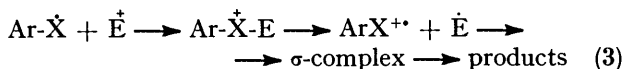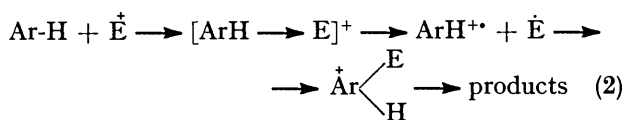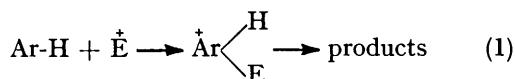# Electrophilic *ipso*-Substitutions.   Part 2.[1]   Reactions of 3-Substituted Indoles and 4-Substituted *NN*-Dimethylanilines with Arenediazonium Ions

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3-Substituted indoles and 4-substituted *NN*-dimethylanilines react with arenediazonium ions to form 3-arylazo-indoles and 4-arylazo-*NN*-dimethylanilines, respectively. The formation of the σ-complex intermediate was interpreted both as electrophilic *ipso*-attack and as coupling of two radicals deriving from an electron transfer process. Both mechanisms are discussed on the basis of the experimental evidence and on the substrate oxidation potentials. The leaving abilities of the substituents are discussed on the basis of the experimental results.

ELECTROPHILIC aromatic substitution reactions have previously been discussed in terms of an electrophilic attack which leads to a σ-complex or Wheland intermediate [equation (1)].[2,3]   In recent years several authors [4-6] have suggested that electrophilic substitution on reactive aromatic compounds occurs through an electron transfer to form an aromatic cation radical [equation (2)].   This new reaction path was proposed on the basis of the formation of the intermediate cation radical detected by e.s.r. spectroscopy and the CIDNP method,[4a-c] or of the ionization and oxidation potentials of the aromatic substrates,[5a,b] or of the product composition.[6a,b]   In addition, reactions between some aromatic amines and arenediazonium ions are interpreted as shown in equation (3).[7a,b]

$$Ar\text{-}H + \overset{+}{E} \longrightarrow \overset{+}{Ar}\Big\langle{}^{H}_{E} \longrightarrow products \quad (1)$$

$$Ar\text{-}H + \overset{+}{E} \longrightarrow [ArH \longrightarrow E]^{+} \longrightarrow ArH^{+\cdot} + \overset{\cdot}{E} \longrightarrow$$
$$\longrightarrow \overset{+}{Ar}\Big\langle{}^{E}_{H} \longrightarrow products \quad (2)$$

$$Ar\text{-}\overset{\cdot}{X} + \overset{+}{E} \longrightarrow Ar\text{-}\overset{+}{X}\text{-}E \longrightarrow ArX^{+\cdot} + \overset{\cdot}{E} \longrightarrow$$
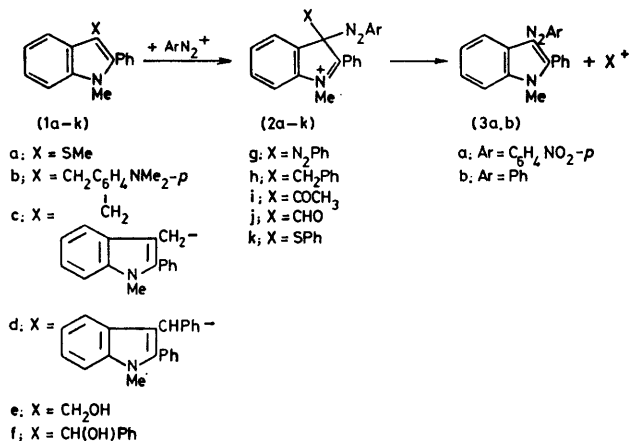$$\longrightarrow \sigma\text{-complex} \longrightarrow products \quad (3)$$

The *ipso*-substitution reactions of 3-substituted indoles (1a—k) and 4-substituted dimethylanilines (4a—f) with arenediazonium salts, described in this paper, throw light on the above reaction mechanism.

RESULTS

3-Substituted indoles (1a—k), on treatment with arenediazonium salts in aqueous ethanol, gave 3-arylazoindoles (3a,b) (Scheme 1). The product yields are reported in Table 1.

