Alkyl Nitrenes from *N*-Alkylbenzoquinone Imine *N*-Oxides

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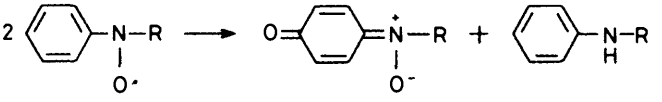
Alkyl nitrenes have been generated by photolysis of two *N*-t-alkylbenzoquinone imine *N*-oxides. These mainly abstract hydrogen to give the corresponding amines which are trapped by reaction with benzoquinone. Intramolecular hydrogen abstraction followed by cyclisation to give a pyrrolidine is a minor process in one case.

Attempts to generate α-substituted benzyl nitrenes in this way led mainly to the production of substituted benzyl radicals by C–N bond cleavage of the *N*-benzylbenzoquinone imine *N*-oxides.

ALKYL nitrenes are most commonly produced by photolysis of azides.[1] The multiplicity of the species formed, or whether it is the result of reaction of nitrenes or of excited azides, is not always clear. Accordingly, we have sought a new route by extending our quinone imine *N*-oxide method [2] to the generation of alkyl nitrenes.

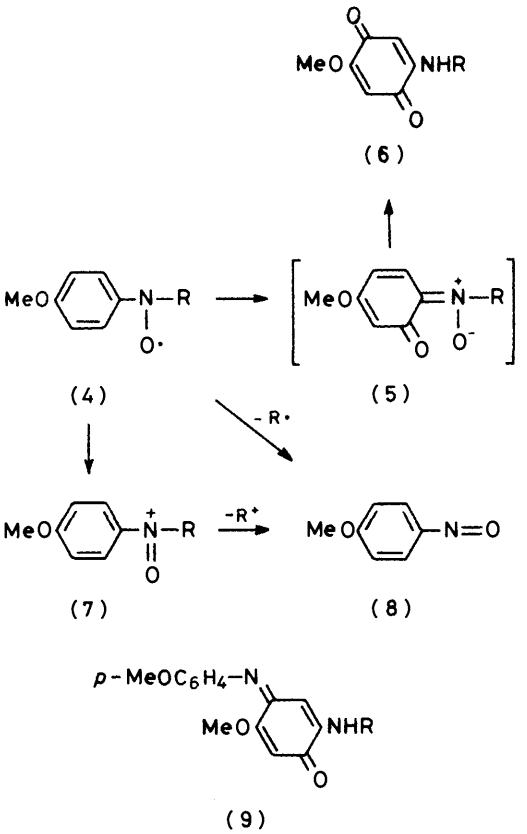
N,N'-Dialkylbenzoquinone di-imine *N,N'*-dioxides are less accessible than their aryl analogues and hence the more readily available *N*-alkylbenzoquinone imine *N*-oxides (2) were used. For simplicity two *N*-t-alkylbenzoquinone imine *N*-oxides (2; R = Bu^t and Oct^t; Oct^t = $CMe_2CH_2Bu^t$) were chosen since these were easier to prepare and should give t-alkyl nitrenes which undergo fewer reactions than their primary and secondary analogues [1] (*e.g.* no aldimine formation). There is the additional possibility with compound (2; R = Oct^t) that the resulting alkyl nitrene could form a pyrrolidine, a reaction still to be established for alkyl nitrenes.[3]

Preparation of N-*t-Alkylbenzoquinone Imine* N-*Oxides* (2; R = Bu^t, Oct^t).—Quinone imine *N*-oxides are usually



(1) (2) (3)

major products of the spontaneous decomposition of t-alkyl aryl nitroxides (1) with a free *para*-position [4a] or with a *para*-substituent (Cl, Br) which is easily displaced.[4b] We have prepared a number of these compounds in this way, but since the nitroxide gives equal amounts of the corresponding secondary amine (3) and quinone imine *N*-oxide (2), isolated yields of the latter product are 40—50% at best. Oxidation of *p*-methoxyphenyl t-butyl nitroxide (4; R = Bu^t) with an excess of silver(II) oxide gave a much higher yield of quinone imine *N*-oxide (2; R = Bu^t) and because of this we initially attempted a similar preparation of the t-octyl analogue (2; R = Oct^t). Oxidation of the appropriate hydroxylamine proceeded *via* the nitroxide (4; R = Oct^t) (a_N = 12.75, $a_{o\text{-}H}$ = 2.0, $a_{m\text{-}H}$ = 1.0 G) and yielded a complex mixture of products from which the desired quinone imine *N*-oxide (2; R = Oct^t) was isolated in only 9% yield. The major product was the t-octylaminobenzoquinone (6; R = Oct^t) (31%) with minor amounts of a quinone imine [probably (9; R = Oct^t)], *p*-nitrosoanisole (8), and benzoquinone oxime (see Experimental section for spectroscopic details). The t-octylaminobenzoquinone (6; R = Oct^t) is a decomposition product of the nitroxide (4; R = Oct^t) and its formation *via* isomerisation of the *o*-quinone imine *N*-oxide (5; R = Oct^t) under the influence of the nitroxide (4; R = Oct^t) can be accounted for as previously described [5] for the corresponding aminoquinone from *p*-methoxyphenyl t-butyl nitroxide (4; R = Bu^t). *p*-Nitrosoanisole was an unexpected product and must arise either by homolysis of the nitroxide (4; R = Oct^t) or more probably by heterolysis of the oxoammonium ion [6] (7; R = Oct^t), an oxidation product of nitroxide (4; R = Oct^t). There are several ways in which the quinone imine (9; R = Oct^t) could arise, none of which has been established, but reaction of the *o*-quinone imine *N*-oxide (5; R = Oct^t) with nitrosoanisole

