Nitroxide Radicals. Part XII.[1] Decomposition of *ortho*-, *meta*-, and *para*-Halogenophenyl t-Butyl Nitroxides

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The spontaneous decomposition of t-butyl *p*-halogenophenyl nitroxides and the hydroxylamines from which they are derived produces mainly *p*-benzoquinone t-butylimine *N*-oxide, the corresponding amine, and hydrogen halide or molecular halogen. Primary studies indicate that the rates of decomposition under comparable conditions in benzene solution increase in the order *p*-I < *p*-F < *p*-Cl < *p*-Br. Under certain conditions small quantities of amino-quinones and quinone imines have also been isolated. The principal decomposition route entails *O*-to-*para*-*C* coupling with subsequent homolytic fragmentation of the intermediate cyclohexadiene. The isomeric *meta*-bromo- and -chloro-radicals also decompose mainly in this way although *O*-to-*ortho*-*C* coupling also occurs, as shown by analysis of the minor products. *ortho*-Bromo- and chlorophenyl t-butyl nitroxides are sufficiently stable to be crystallised and analysed.

ALTHOUGH displacement of halogen attached to an aromatic ring is frequently encountered in free radical reactions, the way in which such a displacement occurs is not well understood. Among the most easily studied reactions of this type are those involving relatively stable halogenated aromatic π-radicals, which frequently dimerise or couple with other radicals with immediate or eventual loss of halogen. The classic example [2] is that of *p*-bromophenyldiphenylmethyl which spontaneously dimerises ('head-to-tail') to give a bromocyclohexadiene. In the presence of an excess of the silver used to generate the initial triphenylmethyl from its halide this intermediate is debrominated slowly to give a dimeric triphenylmethyl. Other more recent examples include the dimerisation (*para*-*C*-to-*para*-*C*) of 2,6-di-t-butyl-4-halogenophenoxyls [3] which ultimately yields a diphenoquinone and the coupling (*N*-to-*para*-*C*) of *p*-(dimethylamino)phenylaminyl with *p*-halogenophenoxyls to give halogen-free quinone imines.[4] Oxidation of *p*-halogenophenols to *p*-benzoquinones by the inorganic nitroxide, Fremy's salt,[5] and the production of *p*-benzoquinone *p*-chlorophenylimine *N*-oxide on attempted preparation of bis-4-chlorophenyl nitroxide by oxidation of bis-4-chlorophenylamine with peroxybenzoic [6] acid suggests that oxidative dehalogenation of halogenoaryl π-radicals by nitroxides is a general reaction. With a view to investigating the way in which such displacements occur and the factors which control them we have prepared and examined the modes of decomposition of a series of *ortho*-, *meta*-, and *para*-halogenophenyl t-butyl nitroxides.

RESULTS

Apart from *N*-*p*-fluoro- and *p*-chloro-phenyl-*N*-t-butylhydroxylamines (**1**; X = F or Cl) which decomposed spontaneously at room temperature during 1—3 days to brown oils, the hydroxylamines listed in Table 3 were stable indefinitely in the solid state. They were converted into the corresponding nitroxides by oxidation with silver(I) oxide in benzene solution. The *para*- and

[1] Part XI, A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 3322.
[2] M. Gomberg and F. F. Blicke, *J. Amer. Chem. Soc.*, 1923, **45**, 1765 and earlier papers.
[3] K. Ley, E. Müller, R. Mayer, and K. Scheffler, *Chem. Ber.*, 1958, **91**, 2670, 2682.
[4] S. Hunig and W. Daum, *Annalen*, 1955, **595**, 131.
[5] H. J. Teuber and O. Glosauer, *Chem. Ber.*, 1965, **98**, 2643.
[6] K. Tokumaru, H. Sakuragi, and O. Simamura, *Tetrahedron Letters*, 1964, 3945.

meta-halogenophenyl nitroxide radicals were extremely sensitive to heat, decomposing vigorously and in one case (*p*-fluoro) violently to intractable tars when their solutions were evaporated to dryness above 40°.

The principal organic products from the decomposition of the *p*-halogenophenyl-hydroxylamines and nitroxides under the controlled conditions outlined in Table 1 were the corresponding amines (6) and the quinone imine *N*-oxide (4), both easily identified from their spectra.[7] Hydrogen halide was also obtained from all but the *p*-iodophenyl-hydroxylamine and nitroxide, which yielded iodine instead. Additional products obtained from the decomposition of *p*-chloro- and *p*-bromo-phenyl nitroxides in the absence of solvent have been identified as the 3-halogenoquinone imines (9; X = Cl or Br) and amino-quinones (12; X = Cl or Br). The structures of the quinone imines were deduced mainly from their i.r. ($\nu_{max.}$ 1650 cm^{-1}) and n.m.r. spectra and by their ease of hydrolysis with acid to halogeno-quinones. The position of the halogen was established by oxidation of the bromo-quinone imine (9; X = Br) with perbenzoic acid to the corresponding quinone imine *N*-oxide [8] which was identical with that obtained by decomposition of t-butyl *m*-bromophenyl nitroxide (see later). The purple amino-quinones (12; X = Cl or Br) showed significant i.r. absorption at 3360, 1675, 1635, and 1615 cm^{-1} and two singlets (τ 2·8 and 4·1) in the n.m.r. spectrum attributable to the quinonoid protons. The relative position of the halogeno- and t-butylamino-substituents was confirmed by reductive acetylation of the quinone to the diacetate (13) whose n.m.r. spectrum showed signals at τ 2·46 and 2·98 from two *para*-coupled (J 0·3 Hz) aromatic protons. Structure elucidation in this work was aided by the sensitivity of the position of the t-butyl resonances to the number and type of groups or atoms bonded to the nitrogen atom.[9] The hydroxylamines (1), amines (6), imines (9), amino-quinones (12), and imine *N*-oxides (4) give t-butyl signals near τ 8·9, 8·7, 8·6, 8·5, and 8·3, respectively.

Decomposition of *m*-chloro- and *m*-bromo-phenyl t-butyl nitroxides (23; X = Cl or Br) gave principally the corresponding amines (24; X = Cl or Br) (23 and 29%, respectively) and 1,4-benzoquinone t-butylimine *N*-oxides (25; X = Cl or Br) (38 and 12%, respectively), accompanied by small quantities of 2-(t-butylamino)-1,4-benzoquinone (29) (2—4%). The purple halogeno-amino-quinone (31; X = Br), whose n.m.r. spectrum showed signals due to two non-equivalent, weakly coupled (J 3 Hz) quinonoid protons, and the parent quinone imine *N*-oxide (4) were also minor products from the *meta*-bromo-radical. Attempts to separate and identify several unstable highly coloured (mostly purple) minor components from these mixtures was unavailing. Spectroscopic data for one of the more abundant of these is given in the Experimental section.

o-Chlorophenyl and *o*-bromophenyl t-butyl nitroxides (32; X = Cl or Br) were by far the most stable radicals examined in this series. Both were isolated, crystallised, and analysed, and underwent little decomposition in the solid state unless heated. In solution, decomposition was slow and then only partial after some weeks. Apart from the corresponding *o*-halogeno-amines (33; X = Cl or Br), the product mixtures contained numerous coloured materials only one of which was common to both mixtures. This, an orange crystalline solid, did not contain halogen (mass spectrum and analysis) and had a molecular formula, $C_{20}H_{24}N_2O_3$, which corresponded to that of an 'anhydro-dimer' of the *ortho*-quinone imine *N*-oxide (34). Its n.m.r. spectrum showed signals from two t-butyl groups at τ 8·22 and 8·6 [$Bu^tN^+(O^-)$= and Bu^tNH–, respectively], one N–H at τ 5·83, and five aromatic and/or quinonoid protons in

TABLE 1

Yields (%) * of decomposition products from t-butyl *p*-halogenoaryl nitroxides and the corresponding hydroxylamines

