Aryl Nitrenes from *N,N'*-Diarylbenzoquinone Di-imine *N,N'*-Dioxides and *N*-Arylbenzoquinone Imine *N*-Oxides

By **Alexander R. Forrester,* Munro M. Ogilvy,** and **Ronald H. Thomson,** Chemistry Department, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

Photolyses of the title quinone imine *N*-oxides give mainly azoarenes formed by dimerisation of triplet aryl nitrenes.

THERMOLYSIS and photolysis of azides, and deoxygenation of aryl nitro- and nitroso-compounds,[1] are the principal methods used for production of aryl nitrenes. We now describe an alternative photolytic route to such intermediates.

Irradiation of the *N,N'*-diaryl-*p*-benzoquinone di-imine *N,N'*-dioxides (1; R = H and R = OMe) in benzene at room temperature through quartz gave the corresponding quinone imine *N*-oxides (3; R = H and OMe), benzoquinone, and azo-compounds (4; R = H and OMe) (54 and 75% respectively) (see Table 1). Small amounts of highly coloured products, thought to be the corresponding 2,5-diarylamino-*p*-benzoquinones (5; $R^1 = H$, $R^2 = Ph$, and $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$), were also detected (t.l.c.). When diethylamine was used as solvent the azo-compounds (4; R = H and OMe) (28 and 43%, respectively) were the main products and these were accompanied by 2,5-bis(diethylamino)-*p*-benzoquinone (5; $R^1 = R^2 = Et$) (25 and 43%, respectively), the 2-diethylamino-3*H*-azepines (6; R = H and R = OMe), aniline (8%), and *p*-anisidine (14%), respectively. In aniline solution the quinone di-imine *N,N'*-dioxide (1; R = H) gave mainly azobenzene (22%) and 2,5-dianilino-*p*-benzoquinone (5; $R^1 = H$, $R^2 = Ph$) (23%).

The results with benzene as solvent are generally similar to those of Pedersen,[2] minor differences in relative yields presumably being due to differences in the irradiation procedures. Previous suggestions [1,2] that these arise by fragmentation of intermediate oxaziridines as indicated [(1)→(2)→(3)→(4)] is supported by the results from irradiation of the quinone di-imines (1) in amine solvents. The observed decrease in yield of azo-compound and formation of aromatic amine when diethylamine replaced benzene as solvent is consistent with the participation of a triplet aryl nitrene for which hydrogen abstraction is an alternative to dimerisation. Azepine formation is an established reaction of singlet nitrenes [3] in nucleophilic solvents and the low yields obtained in the amine solvents confirm that the amounts of the singlet species produced in these photolyses are small. Splitter and Calvin's [4] experience on photolysis of oxaziridines in diethylamine, was similar.

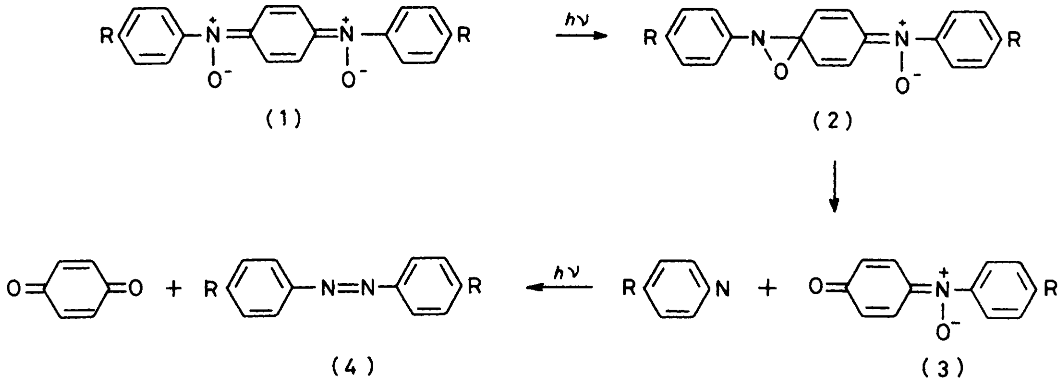
The products derived from biphenyl-2-ylnitrene and the spin states responsible for these products are well-established [5] making this nitrene particularly appropriate for mechanistic studies. Preparation of the benzoquinone imine *N*-oxide precursor (8) of this nitrene was achieved by oxidation of biphenyl-2-ylphenylhydroxylamine with Fremy's salt. The nitroxide (7) initially produced could react further with Fremy's salt to give either of the quinone imine *N*-oxides (8) or (9). The n.m.r. spectrum of the product showed signals from four quinonoid protons (Table 2) and is clearly due to the former of these oxides (8). The $a_{o\text{-H}}$ (2.63 G) and $a_{p\text{-H}}$ (2.63 G) values of the unsubstituted rings of the nitroxide (7) are much larger than those of the corresponding protons in diphenyl nitroxide [6] ($a_{o\text{-H}} = a_{p\text{-H}} = 2.0$ G) although there is little difference in their a_N values (10.5 and 10.9 G, respectively). The spectrum of compound (7) showed further splittings attributable to two *meta*-

