# Reactivity and Structure of *N*-Phenyl-1-naphthylamines and Related Compounds. Part 3.[1] Reaction with Oxygen-centred Radicals

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Comparison is made between products obtained by oxidation of *N*-phenyl-1-naphthylamines and 1-naphthyl phenyl nitroxides with peroxyl radicals. It is concluded that oxidation of the amines does not proceed to a considerable extent *via* the nitroxides. Comparison is also made of products obtained from these amines and nitroxides by oxidation with Fremy's salt.

Use of *N*-phenyl 1- and 2-naphthylamines as antioxidants is widespread [2-5] and the patent literature is replete with examples of their use. During autoxidation peroxyl radicals abstract hydrogen from the N–H group giving an aminyl [6] which, depending on *inter alia* the conditions may dimerise, react with a second peroxyl on nitrogen to give a nitroxide [7] or on carbon to give a quinonoid product.[8] The nitroxide, in turn, could also react with peroxyl radicals to give a quinone imine *N*-oxide.[9] The quinonoid products by analogy with simple quinones would also be expected to react with peroxyl radicals.[10] Kinetic e.s.r. evidence indicates [6] that (*a*) reaction of peroxyl radicals with the amines is much faster than reaction with the corresponding nitroxides, (*b*) the intermediate aminyls react with peroxyls predominantly on carbon rather than on nitrogen, and (*c*) the quinonoid products react relatively slowly with peroxyl radicals. We have now attempted to confirm these conclusions by examining the products formed on reaction of a number of *N*-phenyl-1-naphthylamines and the corresponding nitroxides with peroxyl radicals. For comparison, products obtained using another oxygen-centred radical, Fremy's salt, are also described.

It is instructive to consider first, products obtained previously by oxidation of *N*-aryl-1-naphthylamines with several inorganic oxidising agents and by air. Early workers claimed that with neutral permanganate the corresponding tetra-arylhydrazines were formed.[11] However, Peeler [12] subsequently showed that lead(IV) oxide, permanganate, and air [$Cu^{II}$ catalysed] oxidized *N*-phenyl-1-naphthylamine to a polymer and a C(4)–C(4) coupled dimer. Chromic acid gave only the latter. When the 4-naphthyl position was blocked by the presence of a methyl group oxidation with lead(IV) oxide gave an N–C(2) coupled dimer. When both the 2- and the 4-naphthyl positions were blocked by methyl substituents an N to *para*-C coupled product was obtained.