Ar	Conditions †	Decomposition time	HX	Amine (6)	Quinone imine *N*-oxide	Other products
p-FC_6H_4	(a)	2 h	36	32	42	
	(b)	3 days	45	41	52	
	(c)	10 days	86	81	81	
	(d)	21 days	73	71	70	
p-ClC_6H_4	(a)	2 h	58	57	47	19·4 (9; X = Cl); 8·4 (12; X = Cl)
	(b)	5 days	62	57	60	
	(c)	21 days	87	82	76	
	(d)	21 days	n.d.‡	n.d.	1·9	
p-BrC_6H_4	(a)	2 h	46	48	37	25·4 (9; X = Br); 14·4 (12; X = Br)
	(b)	8 days	55	79	59	
	(c)	27 days	89	93	80	
	(d)	21 days	n.d.	n.d.	0·25	
p-IC_6H_4	(a)	2 h		0	0	
	(b)	1 day		50	20	I_2 > 100
	(c)	24 days		71	62	I_2 39

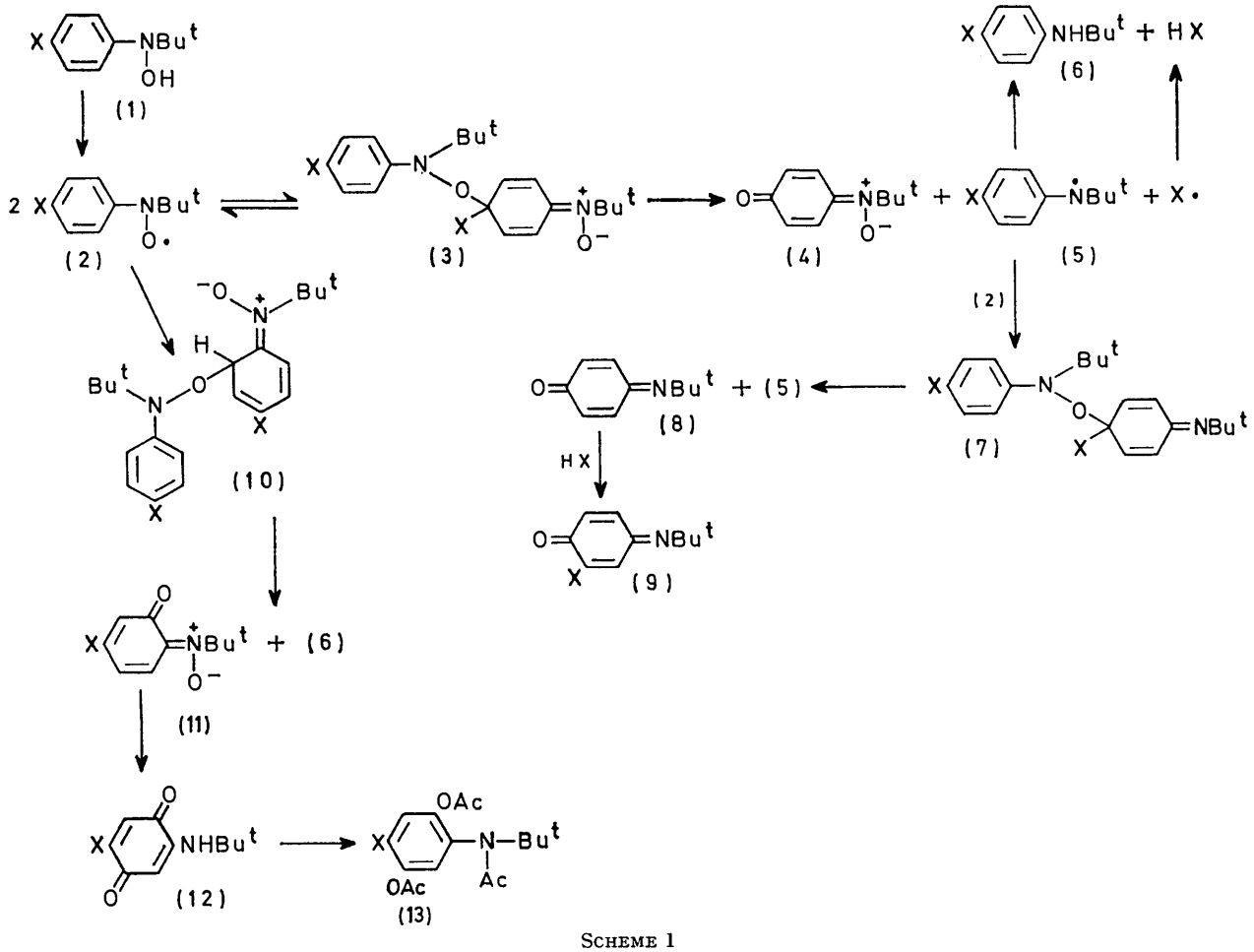
* Yields are based on 2 mol of nitroxide giving 1 mol of each of the products and are the average of two separate determinations. † Decomposition of (a) nitroxide in the absence of solvent; (b) 0·1M-nitroxide in benzene; (c) 0·1M-hydroxyalmine in benzene in air; (d) 0·1M-hydroxylamine in benzene in the absence of air. ‡ Not determined.

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

[8] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1957, **79**, 2295.

[9] (*a*) W. D. Wilk, A. L. Allred, B. A. Koven, and J. A. Marshall, *J. Chem. Soc.* (*B*), 1969, 565; (*b*) W. Horspool, *Quart. Rev.*, 1969, **23**, 204.

the range τ 4·3—3·5. The presence of very strong absorption at 1780 cm^{-1} (four-membered ring ketone?) as well as other lesser bands at 3380 (NH) and 1680 and 1630 cm^{-1} (quinonoid carbonyl) in its i.r. spectrum makes it difficult to formulate a reasonable structure for this product. Although *ortho*-quinones form dimers fairly easily, no dimer with a four-membered ring appears to have been isolated.



SCHEME 1

TABLE 2

Coupling constants (G) of t-butyl halogenoaryl nitroxides [a]

Ar	a_N	$a_{o\text{-}H}$	$a_{m\text{-}H}$	$a_{p\text{-}H}$	a_{other}
p-FC_6H_4	12·5	1·8	0·95		a_F 3·7
p-ClC_6H_4	12·0	2·05	1·0		
p-BrC_6H_4	11·9	2·05	1·0		
p-IC_6H_4	12·0	2·0	1·0		
m-ClC_6H_4	11·7	2·0	0·9	2·0	
m-BrC_6H_4	11·75	2·05	0·9	2·05	
o-ClC_6H_4	13·9	−0·74*	0·47* and 0·82*	−0·29*	a_H^{But} −0·25*
o-BrC_6H_4	13·9	−0·76*	0·43* and 0·87*	−0·27*	a_H^{But} −0·26*

[a] E.s.r. and n.m.r. spectra (marked *) measured for solutions in carbon tetrachloride.

Nitrogen and proton coupling constants have been evaluated by e.s.r. and/or n.m.r. measurements for all of the radicals examined, and are listed in Table 2. Since this work was begun spectra of nearly all these radicals have been reported and adequately discussed by others.[10-12] Our measurements made on radicals generated in an unambiguous way generally confirm these results and are given here so that they may be used as required in the Discussion section.

