Nitroxide Radicals. Part XIV.[1] Decomposition of 1- and 2-Naphthyl t-Butyl Nitroxides

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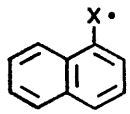
The spontaneous decomposition of 2-naphthyl t-butyl nitroxides yields mainly the corresponding secondary amines and 2-t-butylamino-1,4-naphthoquinones. The latter arise from intermediate 1,2-naphthoquinone t-butylimine *N*-oxides [formed by initial O-to-C(1) coupling of the nitroxide], which are isomerised by a process which is initiated by the nitroxide. 1-Naphthyl t-butyl nitroxide behaves in an analogous fashion, giving the corresponding secondary amine and 4-t-butylamino-1,2-naphthoquinone.

THE title radicals fall into a class of aromatic π-radical which may be represented by the general formulae (1) and (2). Usually such radicals couple in a variety of ways, depending on the nature of X and the conditions under which they are formed. Thus the 1-naphthylmethyl radical (1; X = CH_2) couples in the gas phase CH_2 to CH_2 and CH_2 to C(4) whereas its



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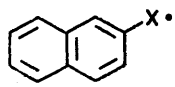


(2)

2-naphthyl isomer (2; X = CH_2) couples CH_2 to CH_2, CH_2 to C(1), and CH_2 to C(3). In both cases disubstituted ethanes and ethylenes and polycyclic hydrocarbons are formed;[2] the aminyl (2; X = NPh) readily couples C(1) to C(1) and C(1) to N (but not N to N) to give dimers;[3] 1-naphthoxyl (1; X = O) gives all possible '*ortho*'- and '*para*'-coupled dimers but no C-to-O coupled products whereas 2-naphthoxyl (2; X = O) gives mainly C(1)-to-C(1) coupled binaphthols accompanied by much less of the O-to-C(1) coupled ether;[4] much less is known about naphthylthio-radicals (1 and 2; X = S) which appear to couple exclusively S to S to give disulphides.[5] We now report on the coupling reactions of a number of 1- and 2-naphthyl t-butyl nitroxides (1 and 2; X = Bu^tNO), whose e.s.r. spectra we have previously described.[1] Such processes are of particular interest since they have bearing on the mechanism by which naphthylamines inhibit autoxidation of, for example, hydrocarbons.

Results.—The naphthyl nitroxides listed in Table 1 were prepared from the corresponding hydroxylamines by oxidation with silver oxide and were allowed to decompose at 30° in the dark during 14 days both as the neat oils and in solution (0·5M) in benzene. Under these conditions all but the 8-t-butyl-2-naphthyl radical (3; $R^1 = Bu^t$, R^2 = H) decomposed substantially to the corresponding amine (6) and 2-t-butylamino-1,4-naphthoquinone (7) [except the 1-naphthyl nitroxide (32) which gave 4-t-butylamino-1,2-naphthoquinone (36)]. Generally, reaction proceeded more rapidly in the absence of solvent but yields were higher when a solvent was used. The amines were identified by comparison with authentic samples produced by hydrogenation of the hydroxylamines over Raney nickel and the aminoquinones by their spectroscopic properties, especially i.r. (NH and CO absorption) and n.m.r. (quinonoid proton signal τ 4·04—4·11). An additional red product, $C_{30}H_{34}N_2O_4$, was obtained from the methoxy-2-naphthyl nitroxide (3; R^1 = H, R^2 = OMe). This was assigned structure (10) since its n.m.r. spectrum showed the correct number of Bu^t, OMe, and aromatic proton resonances and no signal attributable to a quinonoid proton. The 1-naphthyl nitroxide (32) gave the 1,4-quinone imine *N*-oxide (33) as a minor product easily identified from its characteristic u.v. ($\lambda_{max.}$ 388 nm), i.r. ($\nu_{max.}$ 1645 cm^{-1}), and n.m.r. [τ 8·21, $Bu^t\overset{+}{N}(\overset{-}{O})$=] spectra.

A kinetic investigation of the rate of decomposition of the 2-naphthyl t-butyl nitroxide (3) in carbon tetrachloride established that, in the concentration range 0·02—0·20M at 30°, the reaction is a second-order decay in one component. Rate constants for the decompositions are given in Table 2. From measurements over the temperature range 303—318 K the Arrhenius activation energy for the decomposition of the parent 2-naphthyl nitroxide was calculated as 52·3 ± 11·8 kJ mol^{-1}. Similar measurements on the 8-t-butyl-2-naphthyl nitroxide showed that in the temperature and

[1] J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J.C.S. Perkin II*, 1973, 718.
[2] K. F. Lang and H. Buffleb, *Chem. Ber.*, 1958, **91**, 2866.
[3] R. F. Bridger, *J. Amer. Chem. Soc.*, 1972, **94**, 3124.
[4] H. Musso, *Angew. Chem. Internat. Edn.*, 1963, **2**, 723.
[5] A. A. Oswald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, 1961, **26**, 3969; A. S. Hay, Fr.P. 1,337,285/1963 (*Chem. Abs.*, 1964, **60**, 2843).

concentration ranges used this nitroxide did not decompose to a detectable extent.

Discussion.—We have shown previously that phenyl t-butyl nitroxides couple O to *para*-C to give cyclohexadiene intermediates, which fragment spontaneously to secondary amines and *para*-quinone imine *N*-oxides.[6] When such coupling is prevented by the presence of certain *ortho*- or *para*-substituents, other reactions (disproportionation) may occur or the radical may have an exceptionally long life. Clearly the latter is not the case for most of the 2-naphthyl t-butyl nitroxides examined here. The stabilising effect of an 8-alkyl substituent, evident from the kinetic and product studies (Tables 1 and 2) suggests that the rate-controlling step involves reaction at the 1-position. This is, of course, the position of highest unpaired spin density in the ring and the position at which coupling occurs most frequently with other naphthyl π-radicals of type (2). However, O-to-'*ortho*'-C [C(1)] coupling followed by fragmentation (Scheme 1) would lead to secondary amine (6) and 1,2-quinone imine *N*-oxide (5), and the latter is not a product of the decompositions, although it is an isomer of one of the products, the amino-quinone (7). *ortho*-Quinone imine *N*-oxides are unknown and hence the possibility that they may isomerise or be isomerised easily to the corresponding amino-quinones has not been tested. Accordingly we set out to establish that the former were indeed intermediates in the decompositions of the 2-naphthyl nitroxides and that they were the source of the amino-quinones.

TABLE 1

Yields * (%) of decomposition products from naphthyl t-butyl nitroxides of the types (1 and 2; X = Bu^tNO)

Naphthyl	Conditions †	Naphthylamine	Bu^tNH-quinone	Unchanged nitroxide	Other products
2-Naphthyl	(a)	61	74		
	(b)	79	75	13	
8-Me	(a)	56	60	6	
	(b)	29	46	32	
8-Bu^t	(a)	61	62·5	85	
	(b)	‡	‡	92	
6-MeO	(a)	53	64		
	(b)	49	62	6	(10) 4·5
4,5-Me_2	(a)	59	41		
	(b)	62	41		
1-Naphthyl	(a)	24	16		(33) ‡
	(b)	31	5		(33) ‡

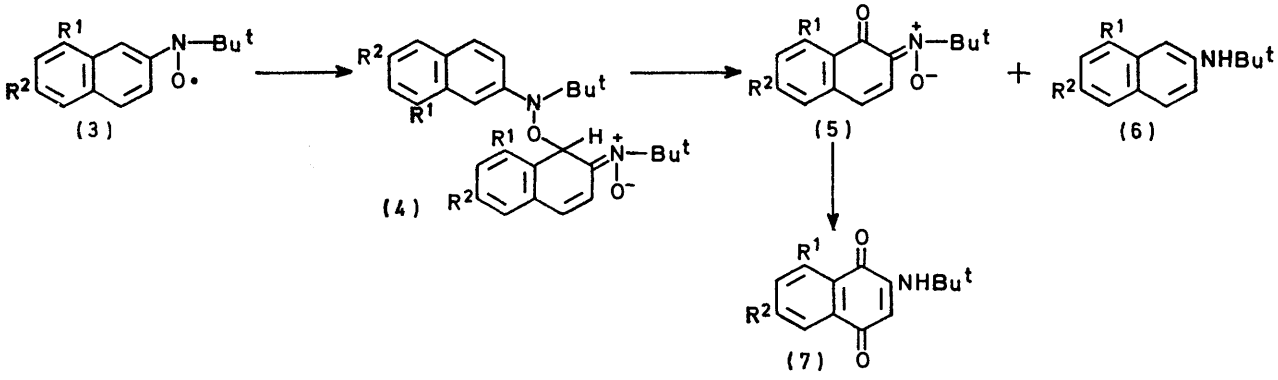
* Yields are based on 2 mol of nitroxide giving 1 mol each of amine and aminoquinone and are calculated on the weight of radical consumed; the values are the average of two separate determinations. † (a) Neat oil; (b) 0·5M solution in benzene. ‡ Unestimated small amount.

