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Photolysis of Imidazole *N*(3)-Oxides. Formation of Unsymmetrical Benzil Di-imines; X-Ray Crystal Structure of One Such Di-imine

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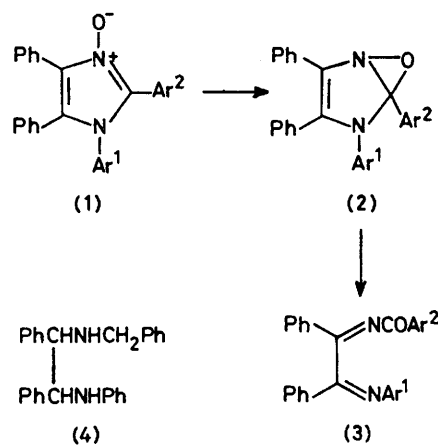
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Summary Irradiation of a series of tetra-aryl substituted imidazole *N*-oxides, in both polar and non-polar media, affords unsymmetrical benzil di-imine derivatives, suggesting that fused oxaziridines are intermediates.

WHEREAS the photochemistry of six-membered aromatic amine oxides has been exhaustively studied,¹ that of monocyclic five-membered analogues has not hitherto been systematically investigated.† Almost without exception, the six-membered amine oxides rearrange *via* well established pathways in which oxaziridine intermediacy is widely assumed. Compelling, independent evidence in support of oxaziridine participation has only recently been demonstrated.²

Since many of the photochemical degradation sequences common in the azine series (*e.g.*, tautomeric oxaziridine-oxazepin ring-opening) are formally improbable in the azole series, we undertook and report here the preliminary results of a study of the photolability of an accessible series of 1,2-diaryl-4,5-diphenylimidazole *N*-oxides (**1a–g**).

Thus, illumination (450 W Hanovia immersion arc) of a dilute methanol, acetone, or benzene solution (1 mM, 1.5 h) of the imidazole *N*-oxide, followed by chromatographic purification affords (65–75%) the respective isomeric β -benzil di-imine derivatives (**3a–g**). No products resulting from deoxygenation were detected. The structures (**3**)



Ar ¹	Ar ²
a; Ph	Ph
b; Ph	<i>o</i> -Tolyl
c; <i>p</i> -Tolyl	Ph
d; Ph	<i>p</i> -Anisyl
e; <i>p</i> -Anisyl	Ph
f; <i>p</i> -Bromophenyl	Ph
g; <i>p</i> -Chlorophenyl	Ph

† *N*-Oxide migrations have been observed with a benzotriazole *N*(3)-oxide (M. P. Serve, W. A. Feld, P. G. Seybold, and R. N. Steppel, *J. Heterocyclic Chem.*, 1975, **12**, 811), with a series of thiadiazole *N*(2)-oxides (H. P. Braun, K. P. Zeller, and H. Meier, *Annalen*, 1975, 1257), and with several benzofuroxan derivatives (G. Calzaferri, R. Gleiter, K. H. Knauer, H. D. Martin, and E. Schmidt, *Angew. Chem. Internat. Edn.*, 1974, **13**, 86). Benzimidazole *N*-oxides are known to rearrange to benzimidazolones (R. Fielden, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1973, 702; M. Ogata, H. Matsumoto, S. Takahashi, and H. Kano, *Chem. and Pharm. Bull. (Japan)*, 1970, **18**, 964).

were confirmed principally from i.r. and mass spectral data[†] and the β -configuration was finally established by a single crystal X-ray diffraction analysis on (3a), the molecular structure of which is illustrated in the Figure.

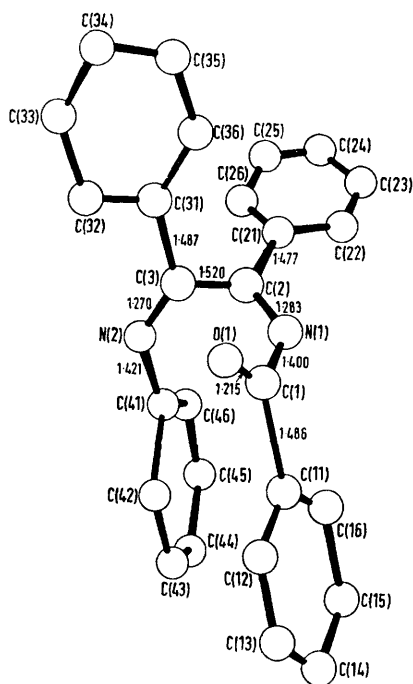


FIGURE. Molecular structure of (3a).

Crystal data: (3a), $C_{27}H_{20}N_2O$, pale yellow rectangular blocks; monoclinic, space group $P2_1/c$, $a = 12.513$, $b = 15.456$, $c = 10.775$ Å, $\beta = 94.10^\circ$, $Z = 4$. Intensity data

[†] I.r. spectra exhibit four prominent absorptions in the 1680–1590 cm^{-1} region and mass spectra display major ions corresponding to M^+ , $[M - Ar^2CO]^+$, $[M - PhCN]^+$, and $[PhCNAr]^+$. Satisfactory analytical data were obtained for all new compounds.

[§] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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¹ G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.

² C. W. Rees, R. Somanathan, R. C. Storr, and A. D. Woolhouse, *J.C.S. Chem. Comm.*, 1975, 740.

³ A. Padwa and E. Glazer, *J. Amer. Chem. Soc.*, 1972, **94**, 7788.

⁴ J. C. Danilewicz, *J. Chem. Soc. (C)*, 1970, 1049.

were collected on a Hilger and Watts Y290 diffractometer using $Cu-K\alpha$ radiation. The structure was solved by direct methods and the final R value for the 2068 independent reflexions used in the refinement is 0.046.[§]

Chemical support for the above assignment was obtained from metal hydride reduction of (3a) which gave a single crystalline compound (85%, m.p. 110 °C, $C_{27}H_{26}N_2$) shown by 1H n.m.r. spectroscopy to be a single diastereoisomer of the diaminodihydrostilbene (4). The two AB quartets centred at δ 3.72 (J 14.2 Hz) and 4.30 (J 5.2 Hz) are attributable to the benzylic methylene protons (which are magnetically non-equivalent) and to the vicinally related methine protons, respectively.

Benzil di-imine formation can be conveniently rationalised as proceeding through the intermediate oxaziridine which, after N–O cleavage, suffers rupture of the N(1)–C(2) bond of the imidazoline nucleus to give (3). However, the apparent insensitivity towards solvent polarity suggests that the conversion of the oxaziridine (2) into (3) can be alternatively described as a symmetry-allowed ring-opening of an electronically excited oxadiazabicyclo[3.1.0]hexene derivative. There is ample precedent for analogous photo-induced six-electron retrocycloaddition reactions of several 1,3-diazabicyclo[3.1.0]hexenes.³ The stereospecificity with which the (*Z,Z*)-di-imines are formed may well be under symmetry control and arise from one of the two invertomeric oxaziridines. It is also possible, but unlikely, that a di-imine of unspecified stereochemistry is optically pumped to the sterically most crowded configuration, since it is well known⁴ that *anti*- α -oximinoketones can be photochemically isomerised to the *syn*-isomers.