Electrophilic *ipso*-Substitutions. Part 3.[1] Reactions of 3-Substituted Indoles, 4-Substituted *N,N*-Dimethylanilines, and 1- and 3-Substituted Indolizines with Nitrous Acid

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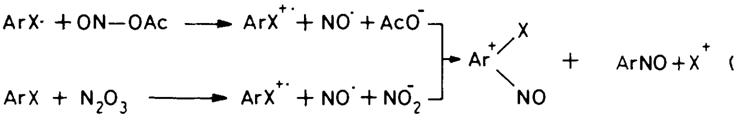
Reactions of 3-substituted indoles, *N,N*-dimethylanilines, and 1- and 3-substituted indolizines with nitrous acid yield products of *ipso*-substitutions, essentially the corresponding nitro-derivatives. An electron transfer process is proposed for the initial step, on the basis of reaction products, e.s.r. evidence, and substrate oxidation potentials.

In previous papers we described electrophilic *ipso*-substitutions of substituted indoles and *N,N*-dimethylanilines with nitronium[2] and arenediazonium[1] ions and also of 3-phenylazoindoles[2] with nitrous acid. Many of the above reactions were interpreted in terms of an electron transfer process, on the basis of the composition of the reaction products, e.s.r. evidence, or the oxidation potentials of the substrates. Since radical cations in general show a low stability,[3] which makes their detection difficult, we consider the nature of the reaction products the most important feature for elucidating the mechanism. In the present paper we describe a study of the title compounds with nitrous acid.

Results and Discussion

All reactions were carried out at room temperature in acetic acid using substrate/reagent (solid $NaNO_2$) in a 1 : 2 ratio, unless otherwise specified.

Reactions of Indoles.—3-Substituted indoles (1a—h) essentially yielded 3-nitroso- (2) and 3-nitro-indoles (3). 3-Formylindole (4) and 3-nitroindole (3) were also formed from (1b) and (1e); 3-nitrosoindole (2), a 3-benzylnitroindole (5), and 1-methyl-2-benzyl-2-phenyl-3-oxoindoline (indoxyl) (6) were formed from (1d) (Scheme 1, Table 1). The formation of 3-nitroso- (2) and 3-nitro-indoles (3), the last derived from oxidation by the excess of nitrous acid, can be explained in terms of an electron transfer process as shown in equation (i), as proposed by others for similar reactions.[4a,b] The species N_2O_3 or ON^-AcO, which can be considered the most likely reagents under the conditions used, could undergo homolytic cleavage, induced by compounds having a low oxidation potential.[5,6] Compound (1a), when treated with $NaNO_2$ in the e.s.r. spectrometer cavity, gave a signal similar to that recorded for the reaction of (1a) with arenediazonium ion and corresponding to the radical cation $(1a)^{+\cdot}$.[1]



$$\left.\begin{array}{l} ArX + ON{-}OAc \longrightarrow ArX^{+\cdot} + NO^{\cdot} + AcO^{-} \\ ArX + N_2O_3 \longrightarrow ArX^{+\cdot} + NO^{\cdot} + NO_2^{-} \end{array}\right] \longrightarrow \overset{+}{Ar}\begin{smallmatrix} X \\ NO \end{smallmatrix} + ArNO + X^{+} \qquad (i)$$

Compound (1d) also yielded the product (6) together with the *ipso*-substitution product (2) and the nitration product (5). Formation of the indoxyl (6), particularly significant in mechanistic terms, can be explained in terms of an intermediate radical cation (7), which undergoes nucleophilic attack by water, forming the intermediate (8)[7,8] (Scheme 2). As for the formation of (6) from (8), there are several examples of rearrangements of 3*H*-indol-3-ols to indolinones,[9] and the migratory power of the benzyl group is well known.[10] The proposed mechanism is supported by the fact that the yield of indoxyl (6) increased when the reaction is carried out in aqueous acetic acid (Table 1). The presence of 3-benzyl-5-nitroindole, (5), the structure of which was confirmed by comparing its ^1H n.m.r. spectrum with that of 1-methyl-2-phenyl-5-nitroindole, could be explained through the intermediate formation of the radical cation (7) as shown in Scheme 2.† An alternative mechanism could involve a 3-hydroxyiminoindole as intermediate, but compounds of this kind do not undergo hydrolysis to form the corresponding indoxyls.[12]

