Reactions of Porphyrins with Nitronium Tetrafluoroborate in Pyridine

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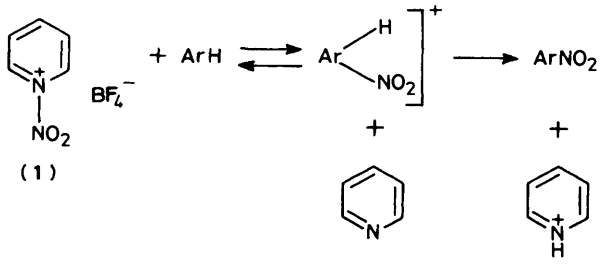
Octaethylporphyrin reacts with nitronium tetrafluoroborate in pyridine at 80 °C to afford the *meso*-nitroporphyrin in 31% yield after 6 h, whereas the zinc complex reacts very rapidly at 20 °C to afford 63% of the *meso*-nitroporphyrin after work-up. *meso*-Tetraphenylporphyrin, however, only reacted slowly with nitronium tetrafluoroborate in pyridine at rather higher temperatures in a sealed tube to afford the β-pyridinium salt of the porphyrin as the major product; again when the zinc complex of tetraphenylporphyrin was used the β-pyridinium salt was formed in 85% yield in a few minutes at 20 °C.

Brief treatment of the tetraphenylporphyrin pyridinium salt with alkali afforded a ring-opened glutaconaldehyde derivative of the β-aminoporphyrin, analogous to the well-known Zincke's compounds which can be obtained from *N*-arylpyridines with alkali. The structures of both the ring-opened products from the pyridinium porphyrin and from *N*-(2,4-dinitrophenyl)pyridinium chloride, were assigned by highfield n.m.r. spectroscopy, including decoupling and n.O.e. difference measurements.

In connection with other studies of electrophilic substitution in porphyrins, especially those occurring at the *meso*-positions,[1] we have recently studied the reaction of nitronium tetrafluoroborate with porphyrins and their metal complexes. Aromatic nitration is commonly carried out with mixtures of concentrated nitric and sulphuric acids, or with alkyl and metal nitrates catalysed by Lewis or Brønsted acids;[2] nitration can also be carried out with nitrate or nitrite ions under oxidising conditions (chemical or electrochemical).

meso-Nitration of simple alkyl porphyrins (unsubstituted in the *meso*-positions) has been carried out in strongly acidic media,[3] but the method suffers from the disadvantage that under these conditions the porphyrins are converted into their relatively unreactive dications. Attempts to nitrate porphyrin free bases with nitronium tetrafluoroborate in sulpholane were not very successful, although the more reactive chlorins were nitrated under these conditions at the *meso*-positions adjacent to the reduced ring.[4] More recently the metallo-complexes of porphyrins have been successfully nitrated with nitronium tetrafluoroborate in acetonitrile,[5] but attempts in our laboratories to nitrate porphyrin free bases under these conditions afforded only the corresponding dications. For this reason we turned to the use of pyridine as a solvent for the nitronium tetrafluoroborate reactions.

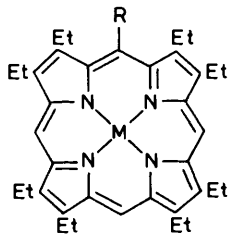
Nitronium tetrafluoroborate reacts with pyridine to give the 1-nitropyridinium salt[6] (**1**), and Olah[7] has reported the use of this compound and analogous salts (*e.g.* 1-nitroquinolinium salts) to effect 'transfer nitration of benzene and toluene.' These salts have the advantage that reactions can be carried out under essentially neutral conditions, since after nitration the displaced proton will bind with the liberated aromatic base [Equation (1)].



