Electrochemical Reactions. Part 23.[1] Intramolecular Radical Substitution during the Reduction of 2-Halogeno-*N*-methyl-*N*-naphthylbenzamides

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Phenyl radical intermediates formed by the reductive cleavage of the carbon–halogen bond in 2-halogeno-*N*-methyl-*N*-(1-naphthyl)benzamides undergo intramolecular substitution to give *N*-methyl-2-(1-naphthyl)-benzamide, and no *N*-methylbenzo[*c*]phenanthridone is formed. Reduction of 2-halogeno-*N*-methyl-*N*-(2-naphthyl)benzamides gives *N*-methyl-2-(2-naphthyl)benzamide, *N*-methylbenzo[*a*]phenanthridone, and *N*-methylbenzo[*b*]phenanthridone. These results complete our comparison of this electrochemical reaction with related radical Pschorr cyclisations. Further reduction of these initial reaction products occurs so that only qualitative conclusions can be drawn from the product yields.

PREVIOUS studies on the electrochemical reduction of 2-halogeno-*N*-methylbenzanilides [2] and 2-chloro-*NN*-diphenylbenzamides [3] showed that the phenyl radical initially formed by reductive cleavage of the carbon–halogen bond can be trapped in good yield by reaction with the adjacent benzene ring. This study was begun in order to compare the reaction products with those obtained by Hey [4] where the intermediate phenyl radical was generated in a more conventional manner from a diazonium salt. It confirms that σ-radicals are intermediate in the electrochemical reaction although since they undergo very fast subsequent reactions their presence cannot be demonstrated by purely electrochemical techniques. We complete the comparison with Hey's work by an examination of the amides (1) and (7) derived from 1- and 2-aminonaphthalene. A summary of the literature on the electrochemical reduction of aryl halides was given in our previous papers.[2,3]

TABLE 1

N.m.r. data and yields of reduction products for 2-halogeno-*N*-methyl-*N*-naphthylbenzamides

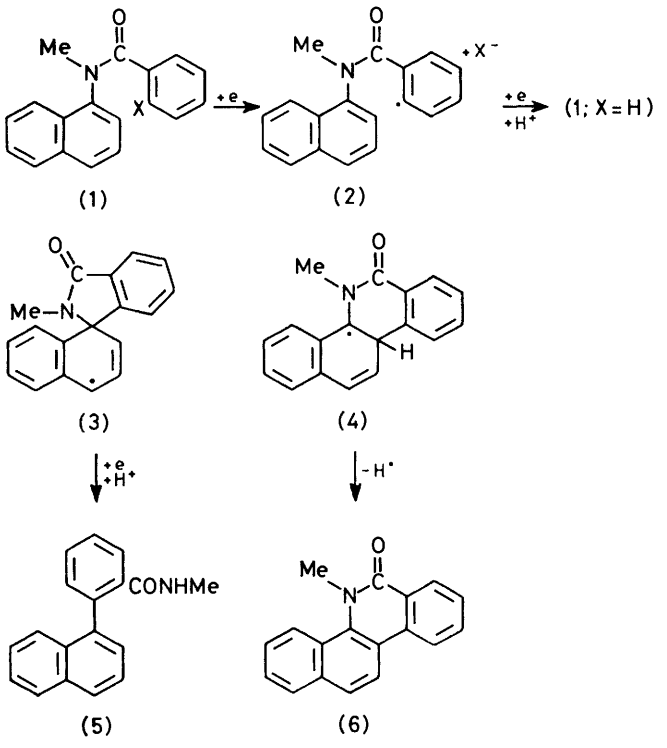
	T_c (°C)	N–Me signals (τ; $CDCl_3$) *syn*	*anti*	*syn* : *anti*	Relative yields (isolated yields in parentheses) Phenyl-naphthalene (5) or (11)	Benzo[*c*]-phenanthridone (6)	Benzo[*b*]-phenanthridone (13)	Benzo[*a*]-phenanthridone (12)
(*a*) *N*-Methyl-1-naphthylamine derivatives								
2-Chlorobenzoyl		6.43	6.72 [a]	87 : 13	100	0		
2-Bromobenzoyl	130	6.44	6.72 [a]	85 : 15	100 (69)	0		
2-Iodobenzoyl		6.42	6.74 [a]	86 : 14	100 (20)	0		
(*b*) *N*-Methyl-2-naphthylamine derivatives								
2-Chlorobenzoyl		6.41	6.70 [b]	89 : 11	63		28	9
2-Bromobenzoyl	50	6.40	6.70 [b,c]	86 : 14	46 (23)		30 (12)	24
2-Iodobenzoyl	50	6.39	6.70 [b]	85 : 15	58		31	16