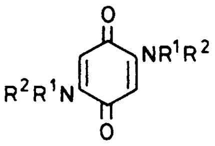
TABLE 1

Products from *N,N'*-diarylbenzoquinone di-imine *N,N'*-dioxides and *N*-arylbenzoquinone imine *N*-oxides

		Products/%			
N-Oxides	Solvent	Quinone imine *N*-oxide (2)	Quinone (3)	Azo-compound (4)	Other
(1; R = H)	C_6H_6	41	31	54	(5; $R^1 = H$, $R^2 = Ph$) [a]
(1; R = OMe)	C_6H_6	17	61	75	(5; $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$) [a]
(1; R = H)	Et_2NH			28	(6; $R^1 = R^2 = Et$, R = H) 1; $PhNH_2$, 8; (5; $R^1 = R^2 = Et$) 26
(1; R = OMe)	Et_2NH			43	(6; $R^1 = R^2 = Et$, R = OMe) 1 $p\text{-MeOC}_6H_4NH_2$, 14 (5; $R^1 = R^2 = Et$) 43
(1; R = H)	$PhNH_2$			22	(6; R = H, $R^1 = H$, $R^2 = Ph$) 1, (5; $R^1 = H$, $R^2 = Ph$) 23
(8)	C_6H_6		41	52	(9) 10
(8)	C_6H_6/O_2		50	24	(9) 31
(8)	C_6H_6/pyrene			49	(9) 8

[a] Detected by t.l.c. but not isolated.




(5)

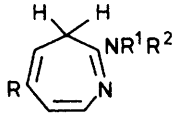
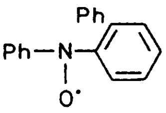

(6)

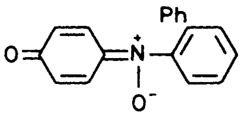
TABLE 2

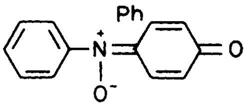
N.m.r. spectra of *N*,*N'*-diarylbenzoquinone di-imine *N*,*N'*-dioxides and *N*-arylbenzoquinone imine *N*-oxides

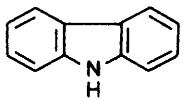
	δ				*J* (Hz)			
N-Oxide	$H_{2,6}$	$H_{3,5}$	ArH	Other	$J_{2,3}$	$J_{5,6}$	$J_{2,6}$	$J_{3,5}$
(3; R = H)	8.02 q	6.63 q	2.46 s		10	11	3	1.5
	7.19 q	6.22 q						
(3; R = OMe)	7.99 q	6.59 q	7.44	4.12 (OMe)	10	10	3	1.5
	7.47 q	6.22 q	7.00 d					
(8)	7.80 q	6.41 q	7.58—7.25 m		9	8.5	3	1.5
	6.78 q	5.99 q	7.30 s					
(1; R = H)		7.28 s	7.50 s	3.88 (OMe)				
(1; R = OMe)	7.26 s		7.43 d					
			6.97 d					