4-Substituted *NN*-dimethylanilines (4a—f) also reacted with arenediazonium salts to form 4-arylazo-*NN*-dimethyl-anilines (6a—c) (Scheme 2) under the above conditions. The product yields are reported in Table 2.   In the reaction between (4e) and *p*-nitrobenzenediazonium salt, compounds (10) and (11) were isolated together with compound (6a) (Scheme 3).   All the reactions in Schemes 1 and 2 were also carried out in the e.s.r. cavity.   Only in the case of (1a) did we record an intense and well resolved signal, corresponding to radical cation (7) [Figure (a)].   For the other compounds,

(1a—k)   (2a—k)   (3a,b)

a: X = SMe
b: X = CH$_2$C$_6$H$_4$NMe$_2$-*p*
c: X = CH$_2$ [structure]
d: X = CHPh [structure]
e: X = CH$_2$OH
f: X = CH(OH)Ph

g: X = N$_2$Ph
h: X = CH$_2$Ph
i: X = COCH$_3$
j: X = CHO
k: X = SPh

a: Ar = C$_6$H$_4$NO$_2$-*p*
b: Ar = Ph

SCHEME 1

poorly resolved signals were recorded and for compounds (1j and k) in particular, no signal was observed at all.

Half-wave oxidation potentials $(E_{\frac{1}{2}})$ of compounds (1a—k) and (4a—f) were determined by anodic oxidation

TABLE 1

Reactions between indoles (1a—k) and arenediazonium ions

Indole	Ar–N$_2$+	Reaction time (h)	Product [yield (%)]
(1a)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [85]
(1b)	Ar = C$_6$H$_4$NO$_2$-*p*	2	(3a) [90]; (6a) [95]
(1c)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [42]
(1d)	Ar = C$_6$H$_4$NO$_2$-*p*	12	(3a) [67]
(1d)	Ar = C$_6$H$_5$	90	(3b) [45]
(1e)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [84]
(1e)	Ar = C$_6$H$_5$	16	(3b) [82]
(1f) *	Ar = C$_6$H$_4$NO$_2$-*p*	12	(3a) [trace]
(1g)	Ar = C$_6$H$_4$NO$_2$-*p*	48	(3a) [10]
(1h)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [trace]
(1i)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [26]
(1j)	Ar = C$_6$H$_4$NO$_2$-*p*	24	(3a) [9]
(1k) *	Ar = C$_6$H$_4$NO$_2$-*p*	12	(3a) [trace]

* The low yields are due to the low solubility of the starting materials in the reaction medium.

(see Experimental section).[8]   The $E_{\frac{1}{2}}$ values for 3-substituted indoles (1a—k) were in the range 1.13—0.33 V and the sequence was (1j) > (1i) ≫ (1g) > (1f) ≥ (1k) ≥ (1e) > (1h) ≥ (1d) > (1c) ≥ (1a) > (1b).   The $E_{\frac{1}{2}}$ values for 4-substituted *NN*-dimethylanilines were in the range 0.44—0.24 V and the sequence was (4f) ≥ (4e) > (4d) > (4b) >
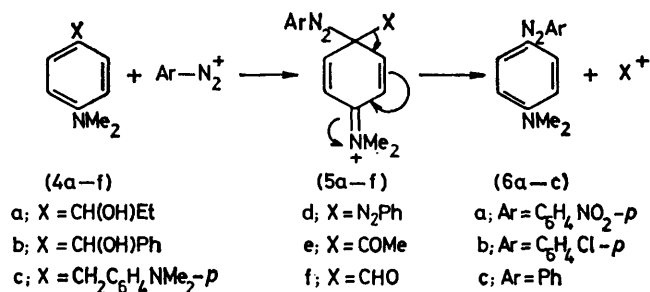
TABLE 2