[a] At 30 °C. [b] At −20 °C. [c] At T_c, b_e = 1.81 Hz, $\Delta\nu$ (*syn*, *anti*) = 18.0 Hz, K = 0.12; hence $t_{\frac{1}{2}}$ *syn*→*anti* = 0.21 s.

RESULTS AND DISCUSSION

Slow rotation about the amide bond occurs in these substrates and the equilibrium between *syn*- and *anti*-forms can be investigated by n.m.r. spectroscopy.[5] For the *N*-methylbenzanilides the upfield N–Me resonance is due to the *anti*-rotamer [2] and we have assumed that this situation will hold also for the *N*-methyl-*N*-naphthylbenzamides, n.m.r. data for which are given in Table 1. The products from electrochemical reduction confirm this assignment. The form of the *N*-methyl-*N*-naphthylbenzamide with *syn* phenyl and naphthyl rings is the predominant rotamer at equilibrium, and the temperature at which coalescence of the N–Me signals occurs is higher for the 1-naphthyl than the 2-naphthyl compound. This is in agreement with the general observation that the barrier to rotation about the amide bond is raised when steric effects force one substituent, here 1-naphthyl, out of the plane of the amide group, decreasing conjugation and giving the amide bond more double-bond character. The rate constant k (3.3 s^{-1}) for the *syn* to *anti* conversion of (1; X = Br) was calculated at the coalescence temperature T_c by the method of Jaesche.[6] Values of the natural line width b_e, the equilibrium constant K { = [*anti*-rotamer]/[*syn*-rotamer]}, and the chemical shift difference, Δν, between the two N–Me signals were taken at a range of temperatures and then extrapolated to the coalescence temperature from the region where they are linearly dependent on temperature. Substitution of these results (Table 1), into Jaesche's diagram afforded the value of k. Clearly the conversion rate at room temperature will be much slower than any radical reactions initiated by the addition of an electron to (1; X = Br), so that the yields of reduction products should reflect the proportions of *syn*- and *anti*-rotamers at equilibrium; only the *syn*-rotamer can undergo the intramolecular cyclisation.

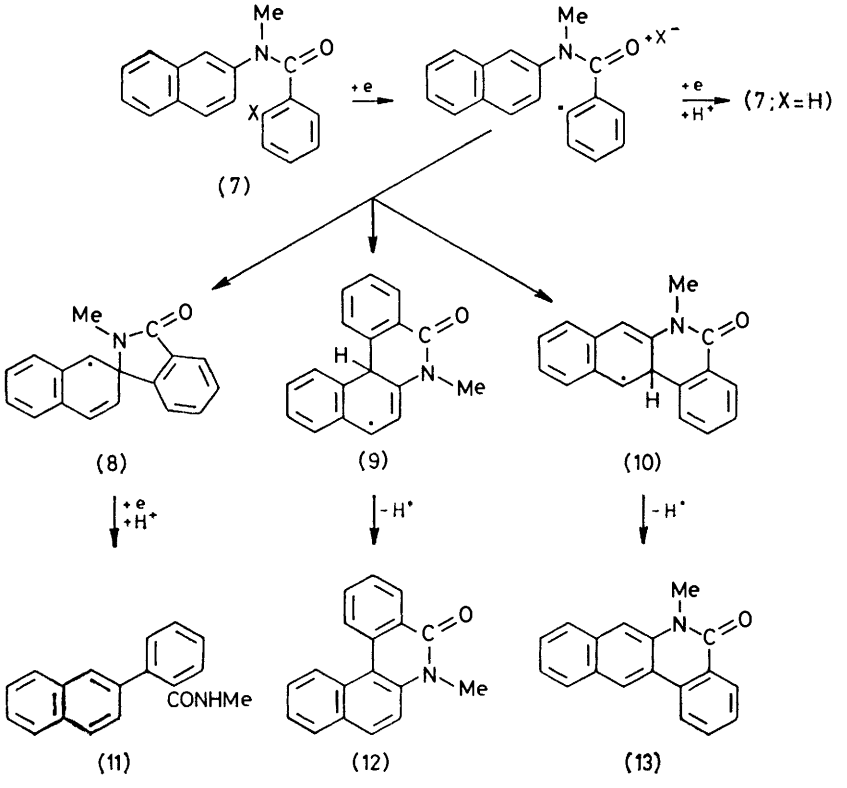
1-*Aminonaphthalene Derivatives*.—Electrochemical re-