protons (0.80 G) and the *ortho*- and *para*-protons of the substituted ring (0.80 G). These values indicate that the biphenyl-2-yl ring of the nitroxide (7) is twisted out of conjugation with the nitrogen; this leads to increased unpaired spin density on the unsubstituted ring and hence the likelihood of Fremy's salt reacting at the *para*-position of that ring is greater.


(7)


(8)


(9)


(10)

Irradiation of the *N*-oxide (9) in benzene gave 2,2'-azobiphenyl (52%), carbazole (9%), benzoquinone (41%), and a trace of 2-aminobiphenyl. Carbazole, which is an established product of singlet biphenyl-2-ylnitrene,[5] does not react with benzoquinone under these conditions. Pyrene and piperylene, both known[7] quenchers of triplet 2-azidobiphenyl, did not alter the course of the reaction. However, when oxygen, previously used to quench triplet oxaziridines,[4] was bubbled through the solution during photolysis, the yield of carbazole was increased to 31% at the expense of the 2,2'-azobiphenyl (24%). This result further confirms the suggestion that dimerisation is a reaction of the triplet and intramolecular cyclisation a reaction of the singlet nitrene.

EXPERIMENTAL

U.v. and n.m.r. spectra were measured for solutions in ethanol and deuteriochloroform, respectively, and i.r. spectra for Nujol mulls, unless stated otherwise. Petroleum refers to light petroleum, b.p. 60—80 °C and ether to diethyl ether.

Preparation of Starting Materials.—*N*,*N'*-Diphenyl- and *N*,*N'*-bis-(4-methoxyphenyl)-*p*-benzoquinone di-imine *N*,*N'*-dioxides and *N*-phenyl- and *N*-(4-methoxyphenyl)-*p*-benzoquinone imine *N*-oxides were prepared by literature methods.[8]

N-(*Biphenyl*-2-*yl*)-p-*benzoquinone Imine N-Oxide* (8).—To a stirred ethereal solution of biphenyl-2-ylmagnesium bromide [prepared from magnesium (1.4 g) and 2-bromobiphenyl (8 g, 0.034 mmol) in ether (50 ml)] cooled to −20 °C under nitrogen, nitrosobenzene (3.6 g, 0.033 mol) in ether (100 ml) was added, dropwise, during 0.5 h. The mixture was allowed to warm to room temperature before it was poured onto ice–water. The ethereal layer was separated and the aqueous layer was extracted with ether (3 × 50 ml) which had been previously flushed with nitrogen. The combined ethereal fractions were dried ($MgSO_4$), and the solvent was removed under reduced pressure to give the crude hydroxylamine (positive tetrazolium test) as a red oil.

A solution of this red oil in methanol (50 ml) was added to one of Fremy's salt (25 g) in an aqueous 0.25M-solution of potassium dihydrogen phosphate (100 ml). The resulting solution was shaken for 0.5 h before it was extracted with chloroform (3 × 100 ml). The dried extracts were evaporated and the residue was chromatographed on neutral alumina (column). Elution with benzene gave (i) a deep-red oil containing biphenyl-2-yl phenyl nitroxide (see text) (0.4 g) and (ii) N-(*biphenyl*-2-*yl*)-p-*benzoquinone imine* N-*oxide* (8) (2.3 g, 26%) as orange needles, m.p. 143—144 °C (from petroleum) (Found: C, 78.7; H, 5.1; N, 4.9. $C_{18}H_{13}NO_2$ requires C, 78.5; H, 4.8; N, 5.1%); $\lambda_{max.}$ 257 and 380 nm (log ε 3.95 and 4.40); $\nu_{max.}$ 1 625 cm^{-1}; ^{1}H n.m.r. data given in Table 2.