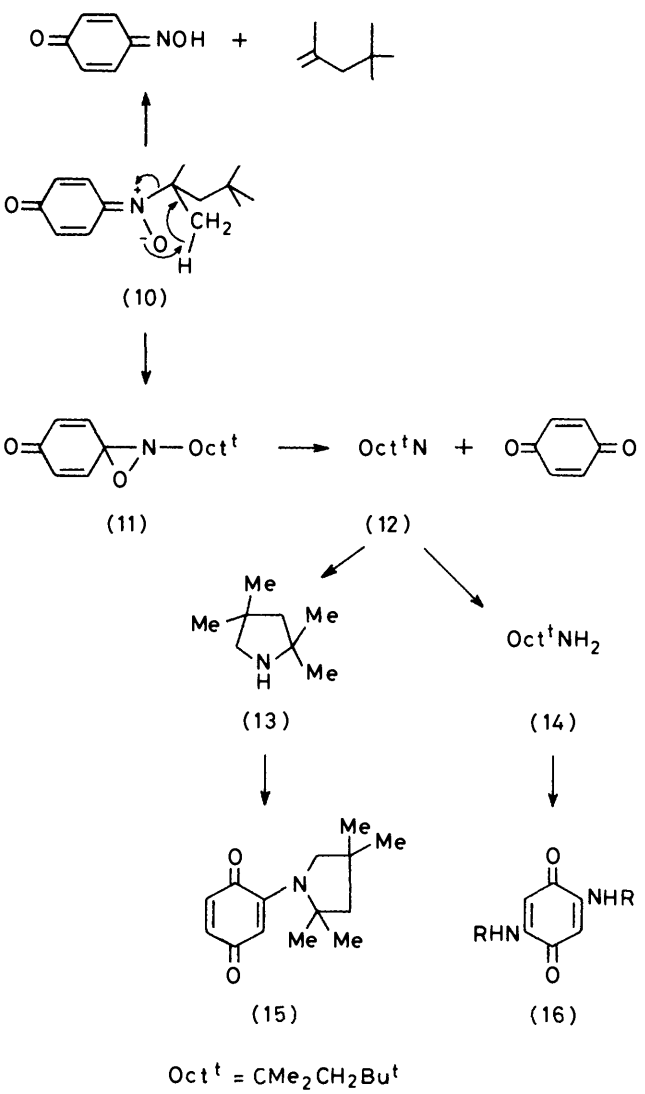


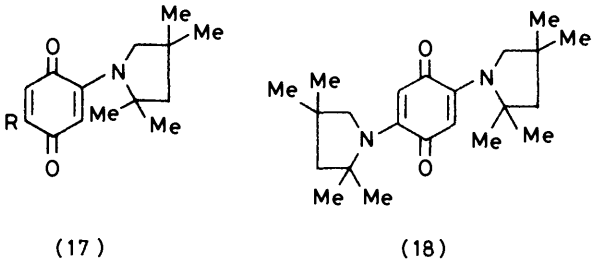
(6) (4) (5) (7) (8) (9)

is a likely possibility. Benzoquinone oxime is a thermal decomposition product of the quinone imine *N*-oxide (2; R = Oct^t). Although the quinone imine *N*-oxide (2; R = Oct^t) was produced in higher yield by spontaneous decomposition of phenyl t-octyl nitroxide (1; R = Oct^t) (a_N = 12.2; $a_{o,p\text{-}H}$ = 2.0, $a_{m\text{-}H}$ = 0.95 G), the best (almost quantitative) yields were obtained when the nitroxide (1; R = Oct^t) or its hydroxylamine precursor were oxidised with an excess of the readily available Fremy's salt.[7] The method is analogous to that used for the preparation of quinones from phenols and amines.[7]

The quinone imine *N*-oxides (2; R = Bu^t and Oct^t) were obtained as orange crystalline solids, the n.m.r. spectra of which showed the non-equivalence of the four quinonoid protons.[4a,8] Although compound (2; R = Bu^t) was stable indefinitely in the dark, the higher homologue (2; R = Oct^t) decomposed on standing to *p*-benzoquinone oxime and 2,4,4-trimethylpent-1-ene. In solution in deuteriobenzene decomposition was complete after 8 days at room temperature and after 10 min at 80 °C. The thermodynamically more stable pentene was not detected (n.m.r.). Similar elimination reactions are common for tertiary amine *N*-oxides.[9] Since *N*-t-butylbenzoquinone imine *N*-oxide was stable in solution even at 80 °C we presume that elimination occurs with [10 (= 2); R = Oct^t] because the preferred conformation has the hydrogens of the methylene group and the oxygen suitably disposed for reaction, as indicated in structure (10).

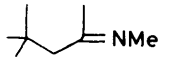
Photolysis of N-*Alkylbenzoquinone Imine* N-*Oxides*.—We anticipated the formation of t-octylamine and 2,2,4,4-tetramethylpyrrolidine, and hence the diaminoquinones (16; R = Oct^t) and (18), on photolysis of the quinone imine *N*-oxide (2; R = Oct^t) by attempting to prepare the diaminoquinones (16; R = Oct^t) and (18). Although the first of these was easily obtained from the amine and *p*-benzoquinone in the usual way,[10] the latter was not. In chloroform solution, using a 2 : 1 ratio of pyrrolidine to benzoquinone, the purple monopyrrolidinylquinone (15) and the red phenoxypyrrolidinylquinone (17; R = OC_6H_4OH-*p*) were the main products. That the last-named compound (17; R = OC_6H_4OH-*p*) arose by the reaction of quinol with compound (15) was easily confirmed in a separate experiment. When oxidising conditions were used (cupric acetate and oxygen with methanol as solvent) formation of the quinone (17; R = OC_6H_4OH-*p*) was suppressed but a new product, identified as the methoxyquinone (17; R = OMe), was obtained. Under neither set of conditions was any of the expected 2,5-dipyrrolidinylbenzoquinone (18) detected. However, a small amount of a red quinone, identified as compound (18), was slowly formed on heating a mixture of 2,2,4,4-tetramethylpyrrolidine with either benzoquinone or the monopyrrolidinylquinone (15) in chloroform for several days. Pyrrolidine reacts rapidly with *p*-benzoquinone to give the corresponding 2,5-dipyrrolidinylbenzoquinone [10] without accumulation of significant amounts of the monopyrrolidinylbenzoquinone. Hence, we attribute the low reactivity of the tetramethylpyrrolidine towards quinone (15) to steric hindrance by the geminal dimethyl groups. Reaction of the monopyrrolidinylquinone (15) with smaller nucleophiles such as dimethylamine, diethylamine, and even methanol, was not significantly impeded. Di-isopropylamine is similarly unreactive towards benzoquinone.[10] Usually monoalkylaminobenzoquinones can only be prepared with difficulty,[11a] reaction proceeding to the 2,5-dialkylamino-





benzoquinone without useful concentrations of the monosubstitution product accumulating.

Irradiation of the *N*-t-octylbenzoquinone imine *N*-oxide (2; R = Oct^t) in benzene gave as the main products benzoquinone (22%), benzoquinone oxime (43%) (a thermal product), and di-t-octylaminobenzoquinone (16; R = Oct^t) (8%). Presumably reaction occurs *via* the oxaziridine intermediate [12] (11) which fragments to octyl nitrene. Hydrogen abstraction by the nitrene, either from the alkene formed by thermal elimination or from the small quantity of toluene present in AnalaR benzene,[11b] would yield the amine (14) and hence the diaminoquinone (16; R = Oct^t). A small but significant amount (*ca.* 1%) of the purple pyrrolidinylquinone (15) was also isolated, providing evidence for intramolecular hydrogen abstraction by the nitrene (12) reacting in its triplet state. Although it is likely that some of the quinone (15) is being destroyed during photolysis,[11d] the ultimate fate of much of the nitrene was not established. Neither of the possible rearrangement products, the imines (19) or (20), nor their hydrolysis products, the corresponding ketones, could be detected. If these are formed they must react further.



