Nitroxide Radicals. Part 21.[1] Spontaneous Decomposition of *N*-Aryl 1- and 2-Naphthyl Nitroxides

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N-Aryl 1-naphthyl nitroxides self-react in solution to give the corresponding secondary amines and *N*-aryl-1,4-naphthoquinone imines. When reaction at the 4-naphthyl position is hindered by substituents benzoquinone imines are also produced. *N*-Phenyl 2-naphthyl nitroxide under similar conditions gives the corresponding amine and 2-phenylamino-1,4-naphthoquinone *via* a 1,2-naphthoquinone imine *N*-oxide intermediate.

Phenyl naphthyl nitroxides are produced during autoxidation of the antioxidants *N*-phenyl 1- and 2-naphthylamines.[2,3] The significance of nitroxide formation and the subsequent fate of the nitroxides during autoxidation has yet to be fully explained. With this aim we have undertaken an examination of the reactions of nitroxides with oxygen-centred radicals, including self-reactions and report on this herein.

The nitroxides were generated from the corresponding hydroxylamines (1) by oxidation with silver oxide or air. The precursor hydroxylamines, prepared from the corresponding naphthyl Grignard reagent and nitrosoarene, could not be isolated because of their rapid oxidation to the nitroxide during chromatographic purification. Of the five nitroxides examined only two (2c) and (2d) were sufficiently stable to be isolated in crystalline form. The others were obtained as chromatographic fractions (purity *ca.* 80—90%; t.l.c.) which could not be further purified because of their continuous decomposition in solution. These were stored in dilute solution at low temperature.

When solutions of the nitroxides were left at room temperature decomposition of all but (2c) began immediately. The rate of decomposition depended on the number and position of the substituents hence the solutions were left for between 6 and 20 days to ensure that sufficient of the products had accumulated to allow their separation and identification. Under these conditions the nitroxide (2c) underwent no appreciable change. The others gave significant amounts of 1,4-naphthoquinone imine (7) and secondary amine (5) accompanied by a large number of minor coloured products which were not isolated. Two additional products the benzoquinone imine (4e) and its *N*-oxide (3e) were isolated from the nitroxide (2e). Yields (in mmol) and mole ratios of the major products are given in Table 1.

If the decomposition of the 1-naphthyl phenyl nitroxides (2) had followed the same course as that of diphenyl- or t-butyl phenyl nitroxides[4] equimolar amounts of *N*-phenyl-1-naphthylamine (5) and 1,4-naphtho- or 1,4-benzo-quinone imine *N*-oxides (6) and (3) would have been produced. Clearly, this does not occur and with only one nitroxide (2e) was there any significant amount of quinone imine *N*-oxide formed. Generally, reaction occurred preferentially at the 4-naphthyl rather than the *para*-phenyl position. Coupling at *para*-phenyl only occurred when there was both steric hindrance to reaction at the 4-naphthyl carbon atom and a free *para*-phenyl position as in nitroxide (2e). This radical behaves, to some extent at least, like diphenyl nitroxide giving a benzoquinone imine *N*-oxide although it also behaves like the other nitroxides in the series giving a naphthoquinone imine (7e) as well.

