Photolysis of *N*-Alkoxybenzoquinone Imine *N*-Oxides

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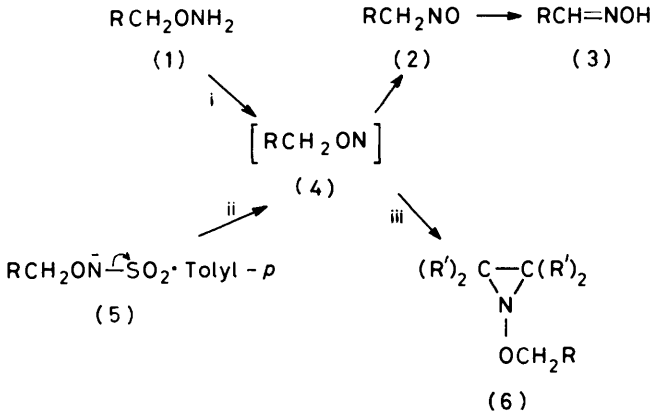
Photolyses of a series of *N*-alkoxybenzoquinone imine *N*-oxides give products arising mainly from alkyl radicals, the solvent, and the several quinonoid species present in the reaction mixture. The alkyl radicals may be derived by fragmentation of the corresponding alkoxynitrenes which also rearrange to nitroso-compounds and hence to oximes.

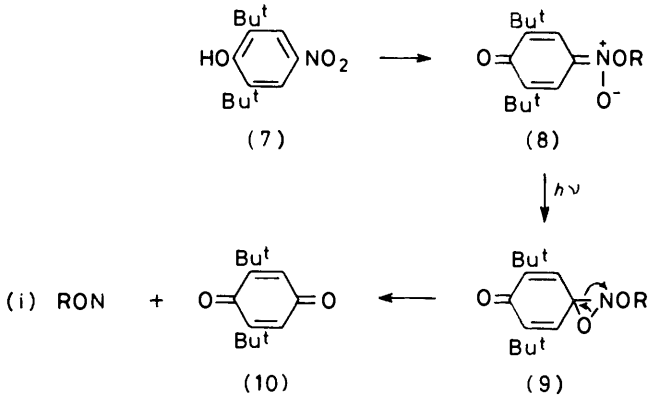
CONCLUSIVE evidence for the generation of alkoxynitrenes (4) has been difficult to obtain. Products formed on oxidation of the alkoxyamines (1) with lead tetra-acetate [1-3] and by thermolysis of salts of *N*-sulphonyl-*O*-alkylhydroxylamines [4] (5) could arise *via* transient oxynitrenes, but the evidence is not conclusive for nitrenes (Scheme 1). Lead alkoxyaminotriacetates



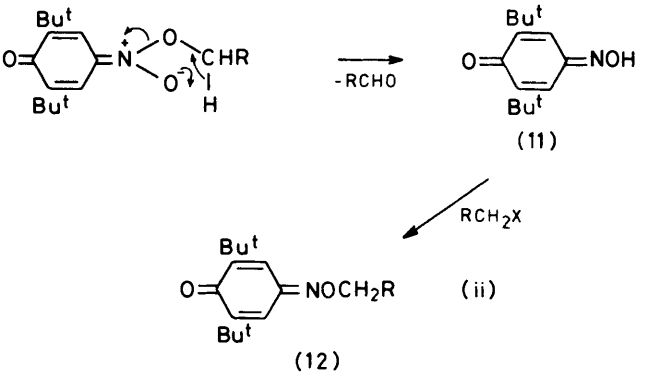
SCHEME 1 *Reagents*: i, $Pb(OAc)_4$; ii, Heat; iii, $(R')_2C{=}C(R')_2$

$[Pb(NHOCH_2R)(OAc)_3]$ may be the reactive species in some cases and formation of the oxime (3) from the sulphonylamine (5) *via* the nitroso-tautomer (2) may involve O ⟶ N migration of alkyl with concerted loss of *p*-toluenesulphinate.[3,4] By analogy with previously described *N*-alkyl- and *N*-aryl-quinone imine *N*-oxides,[5] and certain *aci*-nitro-compounds [6] the *N*-alkoxybenzoquinone-imine *N*-oxides (8) should yield alkoxynitrenes *via* the oxaziridine (9) on irradiation [reaction (i)]. We have prepared and examined the photochemistry of a series of such nitronic esters.†