Because the oxidation potentials ($E_{\frac{1}{2}}$) of compounds (1a) and (1d) are 0.51 and 0.62 V, respectively, and since the $E_{\frac{1}{2}}$ values of compounds (1b), (1c), (1e), and (1f) are in the 0.52—0.67 V range, we believe that an electron transfer process might be involved in these cases also. The 3-substituted indoles (1g) and (1h), which have high $E_{\frac{1}{2}}$ values (1.02 and 1.13 V, respectively), did not react at all at room temperature. In the case of (1g) traces of 3-nitroindole (3) were obtained after the reaction mixture was heated at 60 °C for 72 h.

Reaction of N,N-*Dimethylanilines.*—*N,N*-Dimethylanilines (9a—e) yielded in every case a 4-nitro-*N,N*-dimethylaniline (10) (Scheme 3, Table 2). Despite the fact that no e.s.r. evidence was obtained for these reactions, the products and the oxidation potentials point to an electron transfer mechanism. Compounds (9d) and (9e), which show the highest oxidation potentials in the series[1] ($E_{\frac{1}{2}}$ 0.77 and 0.76 V, respectively), gave the corresponding *N*-nitroso derivatives (13) and (15), derived from the demethylated *N,N*-dimethylanilines (1d) and (1e), with nitrous acid. In fact, 4-acetyl-*N*-methylaniline (16) treated with nitrous acid gave the corresponding *N*-nitroso derivative (13) in quantitative yield. The mechanism of demethylation of *N,N*-dimethylanilines has been considered from several different viewpoints.[13] Recently this reaction was interpretated in terms of an intermediate radical cation, as demonstrated by anodic[14] and chemical oxidation.[15,16] Thus, the formation of 4-nitro-*N,N*-dimethylaniline (10) could be explained by a mechanism which in-

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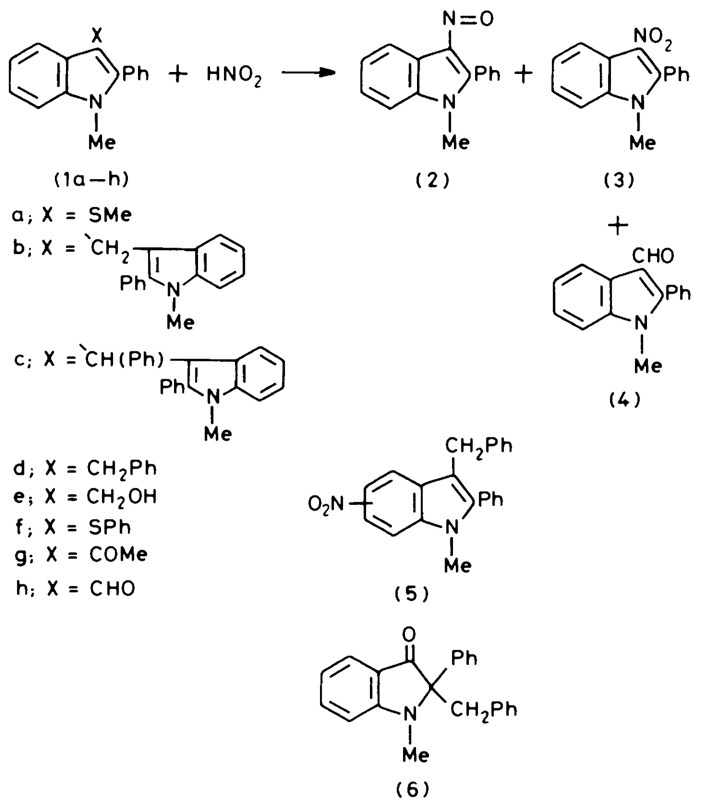
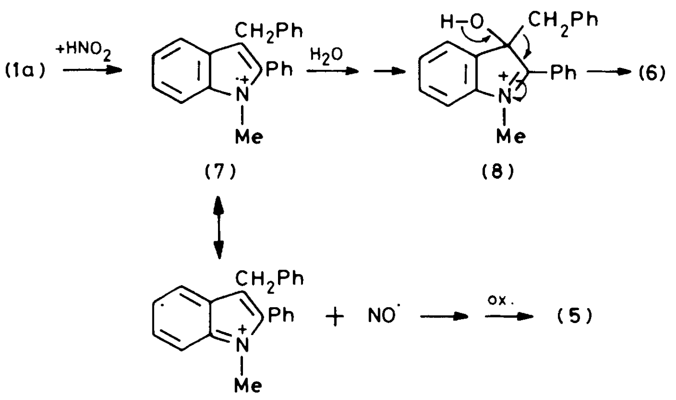
† Since indoles give 5-nitro derivatives when nitrated in sulphuric acid,[11] we tried to prepare compound (5) by direct nitration of (1d), but only 1-methyl-2-phenyl-3-(4-nitrobenzyl)-5-nitroindole and 1-methyl-2-phenyl-3-(4-nitrobenzyl)indole were isolated.