## Results and Discussion

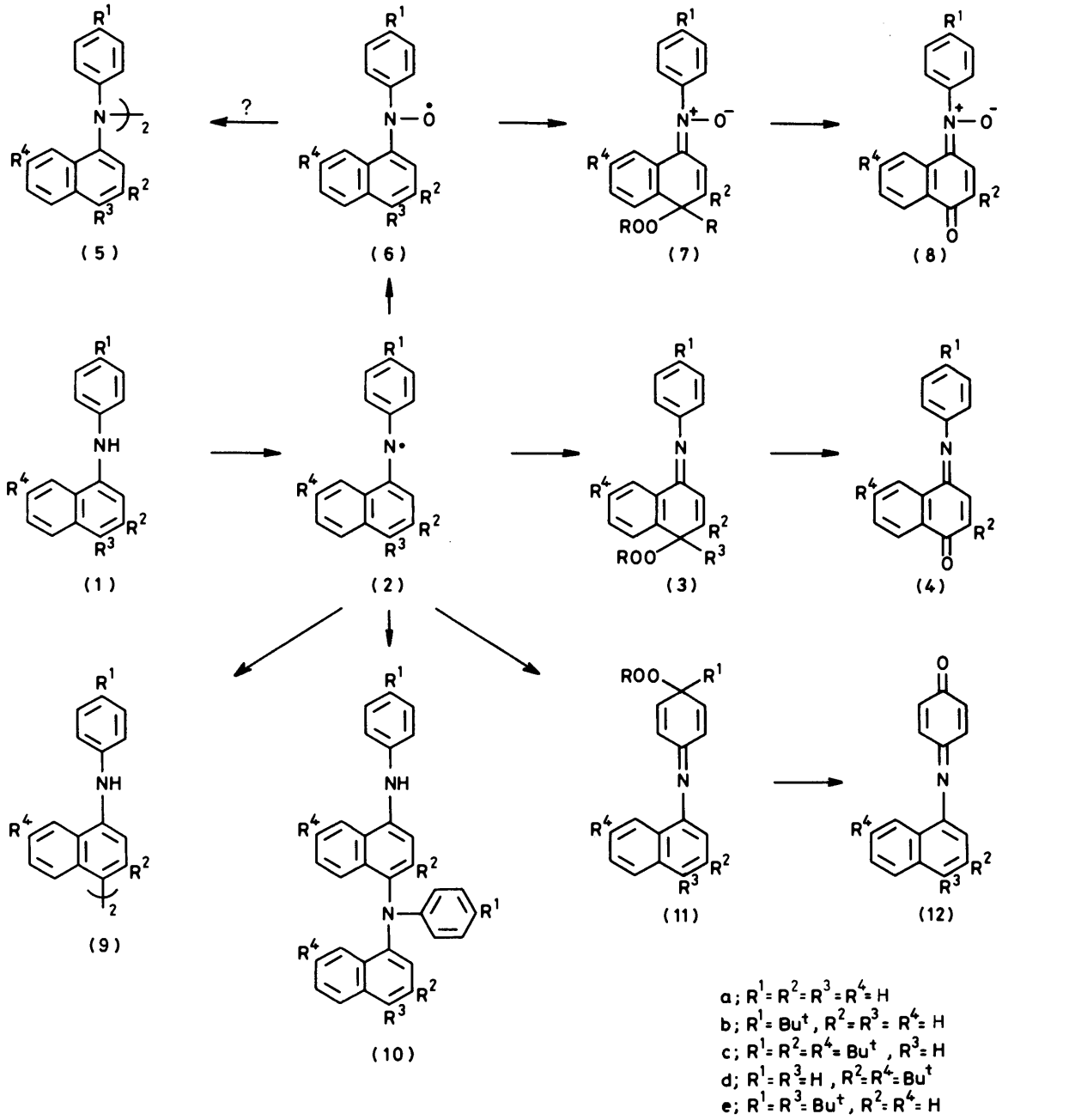
*N-Phenyl-1-naphthylamines.*—The amines [13] (1a—e) were oxidised with t-butyl hydroperoxide in the presence of cobalt toluate.[10] The initial ratio of t-butyl hydroperoxide to amine was 2 : 1 or 3 : 1 but with the amines (1c,d) further additions of hydroperoxide were necessary because reaction was so slow.

The amines (1c) and (1d) reacted cleanly to give the corresponding *N*-aryl-1,4-naphthoquinone imines [13] (4c) and (4d) in high yield (90%). Amines (1a) and (1b) also gave the quinone imine (4a,b) but in much lower yield (<10%). The product mixtures from the latter pair of amines were complex (deep blue) and not all of the products were separated and identified. Because the amine (1a) was the more readily available it was oxidised on a much larger scale than (1b) and hence a larger number of its side-products were examined. Two dehydro-dimers (22%) ($C_{32}H_{24}N_2$; mass spec.) were the main products from the amine (1a). One of these formed a diacetyl and the other a monoacetyl derivative and hence are assigned structures (9a) and (10a), respectively. Only the dehydro dimer (9b) was obtained from the amine (1b). Several minor coloured products were also obtained from the amine (1a). A yellow one gave a mass spectrum indicative of a t-butoxylated *N*-phenylnaphthoquinone imine. Comparison of its n.m.r. spectrum with those of a series of *N*-aryl-1,4-naphthoquinone imines [13] indicated that the t-butoxy group was attached to C-3 (sharp singlet at δ 6.8 corresponding to 2-H) and hence structure (13a) was assigned. One of the two other minor coloured products isolated was shown to be phenylaminonaphthoquinone imine (14a) and the other ($C_{16}H_9NO_2$) the phenoxazone (17a). The latter showed carbonyl but no NH absorption in the i.r. region and a sharp singlet at δ 6.31 attributable to a quinonoid proton in its n.m.r. spectrum. The only coloured product isolated from oxidation of the amine (1b) was the quinone imine corresponding to (4b) although many others were present in the deep blue product mixture.