Synthesis.—Two general methods were devised for the preparation of the nitronic esters (8).[7] The nitrophenol (7) and an alkyl halide were either heated under reflux in acetone over potassium carbonate or left at room temperature in dimethylformamide over potassium carbonate. Neither procedure was particularly efficient (usually *ca.* 25%), and both required a subsequent, rather wasteful chromatographic separation, but many attempts to improve yields *inter alia* by change of solvent and base were unrewarding. In this respect, a subsequently reported [7] alkylation of compound (7) using an alcohol in the presence of triphenylphosphine and diethyl azodicarboxylate appears to be a superior synthetic



route to the nitronic esters (8). An impurity in our preparation was the ether (12) which was formed by alkylation of the quinone oxime (11), the latter being a thermal degradation product of the nitronic ester (8) [reaction (ii)].[8] Predictably, only the t-butyl ester (8; R = Bu^t) did not decompose in this way and was by far the most stable of the nitronic esters examined. Typically, the ethyl ester has $t_{\frac{1}{2}}$ (60 °C) 6.5 h and $t_{\frac{1}{2}}$ (70 °C) 1.25 h. All the alkyl esters show $\lambda_{max.}$ 365 nm and have n.m.r. spectra with non-equivalent quinonoid proton signals. The analogous aryl esters could not be prepared by treatment of the nitrophenol (7) with diphenyliodonium bromide, aryldiazonium salts, or benzyne, nor by oxidation of nitroaryl ethers of the quinone oxime (11) with peroxy-acids.



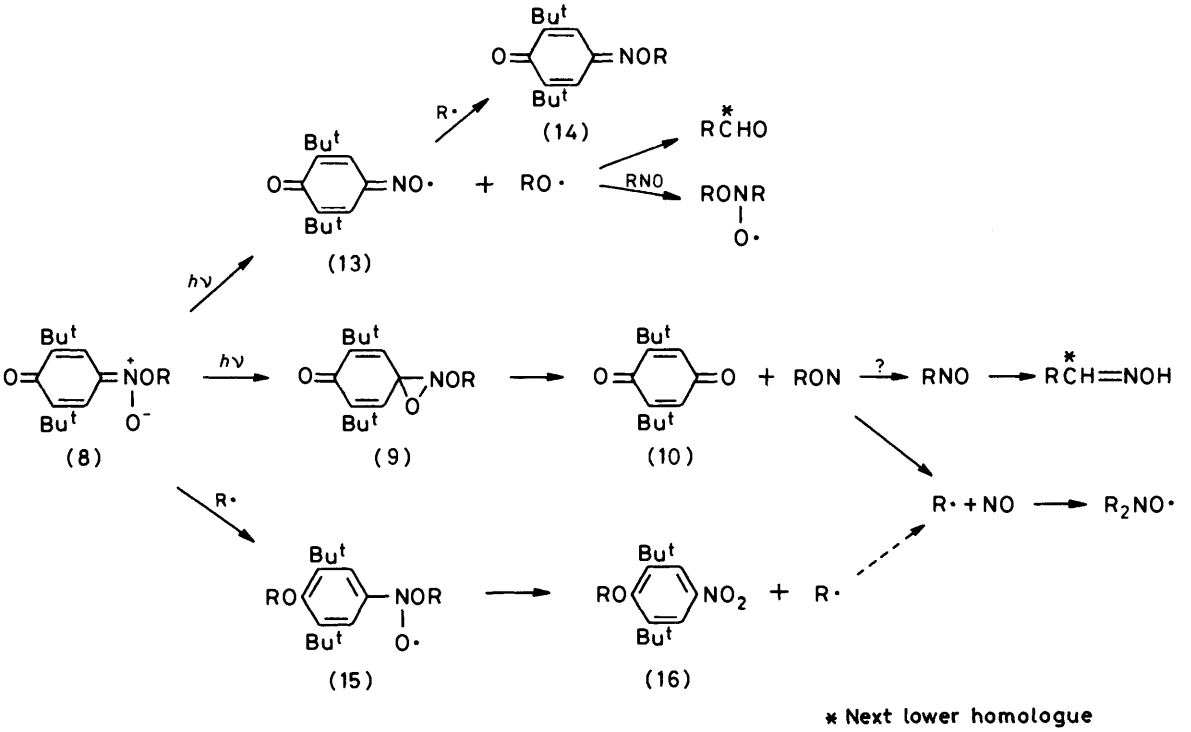
† Nitronic esters have been named systematically as substituted *aci*-nitro-compounds in the Experimental section.