Equation (1)

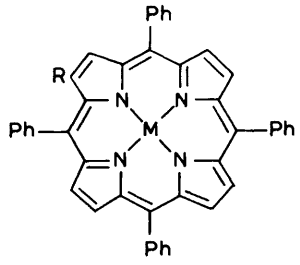
Octaethylporphyrin (**2a**) was dissolved in a mixture of chloroform and pyridine (as it is not very soluble in neat pyridine) and treated with an excess of nitronium tetrafluoroborate at 80 °C. The reaction was followed by changes in the visible spectrum and by t.l.c., and the products were worked up after 6 h and separated by chromatography; some decomposition had occurred but the main product was *meso*-nitro-octaethylporphyrin (**3a**) (31%), some octaethylporphyrin (14%) being recovered. The structure of the *meso*-nitro derivative was confirmed by n.m.r. and mass spectrometery and by melting point.[4] Attempts to improve the yield were unsuccessful as little reaction occurred below 80 °C, and at higher temperatures more decomposition occurred. However, when the octaethylporphyrin zinc complex (**2b**) was treated with nitronium tetrafluoroborate in pyridine at 20 °C, an immediate bathochromic shift in the visible absorption bands was observed, and the colour of the solution changed slightly. After work-up, demetallation, and chromatography, *meso*-nitro-octaethyl porphyrin (**3a**) was obtained in 62% yield. In the absence of evidence to the contrary it seems likely that these *meso*-nitrations follow the normal pattern of aromatic electrophilic substitution, *i.e.* formation of σ-complex followed by loss of a proton [equation (1)]..

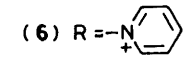
In contrast to the results with octaethylporphyrin (**2a**), *meso*-tetraphenylporphyrin (TPP) (**4a**) proved rather less reactive towards nitronium tetrafluoroborate in pyridine, and the reaction was carried out at 140 °C for up to 3 h before an appreciable change in the visible spectrum of the mixture was observed. On work-up the main product proved not to be the β-nitroporphyrin (**5a**) but the β-pyridinium derivative (45%) (**6a**); this was deduced initially from visible, n.m.r., and mass spectral evidence, and later confirmed by comparisons with the data reported by Shine[8] for the product obtained by treatment of zinc *meso*-tetraphenylporphyrin cation radical with pyridine. A small amount (1%) of the β-nitroporphyrin (**5a**) was also isolated, but when chloroform–pyridine (20:1 v/v) was used as solvent the yield of the β-nitroporphyrin (**5a**) increased to 15%, whilst that of the pyridinium salt (**6a**) decreased to 18%. After 20 h at 100 °C in neat pyridine, the yield of pyridinium salt fell to 26%, some 50% of the TPP being recovered. In chloroform–pyridine (20:1) at 100 °C for 10 h, 20% of the TPP was recovered and 29% of the pyridinium salt (**6a**) and 8% of the β-nitroporphyrin (**5a**) were obtained. The structure of the β-nitroporphyrin (**5a**) was confirmed by comparison (m.p.,

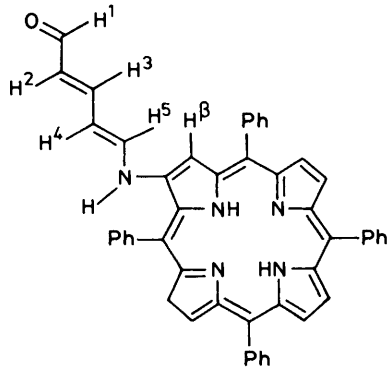


(2) R = H
(3) R = NO_2

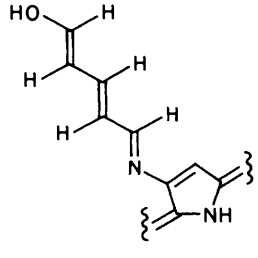
a; M = H_2
b; M = Zn



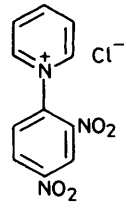
(4) R = H
(5) R = NO_2
(6) R =  Cl^-



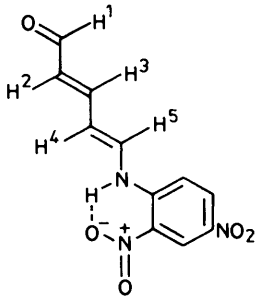
(7a)



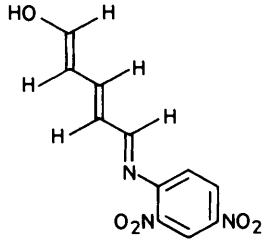
(7b)