duction of 2-halogeno-*N*-methyl-*N*-(1-naphthyl)benzamides afforded 1-methylaminonaphthalene (1; X = H) and the 1-phenylnaphthalene derivative (5). 1-Methylaminonaphthalene arises by reduction of the benzamide function and then hydrolysis of intermediates. The benzoyl residue probably appears as benzaldehyde or a reduction product derived from this. Because of this further reaction of both the starting amide and (1; X = H), we cannot quantitatively relate the yield of (1; X = H) to the proportion of *anti*-rotamer present in the substrate as was done for the benzanilides.[2] However, the isolated yield of (5) from (1; X = Br) was 69%, which confirms our previous deduction that the *syn*-rotamer of (1; X = Br) is the more abundant at equilibrium. The ratio of (5) : (6) reported in Table 1 was determined by n.m.r. spectroscopy using the N–Me signals.

No *N*-methylbenzo[*c*]phenanthridone (6) could be detected from these reactions. This result is in agreement with our previous experience [7] on the reduction of a substituted derivative of (1; X = Br) and with Hey's attempts to cyclise diazonium salts (1; X = $N_2^+BF_4^-$) under reducing conditions in the presence of either copper powder or sodium iodide.[8,9] Hey reported isolated yields of 1.5% for (6) and 70% for a spiro-dimer resulting from union of two radicals (3). In our system radical (3) is reduced further at the electrode with cleavage of a carbon–nitrogen bond so that (5) corresponds to the spiro-dimer product from Hey's reactions.

We have previously found [2] that reduction of 2-halogeno-2′-methyl-*N*-methylbenzanilides gives only a biphenylcarboxamide and no phenanthridone. The amide from 1-aminonaphthalene is behaving like the amide from an *ortho*-substituted aniline. In an explanation of this behaviour, steric effects are considered to rotate the *N*-aryl ring out of the plane of the amide function so that the reacting carbon atoms for the con-

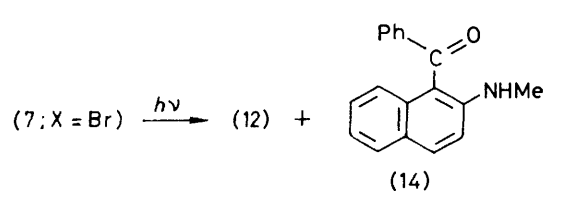


version of (2) to (3) are closer than the reacting carbon atoms for the conversion of (2) to (4), *i.e.* entropy of activation favours the reaction (2) to (3). Also in the naphthalene series radical (3) is more delocalised than (4), so that the enthalpy of activation will also favour the reaction (2) to (3).

The electrochemical reduction of 2-bromo-*N*-methyl-*N*-(1-naphthyl)benzamides is an attractive route for the synthesis of some derivatives of 1-phenylnaphthalene. During reduction of the corresponding 2-iodo-compound, replacement of the halogen by hydrogen becomes the predominant reaction and the isolated yield of (5) falls to about 20%.