Photolyses of Quinone Imine N-*Oxides*.—These were carried out under nitrogen using a Hanovia 500S medium-pressure mercury-vapour lamp in an annular quartz vessel as follows.

N,N′-*Diphenyl*-p-*benzoquinone di-imine* N,N′-*dioxide* (1; R = H). (*a*) The *p*-benzoquinone di-imine *N,N*-dioxide in benzene (250 ml) was irradiated for 6 h at 20 °C. Removal of solvent and chromatography of the residue on neutral alumina (column) gave (i) (petroleum as eluant) azobenzene (4; R = H) (0.334 g, 54%); (ii) (benzene as eluant) *p*-benzoquinone (0.115 g, 31%); and (iii) (chloroform as eluant) *N*-phenyl-*p*-benzoquinone imine *N*-oxide (3; R = H) (0.280 g, 41%). 2,5-Dianilino-*p*-benzoquinone[9] (5; R^1 = H, R^2 = Ph) was detected (t.l.c.) but not isolated.

(*b*) A solution of the quinone di-imine *N,N′*-dioxide (1.0 g) in aniline (250 ml) was irradiated for 6 h. The aniline was distilled off under reduced pressure and the residual gum was dissolved in ether (100 ml). The ethereal solution was extracted with 2M-hydrochloric acid (2 × 25 ml) and the aqueous phase was separated, made alkaline with aqueous sodium carbonate and extracted with ether. The ethereal extracts were dried and evaporated to give 2-anilino-3*H*-azepine[10] (6; R = R^1 = H, R^2 = Ph) (8 mg). The original ethereal solution was chromatographed (p.l.c.) on silica (GF_{254}) with chloroform to give azobenzene (4; R=H) (0.137 g) and 2,5-dianilino-*p*-benzoquinone (5; R^1 = H, R^2 = Ph) (0.230 g).

(*c*) The *p*-benzoquinone di-imine *N,N′*-dioxide (1.0 g) in diethylamine (250 ml) was irradiated for 6 h at 20 °C. After removal of the solvent under reduced pressure the residue was dissolved in ether and extracted with 2M-hydrochloric acid. The acid extracts were neutralised and then extracted with ether. Evaporation of the dried ethereal extracts gave an oil (0.094 g) which, on chromatography (p.l.c.) on silica with benzene as eluant, gave aniline (0.056 g, 8%), and 2-diethylamino-3*H*-azepine[11] (6; R = H, R^1 = R^2 = Et) (7 mg). The ethereal solution was evaporated and the residue was chromatographed on silica (t.l.c.) using dichloromethane to give azobenzene (4; R^1 = H) (0.171 g, 28%) and 2,5-bis(diethylamino)-*p*-benzoquinone[12] (5; R^1 = R^2 = Et) (0.225 g, 26%).

N,N′-*Bis*(4-*methoxyphenyl*)-p-*benzoquinone di-imine* N,N′-*dioxide* (1; R = OMe). (*a*) The quinone di-imine *N,N′*-dioxide (1 g) in benzene (250 ml) was irradiated for 6 h. Work-up as before gave (i) 4,4′-dimethoxyazobenzene (4; R = OMe) (0.518 g, 75%); (ii) *p*-benzoquinone (0.188 g, 61%); and (iii) *N*-(4-methoxyphenyl)-*p*-benzoquinone imine *N*-oxide (3; R = OMe) (0.111 g, 17%). 2,5-Bis-(4-methoxyphenylamino)-*p*-benzoquinone (5; R^1 = H, R^2 = $MeOC_6H_4$-*p*) was detected by t.l.c. but was not isolated.