Scheme 1.



Scheme 2.

Table 1. Reactions of 3-substituted indoles (1a—h) with nitrous acid

Compound	Reaction time (h)	Product [% yield]
(1a)	20	(2) [trace]; (3) [40]
(1b) [a]	20	(3) [30]; (4) [30]
(1c) [a]	20	(2) [37]; (3) [38]
(1d)	4	(2) [24]; (5) [28]; (6) [21]
(1d) [b]	4	(2) [22]; (5) [24]; (6) [32]
(1e)	24	(3) [31]; (4) [30]
(1f)	36	(3) [90]
(1g) [c]	72	(3) [trace]
(1h) [c]	72	No reaction

[a] The substrate-reagent ratio was 1 : 4. [b] Carried out in aqueous acetic acid. [c] Carried out at 60 °C.

volves an electron transfer process like that described for the reactions with arenediazonium ions,[1] and here generalized in equation (i). As to the formation of compounds (11), (12), and (14), the more probable mechanism is that involving a rearrangement of the σ-complex (17), in agreement with that described by others[17] (Scheme 4). The reactions of *N*,*N*-dimethylaniline[18] and compounds (9a)[19] and (9e)[20] with nitrous acid, and the nitrous acid catalysed reaction of *N*,*N*-dimethylaniline with nitric acid,[17] have already been studied; the results, which are in partial agreement with ours, can be explained by our arguments.

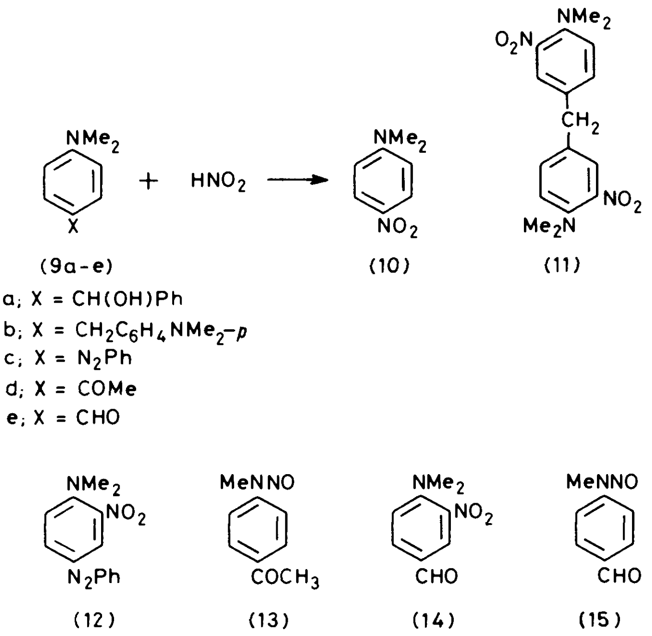
Reactions of Indolizines.—3-Substituted-1-methyl-2-phenylindolizines (19a—d), with nitrous acid under the above conditions, yielded 3-nitroso- (20) and 3-nitro-indolizines (21), and, in the case of (19a), the 3-(*p*-nitrophenyl)indolizine (22), (Scheme 5, Table 3). Since the oxidation potentials ($E_{1/2}$) are in the 0.08—0.16 V range, and are lower than those of the corresponding substituted indoles and *N*,*N*-dimethylanilines, we consider this kind of compound particularly suitable for an electron transfer process.[20,21] For the mechanism of these reactions too, we propose an electron transfer process, followed by radical-pair collapse to the σ-complex intermediate. This supposition is supported by the fact that all reactions gave an intense and unresolved transient e.s.r. signal, and, furthermore, by the higher reactivity of indolizines than of indoles.[22] The fact that the indole (1d), which clearly reacted through an intermediate radical cation (7) (see before), shows an oxidation potential of 0.62 V, the highest $E_{1/2}$ value of the indolizines studied, represents another piece of evidence supporting the proposed mechanism.