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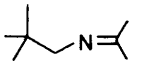

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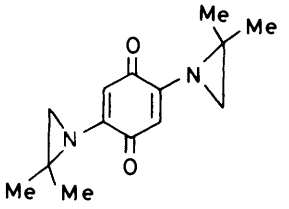

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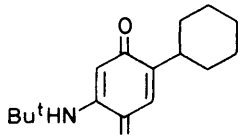

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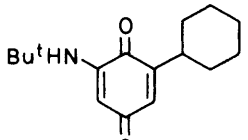

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Photolysis of the quinone imine *N*-oxide (2; R = Oct^t) in cyclohexane gave a higher yield (19%) of the diaminoquinone (16; R = Oct^t), but, again, only a small amount of the monopyrrolidinylquinone (15), in this case accompanied by an equally small amount of the *p*-hydroxyphenoxyquinone (17; X = OC_6H_4OH-*p*). Much intractable material was again produced, but no dipyrrolidinylquinone (18). Cyclohexane is a more convenient source of hydrogen for the nitrene, hence the higher yield of compound (16; R = Oct^t).

Irradiation of the *N*-t-butylbenzoquinone imine *N*-oxide (2; R = Bu^t) in benzene gave mainly benzoquinone (55%). Di-t-butylaminobenzoquinone (16; R = Bu^t) (10%) was also formed, but the diaziridinylquinone (21) was not detected, although an authentic specimen was to hand. The potential rearrangement product 2-methyliminopropane and its hydrolysis product were also absent. In cyclohexane the yield of the diaminoquinone (16; R = Bu^t) was increased to 19% and small amounts of the isomeric quinones (22) and (23) were isolated. Cyclohexylbenzoquinone [13] has been identified as a photoproduct of benzoquinone in cyclohexane and the aforementioned isomers clearly arise by addition of t-butylamine to this photo-product.

Quinone Identification.—Mono(alkylamino)benzoquinones are readily distinguished from di(alkylamino)benzoquinones by their u.v. and i.r. spectra. The former show two u.v. bands in the ranges 470—550 and 300—312 nm and two carbonyl absorptions in the i.r. spectrum, one above and one below 1 650 cm^{-1}, while the latter only show a strong u.v. absorption band in the range 340—380 nm and one i.r. carbonyl band below 1 650 cm^{-1}.

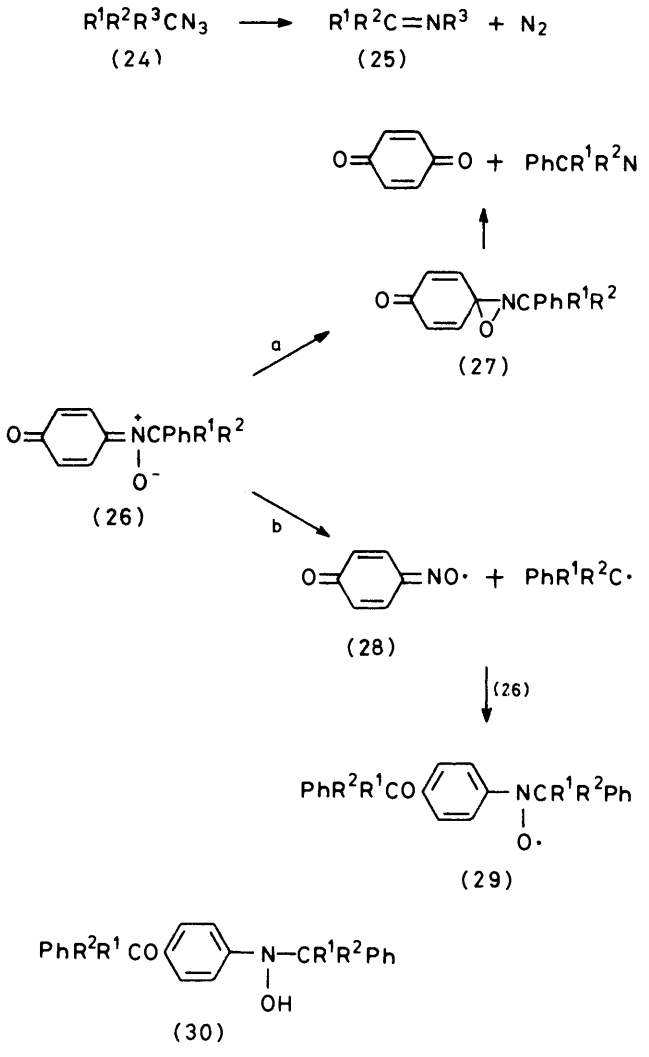
Photolysis of Alkyl Azides.—t-Octyl azide, prepared by transfer of azide from tosyl azide to the anion of t-octylamine,[14] was photolysed in benzene for 4 h and then *p*-benzoquinone (1 mol equiv.) was added to trap nitrene-derived amines. Only the 2,5-bis(t-octylamino)benzoquinone (16; R = Oct^t) was isolated. Pyrrolidinylbenzoquinones (15), (17), and (18) were shown to be absent. Photolysis of n-butyl azide gave a similar result. In benzene it gave mainly the corresponding diaminoquinone (16; R = Bu^t), the yield of which was increased (9 → 17%) by using cyclohexane as solvent. In neither case was the diaziridinylbenzoquinone (21) detected, although in cyclohexane, unexpectedly, a 5% yield of compound (16; R = cyclo-C_6H_{11}) was obtained.

We conclude that photolysis of *N*-alkylbenzoquinone imine *N*-oxides yields alkyl nitrenes, probably in the triplet state, which mainly abstract hydrogen to give alkylamines which are trapped by reaction with benzoquinone. When t-octyl nitrene was generated in this way, intramolecular hydrogen abstraction also occurred, followed by cyclisation, to give the pyrrolidine. This is a minor process but is important nevertheless since it illustrates the feasibility of a reaction much sought after [15] but never established using azides as the nitrene source. We also failed to observe pyrrolidine formation using t-octyl and n-butyl azides as the nitrene precursors (but see ref. 15*a*).

Photolysis of N-α-*Substituted Benzoquinone Imine* N-*Oxides.*—Photolysis [16] or thermolysis [17] of alkyl azides (24) gives imines (25) by an alkyl, aryl, or hydrogen shift which could either follow or be concerted with loss of nitrogen. Evidence, based mainly on the relative migratory aptitudes of the rearranging groups, indicates that only for the thermolysis [17] is a discrete nitrene involved. To obtain comparative data we studied the photolysis of the quinone imine *N*-oxides (26; $R^1 = R^2 =$ Me; R^1 = Ph, R^2 = Me; R^1 = Me, R^2 = H) which were

prepared from the corresponding hydroxylamines by reaction with Fremy's salt or its tetrabutylammonium analogue.

