Nitroxide Radicals. Part XV.[1] *p*-Methoxy- and *p*-Phenoxy-phenyl t-Butyl Nitroxides

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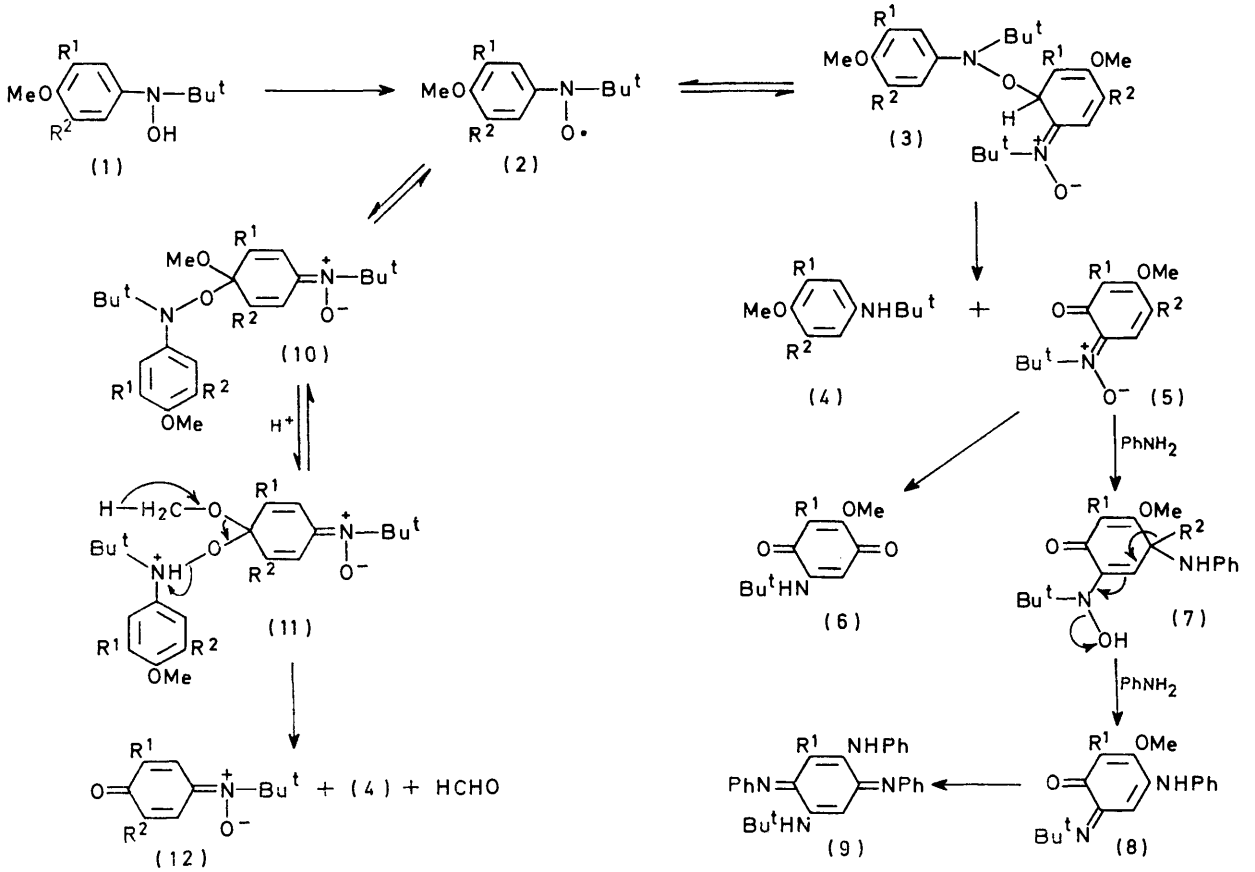
p-Methoxyphenyl t-butyl nitroxides decompose slowly to give 2-methoxy-5-t-butylaminobenzoquinones and *N*-t-butylanisidines by a route involving O-to-*ortho*-C coupling. *p*-Phenoxyphenyl t-butyl nitroxides are much less stable, readily coupling O to *para*-C to give, after displacement of a phenoxyl radical, *p*-benzoquinone t-butylimine *N*-oxide and *p*-phenoxy-*N*-t-butylanilines.

WE have shown previously that aryl t-butyl nitroxides couple O to *para*-C to give, after fragmentation of the initial dimer, *p*-benzoquinone t-butylimine *N*-oxides and t-butylanilines. Such coupling can be inhibited either by introducing an *ortho*-substituent which causes the aryl ring to be twisted out of conjugation with the nitroxide group to a considerable extent,[2] or a t-alkyl or an aryl group which hinders reaction at the *para*-position.[3] We now describe how *p*-methoxy- (but not *p*-phenoxy-) substituents also prevent coupling at the *para*-position and by so doing allow a slower O-to-*ortho*-C coupling to occur, leading eventually to 2-methoxy-5-t-butylaminobenzoquinones by 'rearrangement' of an intermediate *o*-benzoquinone t-butylimine *N*-oxide.