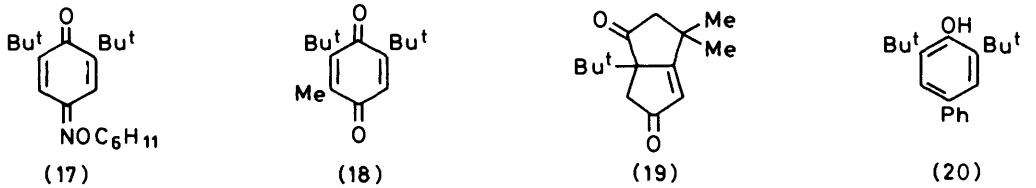
Products formed on irradiation of the nitronic esters (8)

Ester	Conditions [a]	Method of estimation	Products/% (10)	(11)	(14)	(16)	Oxime (3)	Other
(8; R = Me)	6 h/C_6H_6/q	Isolation	65	10	Trace	13		(20) 3; (19) 1
(8; R = Me)	6 h/C_6H_{12}/q	Isolation	40	7	26	10		
(8; R = Me)	4 or 10 h/C_6H_6/q	G.l.c.					1	
(8; R = Et)	6 h/C_6H_6/q	Isolation	67	11			6	(19) 1; (20) 2.5
(8; R = Et)	6 h/C_6H_{12}/q	Isolation	40	10	33		5	
(8; R = Et)	2.5 h/C_6H_6–petrol/q	Isolation	42	32	14			
(8; R = Et)	40 h/[b]/CH_2:CH·CH_2·$CHMe_2$/q	Isolation	34		8	7	2	(17) 8; (18) 3
(8; R = Et)	9 h/C_6H_6/q	N.m.r.	30	19	7		12	
(8; R = Et)	(i) 4 h (ii) 10 h/C_6H_6/p	G.l.c.[c]					(i) 8, (ii) 11	
(8; R = Pr^i)	9 h/C_6H_6/p	N.m.r.	38	←31→				
(8; R = Pr^i)	(i) 4 h (ii) 10 h/C_6H_6/p	G.l.c.					(i) 8, (ii) 12	
(8; R = Bu^n)	6 h/C_6H_6/q	Isolation	66	16			14	(20) 2.5; (19) 1
(8; R = Bu^n)	6 h/C_6H_{12}/q	Isolation	48	13	27		11	
(8; R = Bu^n)	(i) 4 h (ii) 10 h/C_6H_6/p	G.l.c.					(i) 9, (ii) 3	
(8; R = Bu^t)	12 h/C_6H_6/$VOSO_4$	U.v.					*ca.* 20 [d]	
(8; R = $PhCH_2$)	3 h/C_6H_6/q	Isolation	32	33	4	4 (R = H)	3	$PhCH_2Ph$ 10 PhCHO 25

[a] p = Pyrex; q = quartz. [b] 100-W Lamp. [c] 4 h/petrol/q; 4 h/C_6H_6/q; 4 h/C_6H_6/q; 4 h/CH_2:CH·CH_2·$CHMe_2$/p give oxime yields of 2,5,5, and 1%, respectively (g.l.c.). [d] Bu^tNO.

Irradiation Results.—Solutions of the nitronic esters listed in the Table were irradiated at room temperature under nitrogen with a 500-W medium-pressure mercury-vapour lamp through quartz or Pyrex. Product formation was estimated by separation and isolation and/or by n.m.r., e.s.r., g.l.c., and u.v. measurements





SCHEME 2

on the crude reaction mixtures. Complex reaction mixtures were invariably produced, only the principal components of which have been identified.

