Acyl Nitroxides. Part 3.[1] Reactions with Phenols, Alcohols, Ethers, and Sulphides

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Many monohydric phenols are efficiently oxidised to quinones by acyl t-butyl nitroxides in organic solvents. The reaction, which parallels the Teuber oxidation, fails with phenol itself and with some other simple phenols. Diphenylamine gives *N*-phenyl-*p*-benzoquinone imine.

t-Butyl 3,5-dinitrobenzoyl nitroxide is the nitroxide of choice for selectively oxidising allylic and benzylic alcohols to the corresponding aldehydes and ketones. Saturated secondary alcohols may also be oxidised to ketones, but more slowly.

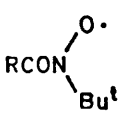
The nitroxides slowly effect α-substitution in ethers; a similar but apparently more rapid, reaction occurs with sulphides.

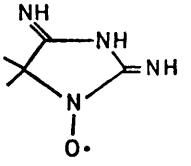
THE preceding paper described a number of free-radical reactions of acyl t-butyl nitroxides.[1] Examples of hydrogen-abstraction reactions and of additions were given, but it was seen that with the less reactive substrates a competing self-reaction of the radical may lead to impaired yields, even when, as with cyclohexane, the substrate is present as the solvent. With more reactive substrates, better yields are obtained, and this led to investigation of possible synthetic applications where selectivity might be achieved by the presence of a site in a molecule particularly vulnerable to free-radical attack.

In view of the inherent stability of acyl nitroxides, and the weakness of the bonds which they form to other atomic centres,[2,3] reactions of these radicals with even the more reactive substrates are likely to be highly selective.

Obvious candidates for investigation as substrates for acyl nitroxide oxidation were the phenols. These are known to be oxidised by the inorganic nitroxide Fremy's radical [$(KOSO_2)_2NO\cdot$], with the formation of quinones, usually in excellent yield.[4] That oxidation (the Teuber reaction) normally involves a heterogeneous system, whereas oxidation with organic nitroxides would allow a homogeneous alternative. Oxidations of phenols using organic nitroxides have been reported before, but yields of quinones were generally disappointing.[5]

In the present work, the relatively reactive benzoyl t-butyl nitroxide (1a) was allowed to react with mono-





(1) a; R = Ph
b; R = $C_{10}H_{21}$
c; R = 3,5-$(O_2N)_2C_6H_3$

(2)

hydric phenols in non-aqueous solvents.[6] In several instances good to excellent yields of quinones were obtained, although for most simple phenols the yields do not compare favourably with those obtained with Fremy's radical.

The results obtained are summarised in Table 1 where comparison is given with the results of other nitroxide oxidations. It is interesting that the most successful of the organic nitroxides previously investigated was porphyrexide (2) which is structurally related to the acyl nitroxides.

The reaction with the acyl nitroxides is presumably similar to that with Fremy's radical, and can be represented as in the Scheme; in successful oxidations with the benzoyl nitroxide, *N*-t-butylbenzohydroxamic acid and *N*-t-butylbenzamide could normally be isolated in good yield.

Phenol itself reacts rapidly with (1a), and both the above by-products could be detected among the reaction products; the amide was isolated in near-quantitative yield. However no trace of 1,4-benzoquinone could be detected in the reaction mixture, and the products from the phenol have not been identified. In some of the successful reactions it was clear that if the substituted quinone was not isolated as soon as reaction was complete the yield deteriorated, but it was easily established that benzoquinone itself did not react rapidly with any of the expected products of phenol oxidation, or with the initial nitroxide. When the progress of the oxidation of unsubstituted phenol was monitored, at no stage was benzoquinone detected.

Somewhat similar observations were made with some other simple phenols, including *p*-cresol. In other cases where the phenol had a blocked *para*-position (*e.g.* β-naphthol and 4-t-butylphenol), an *ortho*-quinone was obtained. The formation of an *ortho*-quinone was also observed from 3-t-butylphenol which suggests a marked steric inhibition of the second (coupling) stage in the Scheme.

Oxidation of 2,4,6-trimethylphenol by two equivalents of (1a) gave a quantitative yield of (5) rather than the expected dienone (4a). Presumably the trimethylphenoxyl radical loses hydrogen to a second nitroxide radical to give the quinone methide (3), which then combines with a further nitroxide radical, and finally acquires a hydrogen atom either from another molecule of trimethylphenol or from the hydroxamic

TABLE 1

Oxidation of phenols with nitroxides (2 equiv.)