The results of the reactions of 1-substituted 2-phenyl-3-

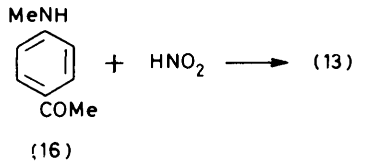
Table 2. Reactions of *N*,*N*-dimethylanilines (9a—e) with nitrous acid

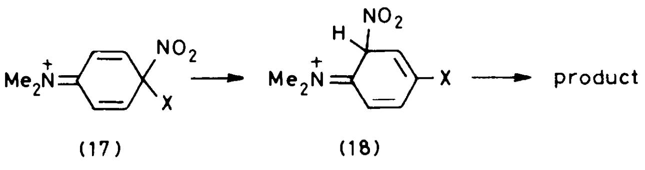
Compound	Reaction time (h)	Product [% yield]
(9a)	14	(10) [30]
(9b)[a]	10	(10) [30]; (11) [20]
(9c)	40	(10) [60]; (12) [24]
(9d)	20	(10) [24]; (13) [67]
(9e)	96	(10) [16]; (14) [9]; (15) [18]

[a] Substrate-reagent ratio 1 : 4.



Scheme 3.



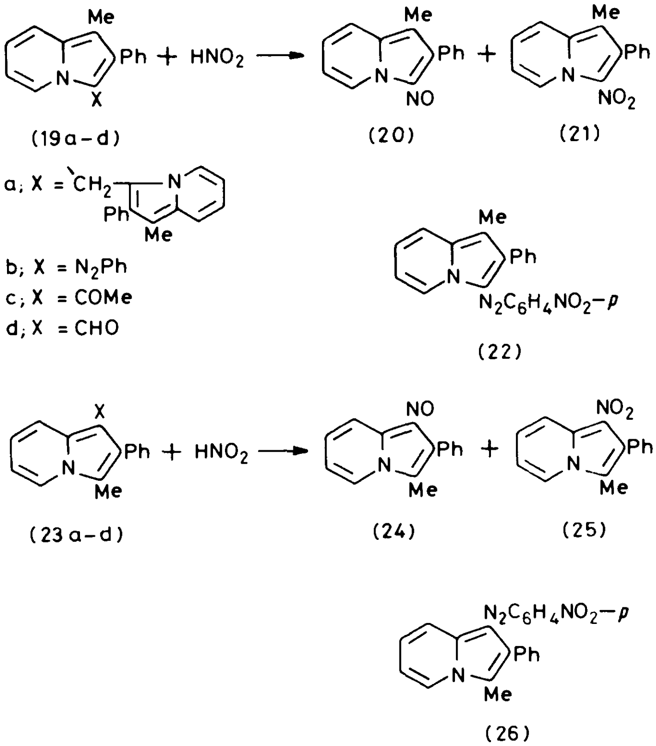


Scheme 4.

Table 3. Reactions of indolizines (19a—d) and (23a—d) with nitrous acid

Compound	Reaction time (h)	Product [% yield]
(19a)[a]	8	(20) [61]; (21) [18]
(19b)	1	(21) [51]; (22) [43]
(19c)	36	(22) [90]
(19d)	48	(22) [47]
(23a)[a]	4	(24) [54]; (25) [13]
(23b)	4	(25) [77]; (26) [trace]
(23c)	5	(25) [68]
(23d)	30	(25) [61]

[a] Substrate-reagent ratio 1 : 4.



Scheme 5.

methylindolizines (23a—d) (Scheme 5, Table 3) with nitrous acid, for which the $E_{\frac{1}{2}}$ values are in the same range (0.18—0.66 V) as those of the indolizines (19a—d), can be interpreted in the same way.