Formation of substantial amounts of 2,6-di-t-butylbenzoquinone in all photolyses provides strong evidence for photofragmentation *via* an oxaziridine intermediate [9] [reaction (i) and Scheme 2]. Complementary alkoxynitrene formation is more difficult to establish since no products [except the oxime ethers (12)] incorporating the RON moiety were isolated or detected, even when the photolyses were effected in an alkene solvent. Indirect evidence for alkoxynitrene participation may be adduced from the isolation and/or detection of the simple aldoximes (3) in most of the photolyses (*cf.* refs. 3 and 4). Such products could arise from alkoxynitrenes by intramolecular $O \longrightarrow N$ migration of an alkyl group, or by fragmentation to nitric oxide and alkyl radicals followed by recombination and tautomerisation. We have no evidence to support the former reaction but, consistent with the latter, there is abundant evidence for the formation of free alkyl radicals, both from product studies (*vide infra*) and e.s.r. results. Thus, the t-butyl ester (8; R = Bu^t), when irradiated (100-W high-pressure mercury-vapour lamp) in the cavity of an e.s.r. spectrometer, gave signals due to di-t-butyl nitroxide (a_N = 15.4 G) and t-butyl t-butoxy nitroxide [10] (a_N = 27.2 G), the signal from the alkoxy nitroxide decaying rapidly when the lamp was shuttered. The primary alkyl esters (8; R = Me, Et, Bu^n, $CH_2CH{=}CH_2$, and $PhCH_2$) gave either no signals, or extremely weak ones, while the isopropyl ester gave a feeble but easily recognisable spectrum due to di-isopropyl nitroxide (a_N = 14.5 and a_H^{CH} = 4.4 G).

Our failure to detect nitroxides on irradiation of the esters (8; R = Me, Et, Bu^n, $CH_2CH{=}CH_2$, and $PhCH_2$) we attribute to the rapid tautomerisation of the product alkyl nitroso-compounds to oximes. Indeed, a similar irradiation of nitrosomethane also gave only weak, unrecognisable signals (*cf.* ref. 10). The tautomerisation removes only one of several competitors for the alkyl radicals. Product analysis (Table) indicates that, among the others, the starting nitronic ester, 2,6-di-t-butylbenzoquinone, the solvent, and the iminoxyl (13) are important. Thus, formation of the nitroaryl ethers (16; R = Me and Et) can be accounted for by addition of the relatively small methyl and ethyl radicals, respectively, to the hindered oxygen of the parent nitronic ester followed by fragmentation of the ensuing *p*-alkoxyaryl alkoxy nitroxide (15).[11] The quinone (18) may arise in a similar way by trapping of alkyl radicals on C, while the isolation of diphenylmethane from the nitro-esters (8; R = $PhCH_2$) in benzene strongly suggests that benzyl radicals are implicated in that photolysis. Trapping of the smaller alkyl radicals by benzene probably also occurs, but the products would not have been detected.

Mediation of alkoxy-radicals in these photolyses, as indicated by the detection of t-butyl t-butoxy nitroxide and isolation of benzaldehyde from the benzyl ester photolysis, indicates that homolysis of the N–O bond of the nitronic ester competes with oxaziridine formation at the photolysis step (*cf.* photolysis of nitrites [12]). The iminoxyl (13), simultaneously produced, was not detected by e.s.r., presumably because it also efficiently traps alkyl radicals to give small but significant yields of the corresponding oxime ethers (14) (see Table).

Although the possibility that oxaziridines photofragment to give nitric oxide, quinone, and alkyl radicals in a concerted fashion cannot be completely discounted, we consider that alkoxynitrenes are produced in our photolyses but that they rapidly fragment to nitric oxide and alkyl radicals, the last-named species being responsible for the complexity of the product mixtures. Since it seems unlikely that such species could be trapped efficiently unless generated at a very low temperature in an inert medium, we are confident that oxynitrenes do not mediate in the formation of alkoxyaziridines when alkoxyamines are oxidised with lead tetra-acetate in alkene solvents,[1-3] nor in other related reactions where high yields of one product are obtained.