TABLE 2

Second-order rate constants for decompositions of 2-naphthyl nitroxides

Nitroxide	Concn. (M)	T/K	10^5k/ l mol^{-1} s^{-1}	Correln. coefft.
2-Naphthyl	0·10	303	4·08	0·998
	0·15	303	3·83	0·999
	0·20	303	3·67	0·994
	0·10	303·2	4·31	0·998
	0·10	310·4	5·86	0·997
	0·10	318	11·4	0·997
8-Me	0·10	303	2·11	0·999
6-MeO	0·10	303	7·67	0·999
4,5-Me_2	0·10	303	25·5	0·999

Decompositions in Aniline.—The 2-naphthyl nitroxides were allowed to decompose in solution in aniline in the expectation that the '*ortho*'-quinone imine *N*-oxides (5) (if formed) would react with aniline as *ortho*-quinones do and so prevent, to some extent at least, amino-quinone formation. Studies of the products from three 2-naphthyl nitroxides are given in Table 3.



SCHEME 1

In general, the yields of amino-quinone were substantially lower than those from the experiments in which benzene was used as solvent, and two additional products, the mono- and di-anils (8) and (9), respectively, were also obtained. These do not arise from the

TABLE 3

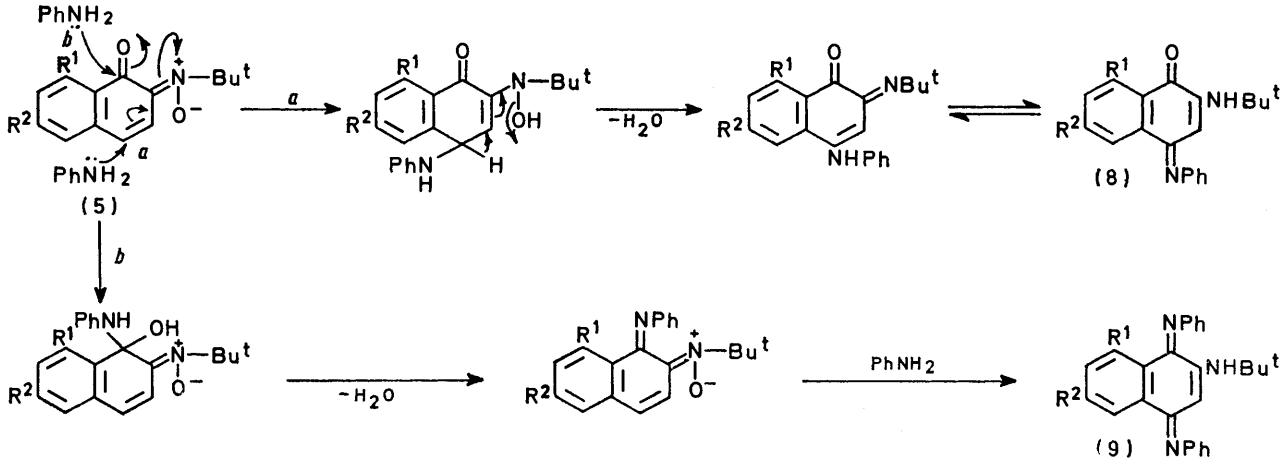
Yields (%) * of products from 2-naphthyl t-butyl nitroxides in aniline

Radical	Bu^tNH-quinone	Naphthylamine	Monoanil	Dianil
2-Naphthyl	39	61	10	1
4,5-Me_2	48	58	4	
6-MeO		4	6	38

* Based on 2 mol of nitroxide giving 1 mol of naphthylamine and 1 mol of amino-quinone or mono- or di-anil.

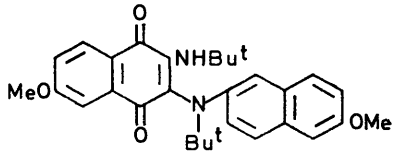
[6] A. Calder and A. R. Forrester, *J. Chem. Soc.* (*C*), 1969, 1459.

amino-quinones (7) since they were not formed when solutions of the corresponding amino-quinones in aniline were left at room temperature or were heated under reflux. Similarly, it was shown that the monoanil (8) is not a precursor of the dianil (9). Hence, monoanil formation can be envisaged as occurring by reaction of aniline at C(4) of the presumed intermediate 1,2-quinone imine *N*-oxide (5) (Scheme 2, path *a*) (this



SCHEME 2

being closely analogous to the reaction of *ortho*-quinones with aniline [7]) and dianil formation as a reaction of aniline initially at the carbonyl group (path *b*) and then



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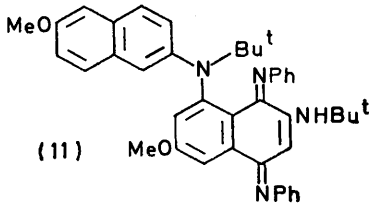


(11)

at the 4-position of the resulting di-imine *N*-oxide. An additional product (26%) formed from the 6-methoxy-2-naphthyl nitroxide (3; $R^1 = H$, $R^2 = OMe$) in aniline has been identified as the 8-naphthylamino-quinone 1,4-dianil (11) mainly on the basis of its mass and n.m.r. spectra. The base peak in the mass spectrum is at $M^+ -227$, which corresponds to loss of the 8-naphthylamino-residue. The n.m.r. spectra of both the dianil (9; $R^1 = H$, $R^2 = OMe$) and this product show a doublet at τ *ca.* 2·04 (J 3 Hz) attributable to H(5) and a singlet at higher field due to H(3); hence the naphthoquinonoid unit in (11) is almost certainly substituted at the 8-position. In a separate experiment it was shown that the 8-substituted dianil (11) is formed by reaction of the parent dianil (9; $R^1 = H$, $R^2 = OMe$) with *N*-t-butyl-6-methoxy-2-naphthylamine (6; $R^1 = H$, $R^2 = OMe$) in aniline. This accounts for the low yield of amine (but not of amino-quinone) in the products of this nitroxide decomposition. Addition of amines at the 8-position of naphthoquinones has been reported [8] but to our knowledge this is the first example of such a reaction with naphthoquinone dianils. Although the above results strongly suggest that there is an '*ortho*'-quinonoid precursor of the t-butylamino-quinone in the nitroxide decompositions the evidence is not exclusive for an '*ortho*'-quinone imine *N*-oxide.

Oxidation of Nitroxides with Fremy's Salt.—In order to obtain more specific evidence for the participation of the '*ortho*'-quinone imine *N*-oxide intermediates (5) their synthesis by an alternative route was undertaken. Oxidation of *N*-alkyl-*N*-phenylhydroxylamines or nitroxides with a free *para*-position with Fremy's salt gives *para*-quinone imine *N*-oxides in good yield in much the same way as phenols are oxidised to quinones with this oxidant.[9] Similar treatment of 2-naphthyl t-butyl nitroxide gave, in addition to the amino-quinone (7; $R^1 = R^2 = H$), a purple product whose n.m.r. spectrum showed a sharp singlet at τ 8·30 characteristic of the $Bu^t\overset{+}{N}(\bar{O})=$ group and signals from six other aromatic and quinonoid protons. I.r. (1638 cm^{-1}), u.v. (450 nm), and accurate mass measurements confirmed that this was the '*ortho*'-quinone imine *N*-oxide (5; $R^1 = R^2 = H$). Similar treatment of N-t-butyl-8-methyl- and -6-methoxy-2-naphthylhydroxylamines gave products (Table 4) with spectral characteristics similar to those already described for (5; $R^1 = R^2 = H$). However, oxidation of 4,5-dimethyl-2-naphthyl t-butyl nitroxide (22) did not lead to the corresponding '*ortho*'-quinone imine *N*-oxide (23a). Instead, the complex

[7] L. Horner and H. Lang, *Chem. Ber.*, 1956, **89**, 2768.
[8] J. H. Bowie and D. W. Cameron, *J. Chem. Soc.* (*C*), 1967, 712.
[9] H. J. Teuber and W. Rau, *Chem. Ber.*, 1953, **86**, 1036 and later papers.

reaction mixture gave the amino-quinone (30) (18%) and a small quantity (1%) of a blue oil of molecular formula $C_{32}H_{36}N_2O_2$. The latter product had one t-butylamino-group (τ 8·51) and one aromatic methyl

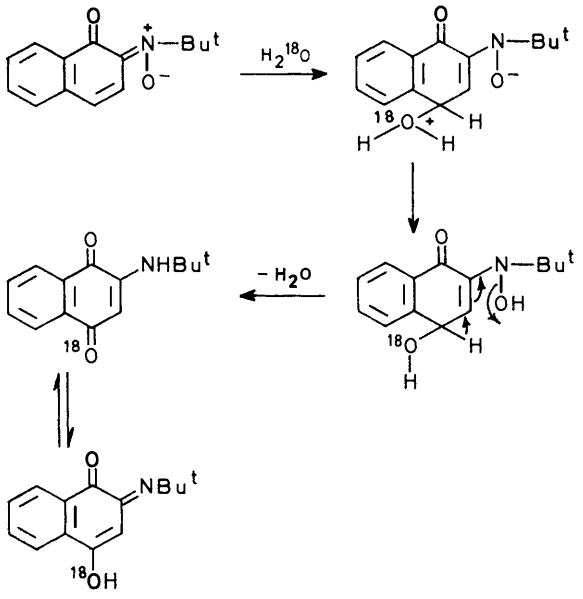
TABLE 4

Yields (%) of products from oxidation of 2-naphthylhydroxylamines with Fremy's salt