Reactions between NN-dimethylanilines (4a—f) and arenediazonium ions

NN-Dimethylaniline	Ar–N$_2^+$	Reaction time (h)	Product [yield (%)]
(4a)	Ar = C$_6$H$_4$NO$_2$-p	3	(6a) [95]
(4a)	Ar = C$_6$H$_4$Cl-p	4	(6b) [85]
(4a)	Ar = C$_6$H$_5$	6	(6c) [86]
(4b)	Ar = C$_6$H$_4$NO$_2$-p	2	(6a) [90]
(4c)	Ar = C$_6$H$_4$NO$_2$-p	3	(6a) [89]
(4c)	Ar = C$_6$H$_4$Cl-p	3	(6b) [80]
(4c)	Ar = C$_6$H$_5$	6	(6c) [75]
(4d)	Ar = C$_6$H$_4$NO$_2$-p	3	(6a) [30]
(4e)	Ar = C$_6$H$_4$NO$_2$-p	6	(6a) [5]; (10) [6] (11) [13]
(4f)	Ar = C$_6$H$_4$NO$_2$-p	3	(6a) [60]

(4c) > (4a). All new compounds were identified on the basis of their analytical and spectroscopic data.

(a)

10 G

(b)
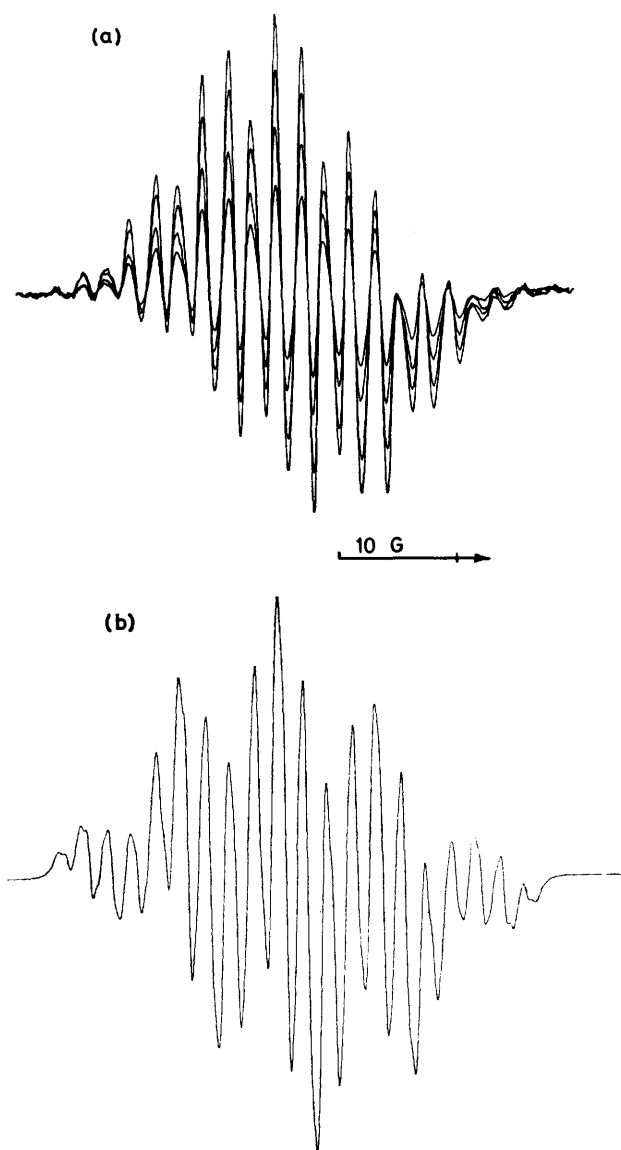
Experimental (a) and computer simulated (b) e.s.r. spectra of cation radical (7)

(4a—f)

a; X = CH(OH)Et
b; X = CH(OH)Ph
c; X = CH$_2$C$_6$H$_4$NMe$_2$-p

(5a—f)

d; X = N$_2$Ph
e; X = COMe
f; X = CHO

(6a—c)

a; Ar = C$_6$H$_4$NO$_2$-p
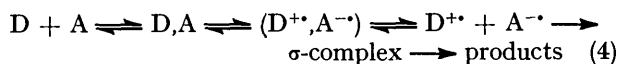b; Ar = C$_6$H$_4$Cl-p
c; Ar = Ph

SCHEME 2

DISCUSSION

Electrophilic *ipso*-substitution reactions of dipyrrylmethanes [9] and di-indolylmethanes [10] with arenediazonium ions have already been studied and interpreted by assuming the formation of a σ-complex intermediate, which leads to *ipso*-substitution products for dipyrrylmethanes and to 3,2-migration products for di-indolylmethanes. The proposed mechanism is in agreement with the classical electrophilic substitution.