Photolysis of the imine (26; $R^1 = R^2 = Me$) in benzene through quartz gave a complex mixture containing benzoquinone, the diaminoquinone (16; R = $PhCMe_2$) (4%), and the hydroxylamine (30; $R^1 = R^2 = Me$), but no imine



nor hydrolysis product thereof. Irradiation in the cavity of an e.s.r. spectrometer showed that there was rapid accumulation of a *para*-substituted phenyl t-alkyl nitroxide, presumably compound (29; $R^1 = R^2 = Me$) ($a_N = 11.5$; $a_{o\text{-}H} = 2.5$ and $a_{m\text{-}H} = 0.8$ g); in similar irradiations of the related *N*-t-butyl- and *N*-*p*-methoxyphenyl-benzoquinone imine *N*-oxides and the benzyl analogue (26; $R^1 = H$, $R^2 = Me$) only very weak nitroxide spectra were detected. This suggests that C–N bond cleavage [18] (route b) of compound (26) predominates over oxaziridine (27) formation (route a) when such cleavage of the quinone imine *N*-oxide gives a relatively stable radical. The quinone imine *N*-oxide (26; $R^1 = Ph$, $R^2 = Me$) behaved similarly. Although there was little e.s.r. evidence for C–N bond cleavage on photolysis of the quinone imine *N*-oxide (26; $R^1 = H$, $R^2 = Me$), the product mixture was exceedingly complex and only benzoquinone and a little acetophenone (a thermal product) from compound (26; $R^1 = H$, $R^2 = Me$) were isolated. In previous work with quinone imine *N*-oxides we did not encounter this difficulty since C–N bond cleavage would have produced aryl or non-stabilised alkyl radicals. This is a disadvantage of quinone imine *N*-oxides as a source of certain nitrenes. However, azides can also suffer from this shortcoming since, for several dialkylaryl azides, C–N predominates over N–N bond cleavage on thermolysis. Because of the inaccessibility and thermal instability of this type of quinone imine *N*-oxide we conclude that they are not suitable sources of substituted benzyl nitrenes.

EXPERIMENTAL

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

Preparation of Hydroxylamines.—*N*-Phenyl-*N*-t-butylhydroxylamine was prepared by the literature method.[4,9]

N-*Phenyl*-N-(1,1,3,3-*tetramethylbutyl*)*hydroxylamine*.—To a stirred solution of phenylmagnesium bromide [prepared from magnesium (1.95 g) and bromobenzene (11.0 g, 0.07 mol)] in tetrahydrofuran (THF) at 0 °C under nitrogen, 2-nitroso-2,4,4-trimethylpentane [19] (10.0 g, 0.07 mol) in THF (50 ml) was added during 30 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 30 min before water was added. The THF was removed under reduced pressure and the aqueous residue was extracted with ether (previously degassed by nitrogen bubbling). The extracts were dried and evaporated to give a solid, crystallisation of which from petroleum gave the *hydroxylamine* (10.8 g, 67%) as plates, m.p. 145—146 °C (Found: C, 76.3; H, 10.8; N, 6.3. $C_{14}H_{23}NO$ requires C, 76.0; H, 10.5; N, 6.3%); $\nu_{max.}$ 3 200 cm^{-1}; δ 1.01 (9 H, s, Bu^t), 1.11 (6 H, s, 2 × Me), 1.63 (2 H, s, CH_2), 5.85 (1 H, br s, OH), and 7.22 (5 H, s, ArH).

N-(4-*Methoxyphenyl*)-N-(1,1,3,3-*tetramethylbutyl*)*hydroxylamine*.—This compound was similarly prepared in 73% yield and obtained as *plates*, m.p. 130—131 °C (from petroleum) (Found: C, 71.4; H, 9.9; N, 5.4. $C_{15}H_{25}NO_2$ requires C, 71.7; H, 10.0; N, 5.6%); $\nu_{max.}$ 3 200 cm^{-1}; δ 1.99 (9 H, s, Bu^t), 1.09 (6 H, s, 2 × Me), 1.60 (2 H, s, CH_2), 3.78 (3 H, s, OMe), 6.76 (2 H, d, ArH), and 7.18 (2 H, d, ArH).

N-(1,1-*Diphenylethyl*)-N-*phenylhydroxylamine*.—To a solution of methyl-lithium [prepared from methyl iodide (2.84 g) and lithium (0.31 g)] in ether (30 ml) a slurry of triphenylnitrone [20] (2.73 g) in THF (50 ml) was added during 30 min; the temperature was maintained at −5 to −10 °C. It was then allowed to rise to 0 °C before the solution was poured into 5M-ammonium chloride solution. The resulting mixture was filtered through phase-separating paper and the filtrate was evaporated to give a red oil. Crystallisation from petroleum gave the *hydroxylamine* as an off-white solid, m.p. 71—73 °C (Found: C, 82.8; H, 6.8; N, 4.8. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.8%);

$\nu_{max.}$ 3 510 cm^{-1}; δ 1.83 (3 H, s, Me), 5.08 (1 H, s, OH), and 6.6—7.5 (15 H, m, ArH).

N-*Phenyl*-N-(1-*phenylethyl*)*hydroxylamine*.—This compound was prepared from α, *N*-diphenylnitrone [19] (9.8 g) and methyl-lithium [from methyl iodide (8.9 g) and lithium (1.03 g)] as described for the preceding hydroxylamine. Crystallisation from petroleum gave a sandy *solid*, m.p. 66—74 °C (Found: C, 77.4; H, 7.3; N, 7.4. $C_{14}H_{15}NO$ requires C, 78.7; H, 7.1; N, 6.6%); $\nu_{max.}$ 3 300 cm^{-1}; δ 1.4 (3 H, br s, Me), 4.55 (1 H, m, CH), 5.7 (1 H, s, OH), and 7.2 (10 H, br s, 2Ph).

N-(1-*Methyl*-1-*phenylethyl*)-N-*phenylhydroxylamine*.—Treatment of *C*-methyl-*C*-phenyl-*N*-phenylnitrone [20] (4.22 g) with methylmagnesium iodide [prepared from methyl iodide (3.4 g) and magnesium (0.58 g)] as described for the preceding hydroxylamine gave the crude product. Chromatography on silica using petroleum as eluant gave the hydroxylamine (positive tetrazolium test, $\nu_{max.}$ 3 300 cm^{-1}) which was contaminated with acetophenone but was sufficiently pure for subsequent oxidation to the corresponding benzoquinone imine *N*-oxide.