(8)



(9a)

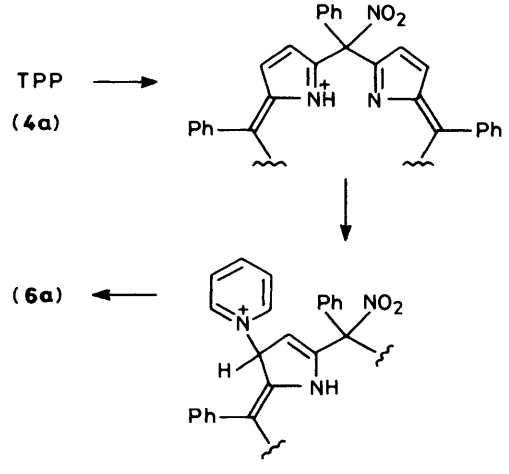


(9b)

n.m.r., and mass spectrometry) with an authentic sample prepared by treatment of zinc *meso*-tetraphenylporphyrin (**4b**) (zinc TPP) with cerium(IV) ammonium nitrate, or thallium(III) nitrate.[9]

When zinc TPP (**4b**) was treated with nitronium tetrafluoroborate (10 equiv.) in pyridine at 20 °C, the colour changed rapidly from red to green (and a bathochromic shift of the visible absorption bands was observed). After a few minutes the product was worked up and on chromatography afforded an excellent yield of zinc TPP pyridinium chloride (**6b**). Traces of zinc nitro-TPP (**5b**) were also found, and a small amount of zinc TPP (3%) was recovered.

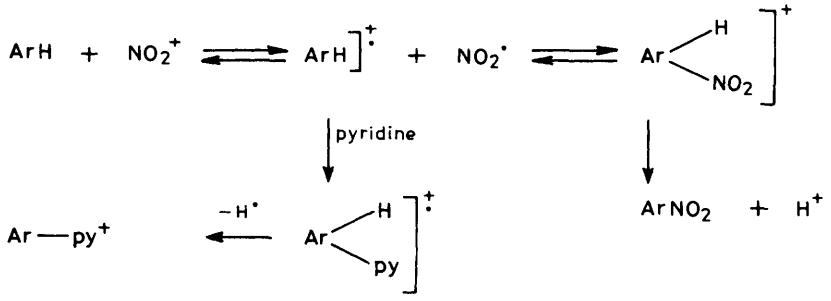
A possible mechanism for the formation of the β-pyridinium salts involves initial electrophilic attack of the nitronium ion at one of the *meso*-positions, and then nucleophilic addition of pyridine at a β-position followed by elimination of a proton and a nitrite ion (see Scheme). In neat pyridine the initial *meso* substitution product would rapidly react with the large excess of pyridine present, whereas in chloroform–pyridine solutions the *meso*-nitro intermediate could either revert to TPP or rearrange



Scheme.

to the β-nitro TPP; alternatively (but presumably more slowly), direct β-nitration of of the TPP could occur. Similar processes would be involved with zinc TPP and nitronium tetrafluoroborate in presence of pyridine.

We also considered the possibility that formation of the β-pyridinium salt involves the intermediacy of a cation radical, as this is the way in which it was originally prepared by Shine.[8] Moreover, such intermediates have been proposed[10] for aromatic nitrations with very reactive nitrating reagents by the 'electron transfer mechanism' [Equation (2)]. However, if a



Equation (2)

cation radical had been produced it would have been expected to react rapidly with nucleophiles (such as pyridine) whereas in the case of OEP, no *meso*-pyridinium salt was formed. We, therefore, concluded that the radical mechanism was unlikely. Direct evidence for the normal electrophilic substitution mechanism was obtained when we followed the reactions of zinc TPP (**4b**) with nitronium tetrafluoroborate spectroscopically in the absence of pyridine, and observed the formation of an intermediate with a spectrum similar to that of an isoporphyrin[11] (with two strong bands at 770 and 856 nm in the near i.r. region).