Hydroxylamine	But NH-quinone	Imine *N*-oxide	Nitroxide
2-Naphthyl	9	22	
8-Me	7	14	28
6-MeO	3	30	13

(τ 7·09) per naphthalene residue and showed i.r. absorption at 1615 and 1610 cm^{-1}. Structure (27), the anhydro-dimer of the quinone methide (23b), is advanced for this product. We consider that this dimer arises from the 1,2-quinone imine *N*-oxide (23a), which may react as the quinone methide (23b) and be oxidatively dimerised to (26). Formation of the blue dimer from the bis-hydroxylamine probably proceeds *via* the corresponding dinitroxide, which would be deoxygenated by coupling with, for example, the parent nitroxide (22) (see later). This reaction sequence is analogous to those suggested for the oxidation of 4-methyl-2,6-di-t-butylphenol to 2,2',6,6'-tetra-t-butylstilbenequinone.[10]

With authentic samples of three 1,2-quinone imine *N*-oxides available it was possible to show (t.l.c.) that these were indeed present in small amount in the decomposition mixtures from the corresponding nitroxides. Further, when left in aniline solution for 4 days the quinone imine *N*-oxides (5; $R^1 = R^2 = H$) and (5; $R^1 = H$, $R^2 = OMe$), like the nitroxides from which they were derived, gave mixtures of the corresponding amino-quinones (7) and naphthoquinone mono- and di-anils (8) and (9), respectively. Hence, although the participation of 1,2-quinone imine *N*-oxides in the decomposition of the nitroxides has been established, the manner by which they rearrange to isomeric amino-quinones has still to be elucidated. Although solutions of the quinone imine *N*-oxides (5; $R^1 = R^2 = H$) and (5; $R^1 = H$, $R^2 = OMe$) in benzene were slowly and apparently spontaneously transformed into the corresponding aminoquinones (the change being accelerated by heat), the rate of change was too slow to account for the yields of amino-quinone formed in the nitroxide decompositions. For example, after 2 weeks in benzene the quinone imine *N*-oxide (5; $R^1 = H$, $R^2 = OMe$) was *ca.* 95% unchanged. Clearly some other species present in these nitroxide decomposition mixtures hastens the transformation. That this was not water carried through from the oxidation of the hydroxylamine to the nitroxide was confirmed by addition of $H_2{}^{18}O$ to a solution of 2-naphthyl t-butyl nitroxide. The mass spectrum of the amino-quinone formed showed no incorporation of the label, thus invalidating Scheme 3.



SCHEME 3

Significantly the isomerisation of the 1,2-quinone imine *N*-oxide (5) was greatly assisted by addition of the corresponding nitroxide. This suggests a mechanism such as that shown in Scheme 4, in which the initial and key step is the addition of the nitroxide (12) to the quinone imine *N*-oxide (13) at the 4-position to give a dienone nitroxide (14). The order and importance of the subsequent steps is difficult to determine since this dienone nitroxide may (a) undergo intermolecular O-to-*ortho*-C coupling with another molecule of nitroxide (12) followed by fragmentation to give the amine (16), the amino-quinone (17), and the quinone imine *N*-oxide (13); (b) undergo addition to another molecule of quinone imine *N*-oxide, followed by fragmentation; or (c) fragment to the quinonoid nitroxide (15), which may then react like the dienone nitroxide in (a) and (b). Irrespective of the exact sequence of events the end result of these reactions is the same, *i.e.* the quinone imine *N*-oxide (13) is transformed into the aminoquinone (17). Addition and conjugate addition of nitroxides to nitrones has been proposed previously to account for products obtained from halogenomethyl nitroxides [11] and from aryl nitroxides with primary and secondary *para*-alkyl substituents.[6]

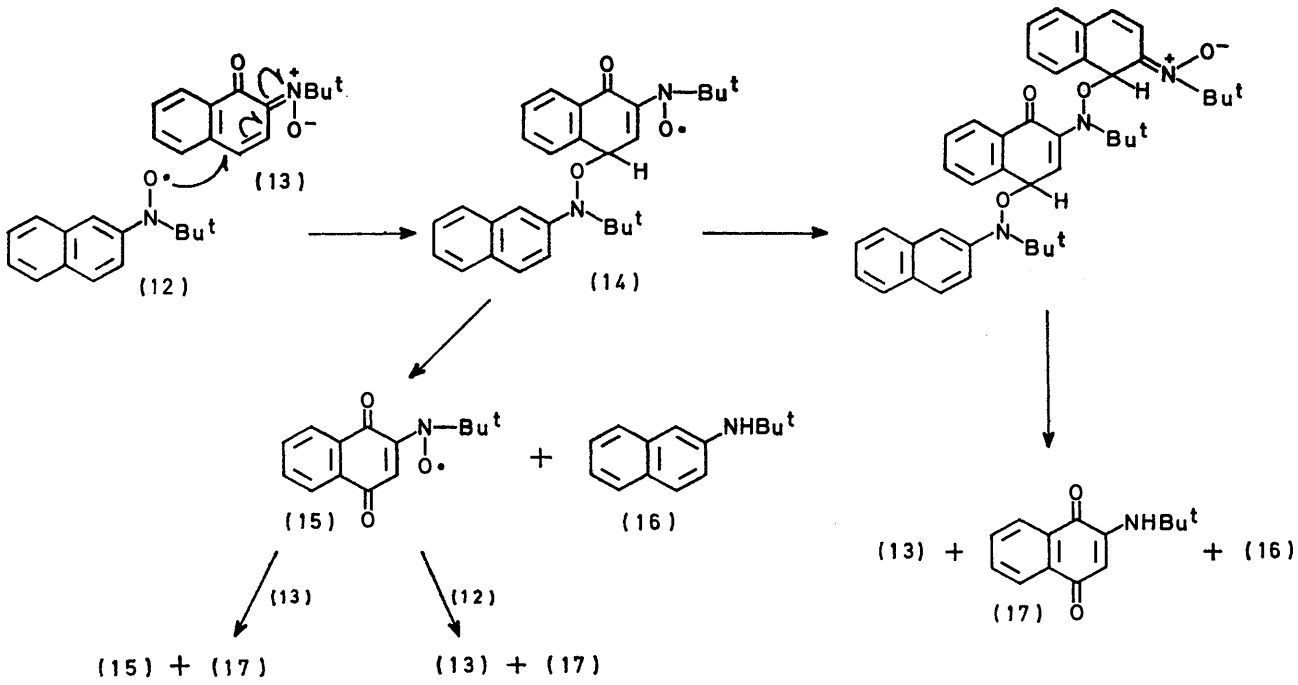
The slow conversion of the quinone imine *N*-oxide (13) into the amino-quinone (17) when apparently no nitroxide is present could be explained in a similar way since quinone imine *N*-oxides are frequently contaminated by traces of the corresponding hydroxyaryl nitroxides.[12] For example, solutions of the 6-methoxynaphthoquinone imine *N*-oxide (18) in carbon

[10] W. Bradley and J. D. Sanders, *J. Chem. Soc.*, 1962, 480.

[11] C. M. Camaggi, R. J. Holman, and M. J. Perkins, *J.C.S. Perkin II*, 1972, 501; J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2709.

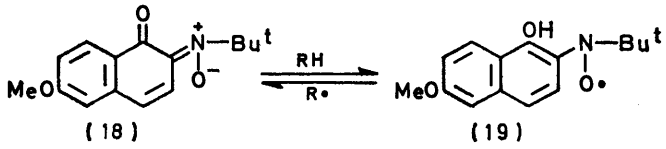
[12] A. R. Forrester, G. R. Luckhurst, and R. H. Thomson, *J. Chem. Soc.* (*B*), 1968, 1311.

tetrachloride gave a weak and poorly resolved e.s.r. spectrum of a nitroxide with a_N 13·5 G, considerably greater than that of the parent nitroxide (11·9 G) but consistent with one bearing a substituent on C(1). dimerise, trimerise, or polymerise.[13] However, formation of the t-butylamino-quinone (17) in the nitroxide decompositions must occur mainly as indicated in Scheme 4, other routes being of minor importance.