Preparation of N-*Alkylbenzoquinone Imine* N-*Oxides*.—(*a*) *N*-(4-Methoxyphenyl)-*N*-(1,1,3,3-tetramethylbutyl)hydroxylamine (5 g; 0.012 mol) in benzene (40 ml) was shaken with silver(I) oxide (26.6 g, 0.093 mol) for 48 h. After removal of the silver residues the solution was evaporated and the residue was chromatographed (p.l.c.) using benzene as eluant to give (i) *p*-nitrosoanisole (0.135 g, 5%), m.p. 24—25 °C (lit.,[22] 23 °C); (ii) *N*-4-methoxyphenyl *N*-(1,1,3,3-tetramethylbutyl) nitroxide (0.55 g, 10%), as a red oil, $\lambda_{max.}$ (EtOH) 305 and 505 nm (log ε 3.92 and 3.04); (iii) N-(1,1,3,3-*tetramethylbutyl*)-p-*benzoquinone imine* N-*oxide* (2; R = Oct^t) (0.42 g, 9%) as orange needles, m.p. 85—86 °C (from petroleum) (Found: C, 71.6; H, 8.7; N, 6.2. $C_{14}H_{21}NO_2$ requires C, 71.5; H, 9.0; N, 6.0%); $\lambda_{max.}$ (EtOH) 386 nm (log ε 4.48); $\nu_{max.}$ 1 620 cm^{-1}; δ 0.98 (9 H, s, Bu^t), 1.73 (6 H, s, 2 × Me), and 2.16 (2 H, s, CH_2); (iv) 5-*methoxy*-2-(1,1,3,3-*tetramethylbutylamino*)-p-*benzoquinone* (6; R = Oct^t (1.59 g, 32%), as red plates, m.p. 95—96 °C (from chloroform–petroleum) (Found: C, 67.8; H, 8.5; N, 5.4. $C_{15}H_{23}NO_3$ requires C, 67.9; H, 8.7; N, 5.3%); $\lambda_{max.}$ (EtOH) 301 and 500 nm (log ε 4.05 and 3.18); δ 1.0 (9 H, s, Bu^t), 1.44 (6 H, s, 2 × Me), 1.71 (2 H, s, CH_2), 3.84 (3 H, s, OMe), 6.15 (1 H, br s, NH), 5.65 (1 H, s, 3-H), and 5.78 (1 H, s, 6-H); (v) 3-*methoxy*-N-(4-*methoxyphenyl*)-6-(1,1,3,3-*tetramethylbutylamino*)-p-*benzoquinone imine* (9; R = Oct^t) (0.21 g, 3%) as red needles, m.p. 89—90 °C (from chloroform–petroleum) (Found: C, 71.2; H, 8.1; N, 7.7. $C_{22}H_{30}N_2O_3$ requires C, 71.4; H, 8.2; N, 7.6%); $\lambda_{max.}$ (EtOH) 312 and 515 nm (log ε 4.18 and 3.53); $\nu_{max.}$ 3 350 and 1 642 cm^{-1}; δ 0.93 (9 H, s, Bu^t), 1.28 (6 H, s, 2 × Me), 1.52 (2 H, s, CH_2), 3.82 (3 H, s, OMe), 3.89 (3 H, s, OMe), 5.6 (1 H, br s, NH), 5.67 (1 H, s, 5-H), 5.86 (1 H, s, 2-H), and 6.4 (4 H, m, ArH); and (vi) *p*-benzoquinone oxime (0.19 g, 8%), m.p. 125—126 °C (lit.,[23] 125—126 °C).

(*b*) *N*-Phenyl-*N*-(1,1,3,3-tetramethylbutyl)hydroxylamine (5 g, 0.022 mol) in methanol (50 ml) was added to a solution of Fremy's salt (25 g) in water (300 ml), followed by 0.25M-potassium hydrogen phosphate (100 ml). After 30 min the reaction mixture was extracted with chloroform until the extracts were colourless. The dried extracts were evaporated to give a red oil, crystallisation of which from petroleum gave *N*-(1,1,3,3-tetramethylbutyl)-*p*-benzoquinone imine *N*-oxide (4.87 g, 92%), as orange needles, m.p. 85—86 °C (from petroleum).

(*c*) *N*-Phenyl-*N*-t-butylhydroxylamine (5 g, 0.028 mol) when treated with Fremy's salt (25 g) as described in (*b*) gave *N*-t-butyl-*p*-benzoquinone imine *N*-oxide,[4a] m.p. 73 °C (from petroleum).

(*d*) *N*-(1-Methyl-1-phenylethyl)-*N*-phenylhydroxylamine (0.908 g, 4 mmol) when treated with Fremy's salt (4 g) as described in (*b*) gave a crude product, chromatography (p.l.c.) of which [with ether–petroleum (2 : 1) as eluant] gave N-(1-*methyl*-1-*phenylethyl*)-p-*benzoquinone imine* N-*oxide* as red needles, m.p. 104—106 °C (from ether–petroleum) (Found: C, 74.1; H, 6.4; N, 5.5. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\lambda_{max.}$ (EtOH) 383 (log ε 4.36); δ 1.9 (6 H, s, 2 × Me), 5.85 (1 H, dd, *J* 10.5, 2 Hz, 3- or 5-H), 6.44 (1 H, dd, *J* 10.5, 2 Hz, 3- or 5-H), 7.03 (1 H, dd, *J* 10.5 and 3 Hz, 6-H), 7.32 (5 H, m, Ph), and 7.89 (1 H, dd, *J* 10.5, 3 Hz, 2-H); *m/e* 241 (M^+, 0.6%), 123 (45), 119 (100), 118 (79), 117 (28), 103 (44), and 91 (56).

(*e*) *N*-Phenyl-*N*-(1-phenylethyl)hydroxylamine, oxidised with Fremy's salt as in (*b*) gave N-(1-*phenylethyl*)-p-*benzoquinone imine* N-*oxide*, as red needles, m.p. 94.5—96 °C (from ether–petroleum) (Found: C, 73.9; H, 5.7; N, 6.5. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%); $\lambda_{max.}$ (EtOH) 380 nm (log ε 4.46); $\nu_{max.}$ 1 618 cm^{-1}; δ 1.78 (3 H, d, *J* 6.5 Hz, Me), 6.04 (1 H, q, *J* 6.5 Hz, *C*HMe), 6.26 (1 H, dd, *J* 10 and 1 Hz, 3- or 5-H), 6.49 (1 H, dd, *J* 10 and 1 Hz, 3- or 5-H), 7.36 (5 H, s, Ph), 7.67 (1 H, dd, *J* 3 and 10 Hz, 6-H), and 7.87 (1 H, dd, *J* 3 and 10 Hz, 2-H); *m/e* 227 (0.6%), 211 (2), 196 (3), 123 (8), and 105 (100).