For the reactions described in this paper we propose an alternative mechanism which is supported by experimental evidence. The e.s.r. signal recorded for the reaction between (1a) and p-nitrobenzenediazonium ion, which decreased in the time, was attributed to the radical cation (7) and interpreted in terms of the following hyperfine splittings: a_H(3H) 8.45 G, a_N(1N) 4.12 G, a_H(3H) 1.87 G, a_H(2H) 0.62 G. The anodic [8] and chemical oxidations (see Experimental section) of (1a) were carried out to confirm unambiguously the formation of radical cation (7).

(1a)   (7)   (8)
RED   SEM   OX
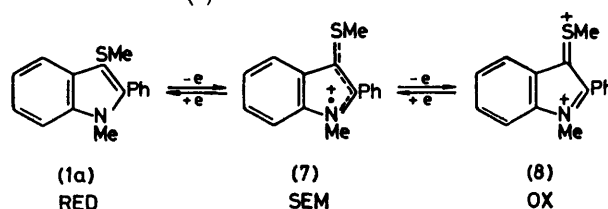
The anodic oxidation of (1a) showed two monoelectronic, reversible steps, the first for the formation of radical cation (7) and the second for the formation of dication (8). In addition, the reversibility of this system was confirmed by mixing equimolar quantities of (1a) and (8), which gave the radical cation (7) quantitatively. Similar systems have already been described in the literature.[11,12]

Radical cation (7) is thus formed during the reaction by an electron transfer process between (1a) (donor = D) and the diazonium ion (acceptor = A) as already described in the literature for phenothiazine and arenediazonium ions.[13] On the basis of this result, the reaction mechanism may be that described by equation (4).[5a,14] This

$$D + A \rightleftharpoons D,A \rightleftharpoons (D^{+\cdot},A^{-\cdot}) \rightleftharpoons D^{+\cdot} + A^{-\cdot} \longrightarrow$$
σ-complex ⟶ products   (4)

proposed mechanism is supported by the fact that com-

pound (1a) has the lowest oxidation potential in the indole series studied, and p-nitrobenzenediazonium ion has the highest electron affinity of the monosubstited arenediazonium ions.[15] Moreover, it is our opinion that, as the $E_{\frac{1}{2}}$ values of 3-substituted indoles (1a—k) increase in the 0.33—1.13 V range, classical electrophilic attack becomes competitive with the electron transfer process.

The reactions between 4-substituted NN-dimethyl-anilines (4a—f) and arenediazonium salts were studied on the basis of the results for the indole series and some result described in the literature.[16,17] Excluding (4e and f), compounds (4a—d) had $E_{\frac{1}{2}}$ values lower than that of 3-methylthioindole (1a), the radical cation (7) of which was obtained during the reaction. For this reason, we assume that the more probable mechanism for the reactions between 4-substituted NN-dimethylanilines and arenediazonium ions is that which involves an electron transfer process [equation (4)], even if no experimental evidence for the formation of a radical cation intermediate was obtained. This supposition is in agreement with our results and is supported by experimental evidence already described in the literature.[7,18,19]

An interesting result was obtained for the reaction between (4e) and p-nitrobenzenediazonium ion (Scheme 3). The formation of p-acetyl-N-methylaniline (9) and of the corresponding diazoamino-derivative (10) confirms the intermediate formation of the radical cation (4e)[+•]. In fact, the demethylation of NN-dimethylanilines is a reaction involving the intermediate formation of a radical cation, as has been demonstrated by anodic [20] and chemical oxidation.[21,22]