DISCUSSION

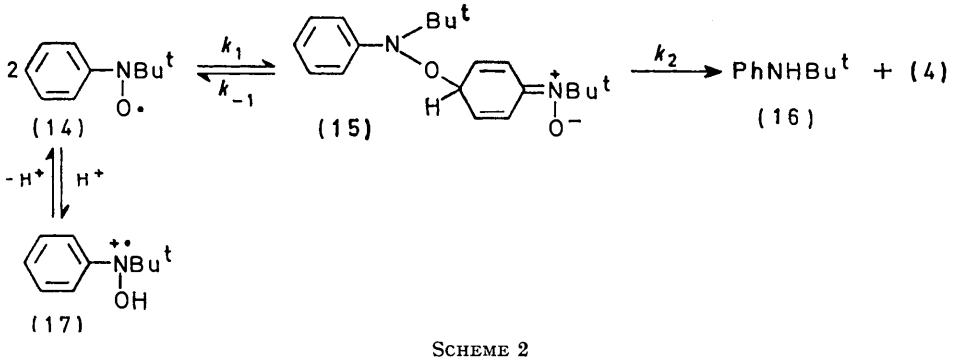
p-Halogenoaryl t-Butyl Nitroxides.—We consider that the initial step in the decomposition the *p*-halogenophenyl t-butyl nitroxides (2) entails intermolecular *O*-to-*para*-*C* coupling (*cf.* decomposition of t-butyl phenyl nitroxide [7]). The ensuing cyclohexadiene dimer (3) then fragments homolytically to give, in addition to the quinone imine *N*-oxide (4), a *p*-halogenophenyl-t-butylaminyl (5) and atomic halogen, hydrogen abstraction by which yields the corresponding amine (6) and hydrogen halide (except with atomic iodine which

[10] H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. chim. France*, 1965, 372.

[11] G. Barbarella and A. Rassat, *Bull. Soc. chim. France*, 1969, 2378.

[12] J. A. Pedersen and K. Torssell, *Acta Chem. Scand.*, 1971, **25**, 3151.

dimerises), respectively. The alternative heterolysis of the dimer (3), which would lead to either halide anion and alkylarylnitrenium cation or halogen cation and alkylarylaminide anion seems much less likely. Formation of the amine (6) from the corresponding nitrenium ion would require the production of the latter in the triplet state [13] and intermediate halogenonium ions (X^+) would halogenate the aromatic amine (6) rather than abstract hydride ion. The main sources of abstractable hydrogen are, presumably, the t-butyl groups of the products (4) and (6) and the nitroxide (2), although in experiments in which AnalaR benzene was used as solvent the low concentration of toluene therein could be a subsidiary source. Such hydrogen abstractions, particularly by non-discriminating atomic fluorine and chlorine would account for the considerable amount of intractable material formed in these decompositions (especially in the absence of solvent) and the moderate yields of amine (6) and *N*-oxide (4) [Table 1, conditions (a) and (b)]. Formation of molecular iodine from compound (2; X = I) rather than hydrogen iodide also attests to a homolytic fragmentation of (3) since hydrogen abstraction by iodine is an appreciably endothermic process.[14] It follows from Scheme 1 that formation of compounds (4) and (6) from the nitroxide (2) should proceed most efficiently in the presence of a good hydrogen donor with which the reactive halogen and t-butylarylaminyl (6) could react. The most convenient donor would be the corresponding hydroxylamine (1) since it would not give rise to additional products whose presence would make analysis of the product mixture more complicated. This situation obtains in the autoxidation of the hydroxylamines (1) in solution in benzene [Table 1, condition (c)] which did indeed produce higher yields of amines (6) and *N*-oxide (4) than obtained from the nitroxides directly. Predictably, these autoxidations proceeded more slowly but more efficiently in good hydrogen-donating solvents such as cumene and triethylamine. For example, decomposition of (1; X = Cl) was complete in benzene but only 64% complete in cumene after 21 days, and the fluorophenylhydroxylamine (1; X = F) gave an 86% yield of the *N*-oxide (4) in cumene (81% in benzene). In the latter case a little bicumyl was also isolated, thus providing further evidence for the mediation of radicals more reactive than nitroxides in these decompositions. Alkyl aryl nitroxides are generally feeble hydrogen abstractors [15] and it was shown in a separate experiment that the nitroxide (2; X = Bu^t) did not react with cumene. The foregoing autoxidations also served to exclude the possibility that the silver formed during the conversion of the hydroxylamines into the nitroxides [Table 1, conditions (a) and (b)] participated in the dehalogenation of the intermediate (3). This contrasts with the behaviour of the cyclohexadiene dimer derived from *p*-bromophenyldiphenylmethyl to which we have already alluded,[3] which does not lose halogen unless treated with metals. As a further consequence of Scheme 1, two molecules of nitroxide (2) should be generated for every one that is consumed if both the radical (5) and the halogen atom abstract hydrogen from the hydroxylamine (1). Hence, solutions of the hydroxylamines (1; X = F, Cl, or Br) containing catalytic quantities of the corresponding nitroxides should decompose spontaneously even in the absence of air. Such was the case. However, decomposition of the hydroxylamines (1; X = Cl or Br) was very slow under these conditions, proceeding to the extent of *ca.* 1·9 and 0·25%, respectively, in 21 days, during which the *p*-fluorophenylhydroxylamine decomposed completely. Complete decomposition of (1; X = Cl or Br) required several months.

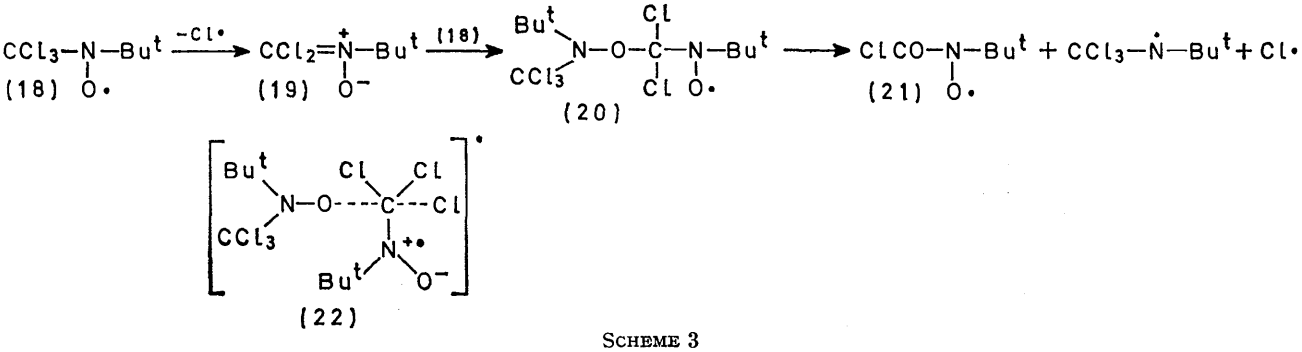


SCHEME 2

From Table 1 the apparent order of rate of decomposition of the nitroxides is *p*-I > *p*-F > *p*-Cl > *p*-Br, but before the factors which determine this order can be appreciated several observations on the decomposition of non-halogenated aryl alkyl nitroxides must be discussed. In view [7] of the stabilising effect (albeit measured only semi-quantitatively) which the introduction of *meta*-methyl substituents had on t-butyl phenyl nitroxide (14) it seemed that the rate-controlling step in its decomposition was simply the initial radical coupling to give (15) (Scheme 2). However, this conclusion is not consistent with the observation that the decomposition of t-butyl phenyl nitroxide (14) in

[13] P. G. Gassman, *Accounts Chem. Res.*, 1970, **3**, 26.
[14] E. S. Huyser, 'Free Radical Chain Reactions,' Wiley, New York, 1970, p. 115.
[15] A. R. Forrester and R. H. Thomson, *J. Chem. Soc.* (*C*), 1966, 1844.

benzene 0·1M with respect to hydrogen chloride is about 20 times as fast as that in the absence of hydrogen chloride. The accelerating effect which acid has on the decomposition of aryl nitroxides has been noted previously [16] and attributed,[17] wrongly in our view, to an increase in unpaired spin density at the *para*-carbon atom in the protonated nitroxide form (17). E.s.r. measurements on t-butyl phenyl nitroxide in 0·1M-hydrogen chloride in benzene revealed that the spin density on the *para*-carbon atom, as indicated by the *para*-hydrogen coupling constant, was not measurably different from that recorded when benzene alone was used as solvent. These facts are best accommodated by Scheme (2) in which acid catalyses the fragmentation [(15) ⟶ (16) + (4)] and the initial radical coupling is an appreciably reversible process. The mechanism is then directly analogous to the S_N2-type process in nucleophilic aromatic substitution for which it has been shown [18] that the overall rate coefficient (k) depends on the rate coefficients of the individual steps as follows: $k = k_1k_2/(k_{-1} + k_2)$. In the case of t-butyl phenyl nitroxide it seems that k_2 and k_{-1} are of comparable magnitude.