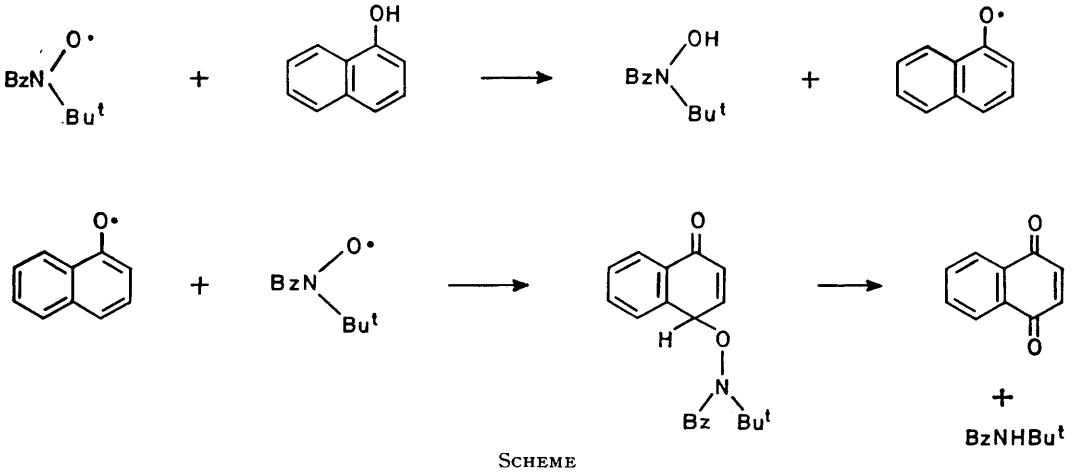
Phenols	Product	Yield (%) using: Fremy's radical [4]	PhCON(Bu^t)O· (this work)	Other nitroxides [5]
Unsubstituted	*p*-Benzoquinone	81	0	0
2,6-Me_2	2,6-Dimethyl-*p*-benzoquinone	75	86 *	
3,5-Me_2	2,6-Dimethyl-*p*-benzoquinone	99	0	
2,5-Me_2	2,5-Dimethyl-*p*-benzoquinone	87	42	61
2-Bu^t	2-t-Butyl-*p*-benzoquinone		60	
3-Bu^t	4-t-Butyl-*o*-benzoquinone		70	
4-Bu^t	4-t-Butyl-*o*-benzoquinone	80	51	
2,6-Cl_2	2,6-Dichloro-*p*-benzoquinone		46	
2,6-$(OMe)_2$	2,6-Dimethoxy-*p*-benzoquinone		60	
3,5-$(OMe)_2$	2,6-Dimethoxy-*p*-benzoquinone	76	60	45
2,4-Bu^t_2	3,5-Di-t-butyl-*o*-benzoquinone		87	
2,3,5,6-Me_4	Duroquinone	87	67	85
α-Naphthol	α-Naphthoquinone	81	72	Trace
β-Naphthol	β-Naphthoquinone	91	84	0
9-Anthranol	Anthraquinone		93	
p-Dihydroxybenzene	*p*-Benzoquinone		91	
3,5-Di-t-butylcatechol	3,5-Di-t-butyl-*o*-benzoquinone		95	

* A yield of 52% was obtained when t-butyl undecanoyl nitroxide (1b) was employed.

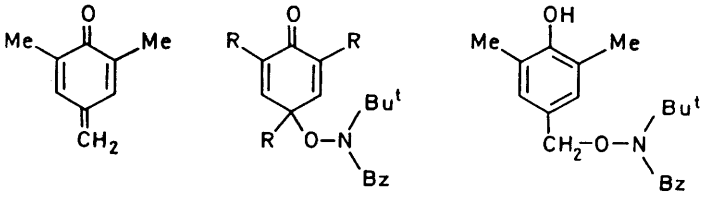
acid which is formed. The formation of a single product has interesting implications for the relative reactivities of the hydrogens in the 2- and 4-methyl groups of the 2,4,6-trimethylphenoxyl radical and of the methylene hydrogens in the phenoxyl radical derived from (3) (since this clearly does not react further).

