Photochemical transformations of cyclic azimines–X-ray crystallographic analysis of intermediates in their sequential phototransformations

Ciaran Byrne,[a] John P. James,*[a] Conor Long[a] and Deborah J. Wilcock[b]

[a] *School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*
[b] *Chemistry Department, Trinity College, Dublin 2, Ireland*

A series of sequential transformations on irradiation of the readily available cyclic azimines 2 lead to saturated pyrrolo[3,2-*b*]indoles 3, the mechanism of which is confirmed by isolation of photolabile intermediates 4 and 7 and two crystallographic determinations.

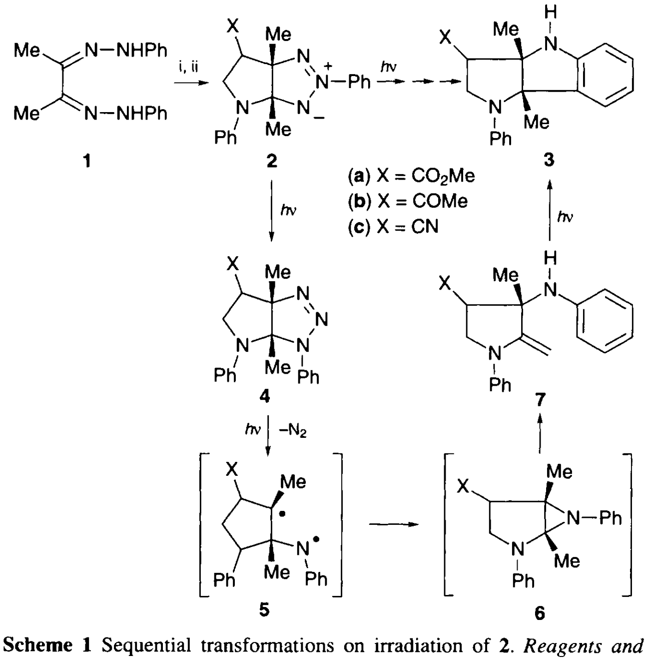
It has recently been reported that the photoisomerization of substituted 2,3a,4,6a-tetraarylpyrrolo[2,3-*d*]-1,2,3-triazoles to either imidazo[4,5-*c*]pyrazoles or tetrahydro-1,2,3,5-tetrazocines depended on the degree of unsaturation of the starting tetraazapentalene.[1,2] Herein we report a completely different photochemical transformation for substituted 3a,6a-dimethyl analogues **2**, which are readily available, ultimately from the bis(phenyl)hydrazone of butane-2,3-dione **1** and a suitable dipolarophile.[3,4]

Irradiation of **2**, using a medium pressure mercury lamp with a pyrex filter, led, after work-up, to the stable pyrrolo[3,2-*b*]indole **3**. This constitutes a new pathway to these sparsely reported benzodiazapentalenes, which have been studied as electrographic photoreceptors and potentially active pharmaceutical agents.[5,6] The reaction appears to proceed *via* an interesting series of sequential phototransformations. Analysis of the reaction pathway was undertaken by isolation and characterisation of photolabile intermediates.

On irradiation, **2** photoisomerised to the 1-phenyl fused triazoline **4** which was isolated in moderate yield. Ring systems of this type have been widely studied with regard to the elimination of molecular nitrogen and the isolation of such a system under photochemical conditions is rare.[7–9] This transformation, a net 1,2-phenyl shift, may involve an intermediate fused triaziridine, formed characteristically on photoinduced electrocyclization of azimines.[10] The product **4** was characterised by IR and ^{1}H and ^{13}C NMR spectroscopic analysis and by X-ray-crystallography (Fig. 1).†

Compound **4**, on further irradiation, underwent photoelimination of molecular nitrogen to form the diradical **5** which then cyclized to the fused aziridine **6**. The intermediate **6** subsequently underwent rearrangement to the observed product, the substituted methylidene pyrrolidine **7**. The structure of **7** was confirmed by X-ray crystallographic analysis (see Fig. 2).† The direction of the electrocyclic ring opening of **6**, may be facilitated by the participation of the pyrrolidine nitrogen lone pair. The eliminative rearrangement of substituted triazolines with methyl substituents in either the C-4 or C-5 position, to yield ring structures with exocyclic double bonds has been reported.[11–13]