SCHEME 3

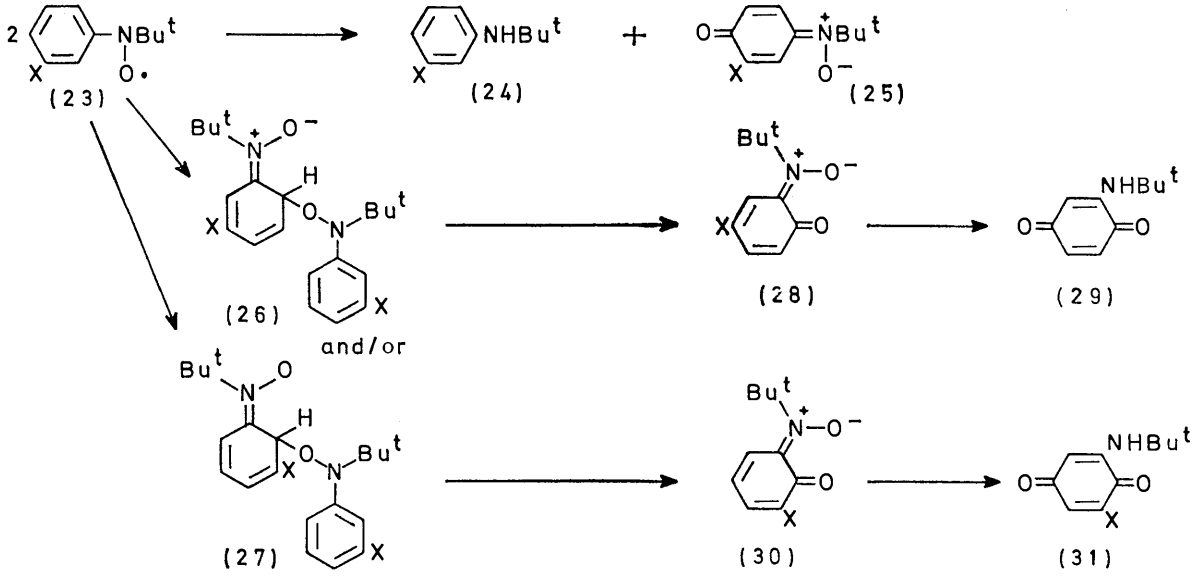
The three main factors likely to affect the rate of decomposition of the t-butyl *p*-halogenophenyl nitroxides are (*a*) the free spin density on the *para*-carbon atom, (*b*) the size of the halogen atom, and (*c*) the ease with which the carbon–halogen bond is broken in the intermediate cyclohexadiene dimer (3). We have little information on factor (*a*) since no ^{13}C splittings were observed in the e.s.r. spectra of the radicals and splitting due to only one halogen ($a_F = 3·7$ G) was detected. Nitrogen and proton couplings did not vary greatly (see Table 2). If factor (*b*) controlled the decompositions the stability of the radicals would be expected to increase in the order *p*-F > *p*-Cl > *p*-Br > *p*-I, whereas if (*c*) predominated this order would be reversed. Hence, it appears that our results place the iodo-nitroxide in an anomalous position, factor (*b*) controlling the rate of decomposition of the fluoro-, chloro-, and bromo-radicals (*cf.* nucleophilic aromatic substitution) and factor (*c*) the decomposition of the iodo-radical. The reasons for this apparent changeover cannot be established from our present results and since the extent to which the fragmentation of (3), like that of (14), is catalysed by the hydrohalide generated during the decomposition is unknown, speculation at this stage would be unjustified. However, this semi-quantitative investigation has provided the basis from which quantitative experiments have been designed. We are currently measuring the rates of decomposition of phenyl and *p*-halogenophenyl t-butyl nitroxides at high dilution in good hydrogen-donating solvents at constant pH. From these results a more reliable order of stability will be obtained.

In our view there is a cogent but as yet unestablished mechanistic link between the mode of decomposition of t-butyl *p*-halogenophenyl nitroxides and recently reported [19,20] oxidative dehalogenations of halogenated aliphatic nitroxides. Thus, the trichloromethyl nitroxide (18) decomposes to the chloroacyl nitroxide (21) by a route thought to involve initial and spontaneous loss of atomic halogen yielding the nitrone (19). The subsequent steps have not been ascertained but addition of a second molecule of nitroxide followed by homolytic fragmentation of (20) seems likely and would be analogous to the fragmentation of the cyclohexadiene (3). In much the same way as oxidative dehalogenation of the aromatic nitroxides in Scheme 1 was compared with nucleophilic aromatic substitution by the addition–elimination sequence, then the foregoing steps can be compared with the S_N1 process in nucleophilic aliphatic substitution. Such a comparison had led us to consider another possibility for the formation of (20). This would be the analogue of the S_N2 process in nucleophilic aliphatic substitution, the nitroxide displacing a chlorine atom in a bimolecular reaction, the transition state for which is represented as (22). As far as we are aware free-radical reactions of this type have not previously been observed (*cf.* ref. 21).

Formation of Minor Products.—In the quinone imines

[16] H. Wieland and K. Roth, *Ber.*, 1920, **53**, 210.
[17] G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *J. Chem. Soc.* (*B*), 1971, 233.
[18] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, London, 1968.
[19] J. W. Hartgerink, J. B. F. N. Engberts, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2707.
[20] C. M. Camaggi, R. J. Holman, and M. J. Perkins, *J.C.S. Perkin II*, 1972, 501.
[21] K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley, New York, 1971.

(9; X = Cl or Br) the relative positions of the halogen and nitrogen are different from those in the initial nitroxides; hence these products must arise by a sequential route involving halogen elimination followed by halogen reintroduction. The most likely participants in the latter step, hydrogen halide and the parent quinone imine (8), did in fact react in this way to give (9; X = Cl or Br). Formation of the parent quinone imine (8) is best accounted for by a direct coupling of



SCHEME 4

the nitroxide (2) with the aminyl (5) followed by halogen elimination from (7) as shown in Scheme 1. The alternative oxidation of the amine (6) by nitroxide is less likely in view of the resistance of the bromo-amine (6; X = Br) to oxidation by Fremy's salt (which is usually a more powerful oxidant than organic nitroxides). It is important to note that these minor products were not detected in decompositions of the hydroxylamines (1; X = Br or Cl), *i.e.* circumstances in which hydrogen abstraction by the aminyl (5) from the hydroxylamine (1) would be expected to be favoured over nitroxide–aminyl coupling.

The *ortho*-quinone imine *N*-oxides (11), formed by *O*-to-*ortho*-*C* coupling of the nitroxides, are isomers and precursors of the purple amino-quinones (12; X = Cl or Br). Their isomerisation to the quinones is an intermolecular process catalysed by the parent nitroxides. We could neither isolate nor detect with certainty the intermediate *ortho*-quinone imine *N*-oxides (11; X = Cl or Br) in these decompositions and our explanation is based on results obtained from a series of naphthyl t-butyl nitroxides which yielded relatively stable intermediates of this type.[22] Significantly, the highest yield of product arising from initial *O*-to-*ortho*-*C* coupling was obtained from that nitroxide (2; X = Br) for which *O*-to-*para*-*C* was most difficult; even then it occurred only under conditions (see Table 1) likely to promote energetically less favourable reactions.