Results.—Unlike other aryl-t-butylhydroxylamines which we have examined, the *N*-*p*-methoxy- and *p*-phenoxy-phenyl-*N*-t-butylhydroxylamines listed in Table 2 gave mixtures of the corresponding nitroxides (2) and *p*-benzoquinone imine *N*-oxides (12) (formaldehyde was also detected with the methoxyphenylhydroxylamines) on oxidation with silver oxide. Analogous oxidative demethylations of anisidines and *p*-methoxyphenols to benzoquinones are well known.[4] Quantitative conversion of the hydroxylamines into the nitroxides was best achieved using alkaline ferricyanide with exclusion of air.



[1] Part XIV, A. Calder, A. R. Forrester, and G. McConnachie, preceding paper.

[2] A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.*, (*C*) 1970, 1277.

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

[4] R. H. Thomson in 'Chemistry of Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1973, ch. 3; M. L. Mihailovic and Z. Cekovic in 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Wiley, New York, 1970, pt. 1, ch. 10.

The *p*-methoxyphenyl nitroxides (2; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Bu^t$; and $R^1 = R^2 = Me$) were much more stable than the parent phenyl t-butyl nitroxide and two of these were sufficiently stable to be crystallised and analysed. Their decomposition in concentrated solution in benzene was slow and required several months for completion, and because of this we did not undertake kinetic analysis of these decompositions. The principal products from the *p*-methoxyphenyl nitroxide (2; $R^1 = R^2 = H$) were the corresponding amine (4; $R^1 = R^2 = H$) and the purple amino-quinone (6; $R^1 = H$) (Table 1), the latter being identified from its i.r. (ν_{CO} 3340 and 1655 cm^{-1}), u.v. ($\lambda_{max.}$ 477 nm), and n.m.r. [τ 8·6 (Bu^t)] spectra. The same t-butylamino-quinone was also obtained (but in much lower yield), together with the corresponding amines (4; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Bu^t$), from the homologous nitroxides (2; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Bu^t$). In contrast, the 4-methoxy-3,5-dimethylphenyl radical (2; $R^1 = R^2 = Me$) in benzene deteriorated little during 5 months and the amine (4; $R^1 = R^2 = Me$), the quinone imine *N*-oxide (12; $R^1 = R^2 = Me$), and the amino-quinone (6; $R^2 = Me$) were not present in the minor decomposition products formed. Authentic specimens of the two first-mentioned compounds were prepared from the nitroxide (2; $R^1 = R^2 = Me$) by hydrogenation (over Raney nickel) and oxidation (with silver oxide), respectively. We have also observed that the previously reported [3] t-butyl *p*-t-butylphenyl nitroxide also gives spontaneously the corresponding t-butylamino-quinone and amine; this result is included in Table 1.

Both *p*-phenoxyphenyl t-butyl nitroxides (15; R = H or Br) decomposed relatively rapidly in benzene solution (0·2M) to give, after 2 days, mainly the amines (17; R = H and Br) and the quinone imine *N*-oxide (18). A small quantity of the amino-quinone (21; R = Br) was also isolated from the 4-(*p*-bromophenoxy)phenyl nitroxide. Surprisingly, under similar conditions, the long-known bis-*p*-methoxyphenyl nitroxide [5] gave bis-*p*-methoxy-phenylamine (24; R = OMe) and the quinone imine *N*-oxide (23; R = OMe) rather than the amino-quinone thus behaving more like the foregoing 4-(*p*-phenoxy)-phenyl nitroxides than the t-butyl methoxyphenyl nitroxides.

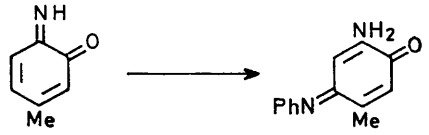
Discussion.—Introduction of a *p*-methoxy (or *p*-t-alkyl) substituent into phenyl t-butyl nitroxide effectively blocks the O-to-*para*-C coupling reaction leading to *p*-benzoquinone imine *N*-oxide, the reaction much favoured by this class of radical.[3] The slower, more hindered O-to-*ortho*-C coupling which gives an *o*-quinone imine *N*-oxide (5) [*via* (3)] then becomes the dominant decomposition route. By analogy with the decomposition of the 2-naphthyl nitroxides already described [1] we consider that 'rearrangement' of the *o*-quinone imine *N*-oxide (5) to the amino-quinone (6) is catalysed by the nitroxide. Although the *o*-quinonoid intermediate (5) could not be detected in the decomposition mixture, nor could it be trapped by complexation with metal salts such as copper(II) acetate, indirect evidence supporting its mediation was gained by allowing the nitroxide (2; $R^1 = R^2 = H$) to decompose in solution in aniline. The resulting diamino-diquinone di-imine (9; $R^1 = H$) we envisage as arising by nucleophilic addition of aniline to the *o*-quinone imine *N*-oxide at C(5) followed by loss of water [(5) ⟶ (7)] in much the same way as *p*-toluidine [6] adds to the *o*-quinone imine (13) to give the substituted quinone imine (14). Nucleophilic substitution of phenyl-amino for methoxy and conversion of the carbonyl into an imino-group [(8) ⟶ (9)] are both known [7] reactions of quinonoid compounds. Significantly, the amino-quinone (6; $R^1 = H$) under comparable conditions in aniline did not yield this product. The *ortho*-coupling mechanism described above finds analogy both in the production of *o*-quinones by oxidation of *p*-methoxy-phenols [8] with Fremy's salt and in the coupling, *N*-to-*ortho*-C, of bis-*p*-methoxyphenylaminyl leading to a di-hydrophenazine derivative.[9] Both O-to-*ortho*-C and O-to-*para*-C (as well as C–C) coupled structures have been