When the β-pyridinium derivative (**6a**) of TPP was treated with dilute potassium hydroxide in methanol, dramatic colour changes occurred, initially from yellow to green, and finally to orange. On working up the reaction mixture we obtained a new compound (*ca.* 30%), which was shown to be the glutaconaldehyde derivative (**7a**) of β-amino TPP by mass and n.m.r. spectrometry and by elemental analysis.

The product was assigned the aminoaldehyde structure (**7a**) following detailed analysis of the ^{1}H n.m.r. spectrum in $CDCl_3$. In addition to the TPP protons, six other protons were seen, two being doublets, the remaining four being quartets or triplets. The lowest field doublet (δ 9.45) was assigned to the aldehyde proton and the doublet at δ 6.75 (exchanging on shaking with D_2O) was assigned to the NH. Decoupling experiments clearly indicated the sequence of the six protons along the side-chain. The alternative imino–enol formation (**7b**) was ruled out because the N=CH proton would be expected to give a doublet at *ca.* δ 7 by analogy with other imines.[12]

Proton 4-H is quite strongly shielded at δ 5.35, suggesting the conformation (**7a**) in which 4-H is shielded by a phenyl ring. Difference nuclear Overhauser measurements confirmed this conformation. Irradiation of the NH enhanced the 4-H signal and the signal for the *o*-protons of a phenyl group. Irradiation of 5-H enhanced the 3-H signal and that of the neighbouring pyrrole proton β^1-H. Other enhancements are listed in the Experimental section and confirm that protons 1, 3, 5, and β^1 lie on one side of the chain, while 2, 4, 6, and the nearby phenyl lie on the other side.

The ready ring-opening of the β-pyridinium TPP salt (**6a**) is reminiscent of the similar ring-opening of simple aryl pyridinium salts under mild alkaline conditions. The classic example is Zincke's salt (**8**), prepared from 2,4-dinitrochlorobenzene and pyridine,[13] which on treatment with aqueous sodium carbonate forms a glutaconaldehyde derivative. This was originally formulated as an equilibrium mixture of the aminoaldehyde (**9a**) and imino–enol (**9b**) forms. We have now re-investigated this reaction and the n.m.r. spectral evidence establishes the aminoaldehyde form (**9a**) in $CDCl_3$ and in $(CD_3)_2SO$. Again the ring-opened pyridine moiety gave a series of six multiplets which could be placed in sequence by decoupling experiments. The aldehyde doublet appears at δ 9.59 ($CDCl_3$) or 9.49 ($(CD_3)_2SO$, close to the position in the TPP-derived compound. However, the NH appeared at much lower field (δ 10.4) in both solvents. This is believed to be due to H-bonding with the neighbouring nitro group on the aryl ring. Nuclear Overhauser enhancements in $CDCl_3$ established that protons 2, 4, and 6 lie on the same side of the side-chain, but proximity of peaks prevented measurements of the enhancements between the side-chain and the aryl ring. In $(CD_3)_2SO$ chemical shifts were sufficiently different to allow more complete Overhauser studies. These confirmed the conformation (**9a**) with protons 2, 4, and 6 on one side of the chain, and protons 1, 3, 5, and 6′ lying on the other side. Particularly significant enhancements were at 6′-H on irradiation of 5-H (23%) and at 5-H on irradiation of 6′-H (20%).

Thus, the n.m.r. results confirm the similarity of the products derived from TPP and from 2,4-dinitrochlorobenzene. Both exist in the aminoaldehyde forms with predominant conformations as indicated.

Experimental

M.p.s were measured on a Kofler block and are uncorrected. Mass spectra were measured with a Varian CH5D spectrometer at 70 e.v. and 50 A for e.i. spectra, and with wire currents 15—20 A for f.d. spectra. Reactions were followed by t.l.c., h.p.l.c., and u.v./visible spectroscopy as appropriate.