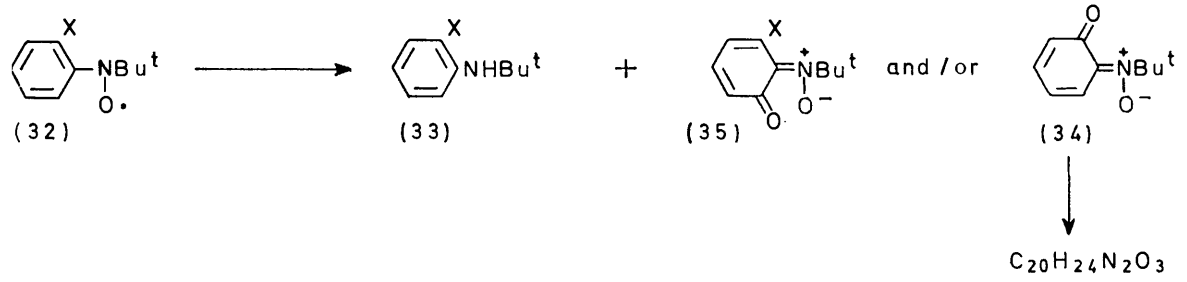
m-*Halogenoaryl t-Butyl Nitroxides*.—The major products (24; X = Cl or Br) and (25; X = Cl or Br) obtained from the two *meta*-halogenophenyl nitroxides (23; X = Cl or Br) are readily accounted for by the *O*-to-*para*-*C* coupling sequence already outlined for t-butyl phenyl nitroxide (Scheme 2). However, yields are considerably lower than those of the corresponding products from that radical. The small quantities of amino-quinones (29) and (31; X = Br) presumably arise by *O*-to-*ortho*-*C* coupling, fragmentation of (26) and (27), and rearrangement of the ensuing *ortho*-quinone imine *N*-oxides (28) and (30) (in one case with displacement of halogen) as described before. Thus, the presence of the *meta*-halogeno-substituent, by inhibiting coupling *via* the *para*-position, aids *ortho*-coupling. The large number of unidentified coloured products in these decompositions almost certainly derive mainly from the highly reactive *ortho*-quinone imine *N*-oxides (28) and (30). Formation of the unsubstituted quinone imine *N*-oxide (4) from the nitroxide (23; X = Br) was surprising and cannot be easily explained. However, it did not arise from an impurity (*ca.* 7% would be required to account for the yield of *N*-oxide) of *p*-bromophenyl or phenyl t-butyl nitroxide in the *m*-bromophenyl t-butyl nitroxide; such impurities were shown to be absent by e.s.r. Although the three radicals under consideration have similar a_N values (Table 2), their spectral widths are significantly different.

o-*Halogenoaryl t-Butyl Nitroxides*.—The relatively high stability of the nitroxides (32; X = Cl or Br) is a direct result of increased unpaired electron localisation. As in *ortho*-alkylaryl t-butyl nitroxides [23] the N–O group is twisted to a large extent out of conjugation with the

[22] A. Calder, A. R. Forrester, and G. McConnachie, unpublished work.

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

aryl ring, unpaired electron density of the *ortho*- and *para*-positions is reduced, and hence bimolecular coupling at these positions is also reduced. The large nitrogen coupling constants (13·9 G) and small ring proton coupling constants (especially for the *para*-position) are manifestations of this twisting [24] (Table 2). From the relatively large quantities of amine (33; X = Cl or Br) and hydrohalide formed it may be inferred that slow *O*-to-*ortho*-*C* coupling predominates. This is also supported by the absence of significant quantities of *para*-quinone imine *N*-oxides, which would have been formed by *O*-to-*para*-*C* coupling and would be expected to be stable. The several minor products presumably arise by further reactions of the intermediate *ortho*-benzoquinone imine *N*-oxides (34) and (35). The available data on the only minor product which was isolated (see Results section) accord with this view.



SCHEME 5

TABLE 3

N-Halogenoaryl-*N*-t-butylhydroxylamines

Ar	Yield (%)	M.p. (°C)	Found (%) C	H	N	Hal	Formula	Required (%) C	H	N	Hal
p-FC_6H_4	54	102—103	65·5	8·0	7·4		$C_{10}H_{14}FNO$	65·5	7·65	7·65	
p-ClC_6H_4	55	106—108	60·1	6·8	7·0	17·5	$C_{10}H_{14}ClNO$	60·1	7·0	7·0	17·6
m-ClC_6H_4	56	121—122	60·0	6·8	6·9	17·7	$C_{10}H_{14}ClNO$	60·1	7·0	7·0	17·6
o-ClC_6H_4	56	110—112	60·1	7·1	7·0	17·6	$C_{10}H_{14}ClNO$	60·1	7·0	7·0	17·6
p-BrC_6H_4	60	117—118	49·2	5·8	5·7	32·6	$C_{10}H_{14}BrNO$	49·2	5·7	5·7	32·8
m-BrC_6H_4	54	121—123	49·5	5·7	5·7	32·8	$C_{10}H_{14}BrNO$	49·2	5·7	5·7	32·8
o-BrC_6H_4	27	96—97	49·4	5·8	5·7	32·8	$C_{10}H_{14}BrNO$	49·2	5·7	5·7	32·8
p-IC_6H_4	61	128—129	41·5	4·5	4·9	43·4	$C_{10}H_{14}INO$	41·2	4·8	4·8	43·6

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 in ethanol (u.v.), Nujol (i.r.), or deuteriochloroform (n.m.r.). Petroleum refers to light petroleum of b.p. 40—60°.

N-Halogenoaryl-N-t-butylhydroxylamines.—The hydroxylamines (Table 3) were prepared by treatment of the corresponding Grignard reagents with 2-methyl-2-nitrosopropane as described previously for alkylaryl-t-butylhydroxylamines.[7] 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.

Decomposition of p-*Halogenoaryl-t-butyl-hydroxylamines and the Corresponding Nitroxides.*—The *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-phenyl butyl nitroxides were obtained by shaking solutions of the corresponding hydroxylamines (250 mg) in benzene (50 ml) with silver oxide (0·55 mol) and magnesium sulphate. After filtration the solutions were (i) evaporated to dryness at room temperature and left for 2 h [conditions (a), Table 1] or (ii) concentrated until 0·1M (0·02M for *p*-iodophenyl t-butyl nitroxide) with respect to the radical and left until decomposition was complete [conditions (b), Table 1]. This required 3, 5, 8, and 1 day(s), respectively, for the *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-phenyl t-butyl nitroxides.

Solutions (0·1M) of the *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-phenyl-t-butylhydroxylamines (250 mg) in benzene were (i) left to decompose in the presence of air for 10, 21, 27, and 24 days, respectively [conditions (c), Table 1] or (ii) thoroughly degassed and left in the absence of air for 21 days [conditions (d), Table 1].

Product Analysis.—The following procedure was used for the products arising from the *p*-fluoro-, *p*-chloro-, and *p*-bromo-phenyl-t-butylhydroxylamines and corresponding nitroxides. The mixtures were diluted with benzene and the resulting solutions extracted with 0·1M-sodium hydroxide (3 × 10 ml), washed with water, and dried ($MgSO_4$). The hydrogen halide was estimated by back titration of the combined alkaline extracts with 0·1M-hydrochloric acid. The organic products in the benzene solution were separated by t.l.c. on silica gel with chloroform as eluant. Yields of *p*-benzoquinone t-butylimine *N*-oxide and amino-quinones (12) were estimated by spectrophotometry ($\lambda_{max.}$ 384 and 500 nm, respectively) and of *N*-t-butylanilines and *p*-benzoquinone t-butylimines by weight.