TABLE 1

Yields * (%) of decomposition products from alkyl aryl and diaryl nitroxides [ArN(Ȯ)R]

		Products		
Ar	R	Amine	Amino-quinone	*p*-Benzoquinone imine *N*-oxide
p-MeO·C_6H_4	Bu^t	70	83	
3-Me-4-MeO·C_6H_3	Bu^t	69	19	
3-Bu^t-4-MeO·C_6H_3	Bu^t	51	12	
p-$Bu^tC_6H_4$	Bu^t	58	96	
p-PhO·C_6H_4	Bu^t	78		81
4-(4-BrC_6H_4·O)C_6H_4	Bu^t	64	3	44
p-MeO·C_6H_4	*p*-MeO·C_6H_4	72		58
p-NO_2·C_6H_4	*p*-NO_2·C_6H_4	85		

* Yields based on 2 mol of nitroxide giving 1 mol of amine and 1 mol of amino-quinone and/or quinone imine *N*-oxide.



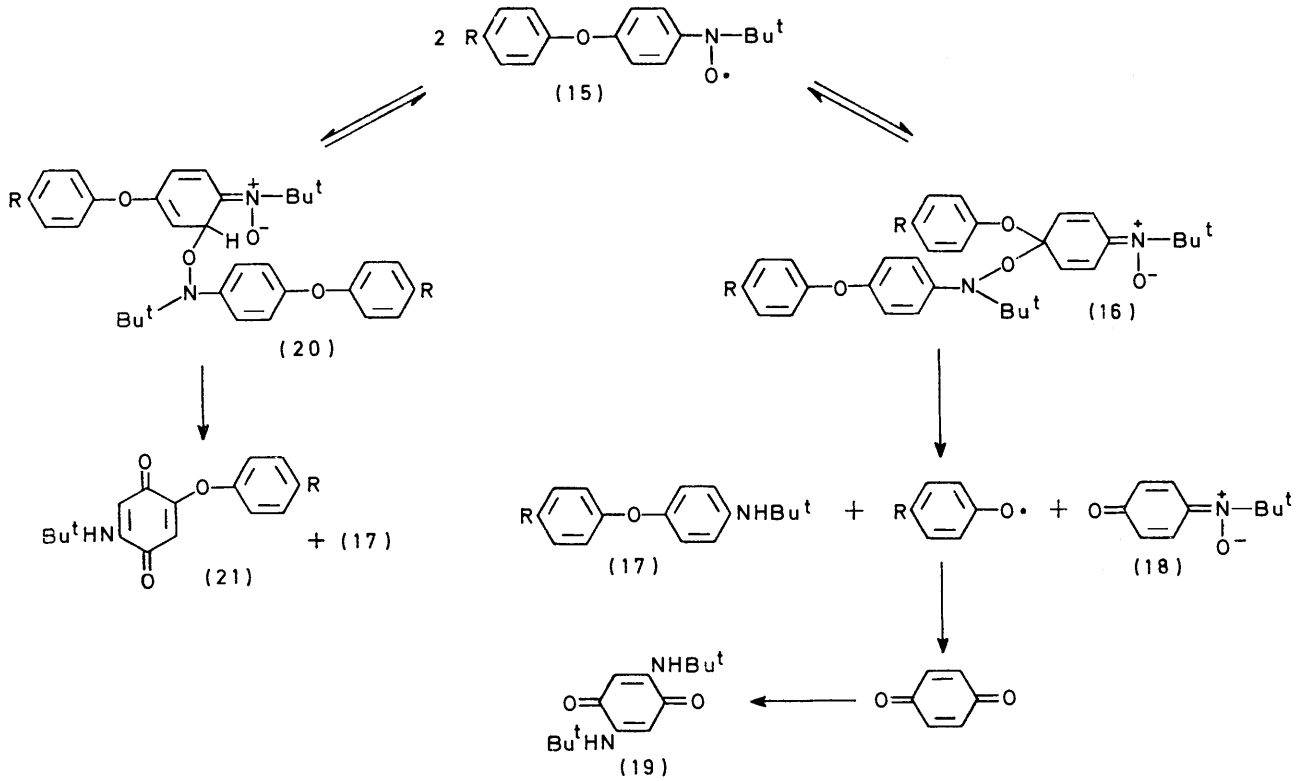
(13) (14)

[5] K. H. Meyer and W. Reppe, *Ber.*, 1921, **54**, 327.
[6] L. Horner and K. Sturm, *Chem. Ber.*, 1955, **88**, 329.
[7] K. T. Finley in 'Chemistry of Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1973, ch. 17.
[8] H. J. Teuber and G. Staiger, *Chem. Ber.*, 1955, **88**, 802.
[9] F. A. Neugebauer and H. A. Fischer, *Chem. Ber.*, 1971, **104**, 886.

proposed [10] for the dimers formed by coupling of *p*-methoxyphenoxyls.