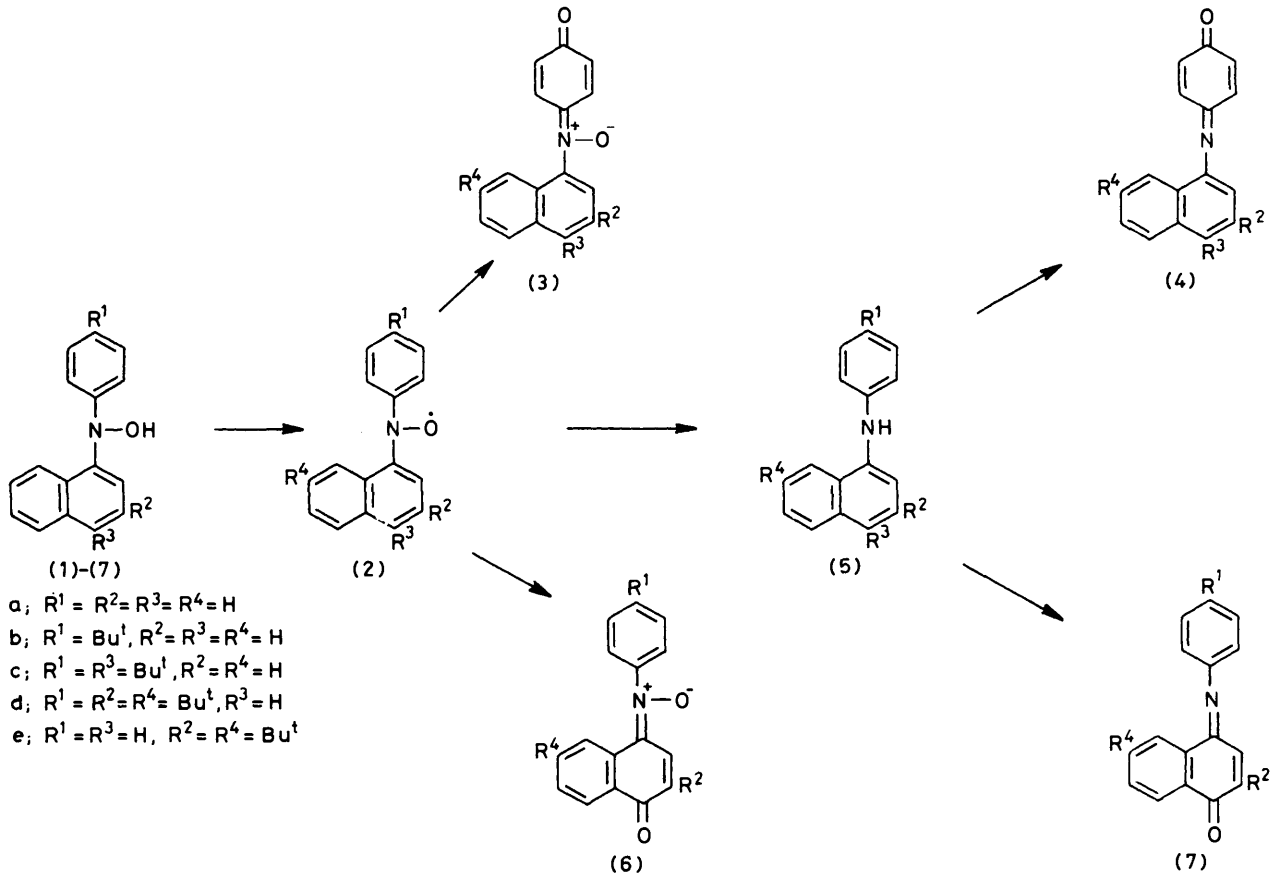
Although naphthoquinone imine *N*-oxides (6) are not major decomposition products it is possible that they are formed as intermediates *en route* to the naphthoquinone imines (7). To test this possibility a series of 1,4-naphthoquinone imine *N*-oxides was prepared from the corresponding quinone imines by oxidation with *m*-chloroperoxybenzoic acid. A similar oxidation of the only benzoquinone imine (4e) isolated gave the corresponding benzoquinone imine *N*-oxide (3e) thus providing confirmation of structure. The quinone imines (7) and their *N*-oxides (6) are easily distinguished spectroscopically since the introduction of the oxygen onto the nitrogen causes a downfield shift of the *peri*-8H (8.3 ⟶ 9.6), a lowering of $\nu_{max.}$ (C=N, C=O) by 5—20 cm^{-1}, and a bathochromic shift of the long wavelength band in the u.v./visible region (330→390 nm) (see Table 2).

Table 1. Yields (mmol) of products from nitroxide (2 mmol) decomposition

Nitroxide	Amine	Quinone imine	
(2)	(5)	(7)	Product ratio
(2a)	0.13	0.90	1 : 6.9
(2b)	0.16	0.51	1 : 3.2
(2d) *	0.63	0.21	1 : 0.33
(2e)	0.37	1.04	1 : 2.8

* Benzoquinone imine (4d) and benzoquinone imine *N*-oxide (3d) also produced.

When a small amount of the naphthoquinone imine *N*-oxide (6d) was added to a solution of the nitroxide (2d) decomposition proceeded normally and the quinone imine *N*-oxide was recovered. Hence, it is not continuously produced and then consumed, for example, by reaction with nitroxide in these decompositions. Similarly, it was shown in a separate experiment that the quinone imine *N*-oxide (6d) did not react with the amine (5d). In view of the small amounts of amine (5) relative to quinone imine (4) produced in the decompositions (Table 1) the possibility that the amine is consumed by reaction with nitroxide was next tested. When a solution of the nitroxide (2d) (1 mol) and the amine (5a) (4 mol) was left for 7 days equivalent amounts of quinone imine (7a) and amine (5d) (0.6 mol) were formed and the amine (5a) was depleted. Similarly when the nitroxide (2c) and an excess of amine (5a) were allowed to react the amine (5c) and the quinone imine (7a) were formed. Hence, the quinone imines (7) are formed from the corresponding amines (5) by (*a*) hydrogen abstraction by the nitroxide (2) followed by coupling of a second molecule of nitroxide at the C-4 naphthyl position of the phenyl naphthylaminyl formed in step (*a*) and fragmentation of the intermediate. The hydroxylamine (1) formed in step (*a*) would undergo spontaneous aerial oxidation giving more nitroxide. From this it follows that hydrogen abstraction from the amine by the nitroxide is faster than O to C self-coupling of the nitroxide. The sequence of reactions leading to the quinone imine (7) does require the initial presence of catalytic amounts