Mixtures from t-butyl-*p*-iodophenylhydroxylamine and the corresponding nitroxide, after dilution with benzene, were extracted with 0·1M-potassium iodide (3 × 50 ml), washed with water, and dried. The iodine in the potassium iodide extracts was estimated by titration with 0·1M-sodium thiosulphate solution and the organic products were separated and estimated as already described.

Products from (i) p-*Fluorophenyl-t-butylhydroxylamine and*

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the corresponding nitroxide. (a) *p*-Benzoquinone t-butylimine *N*-oxide,[7] m.p. 73—74°, $\nu_{max.}$ 1620 cm^{-1}, $\lambda_{max.}$ 384 nm (log ε 4·33); (b) *p*-fluoro-*N*-t-butylaniline, b.p. 58—61° at 0·7 mmHg, $\nu_{max.}$ 3400 cm^{-1}, τ 8·73 (9H, s, Bu^t), 6·98br (1H, s, NH), and 3·1—3·3 (4H, m, ArH); its *benzamide* gave plates, m.p. 123—124° (from petroleum) (Found: C, 75·3; H, 7·0; N, 4·8. $C_{17}H_{18}FNO$ requires C, 75·3; H, 6·65; N, 5·2%), τ 8·51 (9H, s, Bu^t), 3·1—3·3 (4H, m, ArH), and 2·88 (5H, s, Ph).

(ii) p-*Chlorophenyl-t-butylhydroxylamine and the corresponding nitroxide.* (a) *p*-Chloro-*N*-t-butylaniline,[25] $\nu_{max.}$ 3400 cm^{-1}, τ 8·69 (9H, s, Bu^t), 6·72 (1H, s, NH), and 2·8—3·5 (4H, m, ArH); (b) 2-*chloro*-5-(*t-butylamino*)-1,4-*benzoquinone*, purple plates, m.p. 88—90° (from petroleum) (Found: C, 56·3; H, 5·4; Cl, 17·0; N, 6·6. $C_{10}H_{12}ClNO_2$ requires C, 56·2; H, 5·6; Cl, 16·6; N, 6·6%), $\nu_{max.}$ 3360, 1675, 1640, and 1625 cm^{-1}, $\lambda_{max.}$ 282 and 500 nm (log ε 4·07 and 3·41), τ 8·60 (9H, s, Bu^t), 4·28br (1H, s, NH), 4·14 (1H, s, 6-H), and 2·84 (1H, s, 3-H); (c) 3-*chloro*-1,4-*benzoquinone t-butylimine*, needles, m.p. 81—82° (from petroleum) (Found: C, 60·3; H, 6·0; N, 7·0; Cl, 17·6. $C_{10}H_{12}ClNO$ requires C, 60·7; H, 6·1; N, 7·1; Cl, 17·95), $\nu_{max.}$ 1650 cm^{-1}, $\lambda_{max.}$ 273 nm (log ε 4·47), τ 8·50 (9H, s, Bu^t), 3·54 (1H, q, *J* 10·1 and 3·25 Hz, 6-H), 3·17 (1H, d, *J* 3·25 Hz, 2-H), and 2·64 (1H, d, *J* 10·1 Hz, 5-H). This product was separated most conveniently when the decomposition mixture was chromatographed (column) on Camag alumina (pH 10) with benzene as eluant; (d) *p*-benzoquinone t-butylimine *N*-oxide, m.p. 73—74°.

(iii) p-*Bromophenyl-t-butylhydroxyamine and the corresponding nitroxide.* (a) *p*-Bromo-*N*-t-butylaniline, $\nu_{max.}$ 3400 cm^{-1}, τ 8·74 (9H, s, Bu^t), 6·53 (1H, s, NH), and 2·7—3·5 (4H, m, ArH); its *benzamide* gave needles, m.p. 137—139° (from petroleum) (Found: C, 61·4; H, 5·5; Br, 24·2; N, 4·3. $C_{17}H_{18}BrNO$ requires C, 61·4; H, 5·4; Br, 24·1; N, 4·2%), τ 8·53 (9H, s, Bu^t), 2·87 (5H, s, Ph), and 2·6—3·2 (4H, m, ArH); (b) *p*-benzoquinone t-butylimine *N*-oxide, m.p. 73—74°; (c) 2-*bromo*-5-(*t-butylamino*)-1,4-*benzoquinone*, purple plates, m.p. 123—124° (from petroleum) (Found: C, 46·8; H, 4·6; Br, 30·4; N, 5·3. $C_{10}H_{12}BrNO_2$ requires C, 46·5; H, 4·65; Br, 31·0; N, 5·4%), $\nu_{max.}$ 3360, 1675, 1645, 1635, and 1615 cm^{-1}, $\lambda_{max.}$ 296 and 500 nm (log ε 4·03 and 3·41), τ 8·60 (9H, s, Bu^t), 4·25br (1H, s, NH), 4·14 (1H, s, 6-H), and 2·84 (1H, s, 3-H); hydrogenation of this quinone (0·15 g) over platinum followed by acetylation with acetic anhydride in pyridine gave, after chromatography on silica gel in chloroform–benzene (1 : 1), 2,5-*diacetoxy*-4-*bromo*-N-*t-butylacetanilide* as a viscous oil (Found: C, 50·5; H, 5·6; N, 3·1. $C_{16}H_{20}BrNO_5$ requires C, 49·8; H, 5·2; N, 3·6%), $\nu_{max.}$ 1760 and 1650 cm^{-1}, τ 8·6 (9H, s, Bu^t), 8·25 (3H, s, NAc), 7·69 (3H, s, OAc), 7·63 (3H, s, OAc), 2·98 (1H, d, *J* 0·2—0·3 Hz, ArH), and 2·46 (1H, d, *J* 0·2—0·3 Hz, ArH); (d) 3-*bromo*-1,4-*benzoquinone t-butylimine* as plates, m.p. 102—104° (from petroleum) (Found: C, 49·6; H, 4·8; Br, 31·7; N, 6·0. $C_{10}H_{12}BrNO$ requires C, 49·6; H, 4·9; Br, 31·0; N, 5·8%), $\nu_{max.}$ 1645 cm^{-1}, $\lambda_{max.}$ 276 nm (log ε 4·86), τ 8·50 (9H, s, Bu^t), 3·51 (1H, q, *J* 10·1 and 3·25 Hz, 6-H), 2·87 (1H, d, *J* 3·25 Hz, 2-H), and 2·60 (1H, d, *J* 10·1 Hz, 5-H); this product was separated most conveniently by chromatography (column) of the decomposition mixtures on Camag alumina (pH 10) with benzene as eluant. When the foregoing quinone imine (0·04 g) in ether (20 ml) was shaken with 2M-hydrochloric acid (5 ml) for 0·5 h and then the ether evaporated, 2-bromo-1,4-benzoquinone, m.p. 52—53° (lit.,[26] 55—56°), was produced.

(iv) p-*Iodophenyl-t-butylhydroxylamine and the corresponding nitroxide.* (a) *p*-Iodo-*N*-t-butylaniline as an oil, b.p. 85—90° at 0·1 mmHg, $\nu_{max.}$ 3400 cm^{-1}, $\lambda_{max.}$ 264 nm, τ 8·69 (9H, s, Bu^t), 6·57 (1H, s, NH), 3·52 (2H, d, *J* 9 Hz, ArH), and 2·62 (2H, d, *J* 9 Hz, ArH). Its *naphthalene*-1,5-*disulphonate* gave cubes, m.p. >310° (from ethanol) (Found: C, 43·2; H, 4·2; I, 30·0; N, 3·5; S, 7·6. $C_{30}H_{36}I_2N_2O_6S_2$ requires C, 43·0; H, 4·3; I, 30·3; N, 3·3; S, 7·6%); (b) *p*-benzoquinone t-butylimine *N*-oxide.