It seems probable that (4a) is formed, but *reversibly*, since a crystalline dienone (4b) which was isolated (95%) from the oxidation of 2,4,6-tri-t-butylphenol exists (in oxygen-free solution) in equilibrium with a mixture of the nitroxide and tri-t-butylphenoxyl. Reversible coupling of this phenoxyl radical with diphenyl nitroxide has been known for some time.[7]

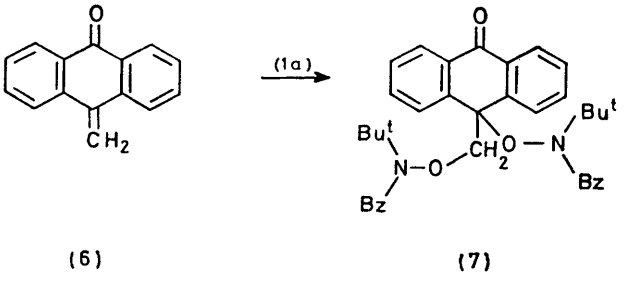
The proposed behaviour of the quinone methide (3) is supported by the reaction of 10-methyleneanthrone (6) towards the nitroxide; there is reversible addition to form a product believed to be (7). No reaction occurs between (6) and *N*-t-butylbenzohydroxamic acid in the absence of nitroxide.



SCHEME



(3) (4) a; R = Me b; R = Bu^t (5)



(6) (7)

Oxidations of quinol to 1,4-benzoquinone and of 3,5-di-t-butylpyrocatechol to the corresponding *ortho*-quinone were also essentially quantitative. Reaction

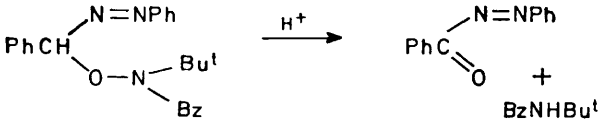
with pyrocatechol itself was equally rapid, and a high yield of *ortho*-benzoquinone was suggested by spectroscopic study. However, in this case isolation of the quinone was difficult, and the nitroxide clearly has no general merit over such oxidants as *o*-chloranil [8] and Fetizon's reagent [9] for the conversion of pyrocatechols to *ortho*-quinones.

Akin to the oxidation of monohydric phenols, is the high-yield conversion of diphenylamine into *N*-phenyl-1,4-benzoquinone imine by the benzoyl nitroxide. However, separation of the product from the accompanying *N*-t-butylbenzamide proved difficult. Isolation of the quinone imine constituted a less serious problem when t-butyl undecanoyl nitroxide (1b) was employed as oxidant, because of the high solubility in hydrocarbon solvents of the nitroxide-derived products. Taking account of the wide range of acyl nitroxides now available, this example highlights the possibility of tailoring a nitroxide reagent to a particular oxidation problem.

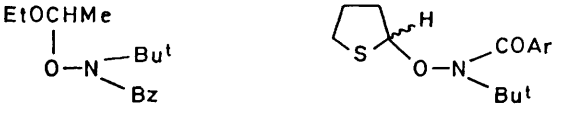
Oxidation of other amines has not been extensively explored. We were unable to identify products from phenothiazine, or from selected indoles. Although these reactions did not appear to parallel those [4b] with Fremy's radical, they have received only cursory attention.

Not unexpectedly, hydrazobenzene reacts rapidly with two equivalents of (1a) to give azobenzene quantitatively, and oxidations of phenylhydrazine and of hydrazine itself are also rapid, although product studies have not been undertaken. Oxidation of *N*-t-butylhydroxylamine gives 2-methyl-2-nitrosopropane.

Oxidation of benzaldehyde phenylhydrazone also occurred cleanly, giving a product (8). A trace of acid



(8)



(9) (10)

apparently causes this to break up into *N*-benzoyl-*N'*-phenyldiazene, and *N*-t-butylbenzamide. The red diazene is itself acid-labile,[10] and was not isolated.

In the course of these experiments, diethyl ether was occasionally used as a solvent for benzoyl t-butyl nitroxide. It rapidly became evident, however, that this was unsuitable since slow reaction of the radical with the solvent occurred. Evidently the hydrogens on C-1 are sufficiently easily abstracted by the nitroxide for the substitution product (9) to be obtained. Presumably this largely reflects a polar effect in the hydrogen transfer, since the CH bond is weakened by only *ca.* 12—13 kJ mol^{-1} by the presence of the oxygen atom.[11] A similar hydrogen abstraction by the more reactive phthalimide *N*-oxyl is probably a key step in the oxidation of ethers to aldehydes by dimethyl azodicarboxylate in the presence of *N*-hydroxyphthalimide, followed by hydrolysis of the product.[12]