Since no 3-alkyl-5-t-butylaminoquinones (6; R^1 = Me and Bu^t) were present in the decomposition mixtures obtained from the nitroxides (2; R^1 = H, R^2 = Me; R^1 = H, R^2 = Bu^t) and the 3,5-dimethylphenyl nitroxide (2; $R^1 = R^2$ = Me) was exceptionally stable it appears that the presence of a 3-alkyl substituent prevents O-to-C coupling at the adjacent *ortho*-position. Hence, decomposition must proceed by O-to-C coupling at the 6-position giving an *o*-quinone imine *N*-oxide (5; R^1 = H, R^2 = Me; R^1 = H, R^2 = Bu^t) which can only yield the observed quinone product (6; R^1 = H) by an oxidative dealkylation process similar to that already outlined [1] for 4,5-dimethyl-1,2-naphthoquinone t-butylimine *N*-oxide. We have no additional evidence in these cases to suggest the exact way in which the methyl and t-butyl groups are displaced but our failure to detect any major products containing these groups strongly suggests that the groups give either highly volatile products or are transferred to a number of the sundry products present in these relatively complex decomposition mixtures. Oxidative displacement of t-butyl and methyl groups by the inorganic nitroxide Fremy's salt has been encountered previously during oxidations of substituted phenols and anilines [11,12] to quinones.

Both the rate and the course of decomposition of *p*-methoxyphenyl t-butyl nitroxide (2; $R^1 = R^2$ = H) were substantially altered when the radical was dissolved in weakly acidic media. In ethanol containing either hydrochloric or acetic acid the radical decomposed completely during 2 days to give the amine (4; $R^1 = R^2$ = H), the quinone imine *N*-oxide (12; $R^1 = R^2$ = H), and formaldehyde; only traces of t-butylamino-quinone (6; R^1 = H) were detected. We have observed [13] previously that acid accelerates the decomposition of aromatic nitroxides and have attributed this to an increase in the rate at which the reversibly formed cyclohexadiene dimer fragments to products on protonation of the tervalent nitrogen atom. To account for the change in reaction products in this case we surmise that the nitroxide (2; $R^1 = R^2$ = H) is in equilibrium with both O-to-*ortho*-C and O-to-*para*-C coupled dimers (3; $R^1 = R^2$ = H) and (10; $R^1 = R^2$ = H), respectively, and that normally the relatively rapid fragmentation of the '*ortho*-dimer' (3) controls the decomposition route. However, in the presence of acid, fragmentation of the '*para*-dimer' (10) is accelerated to a much greater extent than that of the *ortho*-isomer, and the quinone imine *N*-oxide (12; $R^1 = R^2$ = H) and the amine (4; $R^1 = R^2$ = H) result.



Comparison of the stabilities of *p*-t-butylphenyl and biphenyl-4-yl t-butyl nitroxides showed that both *para*-substituents effectively arrest O-to-*para*-C coupling. However, whereas the *para*-phenyl group also prevents O-to-*ortho*-C coupling, and the biphenyl-4-yl t-butyl nitroxide is stable indefinitely, the t-butyl *p*-t-butyl-

[10] J. Petranek and J. Pilar, *Coll. Czech. Chem. Comm.*, 1970, **35**, 830; E. Müller, H. Kaufmann, and A. Rieker, *Annalen*, 1964, **671**, 61; F. R. Hewgill and B. G. Kennedy, *J. Chem. Soc.*, 1965, 2921.

[11] H. J. Teuber and M. Hasselbach, *Chem. Ber.*, 1959, **92**, 674.

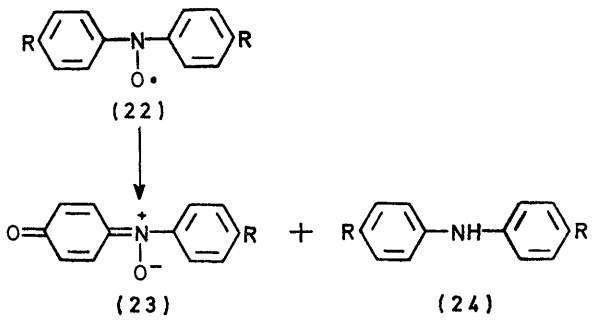
[12] R. Magnusson, *Acta Chem. Scand.*, 1960, **14**, 1643.

[13] A. Calder, A. R. Forrester, and S. P. Hepburn, *J.C.S. Perkin I*, 1973, 456.

phenyl nitroxide, like t-butyl *p*-methoxyphenyl nitroxide decomposed slowly to t-butylamino-quinone and amine. Since there is little difference in the free spin distribution in these radicals (e.s.r.) the difference in their stabilities must be due simply to the steric resistance which their *para*-substituents offer to O-to-*ortho*-C coupling. It is significant that for the unsubstituted radical phenyl t-butyl nitroxide,[3] O-to-*para*-C coupling is so much more rapid than O-to-*ortho*-C coupling that no t-butylamino-quinone can be detected among its decomposition products.[3]