SCHEME 3
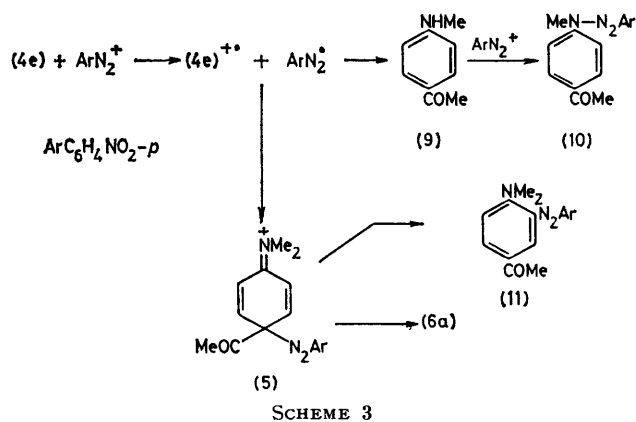
Compound (11) could derive from the intermediate (5) by migration of the diazo-group, as found by others for similar reactions.[10,23] Because compound (9) was not isolated, its formation was demonstrated by reacting it with p-nitrobenzenediazonium ion in the same conditions used for the reaction of (4e) with diazonium ions. Compound (10) was obtained in quantitative yield. Compound (1b), which contains both the NN-dimethyl-aniline and indole groups, can be considered a bidentate system. In fact, when the reagents (1b) and p-nitro-benzenediazonium ion were allowed to react in a ratio of

1 : 2, compound (3a) and 4-(dimethylamino)-4'-nitro-phenylazo-benzene (6a) were isolated in 90 and 95% yields, respectively, whereas, when equimolar amounts of these reagents were reacted, the major products were the azo-benzene derivative (6a) and 3-hydroxymethylindole (1e) together with a small amount of 3-arylazoindole (3a). These results confirmed (i) the reaction mechanism already described by us [1] for the indolymethanes (1c and d), also studied in the present work, and (ii), that the NN-dimethylanilines have the highest reactivity with respect to indoles.

In summary, we do not assume that the electron transfer process precedes the formation of the σ-complex in every case, but the oxidation potential, the e.s.r. evidence [radical cation (7)], and the demethylation in the case of (4e) strongly support an electron transfer process. In addition, the substituent leaving abilities evaluated on the basis of the $ipso$-substitution product yields (all reaction were carried out under the same conditions) follow the sequence of the half-wave oxidation potentials, particularly for the indole series.

EXPERIMENTAL

M.p.s are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer for Nujol mulls. N.m.r. spectra were recorded on a Varian XL 100 spectrometer (tetramethylsilane as internal standard). E.s.r. spectra were recorded on a Varian E4 spectrometer. Mass spectra were recorded on a Varian 112 S instrument. Compounds (1c),[24] (1e),[25] (1g),[26] (1i),[27] (1j),[1] (4a),[28] (4b),[28] (4c),[29] (4d) (C. Erba), (4e),[30] (4f) (Fluka), and (9) [31] were prepared as described in the literature.

1-*Methyl-3-methylthio-2-phenylindole* (1a).—This compound was conveniently prepared (yield 80%) starting from 1-methyl-2-phenylindole using the method described in the literature.[32]

3-(p-*Dimethylaminobenzyl*)-1-*methyl-2-phenylindole* (1b). —NN-Dimethylaniline (21 mmol), 1-methyl-2-phenylindole (20 mmol), acetic acid (5 ml), and absolute ethanol (7 ml) were heated in boiling water for 2 h. The solvent was evaporated under vacuum, and the residue, taken up with benzene, was chromatographed on a SiO_2 column from benzene. Compound (1b) was isolated in 75% yield, m.p. 121° (from ethanol), δ ($CDCl_3$) 2.80 (6 H, s, NMe_2), 3.6 (3 H, s, NMe), 4.05 (2 H, s, CH_2Ar), and 6.6—7.6 (13 H, m, ArH) (Found: C, 84.45; H, 7.2; N, 8.3 $C_{24}H_{24}N_2$ requires C, 84.65; H, 7.1; N, 8.25%). Compound (1b) was also prepared by methylation of 3-(*p*-dimethylaminobenzyl)-2-phenylindole (12) following the method described in the literature.[1]

3-(p-*Dimethylaminobenzyl*)-2-*phenylindole* (12).—This compound was synthesized following a method described in the literature.[33] Starting from 3-(*p*-dimethylaminophenyl)-1-phenylpropan-1-one (20 mmol) and phenylhydrazine (20 mmol) in the presence of PCl_3 (40 mmol), *compound* (12) was isolated in 60% yield, m.p. 128° (from benzene–ligroin), $v_{max.}$ (Nujol) 3 200 cm^{-1} (NH), δ ($CDCl_3$) 2.9 (6 H, s, NMe_2), 4.23 (2 H, s, CH_2Ar), 6.6—7.7 (13 H, m, ArH), 8.15br (1 H, NH) (Found: C, 84.55; H, 7.1; N, 8.6%; M, 326. $C_{23}H_{22}$-N_2 requires C, 84.6; H, 6.8; N, 8.6%; M, 326.4).