The observations above prompted an investigation of the oxidation of alcohols using stoicheiometric quantities (2 equivalents) of acyl nitroxide. The reaction was particularly successful with benzylic and allylic alcohols, especially when the more reactive 3,5-dinitrobenzoyl nitroxide was employed. Only with primary saturated alcohols was the reaction wholly unsuccessful, the product aldehyde here being more reactive than the alcohol. Particularly interesting was the oxidation of *meso*- to benzil without detectable fission of the central bond. Results are summarised in Table 2. Where the

TABLE 2

Oxidation of alcohols by acyl t-butyl nitroxides

Alcohol	Reagent [a]	Product (%) [b]
Bu^{n}OH	(1a)	Pr^{n}CHO (0)
Bu^{n}OH	(1c)	Pr^{n}CHO (*ca.* 10)
Cyclohexanol	(1a)	Cyclohexanone (37)
Cyclohexanol	(1c)	Cyclohexanone (51) [c]
$PhCH_2OH$	(1a)	PhCHO (50)
$PhCH_2OH$	(1c)	PhCHO (61) [c]
$PhCH{=}CHCH_2OH$	(1a)	PhCH=CHCHO (72)
$PhCH{=}CHCH_2OH$	(1c)	PhCH=CHCHO (83) [b]
Cyclohexenol	(1a)	Cyclohexenone (61)
Cyclohexenol	(1c)	Cyclohexenone (93)
Ph_2CHOH	(1a)	Ph_2CO (95) [b]
PhCHOHCHOHPh	(1a) [d]	PhCOCOPh (89) [b]

[a] Two equiv. [b] By g.l.c. except cases marked *b*, which were by isolation. [c] Yield raised by using 2.5—3 equivs. of nitroxide; in no case have yields been optimised. [d] Four equivs. of radical.

dinitrobenzoyl nitroxide was used, a high yield of insoluble *N*-t-butyl-3,5-dinitrobenzohydroxamic acid was obtained. This may readily be re-oxidised to the radical.

In one experiment it was shown that diphenylmethanol could be oxidised to benzophenone by alkaline ferricyanide in a heterogeneous system, using *N*-t-butylbenzohydroxamic acid as a catalyst. Curiously, however, the benzoyl nitroxide could not be induced to catalyse the oxidation of alcohols by *m*-chloroperoxybenzoic acid.[13]

It is well known that sulphur is generally better at stabilising an adjacent radical centre than is oxygen, and this prompted cursory examination of the reaction of acyl nitroxides with the thioether, tetrahydrothiophen. There has been some interest in functionalisation α to sulphur; a recent example occurs in an approach to penicillin total synthesis.[14] With tetrahydrothiophen in excess, the dinitrobenzoyl nitroxide reacts to give α-substitution apparently almost quantitatively. No attempt has yet been made to investigate the chemical manipulation of the product [10; Ar = 3,5-$(O_2N)_2$-C_6H_3].

EXPERIMENTAL

General procedures and instrumentation were as reported in Part 1. Substrates for oxidation were normally purified by crystallisation or distillation prior to use.

Oxidation of Phenols: (i) *Phenol.* (a) Addition of a solution of phenol (sublimed, 97 mg, 1.03 mmol) in dichloromethane (25 cm³) to a stirred deoxygenated solution of benzoyl t-butyl nitroxide (396 mg, 2.06 mmol in 25 cm³ CH_2Cl_2) resulted in a slow colour change from green to golden-yellow. T.l.c. examination at this stage was complicated by rapid decomposition (to a brown-red colour) upon 'spotting' the silica surface. Comparison with pure reference samples, however, revealed formation of both *N*-t-butylbenzamide and *N*-t-butylbenzohydroxamic acid and a trace (*ca.* 5%) of unchanged phenol. 1,4-Benzoquinone could not be detected.

Solvent removal afforded a non-crystallisable brown oil (493 mg, 100%) which was taken up in dichloromethane (50 cm³) and washed with (i) 2M-NaOH (2 × 50 cm³), (ii) water (3 × 50 cm³), and finally dried ($MgSO_4$). Evaporation under reduced pressure afforded a slightly pink solid (197 mg, m.p. >100 °C) which recrystallised from hexane as colourless needles (162 mg). This product was shown (i.r., t.l.c., and mixed m.p.) to be identical with an authentic specimen of *N*-t-butylbenzamide (0.91 mmol, 89%).