Rapid formation of mainly quinone imine *N*-oxide (18) from the *p*-phenoxyphenyl t-butyl nitroxides (15; R = H or Br) strongly suggests that the O-to-*para*-C coupled dimers (16; R = H or Br) are much less stable than their counterparts (10) in the *p*-methoxyphenyl t-butyl nitroxide series. Loss of a phenoxy-group (probably as phenoxyl) from (16; R = H or Br) would be much easier than loss of methoxyl from (10), and this would account for the difference. Since it is known that phenols are oxidised to quinones by nitroxides [14] we considered that the displaced phenoxyl (or phenoxide) should be oxidised, at least to some extent, to *p*-benzoquinone during the decomposition. Although *p*-benzoquinone was indeed present (smell) in the decomposition mixture, only traces could be isolated. The fate of the phenoxyl was more satisfactorily established when the nitroxide (15; R = H) was allowed to decompose in t-butylamine. Under these circumstances the *p*-benzoquinone was trapped as the diamino-quinone (19), isolation of which was much simpler than that of the parent quinone. In a separate experiment it was shown that this diamino-quinone was not formed by the reaction of t-butylamine with the quinone imine *N*-oxide (18). The formation of a small quantity of the t-butylamino-quinone (21; R = Br) from the nitroxide (15; R = Br) indicates that O-to-*ortho*-C coupling to give (20) also occurs with the phenoxyphenyl nitroxides (15; R = H or Br) but that it is a much less favoured process than in the *p*-methoxyphenyl t-butyl nitroxide series.

In view of the apparent stability of the O-to-*para*-C coupled dimer (10) the rapid decomposition of bis-*p*-methoxyphenyl nitroxide (22; R = OMe) to the *p*-quinone imine *N*-oxide (23; R = OMe) and bis-*p*-methoxyphenylamine (24; R = OMe) (and formaldehyde) was unexpected. Particular care was taken to ensure that the mode and rate of decomposition were not being determined simply by traces of acid carried over from the preparation of the nitroxide (from anisole and sulphuric–nitric acid [5]). Although the reasons for this anomalous result are not obvious, since the rate of fragmentation of the O-to-*para*-C dimer should be no greater in this case than for (10), it is worth noting that an analogy does exist. Whereas oxidation of *p*-methoxyanilines [11] with Fremy's salt generally gives *p*-benzoquinones, *p*-methoxyphenols [8] give *o*-benzoquinones. Nevertheless, previous statements [5,15] referring to the high stability of the radical (22; R = OMe) apply only to crystalline samples in which the reactive sites >N–O· and *para*-C are held rigidly apart. A similar misconception concerning bis-*p*-nitrophenyl nitroxide [15] (22; R = NO_2) has also been perpetuated. Although in the solid state this radical is indeed stable for years it is much less so in solution. For example, a 0·25M-solution in chloroform decomposed mainly to bis-*p*-nitrophenylamine during 24 h at room temperature. Neither nitrite nor nitrogen dioxide was detected in the decomposition mixture.



EXPERIMENTAL

T.l.c. refers to separations on silica gel plates. 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°.

TABLE 2

N-Aryl-*N*-t-butylhydroxylamines

Ar	Yield (%)	M.p. (°C)	Found (%) C	H	N	Br	Formula	Required (%) C	H	N	Br
p-MeO·C_6H_4	45	91—90	67·8	9·1	7·3		$C_{11}H_{17}NO_2$	67·7	8·8	7·2	
3-Me-4-MeO·C_6H_3	58	98—99	68·7	8·9	6·7		$C_{12}H_{19}NO_2$	68·9	9·15	6·7	
3,5-Me_2-4-MeO·C_6H_2	51	57—58	69·9	9·5	6·3		$C_{13}H_{21}NO_2$	69·9	9·5	6·3	
3-Bu^t-4-MeO·C_6H_3	64	108—109	72·0	10·1	5·5		$C_{15}H_{25}NO_2$	71·7	10·0	5·6	
4-PhO·C_6H_4	65	110—111	75·0	7·6	5·3		$C_{16}H_{19}NO_2$	74·7	7·4	5·4	
4-(4-BrC_6H_4·O)C_6H_4	65	131—132	57·3	5·3	4·2	23·5	$C_{16}H_{18}BrNO_2$	57·2	5·4	4·2	28·8

N-Aryl-N-t-butylhydroxylamines.—The hydroxylamines in Table 2 were prepared by treatment of the corresponding Grignard reagents with 2-methyl-2-nitrosopropane [16] as

[14] A. R. Forrester and R. H. Thomson, *J. Chem. Soc.* (*C*), 1966, 1844.

[15] H. Wieland and K. Roth, *Ber.*, 1920, **53**, 210.

[16] A. Calder, A. R. Forrester, and S. P. Hepburn, *Org. Synth.*, 1972, **52**, 77.

described previously for *N*-alkylaryl-*N*-t-butylhydroxylamines.[2,3] They were crystallised from hexane and characterised by their i.r. (ν_{OH} 3300—3100 cm^{-1}) and n.m.r. spectra [τ *ca.* 8·9 (Bu^t)] and by their colour reaction with 2,3,5-triphenyltetrazolium chloride.

Aryl t-Butyl Nitroxides.—The hydroxylamine (1 g) in benzene (60 ml) was shaken with potassium ferricyanide (1·5 mol) in 2M-sodium hydroxide (60 ml) for 30 min under nitrogen. The organic layer was then washed with water and dried. Evaporation of the solvent at room temperature gave the corresponding nitroxide [$\lambda_{max.}$ *ca.* 305 and 500 nm (log ε *ca.* 4·0 and 2·9)].