The structure and formation of the minor products (19) and (20) have already been discussed.[13]

EXPERIMENTAL

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

Preparation of Nitronic Esters.—General methods. (*a*) 4-Nitro-2,6-di-t-butylphenol [14] (2.5 g, 10 mmol) in acetone (10 ml) containing potassium carbonate (1 g) was mixed with the alkyl iodide (*ca.* 50 mmol) and the mixture was heated under reflux with stirring for several hours, until most of the nitrophenol had been consumed (t.l.c.). The mixture was evaporated to dryness under reduced pressure at room temperature. The residue was chromatographed on alumina with petroleum as eluant to isolate the oxime ether, and then with ether–petroleum (1 : 50—1 : 10) to allow separation of the nitronic ester.

(*b*) 4-Nitro-2,6-di-t-butylphenol [14] (1—5 g, 4—20 mmol) in dimethylformamide (DMF) (5—25 ml) containing potassium carbonate (0.4—2.0 g) was mixed with a five-fold excess of alkyl bromide and the reaction mixture was stirred at or below room temperature until most of the nitrophenol had been consumed (t.l.c.). It was then poured into water–petroleum (1 : 1 v/v). The water was extracted with petroleum and the combined petroleum extracts were washed, dried, and concentrated. The concentrate was rapidly chromatographed on alumina (activity II or III) and eluted with petroleum followed by ether–petroleum (1 : 20). Further chromatography was usually necessary to obtain pure nitronic ester.

4-(*Methyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Me).—This compound was prepared by method (*a*) with heating for 1.5 h. It was obtained as orange needles, m.p. 105—106 °C (decomp.) (lit.,[15] m.p. 105—106 °C), $\lambda_{max.}$ (CCl_4) 361 nm (log ε 4.45); $\nu_{max.}$ 1 640, 1 610, 1 540, and 1 370 cm^{-1}; δ 1.31 (18 H, s, 2 × Bu^t), 3.97 (3 H, s, OMe), 7.39 (1 H, d, *J* 3 Hz, 3- or 5-H), and 7.58 (1 H, d, *J* 3 Hz, 3- or 5-H).

4-(*Ethyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Et).—This compound was prepared by method (*a*) with heating for 3 h. It was obtained as orange needles, m.p. 54—55 °C (from methanol) (lit.,[16] m.p. 54.5—55.5 °C), $\lambda_{max.}$ (cyclohexane) 249, 257, and 360 nm (log ε 3.5, 3.46, and 4.42); $\nu_{max.}$ 1 640, 1 618, 1 535, and 1 370 cm^{-1}; δ 1.31 (18 H, s, 2 × Bu^t), 1.33 (3 H, t, *J* 7 Hz, Me), 4.42 (2 H, q, *J* 7 Hz, CH_2), 7.40 (1 H, d, *J* 3 Hz, 3- or 5-H), and 7.57 (1 H, d, *J* 3 Hz, 3- or 5-H).

4-(*Isopropyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Pr^i).—This compound was prepared by method (*a*) with heating for 6 h. It was obtained as orange needles, m.p. 50—54 °C (lit.,[16] 62.5—63.5 °C) (Found: M^+, 293.1987. Calc. for $C_{17}H_{27}NO_3$: *M*, 293.1991); $\lambda_{max.}$ (hexane) 362 nm (log ε 4.46); $\nu_{max.}$ 1 641, 1 615, 1 536, and 1 367 cm^{-1}; δ 1.31 (18 H, s, 2 × Bu^t), 1.33 (6 H, d, *J* 6.5 Hz, 2 × Me), 5.22 (1 H, sept., *J* 6.5 Hz, OCH), 7.45 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.61 (H, d, *J* 2.5 Hz, 3- or 5-H); *m/e* 293 (M^+, 2%), 277 (18), 235 (35), 234 (100), 220 (32), 193 (18), 192 (71), 180 (32), 178 (28), and 162 (28).

4-(*Butyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Bu^n).—This compound was prepared by method (*a*) with heating for 3 h. It was obtained as red *plates*, m.p. 52.5—55 °C (Found: C, 70.1; H, 9.3; N, 4.6. $C_{18}H_{29}NO_3$ requires C, 70.3; H, 9.5; N, 4.6%), $\lambda_{max.}$ (CCl_4) 374 nm (log ε 4.30); $\nu_{max.}$ 1 635, 1 610, 1 530, and 1 365 cm^{-1}; δ 0.99 (3 H, t, *J* 6.5 Hz, Me), 1.3 (18 H, s, 2 × Bu^t), 1.4—1.8 (4 H, m, CH_2CH_2), 4.37 (2 H, t, *J* 6.5 Hz, OCH_2), 7.41 5-H). d, *J* 3 Hz, 3- or 5-H), and 7.60 (1 H, d, *J* 3 Hz, 3- or 5-H).