(*f*) A solution of Fremy's salt (0.2 g) and tetrabutylammonium bromide (0.93 g) in water (10 ml) was extracted with methylene chloride and the extracts were added to a solution of *N*-(1,1-diphenylethyl) *N*-phenyl nitroxide (50 mg) in methanol (20 ml) [previously prepared by shaking the corresponding hydroxylamine with silver(I) oxide]. When the colour of the nitroxide had disappeared, water (50 ml) was added and the mixture was extracted with methylene chloride. The extracts were dried and evaporated and the residue was chromatographed (p.l.c.) on silica [ether–petroleum (1 : 1) as eluant]. The bright-yellow band of low R_F was separated and extracted with chloroform to give a solution which showed intense absorptions at $\lambda_{max.}$ 386 nm and $\nu_{max.}$ ($CHCl_3$) 1 622 cm^{-1}, indicative of the presence of *N*-(1,1-diphenylethyl)-*p*-benzoquinone imine *N*-oxide. Evaporation of the solvent gave a solid which decomposed on attempted crystallisation or on storage. Hence the solution was used directly in the photolytic e.s.r. and product work.

Preparation of 2,2,4,4-*Tetramethylpyrrolidine* (13).—1-Hydroxy-2,2,4,4-tetramethylpyrrolidine [24] (4 g, 0.028 mol) in methanol (10 ml) was hydrogenated over Raney nickel. After removal of solvent at low temperature, the residual oil was fractionated. The fraction of b.p. 84—86 °C at 760 mmHg, which was a mixture of the product and 2,2,4,4-tetramethyl-1-pyrroline (δ_{CH} 6.81) in the ratio 3 : 1, was treated with an excess of lithium aluminium hydride in ether during 2 h. Chromatographic (column) separation on neutral alumina of the residue obtained after removal of solvent gave 2,2,4,4-tetramethylpyrrolidine as a pale yellow liquid, b.p. 90—91 °C at 760 mmHg, $\nu_{max.}$ 3 270 cm^{-1}; δ 1.05 (6 H, s, 2 × Me), 1.14 (6 H, s, 2 × Me), 1.40 (2 H, s, CH_2), 2.08 (1 H, s, NH), and 2.63 (2 H, s, NCH_2). The *picrate* had m.p. 128—129 °C (from aqueous alcohol) (Found: C, 47.5; H, 5.6; N, 15.5. $C_{14}H_{20}N_4O_7$ requires C, 47.2; H, 5.7; N, 15.7%).

Preparation of Alkylamino-p-*benzoquinones*.—(*a*) 2-(2,2,-

4,4-*Tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (15). A solution of 2,2,4,4-tetramethylpyrrolidine (1 g, 8 mmol) and *p*-benzoquinone (0.86 g, 8 mmol) in chloroform (15 ml) was stirred at room temperature for 4 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was digested repeatedly with petroleum until the extracts were colourless. Evaporation of the extracts gave a purple oil, crystallisation of which from petroleum gave 2-(2,2,4,4-*tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (0.64 g, 34%) (Found: C, 71.8; H, 8.0; N, 5.9%; M^+, 233.1408. $C_{14}H_{19}NO_2$ requires C, 72.1; H, 8.0; N, 6.0%; *M*, 233.1415); $\lambda_{max.}$ (EtOH) 312 and 530 nm (log ε 3.70 and 3.39); $\nu_{max.}$ (CCl_4) 1 680 and 1 645 cm^{-1}; δ 1.03 (6 H, s, 2 × Me), 1.43 (6 H, s, 2 × Me), 1.72 (2 H, s, CH_2), 3.49 (2 H, s, CH_2), 6.42 (2 H, m, 5- and 6-H), and 5.68 (1 H, d, *J* 0.8 Hz, 3-H). The red residue which was insoluble in petroleum was crystallised from chloroform to give 5-(p-*hydroxyphenoxy*)-2-(2,2,4,4-*tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (17; R = OC_6H_4OH-*p*) (0.21 g, 8%) as red plates, m.p. 198—199 °C (Found: C, 70.5; H, 6.7; N, 4.2%; M^+, 341.1621. $C_{20}H_{23}NO$ requires C, 70.4; H, 6.8; N, 4.1%; *M*, 341.1626); $\lambda_{max.}$ 310 and 530 nm (log ε 3.97 and 3.52); $\nu_{max.}$ 3 280 and 1 665 cm^{-1}; δ 1.12 (6 H, s, 2 × Me), 1.58 (6 H, s, 2 × Me), 1.88 (2 H, s, CH_2), 3.71 (2 H, s, CH_2), 5.92 (1 H, s, 6-H), 5.44 (1 H, s, 3-H), and 6.90 (4 H, m, ArH). When the ratio of benzoquinone to 2,2,4,4-tetramethylpyrrolidine was 1 : 2 the yields of products (15) and (17; R = OC_6H_4OH-*p*) were 45 and 13%, respectively.

To a solution of *p*-benzoquinone (0.86 g, 8 mmol) in methanol (10 ml) containing finely powdered cupric acetate (0.52 g, 2.6 mmol), 2,2,4,4-tetramethylpyrrolidine (2 g, 16 mmol) in methanol (5 ml) was added. The reaction mixture was continuously flushed with oxygen for 4 h before it was filtered. The filtrate was evaporated and the residue was extracted with hot petroleum. The extracts were evaporated and the residue was chromatographed, using dichloromethane as eluant, to give 2-(2,2,4,4-tetramethylpyrrolidinyl-*p*-benzoquinone (0.22 g, 12%) and a small amount of 5-*methoxy*-2-(2,2,4,4-*tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (17; R=OMe) as red plates, m.p. 139—140 °C (from petroleum) (Found: C, 68.6; H, 8.1; N, 5.5. $C_{15}H_{21}NO_3$ requires C, 68.4; H, 8.0; N, 5.3%); $\lambda_{max.}$ 510 and 300 nm (log ε 3.34 and 3.97); $\nu_{max.}$ 1 650 and 1 630 cm^{-1}; δ 1.12 (6 H, s, 2 × Me), 1.57 (6 H, s, 2 × Me), 1.76 (2 H, s, CH_2), 3.72 (2 H, s, CH_2), 3.81 (3 H, s, OMe), 5.49 (1 H, s, 3-H), and 5.81 (1 H, s, 6-H).