(b) Several unsuccessful attempts were made to isolate or identify 1,4-benzoquinone from this reaction. Treatment of phenol with 2 mol equivalents of the undecanoyl nitroxide (1b), for example, produced a similar golden-yellow solution (3 min) but ^1H n.m.r. examination failed to reveal the expected δ 6.78 benzoquinone CH singlet. Instead, a broad phenyl-type pattern was observed in the aromatic region: δ 6.73 and 7.00 (max., relative integrated areas 3 : 2). A similar result was obtained using 2 mol equivalents of t-butyl 4-nitrobenzoyl nitroxide.

Finally, the reaction was repeated using the undecanoyl nitroxide in dry hexane solution and, once the yellow stage had been attained, two further equivalents of phenol were added to induce π-complex formation. No such complex was isolated despite marked solution darkening. A 2 : 1 π-complex was, however, easily isolated from an artificial solution containing 1,4-benzoquinone and phenol at the concentrations used in the oxidation experiment.

(c) Benzoyl t-butyl nitroxide, *N*-butylbenzohydroxamic acid, and *N*-t-butylbenzamide were separately demonstrated to have no effect upon solutions of pure 1,4-benzoquinone. Admixtures of these three compounds similarly showed no reaction with the quinone.

(ii) *α-Naphthol.* A solution of freshly crystallised 1-naphthol (135 mg, 0.94 mmol) in CH_2Cl_2 (15 cm³) was added to neat benzoyl t-butyl nitroxide (360 mg, 1.87 mmol) in one portion. Light petroleum (b.p. 60—80 °C; 20 cm³) was then added to the yellow solution which resulted, and the more volatile solvent was removed using a fast stream of nitrogen. The crystalline solid which formed was recovered by filtration (234 mg), and then subjected to column chromatography [silica gel, PhH–CH_2Cl_2 (9 : 1)] to remove the *N*-t-butylbenzohydroxamic acid present (t.l.c.). Evaporation of the eluted yellow band afforded 1,4-naphthoquinone (107 mg, 72%) as yellow needles, m.p. 123—124 °C (lit. m.p. 125 °C).

(iii) *β-Naphthol.* A solution of freshly crystallised 2-naphthol (138 mg, 0.96 mmol in 20 cm³ dry ether) was added in one portion to the benzoyl nitroxide (369 mg, 1.92 mmol). T.l.c. inspection of the yellow-orange solution which immediately resulted revealed complete removal of both the phenol and the nitroxide, and apparently 'clean' (quantitative) formation of amide, hydroxamic acid, and an orange compound. Petroleum (b.p. 40—60 °C, 5 cm³) was added and, after chilling, a precipitate of orange needles was recovered by filtration, washed with cold hexane (10 cm³), and finally dried [127 mg, 84%, m.p. 145—146 °C (decomp.)]. This product possessed spectral parameters consistent with those reported [15] for 1,2-naphthoquinone [lit. m.p. 146 °C (decomp.)].

(iv) 2,6-*Xylenol.* Recrystallised 2,6-xylenol (82 mg, 0.67 mmol) was added to a solution of the benzoyl nitroxide (259 mg, 1.34 mmol) in dry dichloromethane (25 cm³). Two evaporations to dryness with further CH_2Cl_2 resulted in a rapid colour change from green to yellow, and t.l.c. inspection revealed quantitative removal of the phenol. Column chromatographic separation (silica gel, CH_2Cl_2) of the yellow band afforded, after solvent removal, yellow needles (79 mg, 86%, m.p. 70—72 °C) with spectral parameters consistent with those reported [15] for 2,6-dimethyl-1,4-benzoquinone (lit. m.p. 72—73 °C).

(v) 2,4-*Di-t-butylphenol and* 3,5-*di-t-butylpyrocatechol.* A solution of benzoyl t-butyl nitroxide (269 mg, 1.40 mmol) and 2,4-di-t-butylphenol (144 mg, 0.70 mmol) in carbon tetrachloride (15 cm³) was gently refluxed. After 10 min, t.l.c. inspection of the now red solution revealed both the phenol and the nitroxide to have been removed. Solvent removal under reduced pressure gave a red-green crystallisable oil (413 mg, 100%) which was subjected to preparative t.l.c. (silica gel, CH_2Cl_2). The three product bands were extracted using diethyl ether–CH_2Cl_2 (50 : 50, v/v).