Although the product analyses are inevitably incomplete they do show that the first-formed aminyl predictably reacts with peroxyl at naphthyl rather than at phenyl (Scheme 1). In these cases (1a) and (1b) where the 4-naphthyl position is not hindered dimerisation (N to C-4 and C-4 to C-4) competes with peroxyl radical coupling. Although the exact routes to the minor products (13a) and (17a) were not established they must arise by secondary reactions of peroxyl radicals with the initially formed quinone imine (4). The sequence (4) ⟶ (15) ⟶ (16) ⟶ (17) (Scheme 2) is merely one possibility. The deepening in colour of the reaction mixtures with use of increased quantities of t-butyl hydroperoxide reflects the extent to which primary and secondary products are being consumed by reaction with peroxyl radicals.

Interestingly, reaction with another oxygen-centred radical Fremy's salt [14] proceeds along similar lines. The amines (1a) and (1b) gave the corresponding naphthoquinone imines (4a) and (4b) (46 and 83%, respectively) but the hindered amine (1d) gave the benzoquinone imine (12d). This difference in regiospecificity is readily explained by the difference in effective size of t-butylperoxyl and Fremy's salt. Reaction of the latter at the naphthyl C-4 of (2d) is clearly hindered by the adjacent t-butyl group. When the *para*-position is blocked by t-butyl as in (1c) reaction was very slow and required a large excess of Fremy's salt. The product was a dehydro dimer (mass spec.) which showed no NH absorption in the i.r. region and hence is tentatively assigned the tetra-arylhydrazine structure (5c).

*1-Naphthyl Phenyl Nitroxides.*—Because of the ease of spontaneous decomposition of most of the 1-naphthyl phenyl nitroxides in solution only the substituted nitroxides