4-(*t-Butyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Bu^t).—This compound was prepared by method (*b*) with stirring for 10 d. It was obtained as orange *needles*, m.p. 64—68 °C (Found: M^+, 307.2155. $C_{18}H_{29}NO_3$ requires *M*, 307.2147); $\lambda_{max.}$ (cyclohexane) 250, 259, and 365 nm (log ε 3.5, 3.5, and 4.48); $\nu_{max.}$ 1 637, 1 608, 1 570, and 1 363 cm^{-1}; δ 1.31 (18 H, s, 2 × Bu^t), 1.54 (9 H, s, O-Bu^t), 7.44 (1 H, d, *J* 3 Hz, 3- or 5-H), and 7.51 (1 H, d, *J* 3 Hz, 3- or 5-H); *m/e* 307 (M^+, 3%), 262 (10), 251 (25), 247 (25), 235 (13), 234 (25), 192 (14), 85 (35), 83 (60), and 57 (100).

4-(*Allyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = allyl).—This compound was prepared by method (*b*) with stirring at room temperature for 4 h. It was obtained as red *needles*, m.p. 38—41 °C (Found: M^+, 291.1833. $C_{17}H_{25}NO_3$ requires *M*, 291.1834); $\lambda_{max.}$ (cyclohexane) 248, 257, and 361 nm (log ε 3.56, 3.45, and 4.33); $\nu_{max.}$ 1 639, 1 612, 1 530, and 1 365 cm^{-1}; δ 1.30 (18 H, s, 2 × Bu^t), 4.82 (2 H, d, *J* 6 Hz, OCH_2), 5.2—5.6 (2 H, m, CH_2=), 5.6—6.1 (1 H, m, CH=), 7.35 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.6 (1 H, d, *J* 2.5 Hz, 3- or 5-H).

4-(*Benzyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = $PhCH_2$).—This compound was prepared (72%) by method (*b*) with stirring at room temperature for 6 h or overnight at 5—10 °C. It was obtained as a red *oil* which solidified at *ca.* −10 °C and decomposed on attempted distillation (Found: M^+, 341.1989. $C_{18}H_{29}NO_2$ requires *M*, 341.1990); $\lambda_{max.}$ (cyclohexane) 243 and 362 nm; $\nu_{max.}$ 1 610, 1 528, and 1 366 cm^{-1}; δ 1.30 (18 H, s, 2 × Bu^t), 5.42 (2 H, s, CH_2), 7.44 (1 H, d, *J* 2.5 Hz, 3- or 5-H), 7.46 (5 H, br s, Ph), and 7.64 (1 H, d, *J* 2.7 Hz, 3- or 5-H).