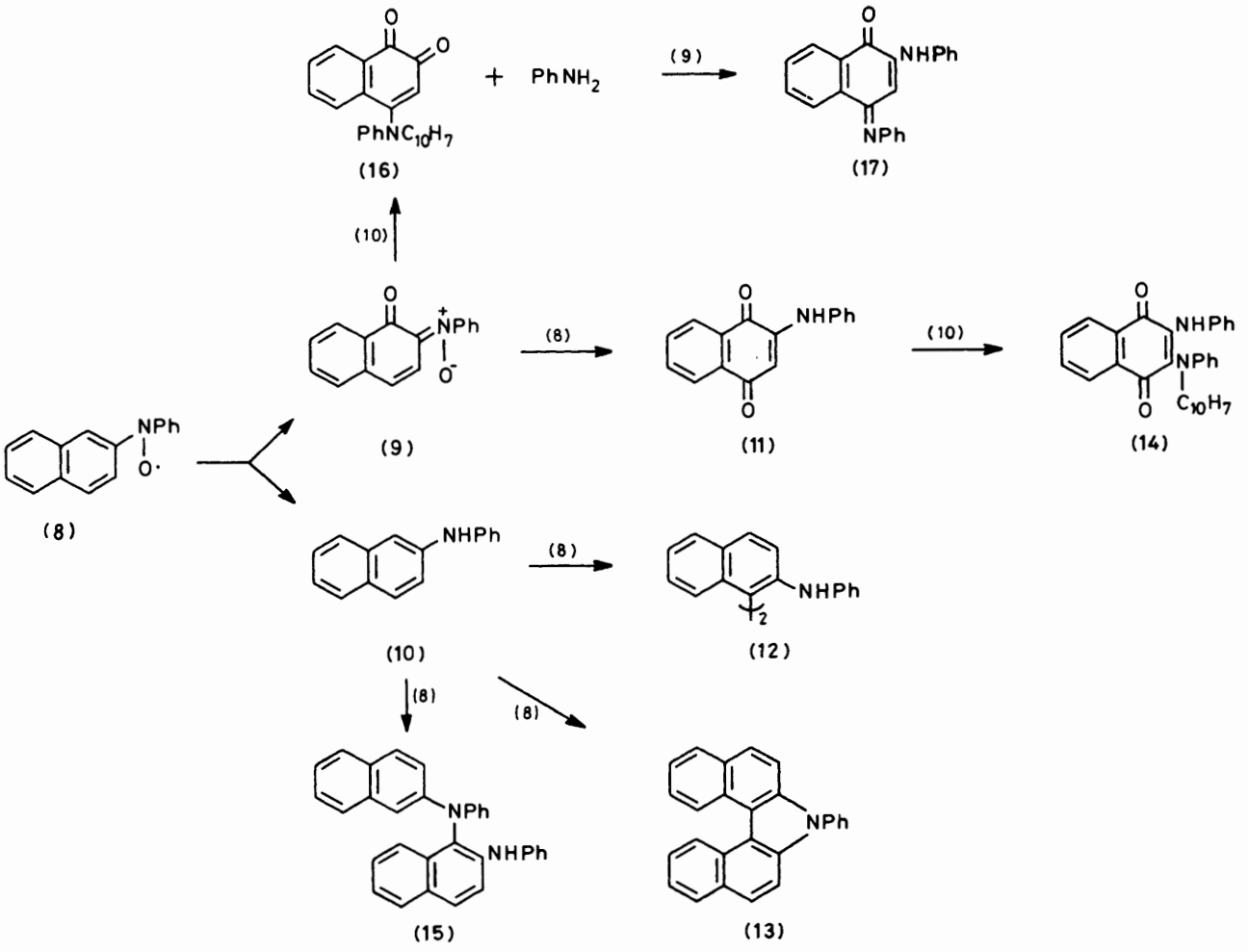
Scheme 1.

Table 2. Spectroscopic data for quinone imines and quinone imine *N*-oxides

Compd.	δ_H Values 2′,6′	3′,5′	4′	2	3	5	6	7	8	Bu^t	$\nu_{max.}$ cm^{-1}	$\lambda_{max.}$ (log ε) nm
(7a)	7.36	*ca.* 6.88	7.24	6.65	7.21	8.45	*ca.* 7.68	*ca.* 7.68	8.16	—	1 660	330 (3.71)
(7b)	7.37	*ca.* 6.71	—	6.61	7.25	8.41	*ca.* 7.63	*ca.* 7.63	8.20	1.34	1 665	330 (3.80)
(7d)	7.4	*ca.* 6.85	—	—	7.14	8.42	—	*ca.* 7.64	8.08	1.25 1.34 1.38	1 641	330 (3.78)
(7e)	7.36	*ca.* 6.92	*ca.* 7.25	—	7.08	8.44	—	*ca.* 7.66	8.1	1.24 1.39	1 655	340 (4.63)
(6a)	7.49	7.49	7.49	6.31	7.29	9.66	7.71	7.71	8.33		1 640	390 (4.2)
(6b)	7.50	7.50	—	6.40	7.30	9.74	7.74	7.74	8.38	1.39	1 645	382 (4.37)
(6d)	7.46	7.46	7.46	—	7.20	9.81	—	7.68	8.26	1.18 1.34 1.40	1 635	390 (4.59)
(20) [c]			7.08—7.96							1.58	1 645	502 (3.75)
(3e) [a]	8.21 6.92	6.15 6.70			7.66—7.84			*ca.* 7.53		1.32	1 625	362 (4.0)
(21) [b]	8.04	6.23								1.58		
					7.4—8.1							
	7.28	6.67									1 625	381 (4.24)