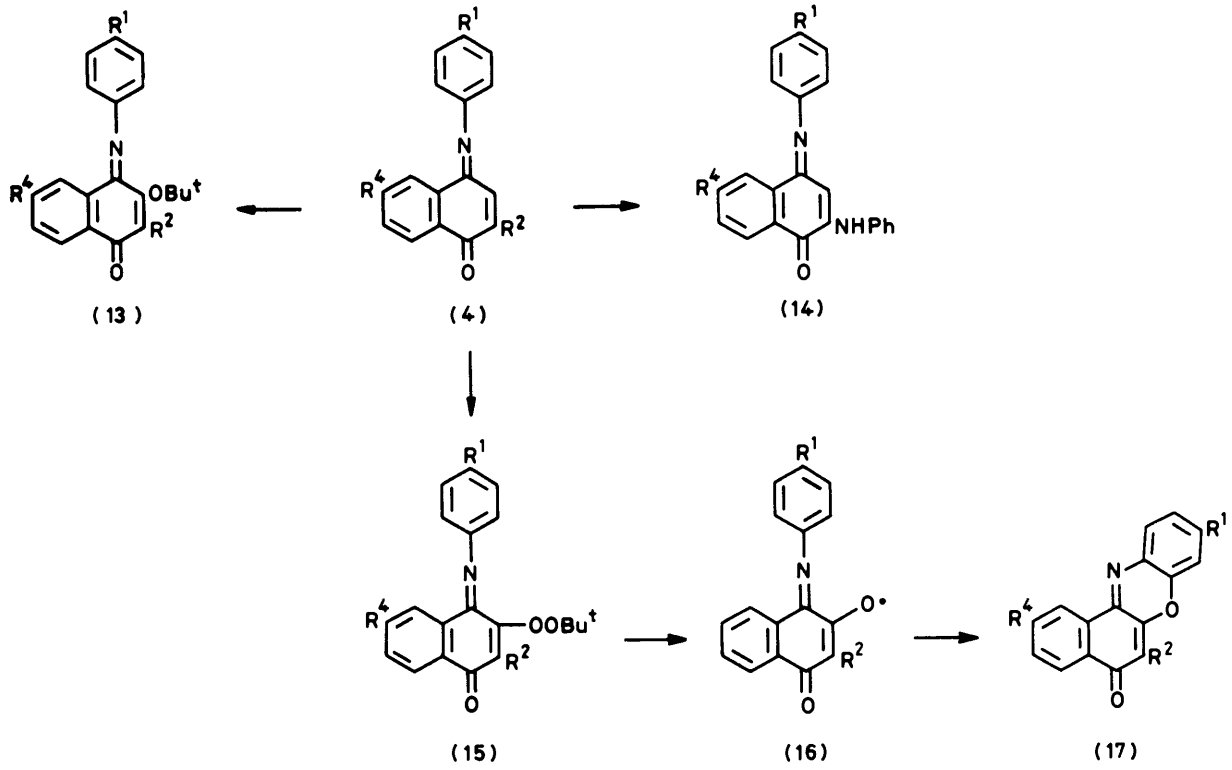



**Scheme 1.**

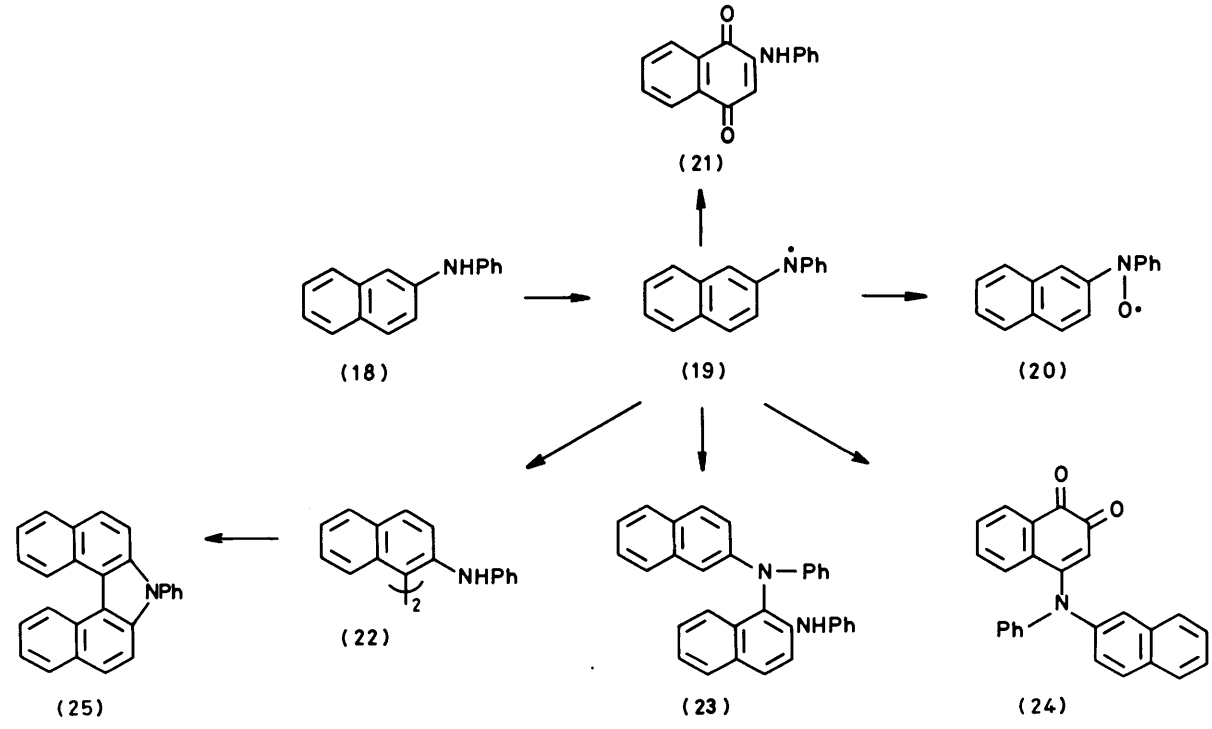
(6c) and (6e) were considered suitable for oxidation with t-butyl hydroperoxide–cobalt toluate. The former slowly gave the naphthoquinone imine *N*-oxide (8c) as the major product (76%) but the latter resisted oxidation under similar conditions. The different products obtained from the amine (1c) and the corresponding nitroxide (6c) is a further indication that oxidation of the amine does not proceed *via* the nitroxide. With Fremy's salt the nitroxides (6a) and (6c) behaved predictably. The former gave the quinone imine *N*-oxide (8a) (54%) whilst the latter failed to react presumably because of steric hindrance to reaction at the naphthyl C-4.

N-*Phenyl-2-naphthyl-amine and -nitroxide*.—Oxidation [10] of *N*-phenyl-2-naphthylamine (18) with t-butyl hydroperoxide in the presence of cobalt toluate gave the products (21)—(25) (Scheme 3). The corresponding nitroxide (20) also gives products (22)—(25) but these are minor compared with the phenylaminonaphthoquinone (21) (21%). Because of the difference in product distribution and kinetic e.s.r. evidence [6] we do not take this result as evidence that oxidation of the amine proceeds mainly *via* the nitroxide. Spontaneous decomposition of the nitroxide (23) during the course of the oxidation produces [13] amine (17) and products (18)—(22) would be derived therefrom.