Bis-(1-*methyl-2-phenylindol-3-yl*)*phenylmethane* (1d).— This compound, already described in the literature,[24] was

conveniently prepared as follows. 1-Methyl-2-phenylindole (2.0 mmol), benzylideneaniline (2.1 mmol), acetic acid (10 ml), and absolute ethanol (7 ml) were heated in boiling water for 1 h. Compound (1d) precipitated quantitatively by cooling.

3-(*Hydroxyphenylmethyl*)-1-*methyl*-2-*phenylindole* (1f).— PhMgBr [obtained from Mg (20 mmol) and bromobenzene (20 mmol) in THF (20 ml)] was added to a solution of 1-methyl-2-phenylindole-3-carbaldehyde (10 mmol) in dried Et_2O (180 ml). After 12 h the mixture was poured into 10% aqueous NH_4Cl (100 ml). The ether layer was separated, dried on Na_2SO_4, and evaporated to dryness. The residue, taken up with benzene, was chromatographed on a silica column using benzene as eluant, m.p. 233° (from methylene chloride–ligroin), yield 70%, δ ($CDCl_3$) 3.35 (3 H, s, NMe), 5.62 [1 H, s, C*H*(OH)Ph], and 8.7—7.9 (15 H, m, ArH +OH) (Found: C, 84.4; H, 6.25; N, 4.6. Calc. for $C_{22}H_{19}NO$: C, 84.3; H, 6.2; N, 4.45%).

3-*Benzyl*-1-*methyl*-2-*phenylindole* (1h).—This compound was prepared by direct methylation of 2-phenyl-3-benzyl-indole (13) following the method described in the literature.[1] Compound (1h) was isolated in quantitative yield, m.p. 55° (from petroleum–ether), δ ($CDCl_3$) 3.62 (3 H, s, NMe), 4.12 (2 H, s, CH_2Ph), and 7.05—7.75 (14 H, m, ArH) (Found: C, 88.8; H, 6.5; N, 4.55%; *M*, 297. Calc. for $C_{22}H_{19}N$: C, 88.85; H, 6.45; N, 4.7%; *M*, 297.3).

3-*Benzyl*-2-*phenylindole* (13).—Starting from 1,3-diphenyl-propan-1-one and phenylhydrazine and following the method described in the literature,[33] compound (13), described in the literature,[34] was isolated in 90% yield.

1-*Methyl*-2-*phenyl*-3-*phenylthioindole* (1k).—Phenylsul-phenyl chloride [35] (1 mmol) in Et_2O (15 ml) was added over 15 min to a solution of 1-methyl-2-phenylindole (1 mmol) in Et_2O (150 ml) and pyridine (1 mmol), at room temperature and with stirring. The mixture was then heated to 35—40° with a steam-bath and then left to stand overnight. The solution was poured into water (100 ml) and the ether layer was separated, dried (Na_2SO_4), and evaporated to dryness. The residue was crystallised from ethanol, m.p. 110°, yield 75%, δ ($CDCl_3$) 3.73 (3 H, s, NMe) and 6.8—7.8 (14, m, ArH) (Found: C, 80.3; H, 5.45; N, 4.3. Calc. for $C_{21}H_{17}$-NS: C, 80.0; H, 5.45; N, 4.45%).

