethylene-Δ²-oxazolin-5-one* crystallised from acetic acid as pale yellow needles, m.p. 131—132 °C (Found: C, 56.7; H, 3.0; N, 4.0. $C_{15}H_{10}BrNO_2$ requires C, 57.0; H, 3.2; N, 4.4%).

2-(2-Bromophenyl)-1-phenyl-4-phenylmethylene-Δ²-imidazolin-5-one (18).—The above azlactone (8.0 g, 1 mol equiv.), aniline (2.27 g, 1 mol equiv.), and anhydrous sodium acetate (2.0 g) were heated in acetic acid (40 ml) under reflux for 3 h. A colourless solid quickly separated and slowly redissolved. The insoluble material (3.7 g) which separated, crystallised from a large volume of ethanol as colourless needles of *2-(2-bromobenzamido)-3-phenylacrylanilide*, m.p. 200—201 °C (Found: C, 62.6; H, 4.1; Br, 18.7; N, 6.6. $C_{22}H_{17}BrN_2O_2$ requires C, 62.3; H, 4.1; Br, 19.0; N, 6.7%); M^+ 422 and 420. Addition of water to the filtrate from the reaction mixture precipitated a gum which crystallised from ethanol to yield yellow needles (3.0 g) of *1-phenyl-2-(2-bromophenyl)-4-phenylmethylene-Δ²-imidazolin-5-one*, m.p. 170—171 °C (Found: C, 65.4; H, 3.8; Br, 19.2; N, 7.0. $C_{22}H_{15}BrN_2O$ requires C, 65.5; H, 3.8; Br, 19.1; N, 7.0%); M^+ 404 and 402.

2-Phenylmethyleneimidazo[1,2-f]*phenanthridin-3*(2H)*-one* (20).—A solution of the Δ²-imidazolin-5-one (0.50 g) in the electrolyte (15 ml) was reduced at a mercury cathode, potential —1.4 V *vs.* s.c.e. Reaction was complete in 3 h and consumed 1.4 F mol^{-1}. The reaction mixture was poured into water and the yellow precipitate (0.40 g) collected. T.l.c. showed this to be a mixture from which crystallisation from ethanol afforded *2-phenylmethyleneimidazo*[1,2-f]*phenanthridin-3*(2H)*-one* (0.22 g) as yellow needles, m.p. 270—271 °C (Found: C, 81.7; H, 4.4; N, 8.5. $C_{22}H_{14}N_2O$ requires C, 82.0; H, 4.4; N, 8.7%) which sublimed at 230 °C/0.1 mmHg; *m/e* 322 (M^+, 79%), 294 (M^+ −CO, 25), 293 (17), 178 (100), 177 (20), 161 (18), and 151 (20).

Reduction of 2-Halogenobenzophenones.—In separate experiments, 2-chloro- and 2-bromo-benzophenone (0.2 g) were reduced in the usual way in dimethylformamide electrolyte (15 ml) at a mercury cathode and the products isolated with ether, washed with water, and dried. The products were analysed by v.p.c. using a Carbowax 20M column at 220 °C; in each case, only benzophenone (R_t 11.6 min) was detected together with starting material. Authentic samples showed the following retention times (min): fluorenone 24, 2-chlorobenzophenone 20.8 and 2-bromobenzophenone 29.8.

Reduction of 1-(2-Bromophenyl)-2-phenylethanone (22).—Reduction as for the 2-halogenobenzophenones gave deoxybenzoin as the only isolable product.

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