The photorearrangement of **7a** in $CDCl_3$ was monitored by ^{1}H NMR spectroscopy on exposure to sunlight. After a few hours the characteristic splitting pattern of the exocyclic double bond was shifted upfield and transformed to a singlet at δ 1.58 which integrated as 3 H. The reaction reached completion after 8 h. Examination of the aromatic region indicated the presence of an *o*-disubstituted benzene ring. The ^{13}C NMR spectrum revealed two methyl groups at δ 21.08 and 21.12 and two bridgehead carbons at δ 74.21 and 74.74. The chemical shift proximity of the latter two carbons support the tricyclic



Scheme 1 Sequential transformations on irradiation of **2**. *Reagents and conditions*: i, $Pb(OAc)_4$ in glacial AcOH; ii, cycloaddition with suitable vinylic dipolarophile, *e.g.* methyl acrylate.

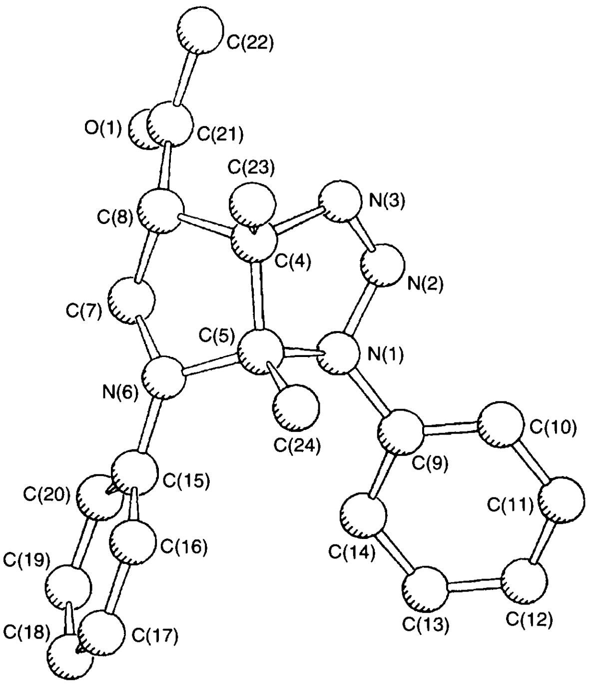


Fig. 1 X-Ray crystal structure of **4b**

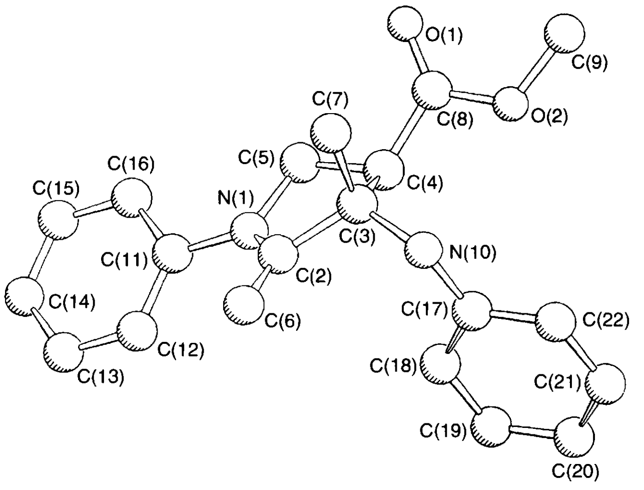


Fig. 2 X-Ray crystal structure of **7a**

structure **3** formed by 5-*exo*-trig ring closure from **7**.[14] The eliminative intramolecular cyclisation of 1-aryl-1,2,3-triazoles leading to polycyclic structures has been well documented.[15,16] The formation of the saturated pyrrolo[3,2-*b*]indole **3** reported herein constitutes a new pathway to this benzodiazapentalene system.‡