Decomposition of t-Butyl p-*Halogenoaryl Nitroxides and the Corresponding Hydroxylamines in Other Solvents.*—(a) *Cumene.* (i) *p*-Chlorophenyl-t-butylhydroxylamine (250 mg) in cumene (12·5 ml) was allowed to autoxidise during 21 days. The *p*-benzoquinone t-butylimine *N*-oxide (74 mg, 64%) formed was determined spectroscopically (390 nm). (ii) *p*-Fluorophenyl-t-butylhydroxylamine (250 mg) in cumene (13·7 ml) was allowed to decompose during 8 days. *p*-Benzoquinone t-butylimine *N*-oxide (105 mg, 86%) was estimated spectroscopically. Chromatography of the product mixture on silica gel with petroleum as eluant gave, in addition to the usual products, 2,3-dimethyl-2,3-diphenylbutane (3 mg), identical (m.p. and i.r. spectrum) with an authentic specimen.[27]

(b) *Cyclohexene. p*-Bromophenyl t-butyl nitroxide in benzene (10 ml) and cyclohexene (250 mg) was allowed to decompose during 8 days. The absence of 3-bromocyclohexene and 1,2-dibromocyclohexane in the product mixture was established by g.l.c., t.l.c., and n.m.r. spectroscopy.

(c) *Triethylamine. p*-Chlorophenyl-t-butylhydroxylamine (300 mg) in triethylamine (20 ml) was shaken with silver oxide (200 mg) for 45 min. After filtration the solution was evaporated to dryness at room temperature and left for 24 h. Chromatography of the mixture gave *p*-benzoquinone t-butylimine *N*-oxide (92 mg, 68%) and *p*-chloro-*N*-t-butylaniline (*ca.* 140 mg, 100%).

Decomposition of Phenyl t-Butyl Nitroxide.—The rates of decomposition of solutions of (*a*) phenyl t-butyl nitroxide (200 mg) in benzene (10 ml) and (*b*) phenyl t-butyl nitroxide (200 mg) in benzene (10 ml) containing hydrogen chloride (concentration 0·1M) were determined by removing samples (0·5 ml) at intervals of 1 h, diluting them to 10 ml with ethanol and measuring the absorption at 390 nm (due principally to *p*-benzoquinone t-butylimine *N*-oxide). The ratio of the slopes of the plots of concentration of quinone imine *N*-oxide against time (6 h) was approximately 1 : 20 (*a* : *b*).

Preparation of 3-*Bromo*-1,4-*benzoquinone t-Butylimine.*—*p*-Benzoquinone t-butylimine *N*-oxide (0·32 g) in ethanol was hydrogenated over Raney nickel for 2 h. After removal of catalyst and solvent the residue was crystallised from benzene–chloroform to give *p*-hydroxyphenyl-t-butylamine (0·101 g, 35%), m.p. 168—171° (lit.,[28] 167—174°), τ 8·77 (9H, s, Bu^t), 6·95 (1H, s, OH or NH), and 3·31 (4H, s, ArH).

The foregoing amine (60 mg) in benzene (10 ml) was shaken with silver oxide (80 mg) for 10 min. Removal of the solvent left *p*-benzoquinone t-butylimine as a yellow oil,

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$\nu_{max.}$ 1665 cm^{-1}, $\lambda_{max.}$ 272 nm, τ 8·54 (9H, s, Bu^t), 3·52 (2H, d, J 10·2, 2- and 6-H), 3·02 (1H, q, J 10·2 and 2·5 Hz, 3- or 5-H), and 2·66 (1H, q, J 10·2 and 2·5 Hz, 3- and 5-H). This product slowly decomposed (rapidly on attempted distillation). Satisfactory analytical figures were not obtained.

A solution of *p*-benzoquinone t-butylimine (60 mg) in chloroform (10 ml) was saturated with hydrogen bromide. The solvent was removed, the residue was dissolved in benzene, and the solution shaken with silver oxide (80 mg). After removal of silver and solvent the residue was crystallised from petroleum to give 3-bromo-1,4-benzoquinone t-butylimine *N*-oxide (33 mg, 40%), m.p. 99—101°, identical (i.r. and n.m.r. spectra) with that isolated from decomposition of *p*-bromophenyl t-butyl nitroxide.

Preparation of 3-*Chloro*-1,4-*benzoquinone t-Butylimine* N-*Oxide*.—3-Chloro-1,4-benzoquinone t-butylimine (120 mg) was treated with perbenzoic acid (120 mg) in chloroform as in the preceding experiment. Chromatography of the complex mixture produced gave the product (10 mg, 8%), m.p. 81—82°, identical (m.p. and i.r. spectrum) with that obtained on decomposition of *p*-bromophenyl t-butyl nitroxide.

Oxidation of p-*Bromophenyl-t-butylamine with Fremy's Salt*.—The amine (0·2 g) in acetone (20 ml) was treated with Fremy's salt (1·2 g) in aqueous 0·13M-sodium hydrogen phosphate (30 ml) and the mixture was shaken for 2 h. The acetone was then removed and the aqueous residue extracted with chloroform. Chromatography of the complex mixture in the chloroform solution on silica gel in benzene gave, in addition to several unidentified coloured minor products, unchanged amine (86 mg, 43%).

Decomposition of m-*Chlorophenyl t-Butyl Nitroxide*.—*m*-Chlorophenyl-t-butylhydroxylamine (3·0 g) in benzene (100 ml) was shaken with silver oxide (1·85 g) and magnesium sulphate for 30 min. After removal of the inorganic residue the solution was concentrated to 20 ml at room temperature and left for 16 h. It was then chromatographed (column) on silica gel.

(i) Elution with petroleum–ether (93 : 7) gave an orange fraction (1·05 g). This was extracted with 2M-hydrochloric acid and the extracts made alkaline. The oil which separated was extracted into ether and the extracts were dried and evaporated to give *m*-chloro-*N*-t-butylaniline (320 mg, 23%) as an oil, b.p. 70—75° at 0·1 mmHg, $\nu_{max.}$ 3420 cm^{-1}, $\lambda_{max.}$ 257 and 306 nm (log ε 4·08 and 3·26), τ 8·67 (9H, s, Bu^t), 6·50 (1H, s, NH), and 3·6—2·8 (4H, m, ArH). Its *naphthalene*-1,5-*disulphonate* formed crystals, m.p. 308—309° (from ethanol) (Found: C, 55·1; H, 5·2; Cl, 10·9; N, 4·2; S, 9·9. $C_{30}H_{36}Cl_2N_2O_6S_2$ requires C, 54·9; H, 5·5; Cl, 10·8; N, 4·3; S, 9·8%). Chromatography (t.l.c.) of the portion insoluble in acid on silica gel in chloroform gave (*a*) an orange fraction (350 mg) with an R_F value (0·7) identical with that of *m*-chlorophenyl t-butyl nitroxide and (*b*) 3-*chloro*-1,4-*benzoquinone t-butylimine* N-*oxide* (60 mg, 4%) as orange plates, m.p. 78—80° (from benzene–petroleum) (Found: C, 56·5; H, 5·9; Cl, 16·8; N, 6·7. $C_{10}H_{12}ClNO_2$ $C_{10}H_{12}ClNO_2$ requires C, 56·7; H, 5·7; Cl, 16·7; N, 6·6%), $\nu_{max.}$ 1628 and 1618 cm^{-1}, $\lambda_{max.}$ 380 nm (log ε 4·51), τ 8·25 (9H, s, Bu^t), 3·61 and 3·39 (1H, d, J 10 Hz, 5-H), 2·19 and 2·11 (1H, q, J 10 and 3 Hz, 6-H), and 1·99 and 1·90 (1H, d, J 3 Hz, 2-H).

(ii) Elution with petroleum–ether (85 : 15) gave a purple fraction which after t.l.c. on silica gel in petroleum–chloroform (3 : 2) yielded a waxy purple solid (130 mg). This product, which slowly decomposed and hence was not fully identified, had the following spectral characteristics: $\nu_{max.}$ 3380, 1690, 1635, and 1630 cm^{-1}, τ 8·6 (9H, s, Bu^t), 4·25 (1H, d, J 3 Hz), 3·22 (1H, d, J 3 Hz), and 4·1—4·3br (1H, s).