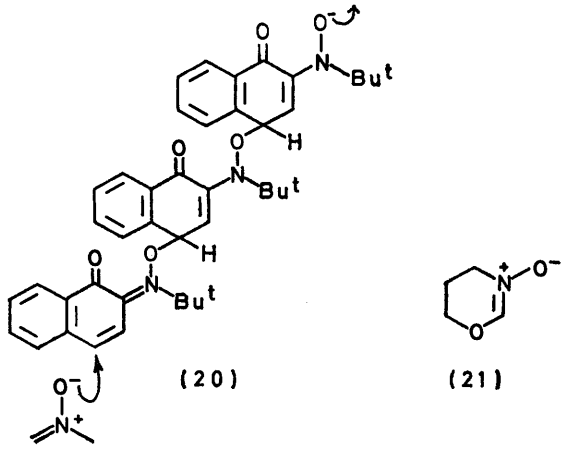


SCHEME 4

This could well be due to the hydroxy-2-naphthyl nitroxide (19). Alternatively, intermolecular oxygen



migration could occur slowly by an ionic pathway by fragmentation of dimeric or telomeric intermediates



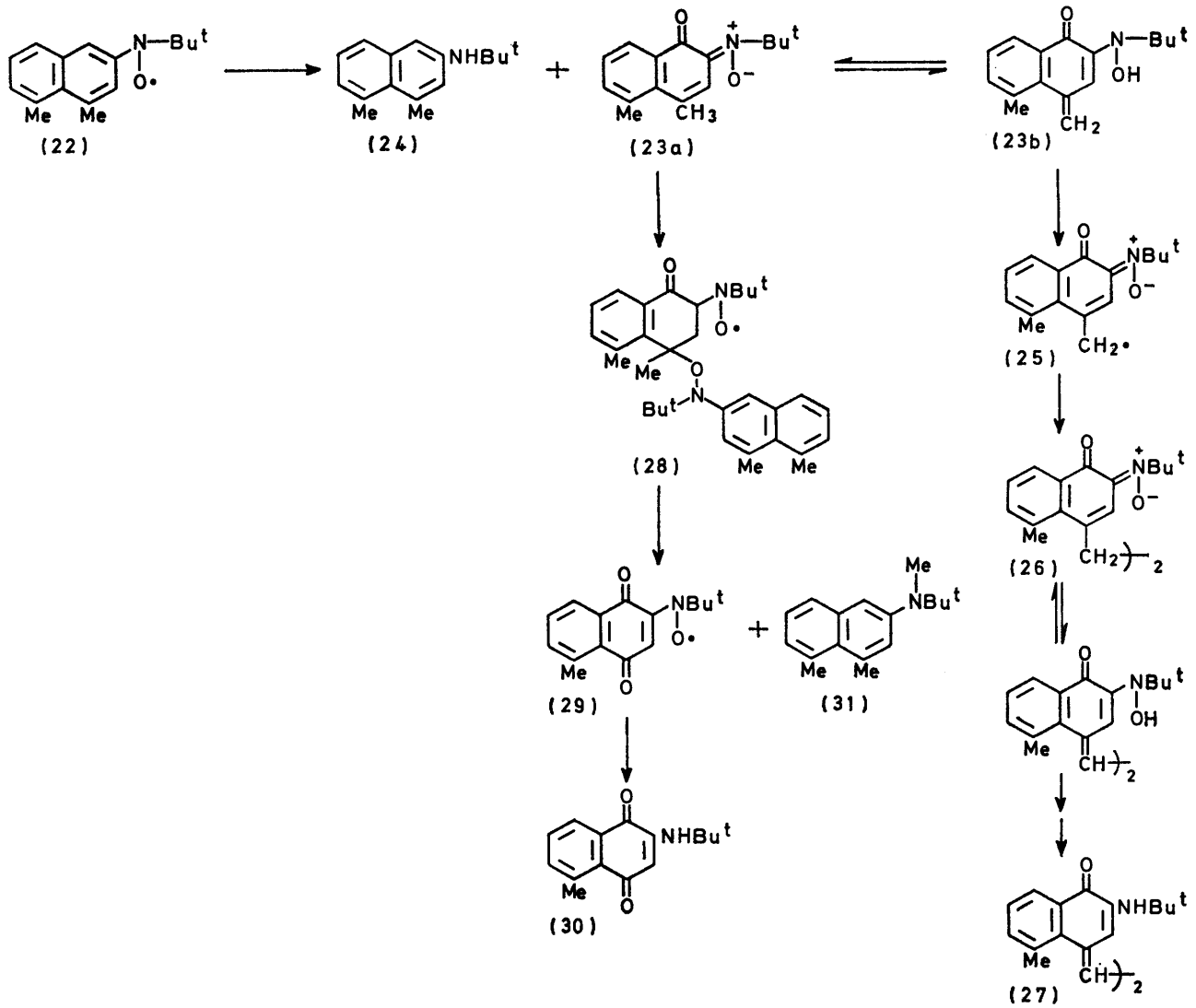
such as (20) formed by self-Michael-type addition of the quinone imine *N*-oxide (12). Analogous cases are known of nitrones [*e.g.* (21)] which spontaneously

An intriguing aspect of the spontaneous decomposition of the 4,5-dimethyl-2-naphthyl nitroxide (22) is the formation of a t-butylaminonaphthoquinone (30) which has no 4-methyl group. For this radical the above mechanism is inadequate since it does not account for the oxidative demethylation required to produce (30) from (23a). Efforts to determine the fate of the methyl group were only partly successful. The n.m.r. spectrum of the crude decomposition mixture obtained when a sample of the nitroxide was left in a sealed tube for several weeks was essentially a composite of the spectra of the amino-quinone (30) and the amine (24). No new intense methyl, methylene, methine, or formyl proton signals were evident. Hence the 4-methyl group of the nitroxide had not been efficiently transferred to or transformed into a single product. Chromatographic separation of the minor products of this decomposition was only slightly more rewarding when the *N*-methyl-*N*-t-butyl-4,5-dimethyl-2-naphthylamine (31) and the dimer (27) were isolated and it was shown that neither *N*-methoxy-*N*-t-butyl-2-naphthylamine (independently produced from the nitroxide and acetyl peroxide) nor formaldehyde (chromotropic acid test) was present.

The poor material balance (with respect to the methyl group) makes it difficult to formulate a reasonable

[13] J. F. Elsworth and M. Lamchen, *J. Chem. Soc.* (*C*), 1968, 2423; G. Eikelmann, W. Heimberger, G. Nonnenmacher, and W. M. Weigert, *Annalen*, 1972, **759**, 183.

reaction scheme for this displacement. Product analysis makes previous mechanisms,[14] which have been adduced for analogous demethylations, inapplicable in this case. Of the several possible reactions which the tautomeric quinone methide ⇌ imine *N*-oxide [(23a) ⇌ (23b)] could undergo with the nitroxide (22), the t-butylnaphthylamine (24), or itself, the were isolated in relatively low yield (Table 1). Since this nitroxide has an unsubstituted '*para*'-position, O-to-C(4) coupling would be expected to occur yielding a 1,4-quinone imine *N*-oxide (33) and the amine (34). However, the quinone imine *N*-oxide (33) is a very minor product of the decomposition and in view of our experience with the 2-naphthyl nitroxides we gave



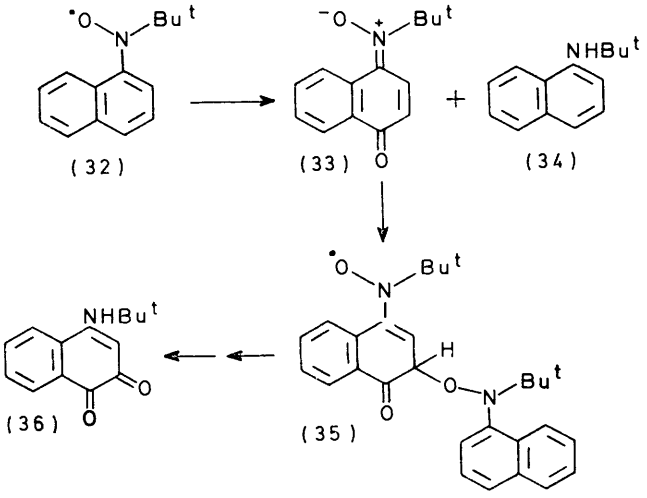
SCHEME 5

addition–elimination sequence (23a) ⟶ (28) ⟶ (29) ⟶ (30) seems to be the only one for which evidence has been obtained. From the relatively low yield of tertiary amine (31) isolated it must be inferred that either this is a minor route or the bulk of the tertiary amine is consumed in further reactions.