Although it may be firmly concluded that oxidation of *N*-phenyl-1- and 2-naphthylamine with t-butyl peroxyl radicals does not proceed to a significant extent *via* the corresponding nitroxide, generalisations about diarylamines should be resisted until there has been a similar investigation of diarylamines which show substantial accumulation of nitroxide (e.s.r.) during peroxy oxidation.[7,8]




Scheme 2.




Scheme 3.

## Experimental

Known compounds were identified by comparison (t.l.c., i.r., m.p.) with authentic specimens. Spectra were measured for Nujol mulls (i.r.) and for solutions in deuteriochloroform (n.m.r.). Petroleum refers to light petroleum b.p. 40—60 °C.

*Oxidation of Amines with Fremy's Salt: General Procedure.*— The amine (1 mmol) in acetone (30 ml) was added to a solution of Fremy's salt (2.5 mmol) in water (40 ml) and 0.16M-potassium dihydrogen phosphate (4 ml) and the mixture was left for 1—5 h. The acetone was removed by distillation

under reduced pressure at room temperature and the aqueous residue extracted with chloroform. The dried extracts were evaporated and the residue was either crystallised or chromatographed (column) on silica using light petroleum–chloroform (1 : 1) as eluant.

(i) N-*Phenyl*-1-*naphthylamine*. This gave *N*-phenyl-1,4-naphthoquinone imine (4a) [13] (46%).

(ii) N-p-*t*-*Butylphenyl*-1-*naphthylamine*. This gave *N*-*p*-t-butylphenyl-1,4-naphthoquinone imine (4b) [13] (83%).

(iii) N-*Phenyl*-3,7-*di*-*t*-*butyl*-1-*naphthylamine*. This gave *N*-(3,7-di-t-butyl-1-naphthyl)-1,4-benzoquinone imine (4d) [13] (46%).

(iv) N-p-*t*-*Butylphenyl*-3,7-*di*-*t*-*butylnaphthylamine*. The amine (1 mmol) was treated with six portions of Fremy's salt (each 2.5 mmol) during 48 h and gave, after chromatography, 1,2-bis(*p*-t-butylphenyl)-1,2-bis(3,7-di-t-butyl-1-naphthyl)-hydrazine (5c) (36%) as a viscous yellow oil (Found: $M^+$, *m/z* 1387.2925. $C_{28}H_{37}N$ requires $M^+$, *m/z* 1387.2924), δ 1.24 (18 H, s, 2 Bu$^t$), 1.28 (18 H, s, 2 Bu$^t$), 1.33 (18 H, s, 2 Bu$^t$), and 7.2—7.9 (18 H, m, ArH); *m/z* 772(%) (*M*) 397(100), 386(32), 372(10), 372(5), 264(10), 218(32), and 178(16).