2-*Aminonaphthalene Derivatives*.—Reduction of 2-halogeno-*N*-methyl-*N*-(2-naphthyl)benzamides is complicated by further reduction of the primary products. The reaction affords up to 30% of 2-methylaminonaphthalene, formed by reduction of the amide link in either the starting material or (7; X = H). Other products isolated were (7; X = H), the 2-phenylnaphthylene derivative (11), and a mixture of *N*-methylbenzo[*a*]phenanthridone (12) and *N*-methylbenzo[*b*]phenanthridone (13). The yield of (7; X = H) was not considered significant and only the relative yields of (11), (12), and (13) were determined by n.m.r. spectroscopy, at 90 MHz using the N–Me signals. Assignment of signals due to (12) and (13) was checked by peak enhancement after the addition of small amounts of the authentic compounds. Both *N*-methylbenzophenanthridones show reduction waves at around −1.95 V *vs.* the saturated calomel electrode (s.c.e.) on cyclic voltammetry. The wave due to (13) was reversible whereas that due to (12) was irreversible under the same conditions. Thus reduction of a mixture of the two will result in preferential destruction of (12). This is because rapid protonation of the first formed radical-anion occurs to give a non-planar intermediate with relief of compression strain between hydrogen atoms on the planar benzo[*a*]phenanthridone skeleton.

A sample of (13) (lit.,[10] m.p. 196 °C), was easily obtained from reduction of the bromo-compound (7; X = Br) by chromatography and crystallisation. A sample of (12) (lit.,[11] m.p. 120 °C) was obtained by photochemical reaction of (7; X = Br) which affords only this phenanthridone along with the photo-Fries rearrangement product (14). The confused earlier literature on the identification of these *N*-methylbenzophenanthridones has been summarised by Hey and Perkins [7] and both compounds have been independently synthesised in the literature there cited.



(14)

Hey [8,9] found that decomposition of the diazonium salt (7; X = $N_2^+BF_4^-$) afforded the two benzophenanthridones (12) and (13) in a ratio of 3.5 : 1, together with a spiro-lactam dimer derived from radical (8). In our case radical (8) is reduced further to (11) and no dimer is formed. At the potential required for reduction of the chloro-compound (7; X = Cl) we expect preferential electroreduction of benzo[*a*]phenanthridone (12), so that the ratio of phenanthridones isolated is not significant. This preferential destruction would not be expected at the reduction potential for the corresponding iodo-compound and, since the ratio of (12) : (13) is the same within experimental error for reaction of the bromo-compound, further reduction is also not significant in the latter case. The ratio of (12) : (13) found for the electrochemical reduction process is 2 : 3, and compound (13) is formed in greater amount.

EXPERIMENTAL

Variable-temperature n.m.r. spectra were obtained with a Varian A60 instrument ($CDCl_3$ as solvent) using sealed sample tubes at elevated temperatures. Analytical n.m.r. spectra were obtained with a Brucker 90-MHz instrument ($CDCl_3$ solvent).

Substrates.—2-Halogeno-*N*-naphthylbenzamides were obtained from the appropriate aminonaphthalene (1 mol) and 2-halogenobenzoyl chloride (1 mol) in pyridine and crystallised from ethanol. Dimethyl sulphate (12 ml) was added dropwise to a refluxing solution of the 2-halogeno-*N*-naphthylbenzamide (8 g) in acetone (100 ml) and aqueous sodium hydroxide (10%, 100 ml). The solution was refluxed for a further 60 min, and then poured into water to precipitate the *N*-methylamide. The products from 1-aminonaphthalene crystallised easily and were recrystallised from ethanol. The products from 2-aminonaphthalene precipitated as oils which were collected in ether, washed with water, dried ($MgSO_4$), and the solvent removed. The product crystallised after some time and was recrystallised from light petroleum (b.p. 60—80 °C). Physical properties and analytical data are collected in Table 2. The *N*-methyl-*N*-naphthylbenzamides were prepared from benzoyl chloride and methylaminonaphthalene.

