# Electrochemical Reactions. Part 20.[1] Intramolecular Cyclisation during the Reduction of 2-Chloro-*NN*-diphenylbenzamides

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The aryl radical formed by reductive cleavage of the carbon–chlorine bond in 2-chloro-*NN*-diphenylbenzamide undergoes exclusive capture by the neighbouring *N*-phenyl group to yield *N*-phenylphenanthridone and biphenyl-2-carboxanilide. 2-Chloro-*NN*-di-4-tolylbenzamide undergoes a similar reaction.

STUDIES [1] on the electrochemical reduction of 2-halogeno-*N*-methylbenzanilides showed that the initially formed phenyl radicals can be trapped in good yield by reaction with the adjacent benzene ring. Hey [2] has

(1; X = Cl)   (2)

(3)

(4)   (5)
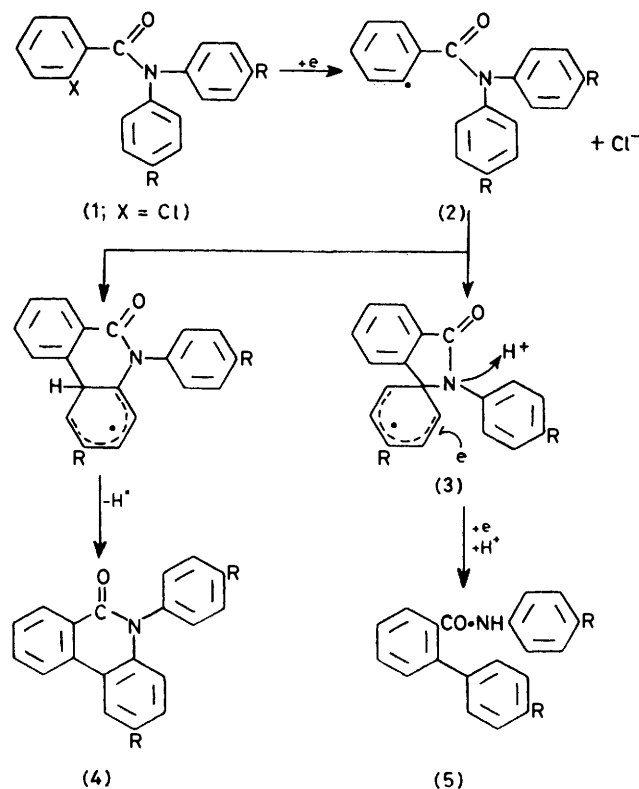
demonstrated that thermal decomposition of the diazonium chloride from 2-amino-*NN*-diphenylbenzamide gives 10-phenylphenanthridone (4; R = H) and 2-hydroxy-*NN*-diphenylbenzamide (1; R = H, X = OH), but decomposition at room temperature on addition of copper powder gives 10-phenylphenanthridone (4; R = H) and biphenyl-2-carboxanilide (5; R = H). The first reaction proceeds by a carbocation mechanism and the second by a free radical mechanism. We wished to compare these reactions with the electrochemical reduction of 2-chloro-*NN*-diphenylbenzamide.

Reduction of 2-chloro-*NN*-diphenylbenzamide at the potential of the first polarographic wave yielded two products, which were separated by preparative t.l.c. and identified as the *N*-phenylphenanthridone (4; R = H) and the anilide (5; R = H). *NN*-Diphenylbenzamide was not present. Chloro-*NN*-di-4-tolylbenzamide gave similar results on electroreduction.

[1] Part 19, J. Grimshaw, R. J. Haslett, and J. Trocha-Grimshaw, preceding paper.

These results indicate very efficient intramolecular trapping of the aryl radical (2) formed by reduction of the carbon–chlorine bond. The intermediate (3) is reduced both electrochemically and also under Hey's conditions with copper power to yield the biphenyl-carboxanilide. The yields (see Table) of this anilide and the *N*-phenylphenanthridone from both our own and Hey's experiments are closely similar. In both sets of experiments, yields were determined after isolation of the products by chromatography.

EXPERIMENTAL

Starting Materials.—2-Chlorobenzoyl chloride and the appropriate diphenylamine were heated for 1 h in refluxing ether containing an excess of pyridine. Evaporation and addition of water precipitated the product. 2-Chloro-*NN*-diphenylbenzamide, m.p. 141—142° (from ethanol) (lit.,[3] 142—143°), showed $E_{\frac{1}{2}}$ − 1.98 V *vs.* s.c.e. on polarography in dimethylformamide (0.1M in tetrapropylammonium perchlorate). 2-*Chloro-NN-di-4-tolylbenzamide* crystallised from ethanol as needles, m.p. 133—134° (Found: C, 75.2; H, 5.4; Cl, 10.7; N, 4.2. $C_{21}H_{18}ClNO$ requires C, 75.1; H, 5.4; Cl, 10.6; N, 4.2%), τ 2.62—2.70 (12 H, aromatic) and 7.77 (6 H, s, CH_3), M^+ 337/335, $E_{\frac{1}{2}}$ −1.98 V *vs.* s.c.e. The polarograms showed other waves with $E_{\frac{1}{2}}$ more negative than −2.6 V.

Electrochemical Reduction.—An H-type electrochemical cell was used with a mercury cathode, platinum anode, and saturated calomel reference electrode. The electrolyte was 0.1M-tetrapropylammonium perchlorate in anhydrous dimethylformamide. A solution of the 2-chloro-*NN*-diphenylbenzamide (2 g) in the electrolyte (15 ml) was reduced at a controlled cathode potential of −2.0 V for 48 h; the current had then fallen to a low value. The catholyte was evaporated under reduced pressure and the residue dissolved in chloroform; the solution was washed with water, dried (Na_2SO_4), and evaporated. The products (total recovery 97%) were separated by chromatography on silica gel plates and elution with dichloromethane. Yields are calculated on the basis of replacement of Cl by H.

Product yields from the electroreduction of 2-chloro-*NN*-diphenylbenzamides compared with yields from decomposition of diazonium salts with Cu (from ref. 2)

Starting material	Product	M.p. (°C)	Yield (%)
(1; R = H, X = Cl)	(4; R = H)	226—227	42
	(5; R = H)	107—109	31
(1; R = H, X = $N_2^+Cl^-$)	(4; R = H)	225	40
	(5; R = H)	109—110	45
(1; R = Me, X = Cl)	(4; R = Me)	176—177	36
	(5; R = Me)	132—133	59
(1; R = Me, X = $N_2^+Cl^-$)	(4; R = Me)	175—176	28
	(5; R = Me)	134—135	58

[2] D. H. Hey and T. M. Moynehan, *J. Chem. Soc.,* 1959, 1563.
[3] A. W. Chapman, *J. Chem. Soc.,* 1927, 1748.