Product Analysis of Decomposition Mixtures from Aryl t-Butyl Nitroxides.—The nitroxide (500 mg), either as the neat oil or moistened with benzene, was allowed to decompose at room temperature in the dark during 5 months (unless stated otherwise). The mixture of products was then separated by t.l.c. on silica gel [chloroform–ether (99 : 1) as eluant]. The yields given are the average values from two separate determinations.

(i) *p*-Methoxyphenyl t-butyl nitroxide gave (a) N-*t-butyl*-p-*anisidine* (147 mg, 70%) as an oil, b.p. 60—65° at 0·1 mmHg, $\lambda_{max.}$ 236 and 288 nm (log ε 3·99 and 3·22), τ 8·8 (9H, s, Bu^t), 7·09br (1H, s, NH), 6·32 (3H, s, OMe), and 3·27 (4H, s, ArH) whose *complex* (2 : 1) with naphthalene-1,5-disulphonic acid gave cubes, m.p. 292—294° (from ethanol) (Found: C, 59·7; H, 6·7; N, 4·5; S, 9·6. $C_{32}H_{42}N_2O_8S_2$ requires C, 59·4; H, 6·5; N, 4·3; S, 9·9%); (b) 2-*methoxy*-5-*t-butylamino*-1,4-*benzoquinone* (200 mg, 83%) as red plates, m.p. 124—124·5° (from hexane) (Found: C, 63·3; H, 7·5; N, 7·0. $C_{11}H_{15}NO_3$ requires C, 63·1; H, 7·2; N, 6·7%), $\lambda_{max.}$ 301 and 477 nm (log ε 4·35 and 2·43), $\nu_{max.}$ 3340 and 1655 cm^{-1}, τ 8·6 (9H, s, Bu^t), 6·15 (3H, s, MeO), 4·38 (1H, s, 6-H), 4·23 (1H, s, 3-H), and 4·0br (1H, s, NH); and (c) unchanged nitroxide (53 mg).

(ii) 4-Methoxy-3-methylphenyl t-butyl nitroxide gave (a) N-*t-butyl*-4-*methoxy*-3-*methylaniline* (151 mg, 69%) as an oil, b.p. 65—70° at 0·1 mmHg, $\lambda_{max.}$ 238 and 289 nm (log ε 3·87 and 3·21), $\nu_{max.}$ 3400 cm^{-1}, τ 8·81 (9H, s, Bu^t), 7·85 (3H, s, Me), 7·0br (1H, s, NH), 6·32 (3H, s, MeO), and 3·39 (3H, s, ArH), whose *complex* (2 : 1) with naphthalene-1,5-disulphonic acid formed cubes, m.p. 302—304° (from ethanol) (Found: C, 60·4; H, 6·8; N, 3·9; S, 9·7. $C_{34}H_{48}N_2O_8S_2$ requires C, 60·5; H, 6·8; N, 4·1; S, 9·5%); (b) 2-methoxy 5-t-butylaminobenzoquinone (45 mg, 19%); and (c) unchanged nitroxide (30 mg).

(iii) 4-*Methoxy*-3-*t-butylphenyl t-butyl nitroxide*, red plates, m.p. 225—230° (from hexane) (Found: C, 71·8; H, 9·8; N, 5·9. $C_{15}H_{24}NO_2$ requires C, 72·0; H, 9·6; N, 5·6%), $\lambda_{max.}$ 303 and 505 nm (log ε 3·92 and 2·84), gave (a) N-*t-butyl*-4-*methoxy*-3-*t-butylaniline* (70 mg, 51%) as an oil, b.p. 75—80° at 0·1 mmHg, $\lambda_{max.}$ 240 and 288 nm (log ε 3·90 and 3·23), $\nu_{max.}$ 3400 cm^{-1}, τ 8·79 (9H, s, NBu^t), 8·67 (9H, s, CBu^t), 7·08br (1H, s, NH), 6·24 (3H, s, OMe), and 3·35—3·2 (3H, m, ArH), whose *complex* (2 : 1) with naphthalene-1,5-disulphonic acid formed cubes, m.p. 284—285° (from ethanol) (Found: C, 62·9; H, 7·5; N, 3·5; S, 8·5. $C_{40}H_{58}N_2O_8S_2$ requires C, 63·2; H, 7·7; N, 3·7; S, 8·5%); (b) 2-methoxy-5-t-butylaminobenzoquinone (15 mg, 12%); and (c) unchanged nitroxide (210 mg).

(iv) 4-*Methoxy*-3,5-*dimethylphenyl* t-*butyl nitroxide*, red plates, m.p. 57—58° (from hexane) (Found: C, 70·5; H, 9·0; N, 6·3. $C_{13}H_{20}NO_2$ requires C, 70·2; H, 9·1; N, 6·3%), $\lambda_{max.}$ 297 and 492 nm (log ε 4·21 and 2·98), was unchanged after 5 months.