Polarography and Electrolytic Reduction.—The polarographic half-wave potentials for the reduction of 2-halogeno-*N*-methyl-*N*-naphthylbenzamides in dimethylformamide are given in Table 2. The supporting electrolyte for electrochemical experiments was 0.1M tetrapropylammonium perchlorate in anhydrous dimethylformamide. An H-type electrolysis vessel was used fitted with a mercury cathode, a salt bridge connection to an s.c.e. reference, and a nitrogen inlet. The anode compartment contained the supporting electrolyte and a platinum anode. For analytical experiments, the *N*-methyl-*N*-naphthylbenzamide (2×10^{-3} mol) was dissolved in the supporting electrolyte (15 ml) and reduced at the following controlled cathode potentials: chloro-compounds −2.1 V, bromo-compounds −1.9 V, and iodo-compounds −1.6 V *vs* s.c.e. Reduction was continued until the current fell to a low value (1.2—1.8 F mol^{-1}). The catholyte was then evaporated to a small volume under vacuum, water (100 ml) was added and the product extracted into ether. The ether was washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and evaporated. N.m.r. analysis of the residue in $CDCl_3$ was carried out and the results are collected in Table 1.

Reduction of 2-*Bromo*-N-*methyl*-N-(1-*naphthyl*)*benzamide*.—The amide (2.0 g) in supporting electrolyte (15 ml) was reduced as described above and the acid washed product chromatographed over alumina. Elution with ether afforded *N*-methyl-*N*-(1-naphthyl)benzamide, m.p. 119—121 °C (lit.,[12] m.p. 121 °C) (Found: C, 82.7; H, 5.9; N, 5.5. Calc. for $C_{18}H_{15}NO$: C, 82.9; H, 5.8; N, 5.4%) which crystallised from ether; τ 6.47 (N–Me), identical with a sample prepared from 1-methylaminonaphthalene and benzoyl chloride. Elution with ether–0.5% methanol afforded *N*-methyl-2-(1-naphthyl)benzamide (yield 69%) which crystallised from ethanol, m.p. 139—140 °C, (lit.,[13] m.p. 139—140 °C); M^+ 261; τ 7.67 (N–Me) (d, *J* 5 Hz).

Reduction of 2-*Bromo*-N-*methyl*-N-(2-*naphthyl*)*benzamide*.—The amide (2.0 g) in supporting electrolyte (15 ml) was reduced as described above and the products isolated with ether and washed with water only. Chromatography on alumina and elution with pentane–ether (1 : 1) yielded 2-methylaminonaphthalene (0.41 g, 33%); M^+ 157; τ 7.12 (s) (N–Me), identified as the picrate, m.p. 146—147 °C (lit.,[14] m.p. 145 °C). Elution with ether gave a phenanthridone fraction from which *N*-methylbenzo[*b*]phenanthridone (13) crystallised, m.p. 194—195 °C (lit.,[8,10] m.p. 196 °C) (0.16 g, 12%); M^+ 259; τ 6.18 (s) (N–Me). Elution with ether —0.5% methanol afforded N-*methyl*-2-(2-*naphthyl*)*benzamide* (Found: C, 82.7; H, 6.0; N, 5.2. $C_{18}H_{15}NO$ requires C, 82.7; H, 5.8; N, 5.4%) (0.30 g, 23%), as needles from ethanol, m.p. 151—152 °C; M^+ 261, τ 7.38 (d, *J* 5 Hz) (N–Me).