1-*Naphthyl t-Butyl Nitroxide*.—Although the stability of the 1-naphthyl nitroxide (32) in solution is similar to that of the 2-isomer, the product mixture which it yielded was much more complex and the *N*-t-butyl-1-naphthylamine (34) and t-butylamino-quinone (36) consideration to the possible 'isomerisation' of the 1,4-quinone imine *N*-oxide to the 4-t-butylamino-1,2-naphthoquinone (36). The former was readily obtained in high yield by oxidation of the 1-naphthyl nitroxide (32) or the corresponding hydroxylamine with Fremy's salt and shown to undergo only an extremely slow spontaneous change to the t-butylaminonaphthoquinone at room temperature in benzene. Heating

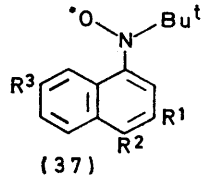
[14] W. M. Horspool, P. Smith, and J. M. Tedder, *J.C.S. Perkin I*, 1972, 1024; H. J. Teuber and G. Steinmetz, *Angew. Chem.*, 1964, **76**, 612.

accelerated the change but even then it occurred much too slowly to account for the formation of the t-butylaminonaphthoquinone isolated from the nitroxide decomposition. Water-catalysed isomeration was again excluded by experiments with $H_2{}^{18}O$ when it was shown that there was no incorporation of ^{18}O into the aminoquinone. However, addition of the nitroxide (32) to solutions of the quinone imine *N*-oxide (33) greatly assisted the isomerisation and hence we postulate Scheme 6, analogous to Scheme 4, in which the key step is the reaction of nitroxide at C(3) of (33). Irrespective of the exact order of the subsequent steps the end result is the formation of t-butylamino-1,2-naphthoquinone



SCHEME 6

(36). The isomerisation (33) ⟶ (36) is even more surprising than the analogous rearrangement for the 1,2-naphthoquinone imine *N*-oxides, since several other 1,4-benzoquinone imine *N*-oxides isolated in this laboratory do not undergo such a change in the presence of nitroxide.[6] In this respect the stability of the adduct radical (35) relative to that of its benzenoid analogue may be crucial. E.s.r. measurements clearly indicate that the nitroxide group in (32), because of interaction of the *peri*-hydrogen atom, is twisted out of conjugation with the ring to a greater extent than it is with t-butyl phenyl nitroxide.[1] This reduces the unpaired spin density at C(4) and hence the likelihood of O-to-C(4) coupling as compared with, for example, t-butyl phenyl nitroxide. However, the low yield of amino-quinone from (32) and the complex mixture of other products produced in the decomposition cannot be explained in this way since 1-naphthyl nitroxides with 4-substituents, *e.g.* (37; $R^1 = R^2 = Me$, $R^3 = H$) and (37; $R^1 = H$, $R^2 = R^3 = Me$) were extremely stable and showed no tendency to couple in other ways which do not involve the 4-position. Therefore the wide variety of other products from the 1-naphthyl nitroxide decomposition must be the result of other reactions which compete with the isomerisation steps shown.



(37)

EXPERIMENTAL

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

Bromonaphthalenes.—1- and 2-Bromonaphthalenes were commercial products. 7-Bromo-1-methyl-,[15] 2-bromo-6-methoxy-,[16] 3-bromo-1,8-dimethyl-,[17] 1-bromo-3,4-dimethyl-[18] and 1-bromo-4,7-dimethylnaphthalenes[19] were prepared by literature methods. *7-Bromo-1-t-butylnaphthalene*, b.p. 100—101° at 0·18 mmHg (Found: C, 63·9; H, 5·6; Br, 30·6. $C_{14}H_{15}Br$ requires C, 63·9; H, 5·7; Br, 30·4%), was prepared from *6-bromo-1,2-dihydro-4-t-butylnaphthalene*, b.p. 88—90° at 0·1 mmHg (Found: C, 63·5; H, 6·4; Br, 30·3. $C_{14}H_{17}Br$ requires C, 63·4; H, 6·5; Br, 30·1%) by dehydrogenation with dichlorodicyanobenzoquinone. The dihydronaphthalene was prepared by the reaction of 7-bromo-1-tetralone with t-butylmagnesium chloride followed by dehydration as described in the literature[15] for its 1-methyl homologue.

N-Naphthyl-N-t-butylhydroxylamines.—The hydroxylamines (Table 5) were prepared by treatment of the corresponding Grignard reagents with 2-methyl-2-nitrosopropane[20] as described previously for alkylaryl-t-butylhydroxylamines.[6] They were crystallised from petroleum and characterised by their i.r. (ν_{OH} 3300—3100 cm^{-1}) and n.m.r. [τ *ca.* 8·9 (Bu^t)] spectra and by their colour reaction with 2,3,5-triphenyltetrazolium chloride.

Preparation and Decomposition of Naphthyl t-Butyl Nitroxides. The nitroxides were obtained by shaking solutions of the corresponding hydroxylamines (1·0 mmol) in benzene with silver oxide (1·2 mmol) and magnesium sulphate. After filtration the solutions were either evaporated at room temperature until solvent was removed and left for 14 days [conditions (a), Table 1] or concentrated to 0·5M with respect to the radical and left for 14 days [conditions (b), Table 1].

Products were separated (t.l.c.) on silica gel (GF_{254}; Merck) with chloroform as eluant. Yields of nitroxides and naphthylamines were obtained by direct weighing and of the amino-quinones spectrophotometrically by measuring the intensities of their visible absorption maxima. The following nitroxides were sufficiently stable to be isolated: *t-butyl 8-t-butyl-2-naphthyl nitroxide*, red prisms, m.p. 57—58° (from hexane) (Found: C, 80·0; H, 8·9; N, 5·4. $C_{18}H_{24}NO$ requires C, 80·0; H, 9·0; N, 5·2%), $\lambda_{max.}$ 271, 310, 357, 552, 584sh, and 618sh nm (log ε 4·07, 4·01, 3·53, 2·57, 2·49, and 2·20); *3,4-dimethyl-1-naphthyl*

[15] M. S. Newman and S. Seshadri, *J. Org. Chem.*, 1962, **27**, 76.
[16] H. E. French and K. Sears, *J. Amer. Chem. Soc.*, 1948, **70**, 1279.
[17] W. J. Mitchell, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 1962, 2526.
[18] C. L. Hewett, *J. Chem. Soc.*, 1940, 293.
[19] E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, 1930, 22.
[20] A. Calder, A. R. Forrester, and S. P. Hepburn, *Org. Synth.*, 1972, **52**, 77.

t-butyl nitroxide, red prisms, m.p. 114—115° (from hexane) (Found: C, 79·1; H, 8·5; N, 6·1. $C_{16}H_{20}NO$ requires C, 79·3; H, 8·3; N, 5·8%), $\lambda_{max.}$ 285, 326, and 440sh nm (log ε 4·28, 3·73, and 1·89); *1-naphthyl t-butyl nitroxide*, deep red cubes, m.p. 74—76° (Found: C, 78·6; H, 7·5; N, 6·5. $C_{14}H_{16}NO$ requires C, 78·8; H, 7·5; N, 6·5%).

(i) *2-Naphthyl t-butyl nitroxide*. This gave (a) *N*-t-butyl-2-naphthylamine, m.p. 43—45° (from petroleum) (lit.,[21] 43—45°), $\nu_{max.}$ 3410 cm^{-1}, τ 8·67 (9H, s, Bu^t), 6·47br (1H, s, NH), and 2·36—3·26 (7H, m, ArH); and (b) *2-t-butylamino-1,4-naphthoquinone*, orange cubes, m.p. 89—90° (from hexane) (Found: C, 73·0; H, 6·7; N, 6·1. $C_{14}H_{15}NO_2$ requires C, 73·3; H, 6·6; N, 6·1%), $\lambda_{max.}$ 235, 271, 330, and 445 nm (log ε 4·19, 4·38, 3·40, and 3·53), $\nu_{max.}$ 3330, 1680, and 1630 cm^{-1}, τ 8·55 (9H, s, Bu^t), 4·04 (1H, s, =CH), 4·0br (1H, s, NH), and 1·8—2·5 (4H, m, ArH), identical with a specimen produced by shaking a solution of 2-ethoxy-1,4-naphthoquinone in ethanol with aqueous t-butylamine.

When 2-naphthyl t-butyl nitroxide (212 mg) in AnalaR acetone (1·5 ml) and ^{18}O-enriched water (0·5 ml; 20% enriched) was left for 14 days the 2-t-butylamino-1,4-naphthoquinone formed showed $M/(M + 2) = 30·4$ in its mass spectrum. 2-t-Butylaminonaphthoquinone similarly produced in acetone–water (not enriched) had $M/(M + 2) = 28·6$.

(ii) *8-Methyl-2-naphthyl t-butyl nitroxide*. This gave (a) *N-t-butyl-8-methyl-2-naphthylamine*, m.p. 54—55° (from hexane) (Found: C, 84·2; H, 8·7; N, 6·9. $C_{15}H_{19}N$ requires C, 84·5; H, 9·0; N, 6·6%), $\nu_{max.}$ 3410 cm, τ 8·59 (9H, s, Bu^t) 7·42 (3H, s, Me), 6·48br (1H, s, NH), and 2·35—3·15 (6H, m, ArH); and (b) *8-methyl-2-t-butylamino-1,4-naphthoquinone*, orange cubes, m.p. 123—125° (from petroleum) (Found: C, 73·9; H, 7·1; N, 5·9. $C_{15}H_{17}NO_2$ requires C, 74·0; H, 7·0; N, 5·8%), $\lambda_{max.}$ 233, 265sh, 271, 287sh, 295sh, 352, and 450 nm (log ε 4·18, 4·23, 4·25, 4·00, 3·91, 3·46, and 3·47), $\nu_{max.}$ 3320, 1670, and 1615 cm^{-1}, τ 8·55 (9H, s, Bu^t), 7·29 (3H, s, Me), 4·07 (1H, s, =CH), 3·95br (1H, s, NH), 2·8—2·3 (2H, m, H-6 and -7), and 8·03 (1H, q, *J* 8 and 2 Hz, H-5).