[a] 4-H = 7.53. [b] 1-H = 8.5 (d, *J* 1.5 Hz). [c] 4-H = 6.54 and 6.75 (d, *J* 10 Hz).

of the amine (5). In those cases where it was not possible to obtain crystalline samples of the nitroxides then small amounts of the amine (5) impurity may well have been present from the Grignard stage. Alternatively, O–C coupling of the nitroxide leading to the quinone imine *N*-oxide and amine may proceed to an extent sufficient to cause initiation of the competing reaction of amine and nitroxide. This is certainly the case for the nitroxide (2e) which gave the benzoquinone imine *N*-oxide (3e). Also, close monitoring (t.l.c.) of the decomposition of the nitroxide (2a) revealed that small quantities of the naphtho-

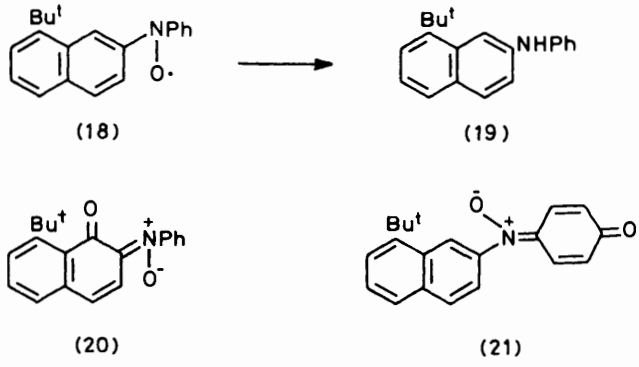


Scheme 2.

quinone imine *N*-oxide (6a) were present almost from the beginning of the decomposition.

2-Naphthyl Phenyl Nitroxide.—When a solution of 2-naphthyl phenyl nitroxide (8) was left at room temperature decomposition was complete within 14 days and a large number of coloured products were produced. The amine (10) (0.23 mol equiv.) and the aminoquinone (11) (0.24 mol equiv.) were the principal products accompanied by small amounts of the carbazole (13), amine dimers (12) and (15), aminoquinones (14) and (16), and aminoquinone imine (17). All of these are known except the red diaminoquinone (14) whose structural assignment was based on mass spectral ($C_{32}H_{22}N_2O_2$), i.r. (1 680 cm^{-1}) and n.m.r. (no quinonoid resonance at δ *ca.* 6.4 evidence (see Experimental section).

Under the same conditions 8-t-butyl-2-naphthyl phenyl nitroxide (18) only decomposed to the extent of 84% and gave three major products. The secondary amine (19) (0.42 mol equiv.) and the quinone imine *N*-oxides (20) (0.13 mol equiv.) and (21) (0.15 mol equiv.). Product (21) showed spectral characteristics typical of a 1,4-benzoquinone imine *N*-oxide, *viz.* $\nu_{max.}$ 1 625 cm^{-1}, $\lambda_{max.}$ 381 nm and n.m.r. signals from both geometric isomers. Each form shows signals from non-equivalent 2′-, 3′-, 5′-, and 6′-protons each proton being coupled to two others giving a pattern of 8 quartets. The 1,2-naphthoquinone imine *N*-oxide (20) is only the second *ortho* quinone imine *N*-oxide to be isolated [5] and is distinguished from the 1,4-benzo- and -naphthoquinone imine



Scheme 3.

N-oxides by its longer wavelength absorption in the visible range ($\lambda_{max.}$ 502 nm) and by its n.m.r. spectrum. Only two quartets were visible outside the broad envelope of aromatic resonances. Since both of these were coupled to signals in the aromatic resonance band but not to each other we conclude that the quinone imine *N*-oxide (20) exists in both isomeric forms and the resolved n.m.r. signals are due to one proton (probably 4-H).

The decomposition of 2-naphthyl phenyl nitroxide (8) like that of its *N*-t-butyl analogue already described,[5] proceeds mainly by O to C-2 coupling with subsequent fragmentation

to the diarylamine (10) and 1,2-quinone imine *N*-oxide (9). The latter subsequently rearranges in the presence of nitroxide to give the aminoquinone (11).[5] The minor amine products (12), (13), (15) arise from coupling of 2-naphthylphenyl aminyl produced presumably by oxidation of the amine (10) by the nitroxide (8). These products are invariably formed in reactions in which 2-naphthylphenyl-aminyls participate.[6] The diaminoquinone (14) is another secondary product which is formed by addition of the amine (8) to the aminoquinone (11). We have shown previously that amino-1,4-naphthoquinone imines such as (17) can be produced by reaction of 1,2-naphthoquinone imine *N*-oxides with aniline [5] and this seems the likely route in this case. The source of the aniline is less clear although some will be produced with the carbazole (13). Formation of the 4-amino-1,2-naphthoquinone (16) is the most difficult to explain. Because it has been shown that addition of the amine (10) to 1,2-naphthoquinone is slow [3] we prefer a route to (16) involving reaction of the quinone imine *N*-oxide (9) with the amine (10) although we have no additional experimental evidence to confirm it.