(*b*) 2,2,4,4-Tetramethylpyrrolidine (2.0 g, 16 mmol) in chloroform (5 ml) was added to a stirred solution of *p*-benzoquinone (0.86 g, 8 mmol) in chloroform (10 ml). The mixture was heated under reflux for 7 d in the dark and constantly flushed with oxygen. Chromatography (p.l.c.) of the crude product using dichloromethane as eluant gave 2-(2,2,4,4-*tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (13) (0.73 g, 39%), and 2,5-*bis*(2,2,4,4-*tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (18) (0.12 g, 4%) as red needles, m.p. 165—166 °C (from petroleum) (Found: C, 73.4; H, 9.4; N, 7.6. $C_{22}H_{34}N_2O_2$ requires C, 73.7; H, 9.6; N, 7.8%); $\lambda_{max.}$ (EtOH) 380 nm (log ε 4.44); $\nu_{max.}$ 1 620 cm^{-1}; δ 1.12 (12 H, s, 4 × Me), 1.58 (12 H, s, 4 × Me), 1.82 (4 H, s, 2 × CH_2), 3.84 (4 H, s, 2 × CH_2), and 5.63 (2 H, s, 3- and 6-H).

(*c*) 2,5-*Bis*-(1,1,3,3-*tetramethylbutylamino*)-p-*benzoquinone* (16; R = Oct^t). To a stirred solution of *p*-benzoquinone (1.08 g, 0.01 mol) in chloroform (25 ml), 1,1,3,3-tetramethylbutylamine (1.3 g, 0.01 mol) in chloroform (10 ml) was added and the mixture was stirred for 2 h. The solvent was evaporated and the residue was digested with petroleum. Evaporation of the petroleum gave the *diamine* (0.94 g, 52%) as red needles, m.p. 138—139 °C (from petroleum) (Found: C, 73.0; H, 10.8; N, 7.9. $C_{22}H_{38}N_2O_2$ requires C, 72.9; H, 10.6; N, 7.7%); $\lambda_{max.}$ (EtOH) 348 (log ε 4.30); $\nu_{max.}$ 3 295 and 1 640 cm^{-1}; δ 1.0 (9 H, s, Bu^t), 1.40 (6 H, s, 2 × Me), 1.72 (2 H, s, CH_2), 5.53 (2 H, s, 3- and 6-H), and 6.85 (2 H, s, 2 × NH).

(*d*) 2,5-*Bis*-(1-*methyl*-1-*phenylethylamino*)-p-*benzoquinone*. To a solution of *p*-benzoquinone (0.216 g) in chloroform (2 ml), 2-amino-2-phenylpropane (216 mg) was added and the mixture was shaken. The *product* (44 mg, 10%) was collected and crystallised from methanol to give red needles, m.p. 295—297 °C (Found: C, 76.7; H, 7.0; N, 7.5. $C_{24}H_{26}N_2O_2$ requires C, 77.0; H, 7.0; N, 7.5%); $\nu_{max.}$ 3 300, 1 645, and 1 576 cm^{-1}; δ 1.66 (12 H, d, 4 × Me), 4.77 (2 H, s, 2 × NH or 3-, and 6-H), 4.77 (2 H, s, 2 × NH or 3- and 6-H), and 7.29 (10 H, br s, 2 × Ph).

(*e*) 2,5-*Bis*-(1-*phenylethylamino*)-p-*benzoquinone*. This compound was similarly prepared (20%). It was obtained as red *needles*, m.p. 197—198 °C (from methanol) (Found: C, 76.1; H, 6.4; N, 8.1. $C_{22}H_{22}N_2O_2$ requires C, 76.3; H, 6.4; N, 8.1%); $\lambda_{max.}$ (EtOH) 240, 342, and 486 nm (log ε 3.91, 4.38, and 2.48); $\nu_{max.}$ 3 270, 1 643, 1 635, and 1 568 cm^{-1}; δ 1.56 (6 H, d, *J* 7 Hz, 2 × Me), 4.46 (2 H, q, *J* 7 Hz, 2 × CH), 5.16 (2 H, s, 3- and 6-H), 6.74 (2 H, br s, 2 × NH), and 7.26 (10 H, br s, 2 × Ph).

Reactions of 2-(2,2,4,4-*Tetramethylpyrrolidin*-1-*yl*)-p-*benzoquinone* (15).—(*a*) The pyrrolidinylbenzoquinone (15) (0.2 g, 8.6 mmol) in chloroform (5 ml) was treated with 1,4-dihydroxybenzene (0.094 g, 8.6 mmol) in chloroform (5 ml) and the mixture was stirred for 6 h in the dark. The solvent was evaporated and the residue was extracted with petroleum. The residue was crystallised from chloroform to yield 5-(*p*-hydroxyphenoxy)-2-(2,2,4,4-tetramethylpyrrolidin-1-yl)-*p*-benzoquinone (0.03 g, 10%).

(*b*) 2,2,4,4-Tetramethylpyrrolidine (0.13 g, 1 mmol) in chloroform (2 ml) was added to a solution of the pyrrolidinylquinone (15) (0.2 g, 8.6 mmol) in chloroform (5 ml) and the mixture was stirred in the dark for 7 d. The solvent was evaporated and the residue was chromatographed (p.l.c.), using dichloromethane as eluant, to give 2,5-bis(2,2,4,4-tetramethylpyrrolidin-1-yl)-*p*-benzoquinone (0.028 g, 9%), identical with that previously prepared.

Photolysis of Benzoquinone Imine N-*Oxides*.—N-(1,1,3,3-*Tetramethylbutyl*)-p-*benzoquinone imine* N-*oxide* (2; R = Oct^t). (*a*) The *N*-oxide (2 g, 8.5 mmol) in benzene (250 ml) was irradiated in an annular quartz vessel fitted with a cooling jacket, using a Hanovia 500S mercury-vapour lamp, at room temperature for 6 h. The solvent was removed and the residue was chromatographed (p.l.c.), using dichloromethane as eluant, to give (*i*) *p*-benzoquinone (0.205 g, 22%); (ii) 2,5-bis(1,1,3,3-tetramethylbutylamino)-*p*-benzoquinone (0.15 g, 5%); (iii) 2-(2,2,4,4-tetramethylpyrrolidin-1-yl)-*p*-benzoquinone (0.011 g, 1%); and (iii) *p*-benzoquinone oxime (0.44 g, 42%).

(*b*) The *N*-oxide (2.0 g, 8.5 mmol) was irradiated in cyclohexane (250 ml) as in (*a*). Work-up as in (*a*) gave (i) *p*-benzoquinone (0.185 g, 21%); (ii) 2,5-bis(1,1,3,3-tetramethylbutylamino)-*p*-benzoquinone (0.236 g, 10%); (iii) 5-(*p*-hydroxyphenoxy)-2-(2,2,4,4-tetramethylpyrrolidin-1-yl)-*p*-benzoquinone (0.034 g, 2%); and (iv) *p*-benzoquinone oxime (0.405 g, 40%).