Preparation of Ethers of 2,6-*Di-t-butyl*-p-*benzoquinone* 4-*Oxime* (11).—These were by-products of the reaction of 4-nitro-2,6-di-t-butylphenol with alkyl bromides. *O*-Methyl-2,6-di-t-butyl-*p*-benzoquinone oxime (12; R = H) was obtained as yellow needles, m.p. 80—81 °C (lit.,[8] m.p. 81—81.5 °C). *O*-*Ethyl*-2,6-*di-t-butyl*-p-*benzoquinone oxime* (12; R = CH_3) was obtained as a yellow oil, b.p. 50—52 °C at 0.1 mmHg (Found: C, 72.8; H, 9.6; N, 5.3. $C_{16}H_{25}NO_2$ requires C,73.0; H, 9·6; N, 5·3%); $\nu_{max.}$ 330 nm (EtOH) (log ε 4.31); $\nu_{max.}$ 1 630 cm^{-1}; δ 1.29 (18 H, s, 2 × Bu^t), 1.32 (3 H, t, Me), 4.37 (2 H, q, CH_2), 6.90 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.41 (1 H, d, *J* 2.5 Hz, 3- or 5-H). *O*-*Isopropyl*-2,6-*di-t-butyl*-p-*benzoquinone oxime* was obtained as a yellow oil, which decomposed on attempted distillation (Found: M^+, 277.2042. $C_{17}H_{27}NO_2$ requires *M*, 277.2041); δ 1.31 (18 H, s, 2 × Bu^t), 1.38 (6 H, d, *J* 6.5 Hz, 2 × Me), 4.57 (1 H, sept., *J* 6.5 Hz, OCH), 6.97 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.47 (1 H, d, *J* 2.5 Hz, 3- or 5-H). *O*-*Butyl*-2,6-*di-t-butyl*-p-*benzoquinone oxime* (12; R = C_3H_7) was obtained as a yellow oil, b.p. 42—45 °C at 0.1 mmHg (Found: C, 74.0; H, 10.2; N, 4.8. $C_{18}H_{29}NO_2$ requires C, 74.2; H, 10.0; N, 4.8%); $\lambda_{max.}$ (CCl_4) 324 nm (log ε 4.34); $\nu_{max.}$ 1 630 cm^{-1}; δ 0.97 (3 H, t, *J* 6.5 Hz, Me), 1.28 (18 H, s, 2 × Bu^t), 1.4—1.97 (4 H, m, CH_2-CH_2), 4.31 (2 H, t, *J* 6.15 Hz, OCH_2), 6.90 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.41 (1 H, d, *J* 2.5 Hz, 3- or 5-H). *O*-*t-Butyl*-2,6-*di-t-butyl*-p-*benzoquinone oxime* was obtained as yellow needles, m.p. 76—78 °C (Found: M^+, 291.2192. $C_{18}H_{29}NO_2$ requires *M*, 291.2198); δ 1.31 (18 H, s, 2 × Bu^t), 1.40 (9 H, s, O-Bu^t), 6.97 (1 H, d, *J* 2.5 Hz, 3- or 5-H), and 7.46 (1 H, d, *J* 2.5 Hz, 3- or 5-H). *O*-*Benzyl*-2,6-*di-t-butyl*-p-*benzoquinone oxime* (12; R = Ph) was obtained as orange needles, m.p. 63—66 °C (from aqueous alcohol) (Found: C, 77.7; H, 8.6; N, 4.3. $C_{21}H_{27}NO_2$ requires C, 77.5; H, 8.4; N, 4.3%); $\nu_{max.}$ (cyclohexane) 319 nm (log ε 4.30); $\nu_{max.}$ 1 630 cm^{-1}; δ 1.30 (18 H, s, 2 × Bu^t), 5.39 (2 H, s, CH_2), 6.99 (1 H, d, *J* 2.5 Hz, 3- or 5-H), 7.45 (5 H, br s, Ph), and 7.55 (1 H, d, *J* 2.5 Hz, 3- or 5-H).

N-*Phenyl*-2,6-*di-t-butyl*-p-*benzoquinone Imine* N-*Oxide*.—The oxime (11) (2.35 g, 10 mmol) in DMF (20 ml) containing potassium carbonate (1 g) was treated with diphenyliodonium chloride (3.2 g) and the mixture was stirred for 17 h. It was then poured into water (40 ml) and petroleum (40 ml), the aqueous layer separated and extracted with petroleum, the combined and dried petroleum extracts evaporated to dryness and the residue chromatographed on alumina. Elution with ether–petroleum (1 : 9) gave the product as red *needles*, m.p. 127—130 °C (Found: C, 77.2; H, 8.0%; M^+, 311.1886. $C_{20}H_{25}NO_2$ requires C, 77.1; H, 8.1%; *M*, 311.1885); $\lambda_{max.}$ (cyclohexane) 257 and 382 nm (log ε 4.0 and 4.17); $\nu_{max.}$ 1 639 and 1 605 cm^{-1}; δ (two isomers) 1.18 and 1.37 (each 9 H, s, Bu^t), 6.95 (1 H, d, *J* 3 Hz, 3-H), 7.56 (5 H, s, Ph), and 7.94 (1 H, d, *J* 3 Hz, 5-H).