Steric hindrance to O to C-1 (naphthyl) coupling is evident with the nitroxide (18). The radical decomposes relatively slowly and there is a competing reaction at C-4 (phenyl). As a result two quinone imine *N*-oxides (20) and (21) are produced in the ratio 0.8 : 1. Interestingly, the *para*-phenyl position is the more reactive despite the greater free spin density [7] at C-1 (naphthyl) ($a_{1\text{-H}} = 2.91$ G and $a_{p\text{-H}} = 1.75$ G) and the relative ease of loss of aromaticity of the naphthyl ring.

The essential difference between the self-decompositions of 1-naphthyl and 2-naphthyl phenyl nitroxides, as outlined in Schemes 1 and 2, is the relative rates at which the nitroxides react (*a*) with the parent amines and (*b*) with the quinone imine *N*-oxides formed after intial O to C coupling. For the 1-naphthyl radical reaction with the amine predominates and for the 2-naphthyl radical reaction with the quinone imine *N*-oxide predominates.

Experimental

I.r. spectra were measured as Nujol mulls (solids) or films (liquids) and n.m.r. spectra were measured for solutions in deuteriochloroform unless stated otherwise. Petroleum refers to light petroleum, b.p. 60—80 °C and ether to diethyl ether throughout. Merck silica gel GF_{254} or HF_{254} was used for chromatographic separations.

Preparation of Starting Materials.—1- and 2-Bromonaphthalenes were purchased and were distilled before use. 1-Bromo-3,7-di-t-butylnaphthalene [8] and 7-bromo-1-t-butylnaphthalene [9] were prepared by literature methods. 1-*Bromo*-4-*t*-*butylnaphthalene* was prepared from 1-t-butylnaphthalene [9] (5.59 g) in chloroform (290 ml) by dropwise addition of a solution of bromine (1.9 ml) in chloroform (80 ml). The mixture was left overnight at room temperature before it was washed successively with a solution of sodium thiosulphate and water. The dried ($MgSO_4$) solution was evaporated and the resulting oil was distilled to give the *product* as an oil (5.8 g, 70%), b.p. 140—142 °C/0.2 mmHg (Found: C, 63.9; H, 5.8; N, 3.0. $C_{14}H_{15}Br$ requires C, 63.9; H, 5.7; N, 3.0%); δ 1.59 (9 H, s, Bu^t), 7.2—7.74 (4 H, m, ArH), and 8.25—8.52 (2 H, m, ArH).

Preparation of N-*Naphthyl*-N-*phenylhydroxylamines* (1) *and Nitroxides* (2).—The naphthylmagnesium bromide, prepared from the corresponding bromonaphthalene (1 mol), 1,2-dibromoethane (0.2 ml), and magnesium (2.2 g-atom) in a 1 : 1 mixture of benzene and tetrahydrofuran, was treated with nitrosoarene (0.45 mol) in tetrahydrofuran dropwise with stirring at −45 °C under nitrogen. The mixture was stirred for 15 min while the temperature rose to room temperature. Cold, deoxygenated water was added and the mixture was concentrated under reduced pressure to remove the tetrahydrofuran. The residue was extracted with ether and the extracts were dried and evaporated. The residue was chromatographed (p.l.c.) during which the hydroxylamine was autoxidised to the corresponding nitroxide. 1-Naphthyl phenyl, *p*-t-butylphenyl 1-naphthyl, and 3,7-di-t-butyl-1-naphthyl phenyl nitroxides could not be obtained in crystalline form and hence they were stored in dilute solution in chloroform at −20 °C. Chromatography indicated that the nitroxides were the major (*ca.* 90%) components in these solutions. p-*t*-*Butylphenyl* 3,7-*di*-*t*-*butyl*-1-*naphthyl nitroxide* gave orange cubes (from hexane), m.p. 67—69 °C (Found: C, 83.2; H, 8.8; N, 3.4%; M^+ 402.2801. $C_{28}H_{36}NO$ requires C, 83.5; H, 9.0; N, 3.5%; *M*, 402.2796); $\nu_{max.}$ 1 362 cm^{-1} (NO). p-*t*-*Butylphenyl* 4-*t*-*butyl*-1-*naphthyl nitroxide* gave red needles, m.p. 97—98 °C (from hexane) (Found: C, 83.0; H, 8.3; N, 4.2%; M^+, 346.2173. $C_{24}H_{28}NO$ requires C, 83.2; H, 8.15; N, 4.05%; *M*, 346.2170); $\nu_{max.}$ 1 365 cm^{-1} (NO). 2-*Naphthyl phenyl nitroxide* gave deep red plates, m.p. 74—75 °C (from cold carbon tetrachloride) (Found: C, 82.0; H, 5.4; N, 5.8%; *M*, 234.0879. $C_{16}H_{12}NO$ requires C, 82.0; H, 5.2; N, 6.0%; *M*, 234.0919); $\nu_{max.}$ 1 375 cm^{-1}. 8-*t*-*Butyl*-2-*naphthyl phenyl nitroxide* was a red oil (Found: M^+, 290.1542. $C_{20}H_{20}NO$ requires *M*, 290.1545); $\nu_{max.}$ 1 370 cm^{-1}.