N-*Methylbenzo*[a]*phenanthridone* (12).—A solution of amide (7; X = Br) (0.22 g) in cyclohexane (400 ml) was irradiated under nitrogen in a quartz vessel with a low-pressure mercury-discharge lamp in a Rayonet reactor assembly for 13 h. The solvent was then removed, the residue dissolved in ether, extracted with dilute hydrochloric acid, washed with water, and dried ($MgSO_4$). After chromatography in ether over alumina, and evaporation of the solvent, the residue of *N*-methylbenzo[*a*]phenanthridone (12) crystallised from ethanol, m.p. 115—117 °C (lit.,[11] m.p. 120°); M^+ 259; τ 6.12 (s) (N–Me). Cyclic voltammetry in dimethylformamide with sweep rate 0.64 V s^{-1} showed an irreversible reduction wave with $E_{\frac{1}{2}}$ —1.98 V *vs.* s.c.e. Under identical conditions *N*-methylbenzo[*b*]phenanthridone (13) showed a reversible reduction–oxidation process with E_0 —1.93 V *vs.* s.c.e.

Basification of the hydrochloric acid extract afforded the photo-Fries rearrangement product (14) which was characterised by the n.m.r. spectrum; τ 0.8 (1 H, br, NH) and 6.93 (3 H, d, *J* 5 Hz, N–Me).

TABLE 2

Data for the halogeno-*N*-naphthylbenzamides and halogeno-*N*-methyl-*N*-naphthylbenzamides

	M.p.	$-E_{\frac{1}{2}}$/V (*vs.* s.c.e.)	Analysis (%) Found	Formula	Required
(*a*) 1-Naphthylamides					
2-Chlorobenzoyl	185—186		C, 72.4; H, 4.4; N, 4.7	$C_{17}H_{12}ClNO$	C, 72.5; H, 4.3; N, 5.0
2-Bromobenzoyl	205—207		C, 62.4; H, 3.8; Br, 24.4; N, 4.14	$C_{17}H_{12}BrNO$	C, 62.6; H, 3.7; Br, 24.5; N, 4.3
2-Iodobenzoyl	233—234		C, 55.0; C, 55.0; H, 3.3; N, 3.9	$C_{17}H_{12}INO$	C, 54.7; H, 3.2; N, 3.8
(*b*) 2-Naphthylamides					
2-Chlorobenzoyl	174—175		C, 72.7; H, 4.4; N, 4.4; N, 4.9	$C_{17}H_{12}ClNO$	
2-Bromobenzoyl	180—181		C, 62.7; H, 3.7; Br, 24.4; N, 4.4	$C_{17}H_{12}BrNO$	
2-Iodobenzoyl	179—180		C, 54.5; H, 3.3; N, 3.8	$C_{17}H_{12}INO$	
(*c*) *N*-Methyl-1-naphthylamides (1)					
2-Chlorobenzoyl	113—115 [a]	2.10; 2.28	C, 72.9; H, 4.9; N, 5.0	$C_{18}H_{14}ClNO$	C, 73.1; H, 4.7; N, 4.7
2-Bromobenzoyl	122—123	2.05; 2.30	C, 63.8; H, 4.3; Br, 23.4; N, 4.1	$C_{18}H_{14}BrNO$	C, 63.5; H, 4.1; Br, 23.5; N, 4.1
2-Iodobenzoyl	141—142	1.66; 2.25	C, 56.0; H, 3.6; N, 3.7	$C_{18}H_{14}INO$	C, 55.8; H, 3.6; N, 3.6
Benzoyl	119—121 [b]	2.31			
(*d*) *N*-Methyl-2-naphthylamides (7)					
2-Chlorobenzoyl	74—76	2.08; 2.28	C, 73.0; H, 4.7; N, 4.5	$C_{18}H_{14}ClNO$	
2-Bromobenzoyl	75—77	2.01; 2.28	C, 63.3; H, 4.0; N, 4.3	$C_{18}H_{14}BrNO$	
2-Iodobenzoyl	75—80	1.66; 2.21	C, 55.7; H, 3.6; N, 3.7	$C_{18}H_{14}INO$	
Benzoyl	83—84 [c]				

[a] Ref. 8, m.p. 113—115 °C. [b] Ref. 12, m.p. 121 °C. [c] G. T. Morgan and F. P. Evans, *J. Chem. Soc.*, 1919, **115**, 1140, give m.p. 84 °C.

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