(*b*) The benzoquinone di-imine *N,N′*-dioxide (1.0 g) in diethylamine (250 ml) was irradiated for 6 h at 20 °C. Isolation of the products as before gave (i) *p*-anisidine (0.091 g, 14%); (ii) 4,4′-dimethoxyazobenzene (4; R = OMe) (0.290 g, 43%); (iii) 2,5-bis(diethylamino)-*p*-benzoquinone (5; R^1 = R^2 = Et) (0.300 g, 43%); and (*iv*) 2-*diethylamino*-5-*methoxy*-3H-*azepine* (6; R = OMe, R^1 = R^2 = Et) (8 mg) as a pale yellow liquid, b.p. 82—86 °C at 0.5 mmHg (Found: C, 67.9; H, 9.2; N, 14.1. $C_{11}H_{18}N_2O$ requires C, 68.0; H, 9.3; N, 14.4%); $\nu_{max.}$ 1 630 cm^{-1}; δ 1.14 (6 H, t, 2 × Me), 2.57 (2 H, d, *J* 6 Hz, 3-H), 3.39 (4 H, q, 2 × CH), 3.56 (3 H, s, OMe), 4.28 (1 H, t, *J* 6 Hz, 4-H), 5.60 (1 H, d, *J* 7 Hz, 6-H), and 7.10 (1 H, d, *J* 7 Hz, 7-H). This product was identical with that obtained on irradiation of *p*-methoxyphenyl azide in diethylamine.

N-*Biphenyl*-2-*yl*-p-*benzoquinone imine* N-*oxide* (8). (*a*) The quinone imine *N*-oxide (0.6 g) in benzene (200 ml) was irradiated for 6 h. After removal of the solvent the residue was chromatographed on silica, using benzene as eluant, to give (i) 2,2′-diphenylazobenzene (0.19 g, 52%); (ii) carbazole (0.033 g, 9%); and (iii) *p*-benzoquinone (0.097 g, 41%). 2-Aminobiphenyl was detected (t.l.c.).

(*b*) The quinone imine *N*-oxide (0.6 g) in benzene (200 ml) containing pyrene (5 g) was irradiated for 6 h. Work-up as before gave (i) 2,2′-diphenylazobenzene (0.175 g, 49%) and (ii) carbazole (0.028 g, 8%).

(*c*) The quinone imine *N*-oxide (0.1 g) in benzene (100 ml), through which oxygen was continuously bubbled, was irradiated for 3 h. The residue obtained after removal of solvent was chromatographed (p.l.c.), using benzene as eluant, to give (i) 2,2′-diphenylazobenzene (0.014 g, 24%); (ii) carbazole (0.019 g, 31%); and (iii) benzoquinone (0.02 g, 50%).

We thank I.C.I. (Pharmaceuticals) Limited for financial assistance and the S.R.C. for a CASE studentship (to M. M. O.).

[2/043 *Received*, 11*th January*, 1982]

REFERENCES

[1] T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes and Arynes,' Nelson, London, 1969 p. 32; P. A. S. Smith in 'Nitrenes,' ed. W. Lwowski, Intersciences, New York, 1970, p. 114.

[2] C. J. Pedersen, *J. Am. Chem. Soc.*, 1957, **79**, 5014.

[3] R. A. Abramovitch and E. P. Kyba in 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, p. 251; C. Wentrup, *Top. Curr. Chem.*, 1976, **62**, 173.

[4] J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1968, 1445.

[5] J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2194; R. J. Sundberg, D. W. Gillespie, and B. A. DeGraff, *J. Am. Chem. Soc.*, 1975, **97**, 6193 and earlier papers by these authors.

[6] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968.

[7] J. S. Swenton, T. J. Ikeler, and B. H. Williams, *J. Am. Chem. Soc.*, 1970, **92**, 3103.

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

[9] M. Martynoff and G. Tsatsas, *Bull. Soc. Chim. Fr.*, 1947, 52.

[10] R. Huisgen, *Angew. Chem.*, 1955, **67**, 756.

[11] W. E. Doering and R. A. Odum, *Tetrahedron*, 1966, **22**, 81.

[12] A. H. Crosby and R. E. Lutz, *J. Am. Chem. Soc.*, 1956, **78**, 1233.