Preparation of N-*Arylnaphthylamines* (5).—These were prepared from the corresponding crude hydroxylamine/nitroxide mixture in ethanol by hydrogenation over palladium/charcoal (10%) at room temperature and atmospheric pressure. The crude amines were purified by chromatography (p.l.c.) using petroleum–chloroform as eluant. *N*-*p*-t-Butylphenyl-1-naphthylamine formed buff needles, m.p. 86—88 °C (from ethanol) (Found: C, 87.3; H, 7.7; N, 5.0. Calc. for $C_{20}H_{21}N$: C, 87.3; H, 7.7; N, 6.1%); $\nu_{max.}$ 3 390 cm^{-1}; δ 1.29 (9 H, s, Bu^t), 5.88 (1 H, s, NH), 6.96 (2 H, d, *J* 9 Hz, ArH), 7.19—7.51 (7 H, m, ArH), and 7.76—8.05 (2 H, m, ArH). N-*Phenyl*-3,7-*di*-*t*-*butyl*-1-*naphthylamine* formed cubes, m.p. 149—151 °C (from ethanol) (Found: C, 86.9; H, 8.8; N, 4.2. $C_{24}H_{29}N$ requires C, 87.0; H, 8.8; N, 4.2%); $\nu_{max.}$ 3 390 cm^{-1}; δ 1.33 (18 H, s, 2 × Bu^t) and 6.8—7.9 (10 H, m, ArH). N-p-*t*-*Butylphenyl*-3,7-*di*-*t*-*butyl*-1-*naphthylamine* formed needles, m.p. 133—134 °C (from ethanol) (Found: C, 86.5; H, 9.6; N, 3.7%; M^+, 387.617. $C_{28}H_{39}N$ requires C, 86.8; H, 9.6; N, 3.6%; *M*, 387.612); $\nu_{max.}$ 3 490 cm^{-1}; δ 1.29 (9 H, s, Bu^t), 1.32 (18 H, s, 2 × Bu^t), 5.84br (1 H, s, NH), and 6.9—7.9 (9 H, m, ArH).

N-p-*t*-*Butylphenyl*-4-*t*-*butyl*-1-*naphthylamine* gave needles, m.p. 138—139 °C (from ethanol) (Found: C, 86.7; H, 9.0; N, 4.2. $C_{24}H_{29}N$ requires C, 87.0; H, 8.8; N, 4.2%); $\nu_{max.}$ 3 390 cm^{-1}; δ 1.30 (9 H, s, Bu^t), 1.63 (9 H, s, Bu^t), and 6.80—7.58 (10 H, m, ArH).

Decomposition of Nitroxides (2).—(i) 1-Naphthyl phenyl nitroxide (750 mg) in chloroform (100 ml) was left at room temperature for 6 days. Chromatography (p.l.c.) using petroleum–chloroform (1 : 1) as eluant gave (a) *N*-phenyl-1-naphthylamine (43 mg); (b) *N*-phenyl-1,4-naphthoquinone imine [10] (312 mg) as red needles, m.p. 102—104 °C (Found: C, 82.3; H, 4.8; N, 5.8. Calc. for $C_{16}H_{11}NO$: C, 82.4; H, 4.8; N, 6.0%). The several other minor coloured bands were not examined.

(ii) p-*t*-*Butylphenyl* 1-*naphthyl nitroxide*. A solution of the nitroxide (730 mg) in chloroform (150 ml) was left at room temperature in the dark for 6 days. Chromatography (p.l.c.) using petroleum–chloroform as eluant gave: (a) *N*-*p*-t-butyl-

phenyl-1-naphthylamine (55 mg) and (b) N-p-*t*-*butylphenyl*-1,4-*naphthoquinine imine* (219 mg) as orange needles, m.p. 145—148 °C (Found: C, 83.1; H, 6.5; N, 4.9%; M^+, 289.1465. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.85%; *M*, 289.1462); *m*/*z* 289(32%) (M^+), 276(6), 275(22), 274(100), 246(3), and 233(3). The numerous, coloured minor products (233 mg) were not investigated. (iii) *Phenyl* 3,7-*di*-*t*-*butyl*-1-*naphthyl nitroxide*. A solution of the nitroxide (580 mg) in chloroform (20 ml) was left at room temperature in the dark for 7 days. Chromatography (p.l.c.) using petroleum–chloroform (6 : 4) as eluant gave (*a*) N-phenyl-3,7-di-t-butyl-1-naphthylamine (170 mg). (*b*) N-*Phenyl*-3,7-*di*-*t*-*butyl*-1,4-*naphthoquinone imine* (60 mg) as orange needles, m.p. 168—169 °C (from hexane) (Found: C, 83.4; H, 7.9; N, 4.2. $C_{24}H_{27}NO$ requires C, 8.34; H, 7.9; N, 4.1%); *m*/*z* 345(100%) (*M*), 331(28), 330(28), 317(4), 316(18), and 288(5). (*c*) Phenyl 3,7-di-t-butyl-1-naphthyl nitroxide (40 mg). (*d*) N-(3′,7′-*Di*-*t*-*butyl*-1′-*naphthyl*)-1,4-*benzoquinone imine* (40 mg) as purple needles, m.p. 159—160 °C (from hexane) (Found: C, 83.3; H, 7.9; N, 4.2. $C_{24}H_{27}NO$ requires C, 83.4; H, 7.9; N, 4.1%); $\nu_{max.}$ 1 642 cm^{-1}; $\lambda_{max.}$ 232, 280, and 515 nm (log ε 3.65, 3.23, and 2.57); δ 1.36 (9 H, s, Bu^t), 1.39 (9 H, s, Bu^t), 6.43, 7.18 (4 H, m, 2′-, 3′-, 5′-, 6′-H), and 7.44—7.84 (5 H, m, ArH); *m*/*z* 345(100%) (*M*), 330(45), 233(4), 165(5), 143(4), and 108(6). (*e*) N-(3′,7′-*Di*-*t*-*butyl*-1′-*naphthyl*)-1,4-*benzoquinone imine* N-*oxide* (200 mg) as orange needles, m.p. 172—179 °C (from hexane) (Found: C, 79.6; H, 7.4; N, 4.0. $C_{24}H_{27}NO_2$ requires C, 79.7; H, 7.5; N, 3.9%); *m*/*z* 361(6%) (*M*), 346(10), 345(35), 331(5), 274(5), 255(56), 254(19), 253(100), 252(4), 230(25), and 182(22).