Conclusions

As stated in the introduction, it is difficult to demonstrate an electron transfer process as the initial step of an electrophilic substitution. However, if we consider that: (i) dinitrogen trioxide and acyl nitrite are good oxidants; (ii) the oxidation potentials of the studied compounds are low; and (iii) the reactivity of indoles and indolizines *versus* nitrosating agents is high; [23,24] then the electron transfer process that we propose for most of the reactions described here can be justified.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer for Nujol mulls. ^{1}H N.m.r. spectra were recorded with a Varian XL 100 spectrometer (tetramethylsilane as internal standard). E.s.r. spectra were recorded with a Varian E4 spectrometer. The mass spectra were recorded with a Varian 112 S instrument. Starting materials (1a),[1] (1b),[25] (1c),[2] (1d),[1] (1e),[26] (1f),[1] (1g),[27] (1h),[2] (9a),[28] (9b),[29] (9c) (C.Erba), (9d),[30] (9e)(Fluka), (19b),[31] (19c),[32] and (23a),[33] were prepared as described in the literature. Compounds (6),[34] (14),[20] (20),[34] and (24) [35] were prepared for comparison purposes.

Table 4. Analytical and spectroscopic data for new compounds

Compd.*	M.p. (°C)	Formula	Found (%) †			$\nu_{max.}$/cm^{-1}	Chemical shift (δ) ‡
			C	H	N		
(5)	Oil	$C_{22}H_{18}N_2O_2$	C, 77.25 (77.15)	H, 5.45 (5.3)	N, 8.2 (8.2)		3.7 (3 H, s, Me), 4.1 (2 H, s, CH_2), 6.83—7.83 (11 H, m, arom.), 7.9 (1 H, pseudo-q, arom., *J* 9.0, 2.0 Hz), 8.4 (1 H, d, arom., *J* 2.0 Hz)
(11)	125 [a]	$C_{17}H_{20}N_4O_4$	C, 59.15 (59.3)	H, 5.75 (5.85)	N, 16.3 (16.25)	1 630 1 530	2.83 (12 H, s, 4Me), 3.80 (2 H, s, CH_2), 6.9 (2 H, d, arom., *J* 9.0 Hz), 7.14 (2 H, pseudo-q, arom., *J* 9.0, 2.8 Hz), 7.5 (2 H, d, arom., *J* 2.8 Hz)
(12)	103 [a]	$C_{14}H_{14}N_4O_2$	C, 62.35 (62.2)	H, 5.35 (5.25)	N, 20.95 (20.75)	1 620 1 530	2.96 (6 H, s, Me), 7.0 (1 H, d, arom., *J* 9.6 Hz), 7.3—8.2 (6 H, m, arom.), 8.36 (1 H, d, arom., *J* 2.4 Hz)
(13)	107 [b]	$C_9H_{10}N_2O_2$	C, 60.45 (60.65)	H, 5.6 (5.65)	N, 15.7 (15.7)	1 680 1 610	2.76 (3 H, s, NMe), 3.5 (3 H, s, COMe), 7.92 (4 H, pseudo-q, arom.)
(19a)	154 [a]	$C_{31}H_{26}N_2$	C, 87.35 (87.3)	H, 6.05 (6.15)	N, 6.5 (6.55)	1 605	2.23 (6 H, s, 2Me), 4.55 (2 H, s, CH_2), 6.13 (2 H, t, arom.), 6.45 (2 H, t, arom.), 7.1—7.56 (12 H, m, arom.)
(19d)	125 [b]	$C_{16}H_{13}NO$	C, 81.75 (81.65)	H, 5.7 (5.55)	N, 5.95 (5.95)	1 650 1 630	2.26 (3 H, s, Me), 6.75—7.7 (7 H, m, arom.), 9.65 (1 H, s, CHO), 9.95 (1 H, d, arom.)
(21)	173 [b]	$C_{15}H_{12}N_2O_2$	C, 71.25 (71.4)	H, 4.85 (4.8)	N, 10.95 (11.1)	1 630	2.16 (3 H, s, Me), 7.05 (1 H, pseudo-q, arom. *J* 6.5, 6.3 Hz), 7.16—7.66 (7 H, m, arom.), 9.7 (1 H, d, arom., *J* 6.6 Hz)
(22)	276 [a]	$C_{21}H_{16}N_4O_2$	C, 70.7 (70.75)	H, 4.35 (4.5)	N, 15.8 (15.7)	1 620 1 600 1 585	3.13 (3 H, s, Me), 7.36—8.16 (13 H, m, arom.) [d]
(23b)	136 [a]	$C_{21}H_{17}N_3$	C, 80.85 (8.1)	H, 5.65 (5.5)	N, 13.35 (13.5)	1 500 1 460	2.5 (3 H, s, Me), 6.6—8.0 (13 H, m, arom.), 8.7 (1 H, d, arom.)
(23c)	115 [c]	$C_{17}H_{15}NO$	C, 81.65 (81.8)	H, 6.05 (6.05)	N, 5.7 (5.6)	1 640 1 620 1 605	1.96 (3 H, s, COMe), 2.26 (3 H, s, Me), 6.83 (1 H, pseudo-q, arom., *J* 7.5, 6.3 Hz), 7.03—7.5 (6 H, m, arom.), 7.76 (1 H, d, arom., *J* 6.3 Hz), 8.55 (1 H, d, arom., *J* 7.5 Hz)
(23d)	163 [c]	$C_{16}H_{13}NO$	C, 81.6 (81.65)	H, 5.4 (5.55)	N, 6.15 (5.95)	1 645 1 620	2.38 (3 H, s, Me), 6.88 (1 H, pseudo-q, arom., *J* 9.0, 6.5 Hz), 7.06—7.5 (6 H, m, arom.), 7.83 (1 H, d, arom., *J* 6.5 Hz), 8.43 (1 H, d, arom., *J* 9.0 Hz), 9.78 (1 H, s, CHO)
(25)	186 [b]	$C_{15}H_{12}N_2O_2$	C, 71.65 (71.4)	H, 4.65 (4.8)	N, 11.25 (11.1)	1 610	2.33 (3 H, s, Me), 7.0 (1 H, pseudo-q, arom., *J* 9.0, 6.6 Hz), 7.2—7.5 (6 H, m, arom.), 7.93 (1 H, d, arom., *J* 6.6 Hz), 8.5 (1 H, d, arom., *J* 9.0 Hz)
(26)	272 [a]	$C_{21}H_{16}N_4O_2$	C, 71.0 (70.75)	H, 4.45 (4.5)	N, 15.75 (15.7)	1 600 1 585	3.25 (3 H, s, Me), 7.0—8.73 (13 H, m, arom.) [d]