(v) t-Butyl *p*-t-butylphenyl nitroxide [3] (91 mg), m.p. 118—119°, gave (a) N-*t-butyl*-p-*t-butylaniline* (13 mg, 58%) as an oil, $\lambda_{max.}$ 242 nm (log ε 4·04), $\nu_{max.}$ 3400 cm^{-1}, τ 8·74 (9H, s, NBu^t), 8·71 (9H, s, CBu^t), 6·75br (1H, s, NH), 3·32 (2H, d, *J* 8 Hz, ArH), and 2·84 (2H, d, *J* 8 Hz, ArH), whose *complex* (2 : 1) with naphthalene-1,5-disulphonic acid formed cubes, m.p. 283—284° (from ethanol) (Found: C, 65·7; H, 7·7; N, 4·2; S, 9·1. $C_{38}H_{54}N_2O_6S_2$ requires C, 65·3; H, 7·7; N, 4·0; S, 9·2%); (b) 2-*t-butyl*-5-*t-butylamino*-1,4-*benzoquinone* (24 mg), 96%) as red plates, m.p. 99—99·5° (from hexane) (Found: C, 71·8; H, 9·1; N, 5·9. $C_{14}H_{21}NO_2$ requires C, 71·5; H, 9·0; N, 5·9%), $\lambda_{max.}$ 274 and 470 nm (log ε 3·91 and 2·32), $\nu_{max.}$ 3360, 1665, and 1630 cm^{-1}, τ 8·71 (9H, s, CBu^t), 8·62 (9H, s, NBu^t), 4·41 (1H, s, 6-H), 3·59 (1H, s, 3-H), and 2·7—2·8 (1H, s, NH); and (c) unchanged nitroxide (42 mg).

(vi) 4-Phenoxyphenyl t-butyl nitroxide (1 g) in benzene (20 ml) after 2 days gave (a) *phenyl* 4-*t-butylaminophenyl ether* (490 mg, 78%) as an oil, b.p. 70° at 0·1 mmHg, $\lambda_{max.}$ 248 (log ε 4·19), $\nu_{max.}$ 3400 cm^{-1}, τ 8·71 (9H, s, Bu^t), 6·96 (1H, s, NH), and 3·3—2·7 (9H, m, ArH), whose *complex* with naphthalene 1,5-disulphonic acid formed cubes, m.p. 290—291° (from ethanol) (Found: C, 65·3; H, 6·1; N, 3·7; S, 8·1. $C_{42}H_{46}N_2O_8S_2$ requires C, 65·4; H, 6·0; N, 3·6; S, 8·3%); and (b) *p*-benzoquinone t-butylimine *N*-oxide [3] (190 mg, 83%).

(vii) 4-(4-Bromophenoxy)phenyl t-butyl nitroxide (500 mg) in benzene (25 ml) gave after 1 day (a) 4-*bromophenyl* 4-*t-butylaminophenyl ether* (152 mg, 64%) as plates, m.p. 54—55° (from hexane), $\lambda_{max.}$ 251 nm (log ε 4·20), $\nu_{max.}$ 3380 cm^{-1}, τ 8·70 (9H, s, Bu^t), 6·44br (1H, s, NH), 3·2 (2H, d, *J* 10 Hz, ArH), 3·19 (4H, s, ArH), and 2·63 (2H, d, *J* 10 Hz, ArH), whose *complex* (2 : 1) with naphthalene-1,5-disulphonic acid gave cubes, m.p. >320° (from ethanol) (Found: C, 55·6; H, 4·8; Br, 17·9; N, 3·0; S, 7·2. $C_{42}H_{44}Br_2N_2O_8S_2$ requires C, 55·5; H, 4·8; Br, 17·6; N, 3·2; S, 7·1%); (b) 2-(4-*bromophenoxy*)-5-*t-butylamino*-1,4-*benzoquinone* (10 mg, 3%) as red plates, m.p. 151—152° (from hexane) (Found: M^+, 349·0314. $C_{16}H_{16}BrNO_3$ requires *M*, 349·0314), $\lambda_{max.}$ 300 and 492 nm (log ε 4·10 and 2·36), $\nu_{max.}$ 3340 and 1660 cm^{-1}, τ 8·60 (9H, s, Bu^t), 5·41 (1H, s, 6-H), 5·23 (1H, s, 3-H), 4·18 (2H, d, *J* 4 Hz, ArH), and 3·71 (2H, d, *J* 4 Hz, ArH); and (c) *p*-benzoquinone t-butylimine *N*-oxide [3] (58 mg, 44%).

(viii) Bis-*p*-methoxyphenyl nitroxide (150 mg) in benzene–chloroform (1 : 1) after 2 weeks gave (a) bis-*p*-methoxyphenylamine [17] (20 mg, 72%), m.p. 99—101°; (b) 1,4-*benzoquinone* p-*methoxyphenylimine* N-*oxide* (14 mg, 58%) as red plates, m.p. 124·5—125° (from hexane) (Found: C, 68·4; H, 4·9; N, 6·4. $C_{13}H_{11}NO_3$ requires C, 68·1; H, 4·8; N, 6·1%), $\lambda_{max.}$ 228, 266, and 388 nm (log ε 3·94, 3·61, and 4·28), $\nu_{max.}$ 1624 cm^{-1}, τ 4·12 (3H, s, OMe), 3·78 (1H, q, *J* 10 and 1·5 Hz, 3- or 5-H), 3·41 (1H, q, *J* 10 and 1·5 Hz, 3- or 5-H), 3·0 (2H, d, *J* 8 Hz, ArH), 2·73 (1H, q, *J* 10 and 3 Hz, 2- or 6-H), 2·56 (2H, d, *J* 8 Hz, ArH), and 2·01 (1H, q, *J* 10 and 3 Hz, 2- or 6-H); and (c) unchanged nitroxide (91 mg).