(iv) p-*t*-*Butylphenyl* 3,7-*di*-*t*-*butyl*-1-*naphthyl nitroxide*. A solution of the nitroxide (384 mg) in chloroform (25 ml) was left at room temperature in the dark for 14 days. Chromatography using petroleum–chloroform (1 : 1) as eluant gave (a) *N*-*p*-t-butylphenyl-3,7-di-t-butyl-1-naphthylamine (73 mg). (b) N-p-*t*-*Butylphenyl*-3,7-*di*-*t*-*butyl*-1,4-*naphthoquinone imine* (200 mg) as orange needles, m.p. 125—126 °C (from hexane) (Found: C, 83.8; H, 8.5; N, 3.5. $C_{28}H_{35}NO$ requires C, 83.7; H, 8.8; N, 3.5%); *m*/*z* 401(89%) (*M*), 387(25), 386(100), and 373(6).

(v) 2-*Naphthyl phenyl nitroxide*. A solution of the nitroxide (745 mg) in benzene (7 ml) was left at room temperature in the dark for 14 days. Chromatography (p.l.c.) using chloroform as eluant gave five major bands and a large number of minor ones which were not investigated.

Band 1 was further purified by chromatography using hexane–diethyl ether (98 : 2) as eluant and gave (a) 7-phenyldibenzo[*c*,*g*]carbazole [11] (8 mg, 1.5%) (Found: M^+, 343.1329. Calc. for $C_{26}H_{17}N$: *M*, 343.1360); (*b*) the *o*-semidine [11] (16) (4 mg, 0.5%) (Found: M^+, 436.1906. Calc. for $C_{32}H_{24}N_2$ *M*, 436.1939); $\nu_{max.}$ 3 370 cm^{-1} and (c) 1,1′-bis(*N*-phenyl-2-naphthyl)amine (5 mg, 0.5%) (Found: M^+, 436.1915. Calc. for $C_{32}H_{24}N_2$ *M*, 436.1939); $\nu_{max.}$ 3 370 cm^{-1}. All were colourless oils.

Band 2 was further purified by chromatography using benzene–hexane (7 : 3) as eluant to yield *N*-phenyl-2-naphthylamine (160 mg, 40%).

Band 3 was further purified by chromatography using benzene–hexane as solvent to yield 2-anilino-1,4-naphthoquinone 4-anil [12] (12 mg, 2.5%) identical (i.r., t.l.c.) with an authentic specimen.

Band 4 after further chromatography using benzene–hexane (1 : 1) as solvent gave 2-anilino-1,4-naphthoquinone [13] (187 mg, 47%) identical (m.p., i.r.) with an authentic sample.

Band 5 after further chromatography using hexane–diethyl ether (4 : 1) as eluant gave 2-*anilino*-3-(N-*phenyl*-2-*naphthyl*-*amino*)-1,4-*naphthoquinone* (4 mg, 0.5%) as a red oil (Found: M^+, 466.1684, $M^+ - 92$, 374.1172. $C_{26}H_{16}NO_2$ requires *M* 406.1681 and $M - 92$ 374.1180); $\lambda_{max.}$ 223, 252, and 486 (log ε 4.47, 4.29, and 3.56); $\nu_{max.}$ 1 680 cm^{-1} and 4-(*N*-phenyl-2-naphthylamino)-1,2-naphthoquinone (26 mg, 4.5%) as purple needles, from cold methanol m.p. 204—206 °C (lit.,[3] 203—207 °C) (Found: M^+, 375.1243, M^+, 347.1297. $M^+ - 57$, 318.1272. Calc. for $C_{26}H_{17}NO_2$ *M*, 375.1259, $C_{25}H_{17}NO$ *M*, 347.1310, and $C_{24}H_{16}N$ *M*, 318.1283); $\nu_{max.}$ 1 690 and 1 630 cm^{-1}; $\lambda_{max.}$ 253, 324infl. 396 and 518 (log ε 4.60, 3.84, 3.57, 3.83); δ 5.97 (1 H, s, =CH) and 7.1—8.2 (16 H, m, ArH).