N.m.r. spectra were measured at 300 or 360 MHz on Bruker instruments, and are given as δ values in p.p.m. from $SiMe_4$. Nuclear Overhauser enhancements were measured by the difference method using standard Bruker software. Low intensity pre-saturation pulses of 5 s duration were applied before each scan. A sequence of 8 pulses at the selected position followed by 8 pulses at a nearby 'blank' position was repeated 64 or 128 times. The summed 'irradiated' and 'blank' free induction decay patterns were subtracted and transformed after processing with a line broadening factor of 1 Hz. Quantitative values for enhancement were obtained from integrals of the difference spectra. In all cases 32 K data points were used over a spectral width of 4 504 Hz.

meso-*Nitro-octaethylporphyrin* (**3a**).—(*a*) Octaethylporphyrin (82 mg) was heated with nitronium tetrafluoroborate (166 mg) in pyridine–chloroform (8:4 v/v; 10 ml) at 80 °C under nitrogen for 6 h. The solution was poured into water, extracted with chloroform, the extracts evaporated to dryness, and the residue taken up in trifluoroacetic acid (2 ml). After a few minutes, dichloromethane (25 ml) was added, and the mixture was shaken with dilute aqueous sodium hydrogen carbonate. The organic phase was worked up with water, dried (Na_2SO_4), evaporated to dryness, and the residue then chromatographed on preparative silica gel t.l.c. plates in toluene–hexane (1:2 v/v). Two porphyrinic bands were obtained and these were scraped off the plate, extracted with dichloromethane and crystallised from dichloromethane–hexane. The first band afforded nitro-octaethylporphyrin (24 mg, 31%), m.p. 255—256 °C (lit.,[4] m.p. 251—252 °C); *m/z* (f.d.) 579 (100%) (M^+); $\lambda_{max.}(CHCl_3)$ 400, 504, 538, 571, and 623 nm; $\delta(CDCl_3)$ 10.17 (s, 2 H, *meso*-H), 9.98 (s, 1 H, *meso*-H), 4.15—3.97 (m, 12 H, 1,4,5,6,7,8-CH_2), 3.75 (q, 4 H, 2,3-CH_2), 1.97—1.83 (m, 18 H, 1,4,5,6,7,8-Me), 1.72 (t, 6 H, 2,3-Me), and −3.77 and −3.85 (br s, 2NH).

The second band was unchanged OEP (11 mg, 14%).

(*b*) Zinc octaethylporphyrin (67 mg) in pyridine (3 ml) was treated with nitronium tetrafluoroborate (145 mg) and stirred under nitrogen at 20 °C. Within a few minutes the colour changed from red to green, and the visible spectral bands underwent bathochromic shifts. The product was worked up in the same manner as for the preceding experiments, followed by preparative t.l.c. on silica gel eluting with toluene–hexane (1:2 v/v). The main porphyrin band was extracted and recrystallised from dichloromethane–hexane to afford nitro-octaethylporphyrin (40 mg, 63%), m.p. 255—256 °C, identical in all respects with the previous product. A small amount of octaethylporphyrin was also recovered.

Reactions of meso-*Tetraphenylporphyrin with Nitronium Tetrafluoroborate.*—(*a*) *In pyridine solution.* Chlorin-free *meso*-tetraphenylporphyrin (240 mg) in pyridine (15 ml) was heated with nitronium tetrafluoroborate (560 mg) at 140 °C for 3 h under nitrogen. After the mixture had been allowed to cool it was poured into dilute hydrochloric acid (2M; 200 ml) and extracted with chloroform (3 × 100 ml). The combined extracts were washed with dilute aqueous sodium hydrogen carbonate and water, and then dried (Na_2SO_4). On evaporation to dryness the chloroform solution afforded a dark residue, which was chromatographed on alumina (Grade III) in toluene solution. The porphyrinic fraction obtained was shown by t.l.c. to contain two components which were separated by preparative thick layer chromatography on silica gel, eluting with toluene. The two bands obtained were extracted from the silica gel with dichloromethane and after evaporation of the solutions to dryness the residues were each crystallised from dichloromethane–hexane to give TPP (43 mg, 18%) and β-nitro-TPP (**5a**) (4 mg, 1%), m.p. >300 °C; $\lambda_{max.}(CHCl_3)$ 425, 528, 561, 602, and 664 nm; *m/z* (f.d.) 659 (M^+). The n.m.r. spectrum accorded with that previously reported.[5]