* All compounds gave correct molecular ion peaks in the mass spectrum. † Calculated in parentheses. ‡ From $CDCl_3$ solutions when not otherwise specified.

[a] From EtOH. [b] From benzene–light petroleum (b.p. 60—80 °C). [c] Light petroleum (b.p. 80—100 °C). [d] From $(CD_3)_2SO$ solutions.

Bis-(1-methyl-2-phenylindolizin-3-yl)methane (19a).—1-Methyl-2-phenylindolizine (15 mmol) and aqueous 37% formaldehyde (12.5 mmol) in dioxane (30 ml), treated as described in the literature[33] for the isomer (23a), gave compound (19a) in 80% yield (Table 4).

1-Methyl-2-phenyl-3-formylindolizine (19d) *and 1-Formyl-2-phenyl-3-methylindolizine* (23d).—$POCl_3$ (1 ml) was added to Me_2NCHO (3.2 g) dropwise at 10—20 °C with stirring. The indolizine (2.07 g in 6 ml of Me_2NCHO) was added to the stirred Vilsmeier reagent, with the temperature kept in the 20—30 °C range. The mixture was then stirred at 35—40 °C for 45 min, poured onto ice, neutralized with aqueous 5% NaOH and extracted with chloroform. The chloroform layer was separated, dried (Na_2SO_4), and evaporated to dryness. The residue, chromatographed on an SiO_2 column (benzene as eluant) gave (19d) or (23d) in 70% or 50% yield respectively (Table 4).