*Oxidation of Amines with t-Butyl Hydroperoxide*.—(i) N-*Phenyl*-1-*naphthylamines*. To a stirred solution of the amine (4.4 g, 20 mmol) and t-butyl hydroperoxide (3.6 g, 40 mmol) in benzene, cobalt toluate was added during 25 min. Stirring was continued for 24 h before the solvent was removed and the residue chromatographed on silica (p.l.c.) using light petroleum–chloroform (6 : 4) as eluant to give (*a*) *N*-phenyl-1-naphthylamine (1.1 g, 25%); (*b*) an oil (0.83 g), $\nu_{max.}$ 3 420 cm$^{-1}$ which on acetylation with acetic acid (8 ml) and acetic anhydride (4 ml) under reflux for 24 h gave 4,4′-*bis*(N-*phenyl*-N-*acetylamino*)-1,1′-*binaphthyl* as needles, m.p. 141—143 °C (from hexane–chloroform) (Found: C, 82.8; H, 5.2; N, 5.6. $C_{36}H_{28}N_2O_2$ requires C, 83.1; H, 5.2; N, 5.4%), $\nu_{max.}$ 1 678 cm$^{-1}$, δ 2.16 (6 H, s, 2$COCH_3$), 7.14—7.74 (18 H, m, ArH), and 8.1—8.2 (2 H, d, *J* 8 Hz, ArH), *m/z* 520(18%) ($M^+$), 478(6), 436(8), 3.43(5), 119(9), and 118(100); (*c*) an oil (100 mg) which on acetylation as in (*b*) gave N-*acetyl*-N,N′-*diphenyl*-N′-1-*naphthyl*-1,4-*naphthylenediamine*, m.p. 139—141 °C (from hexane–chloroform) (Found: C, 85.1; H, 5.2; N, 6.0. $C_{34}H_{26}N_2O$ requires C, 85.3; H, 5.5; N, 5.9%), $\nu_{max.}$ 1 680 cm$^{-1}$, δ 2.0 (3 H, s, $COCH_3$), and 6.64—8.14 (23 H, m, ArH), *m/z* 479(28%), 478(100) ($M^+$), 436(28), 435(45), 362(10), 361(50), and 218(9); (*d*) *N*-phenyl-1,4-naphthoquinone imine (4a) (193 mg); (*e*) N-*phenyl*-3-*t*-*butoxy*-1,4-*naphthoquinone imine* (13a) (46 mg) as yellow cubes, m.p. 102—104 °C (from methanol) (Found: $M^+ - 56$, 249.0792. $M-56$ requires 249.0789), $\nu_{max.}$ 1 669 cm$^{-1}$, $\lambda_{max.}$ 211, 251sh, 292, 340, and 443 nm (log ε 3.32, 3.03, 3.18, 2.78, and 2.43), δ 1.37 (9 H, s, Bu$^t$), 6.48 (1 H, s, 2-H), 6.88 (2 H, dd, *J* 8.0 and 1.0 Hz, 3′,5′-ArH), 7.35 (2 H, d, *J* 8 Hz, 2′- and 6′-ArH), 7.62 (2 H, m, 6,7-ArH), 8.16 (1 H, m, 5-ArH), 8.44 (1 H, m, 8-ArH), *m/z* 305(3%) ($M^+$) 250(8), 249(79), 220(14), 203(9), 193(5), and 173(100); (*f*) *N*-phenyl-2-anilino-1,4-naphthoquinone imine (17a); [15] (*g*) 5*H*-benzo[*a*]phenoxazin-4-one [16] (24 mg, 2%), m.p. 191—193 °C (Found: $M^+$, 247.0633. Calc. for $C_{16}H_{19}NO_2$: *M*, 247.0629), δ 6.31 (1 H, s, 6-ArH), 7.0—8.2 (8 H, m, ArH), *m/z* 248(15%), 247(100) ($M^+$), 219(45), 190(20).

(ii) N-p-*t*-*Butylphenyl*-1-*naphthylamine*. To a stirred solution of the amine (156 mg, 0.56 mol) and t-butyl hydroperoxide (181 mg, 2 mmol), cobalt toluate (2 mg) was added. The reaction mixture was stirred overnight at room temperature before more t-butyl hydroperoxide (103 mg, 1.1 mmol) and cobalt toluate (3 mg) were added. After being stirred for a further 5 h the reaction mixture was chromatographed on silica using hexane–chloroform (1 : 1) as eluant to give (*a*) *N*-*p*-t-butyl-1-naphthylamine (38 mg) and (*b*) a brown oil (88 mg) acetylation of which with acetic acid (1 ml) and acetic anhydride (1 ml) under reflux gave 4,4′-*bis*(N-p-*t*-*butylphenyl*-N-*acetyl*)*amino*-1,1′-*binaphthyl* (35 mg, 38%) as needles, m.p. 140—143 °C (from hexane–chloroform) (Found: C, 83.4; H, 7.05; N, 4.4. $C_{44}H_{44}N_2O_2$ requires C, 83.5; H, 7.0; N, 4.45%), δ 1.26 (18 H, s, 2 Bu$^t$), 2.1br (6 H, s, 2$COCH_3$), *ca.* 7.46 (18 H, m, ArH), and 8.26 (2 H, m, ArH), *m/z* 632(32%) ($M^+$), 590(45), 575(4), 295(18), and 174(100); (*c*) *N*-*p*-t-butylphenyl-1,4-naphthoquinone imine (4b) (22 mg); (*d*) N-p-*t*-*butylphenyl*-2-(p-*t*-*butylanilino*)-1,4-*naphthoquinone imine* (14b) as red needles from hexane–chloroform, m.p. 202—204 °C (Found: $M^+$, 436.2514. $C_{30}H_{32}N_2O$ requires *M*, 436.2512), $\nu_{max.}$ 3 320, 1 658 cm$^{-1}$, $\lambda_{max.}$ 208, 284, 304sh and 492 nm (log ε 3.46, 3.27, 2.76, and 2.76), δ 1.26 (9 H, s, Bu$^t$), 1.31 (9 H, s, Bu$^t$), 6.63 (1 H, s, 3-H), 6.85—7.43 (8 H, m, ArH), 7.6—7.75 (2 H, m, 6,7-ArH), 8.2 (1 H, m, 8-ArH), and 8.61 (1 H, m, 5-ArH), *m/z* 436(94%) ($M^+$) 422(18), 421(100), and 203(16).