(iii) *t-Butyl 8-t-butyl-2-naphthyl nitroxide*. This gave (a) *N-t-butyl-8-t-butyl-2-naphthylamine*, prisms, m.p. 47—49° (from hexane) (Found: C, 84·5; H, 9·8: N. 5·6. $C_{18}H_{25}N$ requires C, 84·6; H, 9·9; N, 5·5%), $\nu_{max.}$ 3400 cm^{-1}, τ 8·58 (9H, s, NBu^t), 8·40 (9H, s, CBu^t), 6·70br (1H, s, NH), and 2·31—3·26 (6H, m, ArH); (b) *8-t-butyl-2-t-butylamino-1,4-naphthoquinone*, orange cubes, m.p. 125—127° (from petroleum) (Found: C, 75·5; H, 8·4; N, 4·8. $C_{18}H_{23}NO_2$ requires C, 75·8; H, 8·1; N, 4·8%), $\lambda_{max.}$ 230, 243sh, 252sh, 266sh, 274, 297sh, 350, and 448 nm (log ε 4·24, 4·21, 4·18, 4·16, 4·19, 3·89, 3·42, and 3·25), $\nu_{max.}$ 3350, 1670, and 1620 cm^{-1}, 8·55 (9H, s, NBu^t), 8·50 (9H, s, CBu^t), 4·09 (1H, s, =CH), 4·00br (1H, s, NH), and 1·8—2·9 (3H, m, ArH). These products could only be obtained in identifiable amounts when a 0·07M-solution of the nitroxide in toluene was heated under reflux for 250 h.

(iv) *6-Methoxy-2-naphthyl t-butyl nitroxide*. This gave (a) *N-t-butyl-6-methoxy-2-naphthylamine*, prisms, m.p. 82—83° (from hexane) (Found: C, 78·3; H, 8·3; N, 6·4. $C_{15}H_{19}NO$ requires C, 78·6; H, 8·3; N, 6·1%), $\nu_{max.}$ 3410 cm^{-1}, τ 8·61 (9H, s, Bu^t), 6·97 (1H, s, NH), 6·13 (1H, s, OMe), and 2·4—3·1 (6H, m, ArH); (b) *6-methoxy-2-t-butylamino-1,4-naphthoquinone*, orange cubes, m.p. 120—121° (from hexane) (Found: C, 69·3; H, 6·4; N, 5·4. $C_{15}H_{17}NO_3$ requires C, 69·5; H, 6·6; N, 5·4%), $\lambda_{max.}$ 227, 272sh, 279, 315, 347, and 457 nm (log ε 4·20, 4·00, 4·23, 3·99, 3·95, and 3·11), $\nu_{max.}$ 3330, 1680, and 1610 cm^{-1}, τ 8·58 (9H, s, Bu^t), 6·09 (3H, s, OMe), 4·11 (1H, s, =CHR), 3·93br (1H, s, NH), 7·02 (1H, q, *J* 9 and 3 Hz, -7), 7·54H (1H, d, *J* 3 Hz, H-5), and 7·94 (1H, d, *J* 9 Hz, H-8); and (c) *6-methoxy-2-t-butylamino-3-(N-t-butyl-6-methoxy-2-naphthylamino)-1,4-naphthoquinone*, brown oil (Found: C, 73·9; H, 6·9; N, 5·6%; M^+, 486·2525. $C_{30}H_{34}N_2O_4$ requires C, 74·0; H, 7·0; N, 5·8%; *M*, 486·2518), $\lambda_{max.}$ 223, 242, 280, 355, and 481 nm (log ε 4·55, 4·65, 4·27, 3·85, and 3·13), $\nu_{max.}$ 3340 and 1645 cm^{-1}, τ 8·59 (9H, s, Bu^t), 8·69 (9H, s, Bu^t), 6·14 (3H, s, OMe), 6·16 (3H, s, OMe), 5·01br (1H, s, NH), and 1·88—3·15 (9H, m, ArH).

(v) *4,5-Dimethyl-2-naphthyl t-butyl nitroxide*. This gave (a) *N-t-butyl-4,5-dimethyl-2-naphthylamine*, yellow oil, b.p. 140—143° at 0·2 mmHg (Found: C, 84·3; H, 9·6; N, 6·2. $C_{16}H_{21}N$ requires C, 84·5; H, 9·3; N, 6·2%), $\nu_{max.}$ 3400 cm^{-1}, τ 8·63 (9H, s, Bu^t), 7·22 (6H, s, 2Me), 5·70br (1H, s, NH), and 2·5—3·4 (5H, m, ArH); (b) *5-methyl-2-t-butylamino-1,4-naphthoquinone*, orange cubes, m.p. 69—70° (from petroleum) (Found: C, 74·0; H, 6·9; N, 5·7. $C_{15}H_{17}NO_2$ requires C, 74·0; H, 7·0; N, 5·8%), $\lambda_{max.}$ 231, 265sh, 272, 298sh, 354, and 456 nm (log ε 4·10, 4·07, 4·11, 3·73, 3·35, and 3·37), $\nu_{max.}$ 3330, 1670, and 1625 cm^{-1}, τ 8·56 (9H, s, Bu^t), 7·23 (3H, s, Me), 4·20br (1H, s, NH), 4·11 (1H, s, =CH), 2·5—2·8 (2H, m, ArH), 1·9—2·2 (1H, m, H-8); and (c) *N-methyl-N-t-butyl-4,5-dimethyl-2-naphthylamine* (9 mg, 4%), prisms, m.p. 44—46°, b.p. 130—135° at 0·6 mmHg, $\lambda_{max.}$ 227, 254, and 288 nm (log ε 4·62, 4·10, and 3·79), τ(CCl_4) 8·85 (9H, s, Bu^t), 7·22 (3H, s, Me), 7·16 (6H, s, 2Me), and 2·4—3·0 (5H, m, ArH). The *complex* (2 : 1) of compound (c) with naphthalene-1,5-disulphonic acid gave cubes, m.p. >300° (from ethanol) (Found: C, 68·4; H, 7·2; N, 3·5; S, 8·2. $C_{44}H_{54}N_2O_6S_2$ requires C, 68·5; H, 7·1; N, 3·6; S, 8·3). The amine (c) was identical with that obtained by heating *N*-t-butyl-4,5-dimethyl-2-naphthylamine (400 mg) and iodomethane (230

TABLE 5

N-Naphthyl-*N*-t-butylhydroxylamines

Naphthyl	Yield (%)	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
2-Naphthyl	52	150—152	78·2	8·1	6·6	$C_{14}H_{17}NO$	78·1	8·0	6·5
8-Me	37	141—142	78·6	8·4	6·1	$C_{15}H_{19}NO$	78·6	8·4	6·1
8-Bu^t	46	159—161	79·6	9·5	5·4	$C_{18}H_{25}NO$	79·6	9·5	5·4
6-MeO	35	143—145	73·3	7·6	7·9	$C_{15}H_{19}NO_2$	73·4	7·8	7·7
4,5-Me_2	76	148—150	79·0	8·7	6·0	$C_{16}H_{21}NO$	79·0	8·7	6·0
1-Naphthyl	42	75—77	78·1	8·0	6·4	$C_{14}H_{17}NO$	78·1	8·0	6·5
3,4-Me_2	56	130—132	79·0	8·5	6·0	$C_{16}H_{21}NO$	79·0	8·7	5·8
4,7-Me_2	29	102—104	79·0	8·7	5·8	$C_{16}H_{21}NO$	79·0	8·7	5·8

[21] A. Bell and M. B. Knowles, U.S.P. 2,692,287/1956 (*Chem. Abs.*, 1956, **50**, 2666).

mg) in methanol (0·5 ml) for 45 min in a sealed tube. The product (125 mg, 29%) was obtained by chromatography (t.l.c.) on silica with chloroform.

(vi) 1-*Naphthyl t-butyl nitroxide*. This gave (a) N-*t-butyl*-1-*naphthylamine*, prisms, m.p. 34—35°, b.p. 98—101° at 0·2 mmHg (Found: C, 84·5; H, 8·7; N, 7·2. $C_{14}H_{17}N$ requires C, 84·4; H, 8·6; N, 7·0%), $\nu_{max.}$ 3440 cm^{-1}, τ 8·57 (9H, s, Bu^t), 6·00br (1H, s, NH), and 2·1—3·2 (7H, m, ArH); (b) 4-*t-butylamino*-1,2-*naphthoquinone*, red needles, m.p. 225—227° (from hexane–chloroform) (Found: C, 73·7; H, 6·6; N, 6·1. $C_{14}H_{15}NO_2$ requires C, 73·3; H, 6·6; N, 6·1%), $\lambda_{max.}$ 241, 278, and 301sh nm (log ε 4·14, 4·13, and 3·92), $\nu_{max.}$ 3300, 1700, and 1620 cm^{-1}, τ 8·48 (9H, s, Bu^t), 4·2br (1H, s, NH), 3·91 (1H, s, H-3), and 1·7—2·5 (4H, m, ArH), identical with a specimen produced by shaking a solution of 4-ethoxy-1,2-naphthoquinone in ethanol with aqueous t-butylamine; and (c) 1,4-*naphthoquinone* 4-*t-butylimine* N-*oxide*, yellow prisms, m.p. 193—195° (from hexane–carbon tetrachloride) (Found: C, 73·6; H, 6·6; N, 6·1. $C_{14}H_{15}NO_2$ requires C, 73·3; H, 6·6; N, 6·1%), $\lambda_{max.}$ 238, 265sh, 276sh, and 388 nm (log ε 3·86, 3·53, 3·57, and 4·27), $\nu_{max.}$ 1645 cm^{-1}, τ (CCl_4) 8·21 (9H, s, Bu^t), 3·71 (1H, d, $J_{2,3}$ 10 Hz, H-3), 2·3—2·6 (2H, m, H-6 and -7), 1·95 (1H, d, $J_{2,3}$ 10 Hz, H-2), and 0·61 (1H, q, J 7 and 2 Hz, H-8). The t-butyl-1- and 2-naphthylamines listed in this section were also conveniently obtained by hydrogenating the parent hydroxylamines in ethanol over Raney nickel.