Reaction between 3-*Substituted Indoles* (1a—k), 4-*Sub-stituted* NN-*Dimethylanilines* (4a—f), *and Arenediazonium Salts. General Procedure.*—The arenediazonium salt solution, obtained from the aniline derivative (3 mmol) in 5N-HCl (20 ml) and $NaNO_2$ (3 mmol) in H_2O (10 ml), neutralized with CH_3CO_2Na, was added to the substrate solution at 8 °C under stirring. After the times reported in Tables 1 and 2, the mixture was extracted with $CHCl_3$. The chloroform layer was separated, dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed on a silica column using benzene as eluant. The isolated products are reported in Tables 1 and 2. Compounds (3a),[36] (3b),[26] (6a),[37] (6b),[16] and (6c) [30] were identified by com-parison with authentic samples prepared as described in the literature. Compound (10) was identified by comparison with an authentic sample prepared by an independent method (see below). Compound (11), m.p. 132° (from benzene–petroleum), was identified from its spectroscopic data, δ ($CDCl_3$) 2.41 (3 H, s, COMe), 3.16 (6 H, s, NMe_2), 6.82 (1 H, d, ArH, *J* 9.0 Hz), 7.82 (1 H, d, ArH, *J* 9.0 Hz), 8.0 (4 H, pseudo q, ArH, *J* 9.6 Hz), and 8.18 (1 H, s, ArH) (Found: C, 61.55; H, 5.1; N, 17.75. Calc. for $C_{16}H_{16}N_4$-O_3: C, 61.5; H, 5.15; N, 17.95%).

4-*Acetyl*-N-(p-*nitrophenylazo*)-N-*methylaniline* (10).—We followed the general procedure starting from *p*-acetyl-*N*-methylaniline [31] (9) (1.0 mmol) and *p*-nitrobenzenediazonium ion (3.0 mmol). Compound (10) precipitated almost quantitatively in the reaction medium, δ ($CDCl_3$) 2.63 (3 H, s, COMe), 3.78 (3 H, s, NMe), 7.88 (4 H, pseudo q, ArH, *J* 9.2 Hz), and 7.93 (4 H, pseudo q, ArH, *J* 8.4 Hz) (Found: C, 60.0; H, 4.7; N, 18.9%; *M*, 298. Calc. for $C_{15}H_{14}N_4O_3$: C, 60.4; H, 4.75; N, 18.8%; *M*, 298.3).

3-*Thioniaphenyl*-1-*methyl*-2-*phenyl*-3H-*indole Diperchlor-ate* (8).—Iodine (5 mmol) and $AgClO_4$ (10 mmol) in CH_3CN (100 ml) were added to a solution of (1a) (2.5 mmol) in CH_3CN (10 ml). The resulting solution, containing the dication (8), was magnetically inactive. All attempts to isolate compound (8) failed. The presence of compound (8) in this solution was demonstrated in the coproportionation reaction (see below).

Cation Radical (7) *by Anodic Oxidation.*—Compound (1a) (*ca.* 1.5 × 10^{-3} mol) in CH_3CN–Et_4NClO_4 (0.1M) was elec-trolysed at the first step potential (0.33 V) using graphite as working electrode and Ag–$AgClO_4$ (0.1M) in CH_3CN as the reference electrode. After 80—90% conversion, a sample was transferred into the e.s.r. cavity giving the signal for cation radical (7).

Cation Radical (7) *by Chemical Oxidation of* (1a).—Iodine (1.5 mmol) and $AgClO_4$ (3 mmol) in CH_3CN (100 ml) were mixed and added to a solution of (1a) (3 mmol) in CH_3CN (10 ml). After 30 min the mixture was filtered. The filtrate was evaporated to a small volume and dried Et_2O was added. The precipitated cation radical (7) was separated by filtration, m.p. 90° (decomp.) (Found: 54.65; H, 4.65; N, 4.05. Calc. for $C_{16}H_{15}ClNO_4S$: C, 54.45; H, 4.3; N, 3.95%).

Cation Radical (7) *by Coproportionation between* (1a) *and* (8).—Cation radical (7) was obtained quantitatively by mixing equal volumes of solutions of (1a) and (8) at the same concentration.

Reactions in the E.s.r. Cavity.—Equimolar solutions of substrate (1a—k) or (4a—f) and arenediazonium salt were each placed in one of the two legs of an inverted U cell similar to that described by Russel,[38] and degassed with nitrogen at 8 °C. The mixed solutions were transferred to the e.s.r. cavity.

Anodic Oxidation.—The $E_{\frac{1}{2}}$ values were measured by polarography in MeCN using graphite as working electrode versus Ag–$AgClO_4$ (0.1M). The reversibility for (1a) was observed by cyclic voltammetry at the scan rate of 0.2 V s^{-1} K^{-1} using the above electrodes.

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