(iii) N-*Phenyl*-3,7-*di*-*t*-*butyl*-1-*naphthylamine* (1c). To a stirred solution of the amine (183 mg, 0.055 mmol) and t-butyl hydroperoxide (165 mg, 1.8 mmol) in benzene (3 ml) cobalt toluate (2 mg) was added. After the reaction mixture had been stirred for 6 h two further additions of t-butyl hydroperoxide (each 116 mg, 1.3 mmol) and cobalt toluate (each 2 mg) were made at 6 h intervals. Chromatography of the crude reaction mixture on silica using hexane–chloroform (1 : 1) as eluant gave *N*-phenyl-3,7-di-t-butyl-1,4-naphthoquinone imine (157 mg, 82%).

(iv) N-p-*t*-*Butylphenyl*-3,7-*di*-*t*-*butyl*-1-*naphthylamine*. To a stirred solution of the amine (368 mg, 1 mmol) and t-butyl hydroperoxide (298 mg, 3 mmol) in benzene (5 ml) cobalt toluate (5 mg) was added. The reaction mixture was stirred for 24 h at room temperature before it was chromatographed on silica using hexane–chloroform (1 : 1) as eluant to give *N*-*p*-t-butylphenyl-3,7-di-t-butyl-1,4-naphthoquinone imine (14c) [13] (302 mg, 80%).

*Oxidation of Nitroxides with t-Butyl Hydroperoxide*.—p-*t*-*Butylphenyl* 3,7-*di*-*t*-*butyl*-1-*naphthyl nitroxide* (6c). To a stirred solution of the nitroxide (204 mg, 0.51 mmol) and t-butyl hydroperoxide (159 mg, 1.8 mmol) in benzene (3 ml) cobalt toluate (3 mg) was added and the reaction mixture stirred for 14 h. Additional t-butyl hydroperoxide (224 mg, 2.5 mmol) and cobalt toluate (3 mg) were then added and stirring was continued for a further 10 h. Chromatography of the reaction mixture on silica using chloroform–petroleum (1 : 1) as eluant gave *N*-*p*-t-butylphenyl-3,7-di-t-butyl-1,4-naphthoquinone imine *N*-oxide (8c) [13] (163 mg) as yellow needles, m.p. 146—148 °C.

Similar treatment of *p*-t-butylphenyl 4-t-butyl-1-naphthyl nitroxide (6e) (0.59 mmol) with t-butyl hydroperoxide (4.8 mmol) and cobalt toluate led only to the recovery of the nitroxide.

N-*Phenyl* 2-*naphthyl nitroxide*. To a stirred solution of the nitroxide (370 mg, 1.6 mmol) and t-butyl hydroperoxide (477 mg, 5.4 mmol) in benzene (5 ml) cobalt toluate (10 mg) was added and the reaction mixture was stirred for 16 h at room temperature. Chromatography of the reaction mixture on silica (p.l.c.) using chloroform–light petroleum as eluant gave 2-phenylamino-1,4-naphthoquinone (21) [13] (103 mg), *N*-phenyl-2-naphthylamine, the anil (18), the *ortho*-quinone (19); the ' dimeric ' amines (20), (21), (22) were present as minor products (t.l.c. comparison) but were not isolated.

*Oxidation of Nitroxides with Fremy's Salt*.—*Phenyl*-1-*naphthyl nitroxide*. The nitroxide (*ca.* 286 mg, 1.22 mmol) in acetone (48 ml) was added to a solution of Fremy's salt (868 mg, 3.24 mmol) in water (50 ml) and M/6 potassium dihydrogen phosphate (6 ml). The reaction mixture was

stirred overnight and then chromatographed on silica using chloroform–petroleum (1 : 1) as eluant to give *N*-phenyl 1,4-naphthoquinone imine *N*-oxide (8a) [13] (162 mg).

Similar treatment of *p*-t-butylphenyl 3,7-di-t-butyl-1-naphthyl nitroxide with Fremy's salt (3 mmol) led only to the recovery of the nitroxide.

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