Evaporation of the separate extracts containing the two most polar components afforded *N*-t-butylbenzohydroxamic acid (124 mg, 0.64 mmol, 91%) and *N*-t-butylbenzamide (117 mg, 0.66 mmol, 95%), both of which were shown to be identical (i.r., t.l.c., and mixed m.p.) with authentic specimens.

Solvent removal from the yellow extract containing the least-polar product gave a red oil which rapidly crystallised to bright red needles (134 mg, 87%, m.p. 111—112 °C). One crystallisation from hexane afforded dark red prisms, m.p. 112—113 °C, with spectral parameters consistent with those reported [15] for 3,5-di-t-butyl-1,2-benzoquinone (lit.,[15] m.p. 111—113 °C).

Oxidation of di-t-butylpyrocatechol in CH_2Cl_2 was rapid and gave the same product (96% after t.l.c.).

(vi) Oxidation of other phenols listed in Table 1 followed procedures adapted from those in (ii) and (iv) above. The yields recorded are of isolated quinones.

(vii) 2,4,6-*Trimethylphenol.* 2,4,6-Trimethylphenol (233 mg, 1.71 mmol) was added in one portion to a freshly prepared solution of the benzoyl nitroxide (658 mg, 3.42 mmol) in dry diethyl ether (30 cm³). Reaction was slow at room temperature (t.l.c.) but gentle reflux for 5 min effected discharge of the green colour, and t.l.c. revealed quantitative removal of both the phenol and the nitroxide. Solvent removal afforded a yellow oil (891 mg, 100%) which was taken up in diethyl ether (30 cm³), washed with 2M-NaOH (2 × 30 cm³) and water (3 × 30 cm³), and dried (Na_2SO_4).

Acidification of the combined alkaline extracts to pH 1 (12M-HCl) and extraction with diethyl ether (2 × 50 cm³) afforded *N*-t-butylbenzohydroxamic acid (323 mg, 98%),

identical by i.r., t.l.c., and m.p. with an authentic pure specimen.

Evaporation of the pale yellow organic layer gave a yellow oil which rapidly crystallised on standing. One recrystallisation from hexane afforded colourless prisms (538 mg, 96%), m.p. 130—132 °C (decomp. >125 °C). From spectroscopic and analytical data this product was identified as N-*benzoyl*-O-(4-*hydroxy*-3,5-*dimethylbenzyl*)-N-*t-butylhydroxylamine* (5); $\nu_{max.}$ (Nujol) 3 260 and 1 623 cm^{-1}; δ($CDCl_3$) 1.59 (s, 9 H, Bu^t), 2.03 (s, 6 H, 2 Me), 4.33 (broad s, 2 H, CH_2), 5.2 (broad, 1 H, OH), 6.18 (s, 2 H, arom), and 7.20—7.65 (m, 5 H, Ph) (Found: C, 73.6; H, 7.7; N, 4.5. $C_{20}H_{25}NO_3$ requires C, 73.4; H, 7.7; N, 4.3%).

(viii) 2,4,6-*Tri-t-butylphenol*. A solution of 2,4,6-tri-t-butylphenol (486 mg, 1.85 mmol) in dry diethyl ether (20 cm^3) was added to neat benzoyl t-butyl nitroxide (713 mg, 3.71 mmol) during 5 min. The pale green solution which resulted (<10% of the nitroxide remained) was washed (2M-NaOH, 3 × 25 cm^3; water, 3 × 25 cm^3) and dried (Na_2SO_4). The alkaline extracts were combined and acidified to give *N*-t-butylbenzohydroxamic acid (303 mg, 84%). Solvent was removed from the organic layer without heating to leave a pale yellow solid (833 mg). Crystallisation from aqueous methanol without heating gave pale yellow needles (795 mg, 95%), m.p. 131—132 °C (decomp., green melt). This product had $\nu_{max.}$ (CCl_4) 1 691, 1 669, 1 648, 1 621, and 1 601 cm^{-1}, considered to accord with the cyclohexa-2,5-dienone *derivative* (4b). The same product was obtained on mixing (N_2) solutions of 2,4,6-tri-t-butylphenoxyl [16] and the nitroxide. When the product was dissolved in CCl_4 (N_2) a blue-green solution was obtained, the colour intensity of which increased on warming but was discharged on cooling. Examination by e.s.r. (N_2) confirmed the presence of the acyl nitroxide and the phenoxyl in the solution.