N-*t*-*Butyl*-p-*benzoquinone imine* N-*oxide* (2; R = Bu^t). (*a*) The *N*-oxide (2.0 g, 11 mmol) in benzene was irradiated at

room temperature for 6 h. Product isolation as before gave (i) *p*-benzoquinone (0.65 g, 54%) and (ii) 2,5-bis(t-butylamino)-*p*-benzoquinone [25] (0.275 g, 10%).

(*b*) The *N*-oxide (2.0 g, 11 mmol) was irradiated in cyclohexane (250 ml) at room temperature for 6 h. Product isolation as before gave (i) *p*-benzoquinone (0.56 g, 47%); (ii) 2,5-bis(t-butylamino)-*p*-benzoquinone (0.52 g, 20%); (iii) 2-*cyclohexyl*-5-*t*-*butylamino*-p-*benzoquinone* (0.075 g, 3%) as red needles, m.p. 72—73 °C (from petroleum) (Found: C, 73.3; H, 9.1; N, 5.2. $C_{16}H_{23}NO_2$ requires C, 73.5; H, 8.9; N, 5.4%); $\lambda_{max.}$ (EtOH) 285 and 505 nm (log ε 4.08 and 3.40); $\nu_{max.}$ 3 340, 1 665, and 1 630 cm^{-1}; δ 1.2—1.8 (10 H, m, 5 × CH_2), 1.38 (9 H, s, Bu^t), 2.8 (1 H, m, CH), 5.62 (1 H, br s, NH), 5.67 (1 H, s, 3-H), and 6.32 (1 H, s, 6-H); (iv) 2-*cyclohexyl*-6-*t*-*butylamino*-p-*benzoquinone* (0.069 g, 2%) as red needles, m.p. 50—52 °C (from petroleum) (Found: C, 73.4; H, 9.0; N, 5.1. $C_{16}H_{23}NO_2$ requires C, 73.5; H, 8.9; N, 5.4%); $\lambda_{max.}$ 285 and 510 nm (log ε 4.08 and 3.40); $\nu_{max.}$ 3 350, 1 670, and 1 640 cm^{-1}; δ 1.2—1.8 (10 H, m, 5 × CH_2), 1.38 (9 H, s, Bu^t), 2.65 (1 H, m, CH), 5.69 (1 H, br s, NH), 5.62 (1 H, s, 3-H), and 6.33 (1 H, s, 5-H).

N-(1-*Methyl*-1-*phenylethyl*)-p-*benzoquinone imine* N-*oxide* (2; R = $CPhMe_2$). The *N*-oxide (0.304 g) in benzene was irradiated as for compound (2; R = Oct^t) for 11 h. Chromatography (column followed by p.l.c.) of the complex product mixture gave 2,5-bis-(1-methyl-1-phenylethylamino)-*p*-benzoquinone (30 mg, 7%), as red needles (from methanol), identical with an authentic specimen, and *N*-(1-methyl-1-phenylethyl)-*N*-*p*-(1-methyl-1-phenylethoxy)-phenylhydroxylamine (48 mg, 10%) as an oil (Found: M^+, 361. $C_{24}H_{27}NO_2$ requires *M*, 361); δ 1.35 (6 H, s, 2 × Me), 1.55 (6 H, s, 2 × Me), 6.15—6.7 (4 H, m, ArH), and 7.0—7.3 (10 H, m, 2 × Ph); *m/e* 361 (M^+, 2%), 243 (2), 125 (8), 119 (100), 103 (9), and 91 (32).

N-(1-*Phenylethyl*)-p-*benzoquinone imine* N-*oxide* (2; R = CHMePh). The *N*-oxide (1.44 g) in benzene (500 ml) was irradiated under nitrogen for 12 h. Analysis of the complex product mixture by u.v. spectroscopy ($\lambda_{max.}$ 375 nm) indicated that 61% of the starting material had been consumed. *p*-Benzoquinone was estimated (46%) by addition of methylamine and measurement of the intensities of the bands at $\lambda_{max.}$ 500 and 550 nm due to 2,5-dimethylaminobenzoquinone. Repeated chromatography (p.l.c.) gave more than 30 products, of which only acetophenone (4%) was identified. 2,5-Bis(1-phenylethylamino)-*p*-benzoquinone was not present in the reaction mixture (t.l.c.).

Preparation of Azides.—A solution of 2-amino-2,4,4-trimethylpentane (6.9 g, 0.054 mol) and freshly prepared potassium t-butoxide (13.4 g, 0.12 mol) in dimethyl sulphoxide (200 ml) was treated with a solution of *p*-toluenesulphonyl azide (11.2 g, 0.054 mol) in dimethyl sulphoxide (40 ml). The mixture was stirred for 12 h and then water (200 ml) was added. The aqueous solution was extracted with ether and the extracts were washed with 2M-hydrochloric acid, 2M-sodium hydroxide, water, and then dried. Evaporation of the ether left a pale yellow liquid which, on distillation at 29—32 °C at 0.22 mmHg, gave 2-*azido*-2,4,4-*trimethylpentane* (1.51 g, 18%) as a colourless liquid (Found: C, 62.2; H, 10.9; N, 27.0. $C_8H_{17}N_3$ requires C, 61.9; H, 11.0; N, 27.1%); $\nu_{max.}$ 2 100 cm^{-1}; δ 0.99 (9 H, s, Bu^t), 1.30 (6 H, s, 2 × Me), and 7.50 (2 H, s, CH_2).

Photolysis of Azides.—(*a*) t-Butyl azide (1 g, 0.01 mol) in benzene (200 ml) was irradiated for 4 h at 20 °C. A solution of benzoquinone (1.08 g, 0.01 mol) in benzene (20 ml) was then added and the mixture was stirred for 4 h. The solvent was evaporated and the residue was chromatographed on silica, using dichloromethane as eluant, to give 2,5-bis(t-butylamino)-*p*-benzoquinone (0.21 g, 9%).

(*b*) Similar irradiation of t-butyl azide (1 g, 0.01 mol) in cyclohexane (200 ml) and work-up as in (*a*) yielded 2,5-bis(t-butylamino)-*p*-benzoquinone (0.15 g, 5%).

(*c*) 2-Azido-2,4,4-trimethylpentane (2 g, 0.0133 mol) was irradiated in benzene (250 ml) for 4 h at 20 °C, and then treated with *p*-benzoquinone and worked up as in (*a*). 2,5-Bis(1,1,3,3-tetramethylbutylamino)-*p*-benzoquinone was the only aminobenzoquinone present in the mixture (t.l.c.).

(*d*) Irradiation of n-butyl azide (2 g, 0.02 mol) in ether (250 ml) at 20 °C for 4 h and treatment of the reaction mixture as in (*a*) gave 2,5-bis(n-butylamino)-*p*-benzoquinone (0.14 g, 7%) as the only coloured product.

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