Decomposition of Naphthyl t-Butyl Nitroxides in Aniline.—General procedure. Solutions (0·5M) of the nitroxides in freshly distilled aniline were left for 4 days at 30° in the dark, after which the aniline was removed by distillation at *ca.* 43° and 0·2 mmHg. The residue was separated by chromatography on silica gel with chloroform or hexane–ether (9 : 1) as eluant.

(i) 2-*Naphthyl t-butyl nitroxide*. This (760 mg) gave (a) 2-t-butylamino-1,4-naphthoquinone (183 mg, 39%); (b) *N*-t-butyl-2-naphthylamine (248 mg, 61%); and (c) a red fraction, further chromatographic separation of which gave 2-*t-butylamino*-1,4-*naphthoquinone* 4-*phenylimine* (125 mg, 10%) as orange prisms, m.p. 101—103° (from ether) (Found: C, 78·6; H, 6·9; N, 8·9. $C_{20}H_{20}N_2O$ requires C, 78·9; H, 6·6; N, 9·2%), $\lambda_{max.}$ 242, 271, 337, and 452 nm (log ε 4·48, 4·13, 3·74, and 3·82), $\nu_{max.}$ 3370, 1660, and 1620, τ(CCl_4) 8·76 (9H, s, Bu^t), 4·53br (1H, s, NH), 4·11 (1H, s, =CH), 2·2—3·3 (2H, m, ArH), 1·94 (1H, q, J 7 and 2 H, H-8), and 1·52 (1H, q, J 7 and 2 Hz, H-5), and 2-*t-butylamino*-1,4-*naphthoquinone* 1,4-*bisphenylimine* (17 mg, 1%), as a red oil (Found: M^+, 381·2200. $C_{26}H_{27}N_3$ requires M, 381·2205), $\lambda_{max.}$ 231, 291, and 444 mm (log ε 4·13, 3·88, and 3·51), $\nu_{max.}$ 3340 cm^{-1}, τ 8·76 (9H, s, Bu^t), 4·18 (1H, s, =CH), 3·83br (1H, s, NH), 2·5—3·3 (13H, m, ArH), 1·46 (1H, q, J 8 and 1·5 Hz, H-5).

(ii) 4,5-*Dimethyl*-2-*naphthyl t-butyl nitroxide*. This (498 mg) gave (a) 5-methyl- 2-t-butylamino-1,4-naphthoquinone (120 mg, 4%); (b) *N*-t-butyl-4,5-dimethyl-2-naphthylamine (135 mg, 58%); and (c) a red fraction, further chromatographic separation of which with hexane–ether (9 : 1) as eluant yielded 5-*methyl*-2-*t-butylamino*-1,4-*naphthoquinone* 4-*phenylimine* (34 mg, 4%), as orange prisms, m.p. 124—125° (from carbon tetrachloride) (Found: C, 79·5; H, 6·7; N, 8·7. $C_{21}H_{22}N_2O$ requires C, 79·2; H, 7·0; N, 8·8%), $\lambda_{max.}$ 242, 271, 345, and 446 nm (log ε 4·45, 4·07, 3·72, and 3·72), $\nu_{max.}$ 3390, 1650, and 1630 cm^{-1}, τ(CCl_4) 8·79 (9H, s, Bu^t), 7·15 (3H, s, Me), 4·71br (1H, s, NH), 4·15 (1H, s, =CH), 2·5—3·3 (7H, m, ArH), 1·96 (1H, q, J 7 and 2 Hz, H-8).

(iii) 6-*Methoxy*-2-*naphthyl t-butyl nitroxide*. This (498 mg) gave (a) *N*-t-butyl-6-methoxy-2-naphthylamine (10 mg, 4%); (b) 6-*methoxy*-2-*t-butylamino*-1,4-*naphthoquinone* 4-*phenylimine* (22 mg, 6%), as orange prisms, m.p. 139—140° (from dichloromethane–cyclohexane) (Found: M^+, 334·1680. $C_{21}H_{22}N_2O_2$ requires M, 334·1681), $\lambda_{max.}$ 250, 262sh, 332, and 462 nm (log ε 4·51, 4·49, 4·36, and 3·90), $\nu_{max.}$ 3355, 1655, and 1615 cm^{-1}, τ(CCl_4) 8·77 (9H, s, Bu^t), 6·04 (3H, s, OMe), 4·48br (1H, s, NH), 4·23 (1H, s, =CH), 2·6—3·26 (5H, m, ArH), 3·01 (1H, q, J 8 and 2·5 Hz, H-7), 2·11 (1H, d, J 2·5 Hz, H-5), and 2·02 (1H, d, J 8 Hz, H-8); and (c) an orange fraction, further chromatographic separation of which with hexane–ether (95 : 5) as eluant gave 6-*methoxy*-2-*t-butylamino*-1,4-*naphthoquinone* 1,4-*bisphenylimine* (160 mg, 38%), as orange prisms, m.p. 168—170° (from carbon tetrachloride) (Found: C, 79·2; H, 6·8; N, 9·9. $C_{27}H_{27}N_3O$ requires C, 79·2; H, 6·7; N, 10·2%), $\lambda_{max.}$ 235, 327, and 430 nm (log ε 4·51, 4·24, and 3·85), $\nu_{max.}$ 3330 and 1618 cm^{-1}, τ(CCl_4) 8·75 (9H, s, Bu^t), 6·12 (3H, s, OMe), 4·32 (1H, s, =CH), 3·88br (1H, s, NH), 2·5—3·6 (12H, m, ArH), and 2·02 (1H, q, J 3 Hz, H-5), and 6-*methoxy*-2-*t-butylamino*-8-(N-*t-butyl*-6-*methoxy*-2-*naphthylamino*)-1,4-*naphthoquinone* 1,4-*bisphenylimine* (11) (180 mg, 28%), as red prisms, m.p. 176—177° (from dichloromethane–hexane) (Found: C, 78·9; H, 7·0; N, 8·7%; M — 227, 409·2139. $C_{42}H_{44}N_4O_2$ requires C, 79·2; H, 7·0; N, 8·8%; M — 227, 409·2154), $\lambda_{max.}$ 237, 263sh, 275, 285sh, 337, and 430 nm (log ε 4·96, 4·46, 4·39, 4·31, 4·11, and 3·64), $\nu_{max.}$ 3345 and 1628 cm^{-1}, τ(CCl_4) 8·91 (9H, s, Bu^t), 8·77 (9H, s, Bu^t), 6·18 (3H, s, OMe), 6·15 (3H, s, OMe), 4·33 (1H, s, =CH), 3·90br (1H, s, NH), 2·5—3·6 (17H, m, ArH), and 2·04 (1H, d, J 3 Hz, H-5). This last product was identical with that obtained in 56% yield by leaving a solution of 6-methoxy-2-t-butylamino-1,4-naphthoquinone 1,4-biphenylimine (10 mg, 0·024 mmol) and *N*-t-butyl-6-methoxy-2-naphthylamine (6 mg, 0·024 mmol) in aniline (1 ml) for 4 days at 30° in the dark.

Preparation of Naphthoquinone Imine N-*Oxides*. (i) *N*-2-Naphthyl-*N*-t-butylhydroxylamine (2·4 g, 11 mmol) in methanol (70 ml) was treated with a solution of Fremy's salt (17 g, 63 mmol) in water (350 ml) and 0·25M-potassium dihydrogen phosphate (150 ml) and the mixture was shaken for 1 h. The resulting precipitate and solution were extracted with dichloromethane and the organic layer was washed with water, dried ($MgSO_4$), and evaporated to dryness below 20°. Chromatographic separation (t.l.c.) of the residue on silica (chloroform as eluant) gave (a) 2-t-butylamino-1,4-naphthoquinone (230 mg, 9%) and (b) a purple oil which after further chromatography on silica with benzene–hexane (4 : 1) gave 1,2-*naphthoquinone* 2-*t-butylimine* N-*oxide* (550 mg, 22%) as orange needles, m.p. 44—45° (from petroleum) (Found: M^+, 229·1108. $C_{14}H_{15}NO_2$ requires M, 229·1102), $\lambda_{max.}$ 291, 351, and 450 nm (log ε 4·04, 3·77, and 3·68), $\nu_{max.}$ 1638 cm^{-1}, τ 8·3 (9H, s, Bu^t), 3·24 (1H, d, J 10 Hz, H-4), 2·4—2·8 (4H, m, ArH), and 1·81 (1H, q, J 7 and 2 Hz, H-8).