A yellow photosensitive oil obtained by elution with ether–petroleum (1 : 49) was a minor product (*ca.* 10%). Its spectroscopic properties were consistent with those expected for *O*-phenyl-2,6-di-t-butyl-*p*-benzoquinone oxime but it was too sensitive to be purified (M^+, 311.1886. $C_{20}H_{25}NO_2$ requires *M*, 311.1885); $\lambda_{max.}$ 360 nm; $\nu_{max.}$ 1 650 and 1 630 cm^{-1}; δ 8.7 (9 H, s, Bu^t), 7.03 (1 H, d, *J* 3 Hz, 3- or 5-H), 7.3 (5 H, br s, Ph), and 7.65 (1 H, d, *J* 3 Hz, 3- or 5-H). On exposure to sunlight for 5 min the band at 360 nm was replaced by one at 273 nm.

Irradiation of Nitronic Esters (*Preparative Scale*).—(a) *With* 4-(*Methyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Me). The nitronic ester (8; R = Me) (2.0 g) in benzene (250 ml) was irradiated in a quartz annular vessel for 6 h at 20 °C. The solvent was removed under reduced pressure at room temperature and the residue was chro-

matographed (p.l.c.) on silica with benzene–hexane (1 : 1) as eluant to give (i) 4-nitro-2,6-di-t-butylanisole (0.255 g, 13.6%), m.p. 80—81 °C (lit.,[16] 80.5—81.5 °C), δ 1.48 (18 H, s, 2 × Bu^t), 3.77 (3 H, s, OMe), and 8.1 (2 H, s, ArH); (ii) unchanged nitronic ester (0.052 g, 3%); (iii) 4-phenyl-2,6-di-t-butylphenol (0.048 g, 3%), m.p. 100—101 °C (lit.,[17] 101—102 °C) (Found: M^+, 282.1979. Calc. for $C_{20}H_{26}O$: M, 282.1983); $\lambda_{max.}$ (EtOH) 266 nm (log ε 3.93); $\lambda_{max.}$ (EtOH–NaOH) 302 nm; δ 1.49 (18 H, s, 2 × Bu^t), 5.22 (1 H, s, OH), and 7.15—7.50 (7 H, m, ArH); (iv) 2,6-di-t-butyl-1,4-benzoquinone (1.12 g, 5%); (v) 2,6-di-t-butyl-*p*-benzoquinone oxime (11) (0.168 g, 10%); (vi) 3,3,-6,6a-tetrahydro-3,3-dimethyl-6a-t-butylpentalene-1,5-dione (19) (0.085 g, 1%), m.p. 90—91 °C (from pentane), spectroscopic details of which are given in ref. 13. Irradiation of the nitronic ester (8; R = Me) in cyclohexane and work-up of the product as in (a) gave the products listed in the Table.

(*b*) *With* 4-(*ethyl*-aci-*nitro*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (8; R = Et). On irradiation the nitronic ester (8; R = Et) gave under the sets of conditions listed in the Table the products shown. The following are new: 3-*methyl*-2,6-*di-t-butylbenzoquinone* (18) (M^+, 248.1774. $C_{16}H_{24}O_2$ requires 248.1776); δ 1.08 (3 H, t, *J* 7.5 Hz, Me), 1.23 (9 H, s, Bu^t), 1.36 (9 H, s, Bu^t), 2.61 (2 H, q, *J* 7.5 Hz, CH_2), and 6.35 (1 H, s, 5-H); O-(4-*methylpent*-1-*en*-3-*yl*)-2,6-*di-t-butyl*-p-*benzoquinone oxime* (Found: M^+, 317.2352. $C_{20}H_{31}NO_2$ requires M, 317.2354); δ 1.04 (6 H, d, *J* 6 Hz, 2 × Me), 1.28 (18 H, br s, 2 × Bu^t), 2.36 (1 H, sept., C*H*Me$_2$), 4.76—5.75 (4 H, m, CH=CH$_2$), 6.93 (1 H, d, *J* 2 Hz, 3-H), and 7.44 (1 H, d, *J* 2 Hz, 5-H); *m/e* 317 (M^+, 40%), 260 (18), 247 (10), 235 (71), 234 (20), 220 (11), 219 (10), 192 (11), 83 (84), and 82 (22). The other nitronic esters, when irradiated under the conditions indicated in the Table, gave known products.

Light Sources.—Both 100-W and 1-kW mercury-vapour lamps were used for the e.s.r. studies, and for preparative work a 500-W medium-pressure lamp in an annular vessel was used.

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