(vi) *Phenyl* 8-*t*-*butyl*-2-*naphthyl nitroxide*. A solution of the nitroxide (410 mg) in benzene (3 ml) was left at room temperature in the dark for 14 days. Chromatography of the product mixture using chloroform as eluant gave (*a*) unchanged nitroxide (65 mg), (*b*) N-*phenyl*-8-*t*-*butyl*-2-*naphthylamine* (140 mg, 85%) as prisms, m.p. 134—135 °C (from pentane) (Found: C, 86.9; H, 7.7; N, 5.1. $C_{20}H_{21}N$ requires C, 87.2; H, 7.7; N, 5.1%); $\nu_{max.}$ 3 380 and 1 623 cm^{-1}; δ 1.53 (9 H, s, Bu^t), 5.8br (1 H, s, NH), and 6.8—8.0 (11 H, m, ArH); (*c*) 8-*t*-*butyl*-1,2-*naphthoquinone* 2-*phenylimine* N-*oxide* (45 mg, 25%) as deep red prisms from cold carbon tetrachloride, m.p. 103—105 °C (Found: M^+, 305.1450. $C_{20}H_{19}NO_2$ requires *M*, 305.1416) and N-(8-*t*-*butyl*-2-*naphthyl*)-1,4-*benzoquinone imine* N-*oxide* (56 mg, 31%) as orange prisms from cold carbon tetrachloride, m.p. 58—60 °C (Found: C, 78.7; H, 6.6; N, 4.3%; M^+, 305.1450. $C_{20}H_{19}NO_2$ requires C, 78.7; H, 6.3; N, 4.6%; *M*, 305.1416).

Preparation of Naphthoquinone Imine N-*Oxides* (6).—The quinone imine (1 mol) in carbon tetrachloride was added to a solution of *m*-chloroperbenzoic acid (1.2 mol) in carbon tetrachloride. If reaction was not complete (t.l.c.) then a further portion of *m*-chlorobenzoic acid (1 mol) was added and the mixture was left overnight. The products were separated by chromatography on silica using chloroform–petroleum as eluant. N-*Phenyl*-1,4-*naphthoquinone imine* N-*oxide* (64%) gave yellow cubes, m.p. 143—144 °C (from ethanol) (Found: C, 77.0; H, 4.4; N, 5.6%; M^+, 249.0787. $C_{16}H_{11}NO_2$ requires C, 77.1; H, 4.45; N, 5.6%; *M*, 249.0789). N-p-*t*-*Butylphenyl*-1,4-*naphthoquinone imine* N-*oxide* gave orange needles, m.p. 175—178 °C (from hexane–chloroform) (Found: M^+, 305.1418. $C_{20}H_{19}NO_2$ requires *M*, 305.1415). N-p-*t*-*Butylphenyl*-3,7-*di*-*t*-*butyl*-1,4-*naphthoquinone imine* N-*oxide* gave orange needles, m.p. 146—148 °C (from ethanol) (Found: C, 80.7; H, 8.5; N, 3.5%; M^+, 417.2669. $C_{28}H_{35}NO_2$ requires C, 80.5; H, 8.45; N, 3.35%; *M*, 417.2667). *N*-(3′,7′-Di-t-butyl-1′-naphthyl)-1,4-benzoquinone imine *N*-oxide gave orange needles, m.p. 178—179 °C.

Reactions of N-*Phenyl*-1-*naphthylamine*.—(i) *With* p-*t*-*butylphenyl* 3,7-*di*-*t*-*butyl*-1-*naphthyl nitroxide*. *N*-Phenyl-1-naphthylamine (400 mg, 1.83 mmol) and the nitroxide (184 mg, 0.46 mmol) were dissolved in chloroform (1 ml). The solution was left for 7 days and then chromatographed using hexane–chloroform (1 : 1) as eluant to give (*a*) *N*-*p*-t-butylphenyl-3,7-di-t-butyl-1-naphthylamine (107 mg, 0.275 mmol); (*b*) unchanged *N*-phenyl-1-naphthylamine (340 mg, 1.55 mmol); and (*c*) *N*-phenyl-1,4-naphthoquinone imine (64 mg, 0.275 mmol).

(ii) *With* p-*t*-*butylphenyl* 4-*t*-*butyl*-1-*naphthyl nitroxide*. The amine (53 mg, 0.24 mmol) and nitroxide (20 mg, 0.06 mmol) were dissolved in chloroform (0.5 ml) and the solution was left for 7 days. Chromatography as in (i) gave small amounts of (*a*) *N*-*p*-t-butylphenyl 4-t-butyl-1-naphthylamine; (*b*) *N*-phenyl-1-naphthylamine; and (*c*) *N*-phenyl-1,4-naphthoquinone imine all identical with authentic samples.

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