Further elution of the original chromatography column with chloroform afforded a green band which changed to yellow-brown on collection of the eluates. This fraction was shaken with saturated brine, and then washed with water, before being dried (Na_2SO_4). The residue, obtained after evaporation of the solvent under reduced pressure, crystallised from dichloromethane–hexane to give β-pyridinium-*meso*-tetraphenylporphyrin chloride (**6a**) (105 mg, 45%), m.p. >300 °C; *m/z* (f.d.) 692 (M^+); $\delta(CDCl_3)$ 9.24 (d, *J* 7 Hz, 2 H, pyr-2,6-H), 9.19 (s, 1 H, porphyrin-3-H), 8.98—8.52 (m, 7 H, porphyrin 7, 8, 12, 13, 17, 18-H, and pyr-4-H), 8.22—8.04 (m, 6 H, phenyl-*o*-H), 7.91—7.68 (m, 13 H, 5,10,15-phenyl m and p-H, 20-phenyl *o*-H, and 3,5-H), and 7.00—7.33 (m, 3 H, 20-phenyl-*m* and *p*-H); $\lambda_{max.}(CHCl_3)$ 425, 526, 560, 606, and 656 nm.

(*b*) *In chloroform–pyridine.*—TPP (106 mg) in chloroform–pyridine (10:0.5 v/v) (10 ml) was heated in a sealed tube with nitronium tetrafluoroborate (233 mg) for 3 h at 140 °C under nitrogen. After work-up as described above followed by chromatography, three products were obtained: (i) TPP (8 mg, 7%), (ii) β-nitro-TPP (18 mg, 15%), and (iii) β-pyridinium TPP chloride (21 mg, 18%).

In a similar reaction in which the mixture was heated at 100 °C for 10 h the products were TPP (20%), nitro-TPP (7 mg, 8%), and pyridinium TPP chloride (27 mg, 29%). The β-nitro TPP was recovered unchanged after being heated for 5 h in pyridine solution at 140 °C, thus showing that it was not an intermediate in the formation of the pyridinium salt.

Reaction of Zinc(II) meso-*Tetraphenyl Porphyrin with Nitronium Tetrafluoroborate.*—Zinc TPP (178 mg) in pyridine (10 ml) was stirred for 10 min with nitronium tetrafluoroborate (347 mg) until the colour of the solution changed from red to green. The solution was partitioned between water (100 ml) and chloroform (100 ml) and the organic phase washed with water and dried ($NaSO_4$). After evaporation of the solvent the residue was taken up in toluene and chromatographed on alumina (Grade III). The first (minor) band eluted was ZnTPP (5 mg, 3%), shown by preparative t.l.c. to contain a trace of the β-nitro ZnTPP (**5a**). The second (main) fraction was eluted with chloroform–methanol (9:1, v/v) and the eluate evaporated to small bulk and washed with brine, and then with water, and dried (Na_2SO_4). After evaporation to dryness the residue was recrystallised from dichloromethane–hexane to give the β-pyridinium zinc tetraphenylporphyrin chloride (**6b**) (172 mg, 85%), m.p. >300 °C; $\lambda_{max.}(CHCl_3)$ 427, 555, and 594 nm.

Demetallation was effected by treatment with trifluoroacetic acid; the metal-free porphyrin was taken up in chloroform and the solution neutralised with aqueous sodium hydrogen carbonate. After treatment with brine, followed by washing with water, the chloroform solution was dried (Na_2SO_4), evaporated to dryness, and the residue crystallised from dichloromethane–hexane to afford β-pyridinium TPP chloride identical in all respects with material prepared directly from TPP as above.

