Nitrenes by Photolysis of Quinone Imine *N*-Oxides

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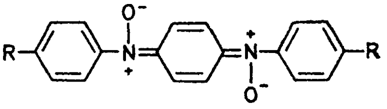
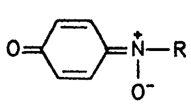
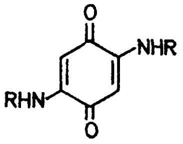
Summary Evidence is presented which establishes that aryl and alkyl nitrenes can be generated by photolysis of benzoquinone imine *N*-oxides.



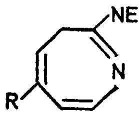
(1) R = H
(2) R = OMe



(3) R = Ph
(4) R = *p*-MeOC$_6$H$_4$
(5) R = *o*-PhC$_6$H$_4$
(6) R = Bu^t



(7) R = Ph
(8) R = *p*-MeOC$_6$H$_4$
(9) R = Bu^t
(10) R = C(Me)$_2$CH$_2$Bu^t
(11) R = Bu^n



(12) R = H
(13) R = OMe

PHOTOLYSIS or thermolysis of azides is the most general method for the generation of nitrenes but it is not always clear whether the products of these reactions arise by way of intermediate nitrenes or directly from the azides. The photolysis of benzoquinone imine *N*-oxides[1] would avoid these ambiguities but conclusive evidence for the participation of nitrenes[2] is lacking.

Irradiation of the di-*N*-oxides (**1**) and (**2**) in benzene solution at 20° for 6 h using a Hanovia S500 mercury-vapour lamp gave (t.l.c.) benzoquinone, azobenzene, or 4,4′-dimethoxyazobenzene, the benzoquinone monoimine *N*-oxides (**3**) or (**4**), and traces of the diaminoquinones (**7**) or (**8**) (see Table). Photolysis in diethylamine solution yielded 2,5-bis(diethylamino)benzoquinone, free amines (aniline or *p*-anisidine), and the azepines (**12**)† or (**13**) in low yield. The *N*-oxide (**5**), on irradiation, gave carbazole as well as benzoquinone and azo-compound. These observations establish the intervention in these reactions of aryl nitrenes which are presumably formed by rearrangement of the *N*-oxides to oxaziranes and collapse[2,3] as shown in (**14**). The production of triplet nitrenes is indicated by the substantial amounts of azo-compounds and amines which were isolated, and by the low yield of azepines. Normally[4]

TABLE

Product yields (%) *from photolysis of benzoquinone imine* N-*oxides*

N-Oxide	Solvent	Benzoquinone	Azo-compound	Monoimine *N*-oxide	2,5-Diamino-benzoquinone	Azepine	Others
(**1**)	C$_6$H$_6$	38	53	41	trace		
(**2**)	C$_6$H$_6$	61	75	17	trace		
(**1**)	Et$_2$NH		28		27[a]	1—2	Aniline, 9
(**2**)	Et$_2$NH		43		36[a]	1—2	*p*-Anisidine, 12
(**5**)	C$_6$H$_6$	41	52				Carbazole,[b] 9
(**6**)	C$_6$H$_6$	55			10		
(**6**)	C$_6$H$_{12}$	48			19		(**18**) + (**19**), 3
(**16**)	C$_6$H$_6$	22			8		(**17**), 43 (**20**), 1
(**16**)	C$_6$H$_{12}$	20			19		(**20**), trace (**21**), 2

[a] 2,5-Bis(diethylamino)benzoquinone. [b] Also 2-aminobiphenyl, trace.

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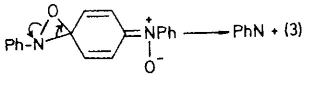
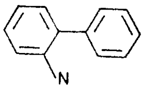
† Satisfactory analyses and spectroscopic data were obtained for all new compounds.

the nitrene (**15**), from (**5**), cyclises in the singlet state, and the relatively large amount of carbazole (9%) obtained was increased to 31% at the expense of the azo-compound (24%) when (**5**) was photolysed in the presence of oxygen (a triplet quencher[3]).



(14)



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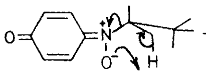

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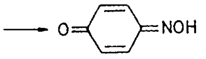

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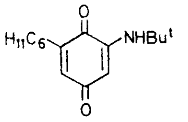

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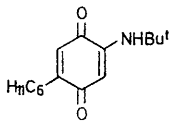

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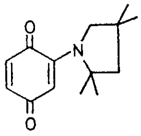

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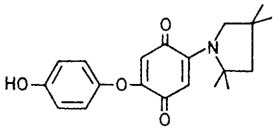

(21)

In parallel with the above results, irradiation of the t-butyl *N*-oxide (**6**) in benzene gave benzoquinone and the diaminoquinone (**9**); in cyclohexane the yield of (**9**) was increased, and the quinones (**18**) and (**19**) were isolated in low yield, being formed by addition of t-butylamine to cyclohexylbenzoquinone.[5] Photolysis of the octyl analogue (**16**) gave the oxime (**17**) as major product‡ (possibly as indicated), the diaminoquinone (**10**), and, significantly, the pyrrolidinoquinone (**20**) in 1% yield. This compound is photo-labile[6] and much of it was probably destroyed during the reaction. In cyclohexane solution only a trace of (**20**) was detected but (**21**) [formed by addition of quinol[7] to (**20**)] was isolated. The isolation of (**10**), (**20**), and (**21**) establishes the formation of the triplet 1,1,3,3-tetramethylbutyl nitrene which abstracts hydrogen both inter- and intra-molecularly. The production of pyrrolidines[8] by photolysis of alkyl azides has never been substantiated,[9] and we found that irradiation of n-butyl azide[8] and of 1,1,3,3-tetramethylbutyl azide, in benzene in the presence of benzoquinone, gave (**11**) and (**10**), respectively, but no pyrrolidinoquinone could be detected in either case. We expect that pyrrolidinoquinones can be obtained from quinone imine *N*-oxides in higher yields by selection of more appropriate starting materials and careful control of conditions.

(*Received*, *7th February* 1972; *Com.* 187.)

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‡ Oxime and alkene were formed slowly but quantitatively even in the absence of light; (**6**) did not decompose in this way even in benzene under reflux.

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