Footnotes

† *Crystal Data* for **4b**: $C_{20}H_{22}N_4O$; M_w 334.42, $F(000) = 712$, monoclinic, $a = 8.4031(9)$, $b = 12.9267(7)$, $c = 16.484(2)$ Å, $\alpha = 90$, $\beta = 96.289(5)$, $\gamma = 90°$, $V = 1779.8(3)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.248$ g cm^{-3}, $\mu = 0.080$ mm^{-1}. For **7a**: $C_{20}H_{22}N_2O_2$: M_w: 322.41, $F(000) = 688$, monoclinic, $a = 8.366(4)$, $b = 25.268(5)$, $c = 8.523(5)$ Å, $\alpha = 90$, $\beta = 107.83(3)$, $\gamma = 90°$, $V = 1715.1(14)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.249$ g cm^{-3}, $\mu = 0.081$ mm^{-1}. X-Ray crystallographic data was collected on an Enraf Nonius CAD4 single crystal diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Structures were solved by direct methods.[17] The structures were refined by full-matrix least-squares on F^2 to a final R value of 0.0415 (wR^2 = 0.0982) and 0.0468 (wR^2 = 0.1196) for **4b** and **7a** respectively.[18] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *Chemical Communications*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/19.

‡ *Physical data* for photoproduct **3a**: 78% yield, mp 114–116 °C; For **3b** 70% yield, mp 152–154 °C; For **4b** 45% yield, mp 108–110 °C; For **4c** 51% yield, mp 136–138 °C; For **7a** 57% yield, mp 164–166 °C.

References

1 R. N. Butler, D. M. Colleran, D. F. O'Shea, D. Cunningham, P. McArdle and A. M. Gillan, *J. Chem. Soc., Perkins Trans. 1*, 1993, 2757.

2 C. Byrne, S. M. Draper, J. P. James and C. Long, *J. Chem. Res. (S)*, 1995, 438; C. Byrne, S. M. Draper, J. P. James and C. Long, *J. Chem. Res. (M)*, 1995, 2501.

3 R. N. Butler, D. Cunningham, J. P. James and P. McArdle, *J. Chem. Soc., Chem. Commun.*, 1983, 763.

4 R. N. Butler, A. M. Evans, A. M. Gillan, J. P. James, E. McNeela and P. McArdle, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2537.

5 S. Furuta and H. Inagaki, *Jpn. Kokai Tokkyo Koho, Jpn. Pat.*, 04 326 360 (*Chem. Abstr.*, 1993, **118**, 180029c).

6 E. Aiello, G. Dattolo and G. Cirrincione, *J. Chem. Soc., Perkin Trans 1*, 1981, 1.

7 M. P. Servé, W. A. Feld, P. G. Seybold and R. N. Steppel, *J. Heterocycl. Chem.*, 1975, **12**, 811.

8 A. Albini, G. F. Bettinetti, G. Minoli and S. Pietra, *J. Chem. Soc., Perkin Trans 1*, 1980, 2904.

9 J. Van Thielen, T. Van Thien and F. C. De Schryver, *Tetrahedron Lett.*, 1977, 3031.

10 G. Kaupp and J. A. Dohle, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 828.

11 A. G. Schultz, J. P. Dittami, S. O. Myong and C.-K. Sha, *J. Am. Chem. Soc.*, 1983, **105**, 3723; A. G. Schultz and S. O. Myong, *J. Org. Chem.*, 1983, **48**, 2432.

12 K. Hirakawa, T. Ito, Y. Okubo and S. Nakazawa, *J. Org. Chem.*, 1980, **45**, 1668.

13 N. Kanomata, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 683.

14 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.

15 G. Mitchell and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 403.

16 J. J. Kulagowski, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2725 and 2733.

17 G. M. Sheldrick, SHELXS 86. Program for Crystal Structure Solution, University of Göttingham, 1986.

18 G. M. Sheldrick, SHELXL 93. Program for Crystal Structure Determination, University of Cambridge, 1992.

Received, 20th November 1995; Com. 5/07568H