Reaction of Pyridinium TPP Chloride with Alkali.—To a solution of pyridinium *meso*-tetraphenylporphyrin chloride (**6a**) (32 mg) in tetrahydrofuran (50 ml) was added methanolic potassium hydroxide [1 ml of a solution of KOH (186 mg) in methanol (25 ml) (3 mol equiv.)]. The mixture was stirred for 10 min at 20 °C and then poured into cold, dilute hydrochloric acid (1M, 10 ml) and extracted with chloroform (2 × 10 ml). The organic extracts were washed with water (2 × 10 ml), dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed by preparative t.l.c. on silica gel plates, eluting with dichloromethane. The first (minor fraction) proved to be too unstable for characterisation, although the f.d. mass spectra showed an intense peak at *m/z* 629. The second (major) fraction was extracted from the plates and crystallised from methylene chloride–hexane to afford the aminoporphyrin derivative (**7a**) (9 mg, 29%); m.p. >300 °C (Found: C, 81.65; H, 5.1; N, 9.6. $C_{49}H_{35}N_5O{\cdot}0.5\ H_2O$ requires C, 81.9; H, 5.05; N, 9.7%); $\lambda_{max.}$ (log $\varepsilon_{max.}$) ($CHCl_3$) 419 (5.23), 471 (4.86), 530 (4.49), 573 (4.26), 599 (4.20), and 655 (3.45) nm; *m/z* 709 (M^+); $\delta(CDCl_3)$ 5.35 (1 H, dd, *J* 12, 13, 4-H), 6.0 (1 H, dd, *J* 8, 15, 2-H), 6.75 (1 H, d, *J* 13, 6-NH), 7.23 (1 H, dd, *J* 12, 15, 3-H), 7.44 (1 H, t, *J* 13, 5-H), 7.7—8.0 (12 H, complex, *m*- and *p*-Ph), 8.02 (1 H, s, β′-H), 8.2 (8 H, d, *J* 7, *o*-Ph), 8.65, 8.74, 8.82, 8.84 (each 1 H, d, *J* 5), and 8.73 (2 H, s, 6 × β-H), and 9.45 (1 H, d, *J* 8, 1-H). N.O.e. enhancements: 6-H→*o*-Ph (3.5%), 6-H→4-H (10%),

5-H→β′-H (9%), 5-H→3-H,* 4-H→6-H (6%), 4-H→2-H (10%), 3-H→5-H,* 3-H→1-H,* 2-H→4-H (5%), 1-H→3-H (10%), and β′-H→5-H (4%).

5-(2,4-*Dinitroanilino*)*penta*-2,4-*dienal* (**9a**).—Pyridine reacted with 2,4-dinitrochlorobenzene, and the resulting 2,4-dinitrophenylpyridinium chloride (**8**) on treatment with aqueous sodium carbonate as described by Zincke *et al.*,[13] afforded the dinitroanilinodienal (**9a**) as orange red crystals from acetone, m.p. 178—179 °C (lit.,[13] 180 °C); δ($CDCl_3$) 6.22 (1 H, dd, *J* 8, 15, 2-H), 6.38 (1 H, dd, *J* 13, 11, 4-H), 7.21 (1 H, dd, *J* 15, 11, 3-H), 7.32 (1 H, dd, *J* 13, 12, 5-H), 7.35 (1 H, d, *J* 10, 6′-H), 8.42 (1 H, dd, *J* 10, 2.5, 5′-H), 9.2 (1 H, d, *J* 2.5, 3′-H), 9.59 (1 H, d, *J* 8, 1-H), 10.46 (1 H, br d, *J* 2, 6-NH). N.O.e. enhancements: 1-H→3-H (14%), 4-H→2-H (13%), 4-H→6-NH (6%); δ[$(CD_3)_2SO$] 6.11 (1 H, dd, *J* 8, 15, 2-H), 6.65 (1 H, t, *J* 12, 4-H), 7.45 (1 H, dd, *J* 15, 12, 3-H), 7.79 (1 H, d, *J* 9, 6′-H), 8.00 (1 H, d, *J* 12, 5-H), 8.45 (1 H, dd, *J* 9, 2.5, 5′-H), 8.85 (1 H, d, *J* 2.5, 3′-H), 9.49 (1 H, d, *J* 8, 1-H), 10.44 (1 H, br s, 6-NH). N.O.e. enhancements: 6-H→4-H (15%), 5-H→3-H (14%), 5-H→6′-H (23%), 4-H→6-H (8%), 4-H→2-H (19%), 3-H→5′-H (10%), 3-H→1-H (23%), 6′-H→5-H (20%), and 6′-H→5′-H (26%).

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* Indicates that n.O.e. enhancements are significant but could not be measured quantitatively because of proximity or overlap of signals.

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