(ix) *Reactions of benzoyl t-butyl nitroxide with* 10-*methyleneanthrone*. A solution of 10-methyleneanthrone [17] (127 mg, 0.61 mmol) in CH_2Cl_2 (15 cm^3), was added dropwise to a stirred solution of benzoyl t-butyl nitroxide (236 mg, 1.23 mmol) in CH_2Cl_2 (5 cm^3) under nitrogen. The colour of the radical rapidly faded, but was not completely discharged. Removal of solvent gave an amorphous, almost colourless solid (362 mg, *ca.* 100%). Crystallisation from hexane–CH_2Cl_2 gave a colourless solid, m.p. 132—133 °C (decomp.) having $\nu_{max.}$ (Nujol) 1 665, 1 646, and 1 640 cm^{-1}. In $CDCl_3$ the initially pale yellow solution rapidly became green; the n.m.r. spectrum was consequently broad: δ($CDCl_3$) 0.81 (s, 9 H, Bu^t), 1.03 (s, 9 H, Bu^t), 4.01 (broad, 2 H, CH_2), 6.80—7.80 (m, 16 H, arom), and 8.0—8.5 (m, 2 H, H-1,8) (Found: C, 75.3; H, 6.3; N, 4.7%. $C_{37}H_{38}N_2O_5$ requires C, 75.2; H, 6.5; N, 4.7%). The data are considered consistent with the *adduct* [(7), 97%]. In dilute solution this product was in equilibrium with the reactants (t.l.c.).

Oxidation of Diphenylamine.—A solution of diphenylamine (507 mg, 3 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of t-butyl undecanoyl nitroxide (1.53 g, 6 mmol) in CH_2Cl_2 (10 cm^3), and the mixture was boiled under reflux until the reactants had been consumed (t.l.c.). The resulting red-brown solution was immediately chromatographed on silica gel. Elution with CH_2Cl_2–diethyl ether (19 : 1) gave a red fraction which on removal of solvent left a red oil. This yielded crystals of *N*-phenyl-1,4-benzoquinone imine (327 mg, 65%) on treatment with hexane (m.p. 102 °C from hexane).

Oxidation of Benzaldehyde Phenylhydrazone.—A solution of freshly crystallised benzaldehyde phenylhydrazone (372 mg, 1.89 mmol) in dry diethyl ether (30 cm^3) was added to a solution of benzoyl t-butyl nitroxide (732 mg, 3.81 mmol) in diethyl ether (10 cm^3). The green colour of the radical was immediately replaced by a golden yellow colour. T.l.c. examination revealed quantitative removal of both reactants, and apparently clean formation of *N*-t-butylbenzohydroxamic acid and a less-polar yellow compound.

The benzohydroxamic acid was removed (t.l.c.) by extraction with 2M-NaOH (3 × 25 cm^3), and the organic layer was then washed with water (3 × 30 cm^3) and dried (Na_2SO_4). Solvent removal under reduced pressure afforded a yellow amorphous solid (731 mg), 118—120 °C. Recrystallisation from aqueous methanol (10% v/v H_2O, 30 cm^3) furnished yellow needles (688 mg), m.p. 125—126 °C. This had $\nu_{max.}$ (CCl_4) 1 654; δ(acid-free $CDCl_3$) 1.54 (s, 9 H, Bu^t), 5.54 (broad, 1 H, not removed by D_2O, >CHO–), and 7.0—7.8 (m, 15 H, 3 Ph) (Found: C, 74.6; H, 6.6; N, 10.9. $C_{24}H_{25}N_3O_2$ requires C, 74.4; H, 6.5; N, 10.9%). These parameters are consistent with the identification of this product as the *azo-compound* (8). Treatment of the product with DCl–D_2O–$CDCl_3$ led to the formation of *N*-t-butylbenzamide and a red product considered to be *N*-benzoyl-*N'*-phenyldiazene. This was not isolated.

Reaction of Benzoyl t-Butyl Nitroxide with Diethyl Ether.—A solution of the nitroxide (340 mg) in dry diethyl ether (500 cm^3) was deoxygenated (N_2), and left in the dark until the colour was discharged (11 days). *N*-t-Butylbenzohydroxamic acid (148 mg, 85%) was then extracted with base; the remaining ethereal solution was dried (Na_2SO_4) and evaporated to leave a pale green oil. P.l.c. (silica gel, CH_2Cl_2) gave a colourless oil with spectroscopic parameters consistent with its formulation as N-*benzoyl*-O-(1-*ethoxyethyl*)-N-*t-butylhydroxylamine* (220 mg, 92%), $\nu_{max.}$ (CCl_4) 1 643 cm^{-1}; δ($CDCl_3$) 0.92 (d, 3 H, CH_3), 1.01 (t, 3 H, CH_3), 1.48 (s, 9 H, Bu^t), 3.10—3.76 (4 q, 2 H, $CH_AH_BCH_3$), 4.48 (q, 1 H, CH), and 7.15—7.70 (m, 5 H, Ph). Irradiation at δ 1.01 reduced the signal at *ca.* δ 3.5 to an AB quartet.