(ix) Bis-*p*-nitrophenyl nitroxide [15] (250 mg) in chloroform (4 ml) after 24 h gave bis-(*p*-nitrophenyl)amine (110 mg, 85%), m.p. 223—224°, identical with an authentic specimen.[18]

Oxidation of N-p-*Methoxyphenyl*-N-*t-butylhydroxylamines with Silver Oxide.*—*N*-(4-Methoxy-2,6-dimethylphenyl)-*N*-t-butylhydroxylamine (1 g) in benzene (30 ml) was shaken with silver oxide (3·0 g) and magnesium sulphate for 30 min. The mixture was filtered and the filtrate evaporated

[17] H. Wieland, *Ber.*, 1909, **41**. 3493.

[18] S. Smiles and T. P. Hilditch, *J. Chem. Soc.*, 1908, **93**, 153.

to dryness at room temperature. Crystallisation of the residue from hexane gave *3,5-dimethyl-1,4-benzoquinone t-butylimine N-oxide* (0·6 g, 58%) as orange plates, m.p. 117—118° (Found: C, 69·8; H, 8·0; N, 6·7. $C_{12}H_{17}NO_2$ requires C, 69·5; H, 8·3; N, 6·8%), $\lambda_{max.}$ 262 and 394 nm (log ε 3·15 and 4·14), $\nu_{max.}$ 1620 cm^{-1}, τ 8·28 (9H, s, Bu^t), 7·93 (6H, m, 2Me), 2·38 (1H, m, 3- or 6-H), and 2·23 (1H. m, 3- or 6-H).

Similar treatment of *N-p*-methoxyphenyl-*N*-t-butylhydroxylamine (1 g) gave 1,4-benzoquinone t-butylimine *N*-oxide [3] (0·7 g, 80%), m.p. 73—74°.

Decomposition of Nitroxides in Other Solvents.—(i) *p*-Methoxyphenyl t-butyl nitroxide (300 mg) in aniline (3 ml) was allowed to decompose during 3 weeks at room temperature. T.l.c. of the resulting mixture in benzene–petrol (1 : 1) gave, in addition to unchanged nitroxide, *N*-t-butylaniside, and small quantities of 2-methoxy-3-t-butylamino-1,4-benzoquinone, a red fraction (155 mg), crystallisation of which from chloroform–hexane afforded *2-anilino-5-t-butylamino-1,4-benzoquinone bisphenylimine* as red needles, m.p. 183—184° (Found: C, 80·1; H, 6·2; N, 13·1. $C_{28}H_{26}N_4$ requires C, 80·4; H, 6·3; N, 13·4%), $\nu_{max.}$ 3300 cm^{-1}, τ 8·94 (9H, s, Bu^t), 4·48 (1H, s, 3- or 6-H), 3·88 (1H, s, 3- or 6-H), 3·5br (1H, s, NH), 3·3—2·5 (15H, m, ArH), and 1·9—1·6 (1H, s, NH).

(ii) In separate experiments (*a*) copper acetate (250 mg), (*b*) potassium acetate (250 mg), (*c*) acetic acid (1 drop), and (*d*) conc. hydrochloric acid were added to a 0·5M-solution of *p*-methoxyphenyl t-butyl nitroxide (200 mg) in ethanol (2 ml). After 2 days it was shown (t.l.c.) that in reactions (*c*) and (*d*) the nitroxide had decomposed completely to *N*-t-butyl-*p*-anisidine and 1,4-benzoquinone t-butylimine *N*-oxide; after 1 week reaction (a) yielded 2-methoxy-5-t-butylamino-1,4-benzoquinone and *N*-t-butyl-*p*-anisidine. Meanwhile reaction (b) showed little change.

(iii) Phenoxyphenyl t-butyl nitroxide (500 mg) in a mixture of benzene (6 ml) and t-butylamine (4 ml) was allowed to decompose during 2 days. T.l.c. in chloroform gave, in addition to 1,4-benzoquinone t-butylimine *N*-oxide and phenyl 4-t-butylaminophenyl ether, 2,5-bis-(t-butylamino)-1,4-benzoquinone [19] (25 mg, 15%).

N-t-Butyl-4-methoxy-2,6-dimethylaniline.—Hydrogenation of *N*-(4-methoxy-2,6-dimethylphenyl)-*N*-t-butylhydroxylamine (1 g) in ethanol yielded a crude product, crystallisation of which from hexane provided the *amine* as plates, m.p. 65·5—66°, $\lambda_{max.}$ 238 and 290 nm (log ε 3·85 and 3·19), $\nu_{max.}$ 3400 cm^{-1}, τ 8·73 (9H, s, Bu^t), 7·8 (6H, s, 2Me), 7·1br (1H, s, NH), 6·33 (3H, s, OMe), and 3·62 (2H, s, ArH). Its *complex* (2 : 1) with naphthalene-1,5-disulphonic acid gave cubes, m.p. 270—272° (from ethanol) (Found: C, 71·6; H, 7·1; N, 4·2; S, 9·1. $C_{36}H_{50}N_2O_8S_2$ requires C, 61·6; H, 7·1; N, 4·0; S, 9·1%).

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[19] G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, N.-Y. Chang, and G. Kaupp, *J. Amer. Chem. Soc.*, 1968, **90**, 4646.