(iii) Elution with petroleum–ether (80 : 20) gave 2-(t-butylamino)-1,4-benzoquinone (77 mg, 4%) as red needles, m.p. 66—67°.

(iv) Elution with petroleum–ether (60 : 40) gave a yellow fraction which after further chromatography on silica gel in benzene–chloroform (1 : 1) yielded 3-chloro-1,4-benzoquinone t-butylimine *N*-oxide (540 mg, 34%), m.p. 78—80°.

Decomposition of m-*Bromophenyl t-Butyl Nitroxide*.—A solution of *m*-bromophenyl t-butyl nitroxide in benzene (20 ml) was prepared by oxidation of the corresponding hydroxylamine (2·5 g) as described for the *m*-chlorophenyl nitroxide and left for 16 h. The mixture was then chromatographed (column) on silica gel.

(i) Elution with petroleum–ether (95 : 5) gave an orange fraction (840 mg) which after t.l.c. in chloroform gave unchanged nitroxide (330 mg) and *m*-bromo-*N*-t-butylaniline (336 mg, 29%) as an oil, b.p. 70—75° at 0·1 mmHg, $\nu_{max.}$ 3400 cm^{-1}, $\lambda_{max.}$ 257 and 308 nm (log ε 4·04 and 3·29), τ 8·70 (9H, s, Bu^t), 6·5br (1H, s, NH), and 3·4—3·0 (4H, m, ArH). Its *naphthalene*-1,5-*disulphonate* formed cubes, m.p. 298—299° (from ethanol) (Found: C, 48·6; H, 5·1; Br, 21·8; N, 3·7; S, 8·6. $C_{30}H_{36}BrN_2O_6S_2$ requires C, 48·4; H, 4·8; Br, 21·5; N, 3·8; S, 8·6%).

(ii) Elution with ether–petroleum (15 : 85) gave a complex brown fraction (130 mg) which was not further examined.

(iii) Elution with ether–petroleum (20 : 80) gave 2-(t-butylamino)-1,4-benzoquinone (27 mg, 2%), m.p. 66—67°.

(iv) Elution with petroleum–ether (60 : 40) gave a yellow fraction (440 mg), t.l.c. of which on silica in chloroform–ether (95 : 5) afforded 3-*bromo*-1,4-*benzoquinone t-butylimine* N-*oxide* (167 mg, 12%) as orange plates, m.p. 96·5—97° (from hexane) (Found: C, 46·8; H, 4·5; Br, 31·3; N, 5·7. $C_{10}H_{12}BrNO_2$ requires C, 46·5; H, 4·6; Br, 31·0; N, 5·4%), $\nu_{max.}$ 1615 cm^{-1}, $\lambda_{max.}$ 269 and 395 nm (log ε 3·50 and 4·39), τ 8·23 (9H, s, Bu^t), 3·6 and 3·38 (1H, d, J 10 Hz, 5-H), 2·19 and 2·11 (1H, q, J 3 and 10 Hz, 6-H), and 1·99 and 1·90 (1H, d, J 3 Hz, 2-H).

(v) Elution with methanol gave a purple mixture which was separated by t.l.c. in chloroform–ether (90 : 10) to give 1,4-benzoquinone t-butylimine *N*-oxide (58 mg), and 2-(N-m-*bromophenyl-t-butylamino*)-6-*t-butylamino*-1,4-*benzoquinone* (25 mg) as a purple oil (Found: *M*, 404·1084. $C_{20}H_{25}BrN_2O_2$ requires *M*, 404·1100), $\nu_{max.}$ 3380, 1690, 1640, and 1620 cm^{-1}, τ 8·63br (18H, s, 2 Bu^t), 4·3 (1H, d, J 3 Hz, 3- or 5-H), and 2·93 (1H, d, J 3 Hz, 3- or 5-H).

Decomposition of o-*Chlorophenyl t-Butyl Nitroxide*.—Oxidation of *o*-chlorophenyl-t-butylhydroxylamine with silver oxide in benzene as previously described gave o-*chlorophenyl t-butyl nitroxide*, as red plates, m.p. 43—43·5° (Found: C, 60·7; H, 6·7; Cl, 17·8; N, 7·3. $C_{10}H_{13}ClNO$ requires C, 60·4; H, 6·5; Cl, 17·9; N, 7·1%), $\lambda_{max.}$ 296 and 495 nm (log ε 3·14 and 1·79). The nitroxide (300 mg) in benzene (5 ml) was allowed to decompose during 1 month. Chromatography of the mixture on silica gel in chloroform–benzene (1 : 1) gave (i) *o*-chloro-*N*-t-butylaniline (25 mg, 34%) as an oil, b.p. 70—75° at 0·1 mmHg, $\lambda_{max.}$ 251 and 302 nm (log ε 4·04 and 3·31), $\nu_{max.}$ 3400 cm^{-1}, τ 8·62 (9H, s, Bu^t), 3·8br (1H, s, NH), and 3·2—2·5 (4H, m, ArH); its *naphthalene*-1,5-*disulphonate* formed cubes, m.p. 269—270° (from ethanol) (Found: C, 54·7; H, 5·7; N, 4·4; S, 9·6. $C_{30}H_{36}Cl_2N_2O_6S_2$ requires C, 55·0; H, 5·5; N, 4·3; S, 9·8%); (ii) *o*-chlorophenyl t-butyl nitroxide (142 mg);

and (iii) the anhydro-dimer of (34) (6 mg), m.p. 247—248° (from hexane) (Found: C, 70·3; H, 7·1%; *M*, 340·1782. Calc. for $C_{20}H_{24}N_2O_3$: C, 70·6; H, 7·1%; *M*, 340·1787), $\nu_{max.}$ 3340, 1780, 1680, and 1640 cm^{-1}, $\lambda_{max.}$ 410 nm (log ε 4·21), τ 8·6 (9H, s, Bu^t), 8·22 (9H, s, Bu^t), 5·83br (1H, s, NH), 4·3—3·9 (4H, m), and 3·5 (1H, m).

Decomposition of o-*Bromophenyl t-Butyl Nitroxide.*—Oxidation of *o*-bromophenyl-t-butylhydroxylamine in benzene with silver oxide as before gave o-*bromophenyl t-butyl nitroxide* as red plates, m.p. 53—54° (Found: C, 49·8; H, 5·3; Br, 33·0; N, 6·0. $C_{10}H_{13}BrNO$ requires C, 49·4; H, 5·4; Br, 32·9; N, 5·8%), $\lambda_{max.}$ 297 and 500 nm (log ε 3·13 and 2·10). The nitroxide (243 mg) in benzene (5 ml) was allowed to decompose during 18 days. T.l.c. of the mixture on silica gel in chloroform gave (i) unchanged nitroxide (70 mg); (ii) *o*-bromo-*N*-t-butylaniline (33 mg, 41%) as an oil, b.p. 75—80° at 0·1 mmHg, $\nu_{max.}$ 3400 cm^{-1}, $\lambda_{max.}$ 254 and 305 nm (log ε 3·97 and 3·32), τ 8·62 (9H, s, Bu^t), 6·0br (1H, s, NH), and 3·8—2·5 (4H, m, ArH); its *naphthalene-1,5-disulphate* formed cubes, m.p. 248—250° (from ethanol) (Found: C, 48·1; H, 4·8; Br, 21·6; N, 3·5; S, 8·5. $C_{30}H_{36}Br_2N_2O_6S_2$ requires C, 48·4; H, 4·8; Br, 21·5; N, 3·8; S, 8·6%); and (iii) the anhydro-dimer of (34) (19 mg), as red plates, m.p. 247—248°.

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