Reaction of Nitroxides with Tetrahydrothiophen.—(a) A solution of benzoyl t-butyl nitroxide (468 mg) in tetrahydrothiophen (15 cm^3) was stirred at room temperature until the colour was discharged (*ca.* 2 h) and solvent was then removed under reduced pressure. The residue was dissolved in diethyl ether, *N*-t-butylbenzohydroxamic acid was extracted with base, and the dried ethereal solution was evaporated to leave a pale yellow oil which crystallised on standing. Colourless crystals, m.p. 81 °C (200 mg, *ca.* 60%), were obtained from hexane, and are considered to be the tetrahydrothiophen *derivative* (10; Ar = Ph), $\nu_{max.}$ (Nujol) 1 640 cm^{-1}; δ(CCl_4) 1.53 (s, 9 H, Bu^t), 0.69—2.65 (m, 6 H), 5.35 (broad 1 H), and 7.08—7.61 (m, 5 H, Ph) (Found: C, 63.9; H, 7.5; N, 5.2%. $C_{15}H_{21}NO_2S$ requires C, 64.5; H, 7.6; N, 5.0%).

(b) A similar reaction was carried out using 3,5-dinitrobenzoyl t-butyl nitroxide. Disappearance of the radical was rapid, and spectroscopic examination of the reaction mixture after removal of excess of tetrahydrothiophen suggested a near quantitative transformation into *N*-t-butyl-3,5-dinitrobenzohydroxamic acid and the dinitrobenzoyl analogue of (10). However, the product decomposed during work-up, and the reaction has not been examined further.

Oxidation of Alcohols. (i) *Diphenylmethanol*. (a) A solution of diphenylmethanol (239 mg, 1.3 mmol) and the

benzoyl nitroxide (430 mg, 2.24 mmol) in dry benzene (15 cm^3) was refluxed for 35 min. After removal of solvent, the residue was separated by p.l.c. (silica gel, CH_2Cl_2). This gave *N*-t-butylbenzohydroxamic acid (415 mg, 96%), recovered diphenylmethanol (25 mg), and benzophenone (195 mg, 92%). (b) A benzene solution of diphenylmethanol (1.0 g in 15 cm^3) was refluxed together with a solution of $K_3Fe(CN)_6$ (7.5 g) in 2M-NaOH (30 cm^3) for 5 h. No oxidation was detected (t.l.c.). *N*-t-Butylbenzohydroxamic acid (100 mg) was added to an identical mixture, and the solution boiled under reflux for $4\frac{1}{2}$ h. From the green benzene layer was isolated benzophenone (0.98 g, *ca.* 100%) as colourless prisms, m.p. 48—49 °C.

(ii) meso-1,2-*Diphenylethane*-1,2-*diol*. The diol (278 mg, 1.30 mmol) and the benzoyl nitroxide (989 mg, 5.18 mmol) in benzene (50 cm^3) were boiled under reflux for 5 h. The solution was diluted with diethyl ether (80 cm^3), washed with 2M-NaOH (3 × 30 cm^3) and water, and then dried. From the alkaline extract was recovered *N*-t-butylbenzohydroxamic acid (862 mg, 86%). The organic solution yielded benzil, m.p. 94—95 °C (from hexane) (241 mg, 89%). Traces of benzoin and *NO*-dibenzoyl-*N*-t-butylhydroxylamine [1] were also detected among the products.

(iii) *Other Alcohols*. Oxidations of liquid alcohols were carried out according to the following general procedure. The alcohol (0.5 mmol) and the nitroxide (*ca.* 1.05 mmol) were dissolved in dry benzene (1 cm^3), and the mixture refluxed until the colour of the radical was discharged. A known quantity of reference material was added for g.l.c. analysis on fluorinated silicone oil or bis-(3,3,5-trimethylcyclohexyl) phthalate. The results are summarised in Table 2. No attempt has been made to optimise yields.

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