(ii) Similar treatment of *N*-6-methoxy-2-naphthyl-*N*-t-butylhydroxylamine (0·5 g) gave (a) 6-methoxy-2-naphthyl t-butyl nitroxide (65 mg, 13%); (b) 6-methoxy-2-t-butylamino-1,4-naphthoquinone (15 mg, 3%), and (c) 6-*methoxy*-1,2-*naphthoquinone* 2-*t-butylimine* N-*oxide* (158 mg, 30%) as brown prisms, m.p. 98—99° (from hexane) (Found: C, 69·2; H, 6·5; N, 5·6%; M^+, 259·1209. $C_{15}H_{17}NO_3$

requires C, 69·5; H, 6·5; N, 5·4%; *M*, 259·1208), $\lambda_{max.}$ 292, 350, and 396 nm (log ε 4·14, 3·89, and 4·09), $\nu_{max.}$ 1633 cm^{-1}, τ(CCl_4) 8·31 (9H, s, Bu^t), 6·15 (3H, s, OMe), 3·36 (1H, d, *J* 2 Hz, H-5), 3·34 (1H, d, *J* 10 Hz, H-4), 3·19 (1H, q, *J* 8 and 2 Hz, H-7), 2·66 (1H, d, *J* 10 Hz, H-3), and 1·90 (1H, d, *J* 8 Hz, H-8).

(iii) Similar treatment of *N*-8-methyl-2-naphthyl-*N*-t-butylhydroxylamine (0·8 g) gave (a) 8-methyl-2-naphthyl t-butyl nitroxide (222 mg, 28%); (b) 8-methyl-2-t-butylamino-1,4-naphthoquinone (113 mg, 14%); and (c) 8-methyl-1,2-naphthoquinone 2-t-butylimine *N*-oxide (30 mg, 7%) as an orange oil, $\lambda_{max.}$ 252, 292, 357, and 438 nm, $\nu_{max.}$ 1638 cm^{-1}, τ(CCl_4) 8·30 (9H, s, Bu^t), 7·27 (3H, s, Me), 3·27 (1H, d, *J* 10 Hz, H-4), and 2·5—3·1 (4H, m, ArH).

(iv) Similar treatment of *N*-4,5-dimethyl-2-naphthyl-*N*-t-butylhydroxylamine (0·5 g) gave (a) 5-methyl-2-t-butylamino-1,4-naphthoquinone (90 mg, 18%) and (b) 1,2-*bis*-(1,4-*dihydro*-8-*methyl*-4-*oxo*-3-*t-butylamino*-1-*naphthylidene*)*ethane* (27) (4 mg, 1%) as a blue oil (Found: M^+, 480·2776. $C_{32}H_{36}N_2O_2$ requires *M*, 480·2777), $\lambda_{max.}$ 224, 253, 340sh, 425, and 622 nm, $\nu_{max.}$ 1615 and 1610 cm^{-1}, τ 8·51 (s, Bu^t), 7·09 (s, Me), and 2·0—3·1 (m, ArH).

(v) Similar treatment of *N*-1-naphthyl-*N*-t-butylhydroxylamine (1·8 g) with Fremy's salt (22·0 g) gave 1,4-naphthoquinone 4-t-butylimine *N*-oxide (1·6 g, 83%). Smaller quantities of Fremy's salt (5·5 and 8·5 g) gave 210 mg (10%) and 410 mg (21%) of this product, respectively.

Reactions of Quinone Imine N-*Oxides*.—(i) *With aniline*. (a) 1,2-Naphthoquinone 2-t-butylimine *N*-oxide (150 mg) in aniline (1·3 ml) was left for 4 days at 30° in the dark. The aniline was then removed at 43° and the residue was chromatographed on silica with hexane–diethyl ether (9 : 1) to give 2-t-butylamino-1,4-naphthoquinone 4-phenylimine (60 mg, 30%) and small quantities of 2-t-butylamino-1,4-naphthoquinone 1,4-bisphenylimine and 2-t-butylamino-1,4-naphthoquinone.

(b) 6-Methoxy-1,2-naphthoquinone 2-t-butylimine *N*-oxide in redistilled aniline (0·1 ml) was left at 30° for 4 days. Work-up as above gave 6-methoxy-2-t-butylamino-1,4-naphthoquinone 1,4-bisphenylimine (9 mg) and traces (t.l.c.) of 6-methoxy-2-t-butylaminonaphthoquinone and 6-methoxy-2-t-butylamino-1,4-naphthoquinone 4-phenylimine.

(ii) *With nitroxide*. (a) 6-Methoxy-1,2-naphthoquinone 2-t-butylimine *N*-oxide (50 mg) and 6-methoxy-2-naphthyl-t-butyl nitroxide (43 mg) in benzene (0·4 ml) were left for 14 days at 30° in the dark. Chromatographic separation gave *N*-t-butyl-6-methoxy-2-naphthylamine (9 mg), 6-methoxy-2-t-butylamino-1,4-naphthoquinone (24 mg), and unchanged *N*-oxide (6 mg). In the absence of *N*-oxide, 6-methoxy-2-naphthyl t-butyl nitroxide (43 mg) in benzene (0·4 ml) gave the corresponding amine (10 mg) and aminoquinone (13 mg), and 6-methoxy-1,2-naphthoquinone 2-t-butylimine *N*-oxide (45 mg) in benzene (0·5 ml) underwent little change during 14 days at 30°, giving only amino-quinone (2 mg) and small amounts of other coloured products. The *N*-oxide (40 mg) in benzene (3 ml) on heating under reflux for 1·5 h gave the amino-quinone (15 mg, 38%).

(b) 1,4-Naphthoquinone 4-t-butylimine *N*-oxide (30 mg) and 1-naphthyl t-butyl nitroxide (2 mg) in benzene (2 ml) were heated under reflux for 20 min. Chromatographic separation of the products gave 4-t-butylamino-1,2-naphthoquinone (10 mg) (spectrophotometry). Similar treatment of the imine *N*-oxide (30 mg) in benzene (2 ml) gave no aminoquinone after 20 min and only 1 mg of aminoquinone after 20 h.

(c) 1,2-Naphthoquinone 2-t-butylimine *N*-oxide (40 mg) and 2-naphthyl t-butyl nitroxide (42 mg) in benzene (0·5 ml) were left for 14 days at 30°. Chromatographic separation gave 2-t-butylaminonaphthoquinone (21 mg) and unchanged *N*-oxide (6 mg). Under identical conditions the imine *N*-oxide (40 mg) in benzene (0·5 ml) gave 2-t-butylaminonaphthoquinone (5 mg) and unchanged imine *N*-oxide.

(iii) *With* $H_2{}^{18}O$. 1,4-Naphthoquinone 4-t-butylimine *N*-oxide (30 mg), AnalaR acetone (0·5 ml), and $H_2{}^{18}O$ (0·5 ml; 17% enrichment) was left for 8 weeks at 30°. Mass spectroscopic measurements on the resulting 4-t-butylamino-1,2-naphthoquinone (8 mg, 27%) gave $M/(M + 2) = 4·50$, compared with 4·55 for a sample similarily produced in aqueous (non-enriched) acetone.

N-*Methoxy*-N-*t-butyl*-4,5-*dimethyl*-2-*naphthylamine*.— 4,5-Dimethyl-2-naphthyl t-butyl nitroxide (100 mg) in carbon tetrachloride (3 ml) at −5° was treated with acetyl peroxide (17 mg) in iso-octane (34 ml) also at −5°. The mixture was allowed to warm and left for 24 h before the solvent was removed. Chromatography of the residue on silica with hexane–ether (90 : 10) gave (a) unchanged nitroxide; (b) 2-t-butylamino-1,4-naphthoquinone (15 mg); and (c) an oil, further chromatography of which on silica with benzene gave N-*methoxy*-N-*t-butyl*-4,5-*dimethyl*-2-*naphthylamine* (8 mg) as an oil (Found: M^+, 257·1787. $C_{17}H_{23}NO$ requires *M*, 257·1780), $\lambda_{max.}$ 252, 290, and 300 sh (log ε 4·35, 4·30, and 3·71), τ 8·83 (9H, s, Bu^t), 7·09 (6H, s, Me), 6·52 (3H, s, OMe), and 2·3—2·9 (5H, m, ArH).

Kinetic Measurements.—The nitroxides were prepared from known weights of the corresponding hydroxylamines, dissolved in freshly distilled carbon tetrachloride solution by shaking with silver oxide. Solutions of the nitroxides, after removal of the silver residues, were degassed for 15 min with a stream of nitrogen, diluted to known volumes, and sealed into e.s.r. tubes. Spectra were recorded at regular intervals, the samples being removed from the thermostatted water-bath for about 5 min on each occasion. Nitroxide concentrations were obtained by doubly integrating the first derivative e.s.r. trace. All e.s.r. tubes were precalibrated using a solution of known concentration of the very stable t-butyl 8-t-butylnaphthyl nitroxide. All kinetic runs were performed in duplicate.

We thank the S.R.C. and the Carnegie Trust for studentships (to A. C. and G. McC., respectively).

[4/733 *Received*, 10*th April*, 1974]