1-Phenylazo-2-phenyl-3-methylindolizine (23b).—2-Phenyl-3-methylindolizine (10 mmol in 140 ml of EtOH) and benzenediazonium chloride (20 mmol in 30 ml of H_2O), treated as described for the isomer (19b), gave compound (23b) in almost quantitative yield (Table 4).

1-Acetyl-2-phenyl-3-methylindolizine (23c).—2-Phenyl-3-methylindolizine (1.6 g), dry sodium acetate (2.0 g), and acetic anhydride (15 ml) were refluxed for 6 h. The mixture was poured into ice and water, stirred for 3 h, and extracted with chloroform. The chloroform layer was separated, dried (Na_2SO_4), and evaporated to dryness. The residue, chromatographed on an Al_2O_3 column (elution with benzene-acetone, 9 : 1) gave (23c) in 80% yield (Table 4).

Reactions of Indoles (1a—h), *N,N-Dimethylanilines* (9a—e), *and Indolizines* (19a—d) *and* (23a—d) *with Nitrous Acid. General Procedure*.—Solid $NaNO_2$ (10 mmol) was added to the substrate (5 mmol in 20—100 ml of acetic acid). After the times reported in Tables 1—3, the mixture was poured into water (100—200 ml), neutralized with solid Na_2CO_3, and extracted with chloroform. The chloroform layer was separated, dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed on an SiO_2 column (elution with benzene or benzene-acetone, 9 : 1). The isolated compounds are reported in Tables 1—3. Analytical and spectroscopic data of new compounds are reported in Table 4. Known compounds were identified by comparison with authentic samples.

Reaction of 4-*Acetyl*-N-*methylaniline* (16) *with Nitrous Acid.*—Solid $NaNO_2$ (4 mmol) was added to a solution of (16)[36] (2 mmol in 15 ml of acetic acid). After 2 h the reaction, worked up as described in the general procedure, gave the corresponding *N*-nitroso derivative (13) in almost quantitative yield.

Reactions in the E.s.r. Spectrometer Cavity.—Acetic acid solutions (10^{-1}M) of (1a—h), (9a—e), (19a—d), and (23a—d) and the corresponding quantities of $NaNO_2$ were placed in one of the two arms of an inverted cell, similar to that described by Russel,[37] and degassed with nitrogen at room temperature. The mixed materials were transferred into the e.s.r. cavity.

Anodic Oxidation.—The reported $E_{\frac{1}{2}}$ values were measured by polarography in MeCN using a graphite or rotating platinum electode *versus* Ag–$AgClO_4$ (0.1M).

Nitration of the Indole (1d) *with* 70% *Nitric Acid in* 96% *Sulphuric Acid.*—70% HNO_3 (4 mmol) was added to a stirred solution of (1d) (3 mmol) in 10 ml of 96% H_2SO_4, at 15 °C. After 15 min the mixture was poured into 100 g of ice, neutralized with solid Na_2CO_3, and extracted with $CHCl_3$. The $CHCl_3$ layer was separated, dried (Na_2SO_4), and chromatographed on a column of silica gel (elution with benzene). The first yellow eluate was 1-methyl-2-phenyl-3-(4-nitrobenzyl)-indole: m.p. 185 °C (from CH_2Cl_2–light petroleum); 8% yield, δ ($CDCl_3$) 3.63 (3 H, s, Me), 4.15 (2 H, s, $-CH_2-$); 7.03—7.56 (11 H, m, arom.) and, 8.1 (2 H, d, AB arom.) (Found: C, 77.25; H, 5.25; N, 8.2. Calc. for $C_{22}H_{18}N_2O_2$: C, 77.15; H, 5.3; N, 8.2%). The second yellow eluate was 1-methyl-2-phenyl-3-(4-nitrobenzyl)-5-nitroindole, m.p. 150 °C (from ethanol); 56% yield, δ ($CDCl_3$) 3.7 (3 H, s, Me), 4.2 (2 H, s, $-CH_2-$), 7.1—7.7 (8 H, m, arom.); 7.96—8.29 (1 H, pseudo-q, H-6 + 2 H, d, AB arom.), 8.39 (1 H, d, H-4, *J* 1.6 Hz) (Found: C, 68.35; H, 4.3; N, 11.0. Calc. for $C_{22}H_{17}N_3O_4$: C, 68.2; H, 4.4; N, 10.85%).

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