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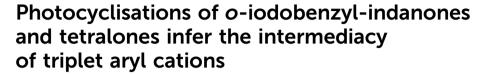


Cite this: Chem. Commun., 2025, **61**, 19229

Received 8th September 2025, Accepted 31st October 2025

DOI: 10.1039/d5cc05185a

rsc.li/chemcomm



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Photocyclisations of aryl iodides to 2-indanones and 2-tetralones give different outcomes to analogous radical reactions implicating the intermediacy of triplet aryl cations. Additions to 2-indanones generally give dibenzoisochromenones by sequential cyclisation, CO extrusion and electrocyclisation. By contrast, 2-tetralones produce benzo[a]phenalenones by ortho-cyclisation.

The homolytic cleavage of aryl iodides by photolysis has a long history and is usually attributed to the formation of an excited triplet state that collapses to give an iodine atom and an aryl radical intermediate (Scheme 1)^{1,2} Rarely, favourable solvent and substituent effects can combine to switch the course of the reaction to give a triplet aryl cation intermediate *via* heterolysis of the excited triplet state or by electron transfer within a short-lived triplet radical pair.³⁻⁶ Indeed, we recently observed such a phenomena in the photocyclizations of benzyl *ortho*-iodoaryl ethers and related compounds, where regiochemical outcomes differed from those given by analogous reactions *via* radical intermediates.^{5,7}

Herein we show how the photocyclisations of 1-(*ortho*-iodobenzyl)-2-indanones 1 give markedly different outcomes to analogous reactions conducted under radical forming conditions (Scheme 2) implicating the intermediacy of triplet aryl cations ³[3].⁸ Thus, while radical reactions mediated by tributyltin hydride for the most part gave dibenzocyclooctananes 7 in high yield *via* a ubiquitous 5-*exo*-trig cyclisation to 4 and fragmentation,⁷ related photocyclisations gave dibenzoisochromenones 11. The dichotomy can be attributed to formation of a triplet aryl cation ³[3] that undergoes a 'carbene like' closure to phenonium ion 6.⁸ Subsequent loss of HI then gives acephenanthrylenone 5, which was evidenced by NMR in crude product mixtures and isolated as a minor component in a few

Substrates bearing an electron releasing substituent at C5 of the indane ring unexpectedly gave more complex product mixtures (Scheme 3). Thus, while prolonged exposure of the C5methyl analogue 1g to UVC light gave an intractable mixture of products, more limited exposure gave acephenanthrylenone 5g in 52% isolated yield together with dibenzocyclooctane 2g (24%). By contrast, analogues 1h and 1i bearing mesomeric donors at C5 gave indenoindenones 15h and 15i (Fig. 1), dibenzocyclooctane 2h and dibenzocycloheptane 15i in modest to low isolated yield. These results lend further support to the intermediacy of triplet aryl cation ³[5] as the mechanistic course followed would be dictated by the ease of collapse of phenonium ion 6 to cation 12 or 13 (Scheme 2). Thus, for 1a-g reactions via cation 12 are favoured, but for 1h, 1i and to a lesser extent 1g, the stabilising influence of the donor substituent promotes formation of cation 13. Loss of a proton then gives dihydroindenoindenone 15 which is prone to homolytic cleavage to biradical intermediate 14,11 giving access to dibenzocyclooctane 7 and dibenzocycloheptane 16 through relaxation to a cyclopropanone and decarbonylation.¹²

Related photocyclisations of 1-(ortho-iodobenzyl)-2-tetralones 17a-k were next investigated and, in each case, gave ring closure to the corresponding benzoanthracenones 21a-k in modest to good yield (Scheme 4 and Fig. 1). In stark

 $\begin{tabular}{ll} Scheme 1 & Aryl iodide photolysis leading to radical and triplet aryl cation intermediates. \end{tabular}$

cases (*e.g.* **5b** Fig. 1 and **5g**, *vide infra*). Attempts to optimise for this product proved unrewarding due to a facile Norrish type 1 cleavage of its 2-indanone core to biradical ³[9]. Decarbonylation to quinodimethane **8**, cyclisation to keteneacetal **10**, and oxidation then gives dibenzoisochromenone **11** as the major product.

Arl \xrightarrow{hv} $^{3}[Arl]^{*}$ $\xrightarrow{homolysis}$ Ar' + 1' $\xrightarrow{homolysis}$ $^{3}[Ar' + 1']$ $\xrightarrow{electron}$ $^{3}[Ar]^{+}1'$

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Scheme 2 Dichotomous reactivity of iodoarenes 1 under photolysis and radical-forming conditions implicates the intermediacy of triplet anylication ³[3].

contrast to analogous reactions conducted under radical forming conditions, we saw none of the ring expansion product 20, suggesting that these reactions also proceed via triplet aryl cation 19 rather than aryl radical 18. Notably, extrusion of carbon monoxide from benzoanthracenones 21 did not occur since the biradical formed by a Norish type 1 cleavage, ³[24], now gives biradical 23 on decarbonylation rather than a quinodimethane. Nor did the outcome appear unduly influenced by substituents on the tetralone ring, indicating that the lower acidity of the benzylic protons in phenonium ion 22, compared to 13, reduces the tendency to form 7*a*,8-dihydrobenzofluorenone 25. The greater propensity for 6-ring closure to tetralones in analogous radical reactions may also be pertinent as it bears testament to the reduction of strain in the tetralone series following ortho-cyclisation. Indeed, for substrates lacking mesomeric donor substituents on the iodinated arene, e.g. 17d/e, reactions may proceed, in part, by C-I bond homolysis and radical cyclisation.

Extensions to related heterocyclic analogues 26–29 were next examined and, for the most part, gave good yields of the *ortho*-cyclisation products 30–33 (Scheme 5 and Fig. 1).¹³ Benzo-oxazinone 29 was an outlier, giving 33 in 24% isolated yield. The dichotomy can again be explained by a switch in the favoured mode of collapse of the phenonium ion intermediate 35, from cation 34 to cation 36.

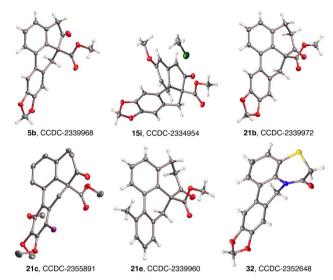


Fig. 1 X-ray crystal structures for **5b** (Scheme 2), **15i** (Scheme 3), **21b**, **c** and **e** (Scheme 4), and **32** (Scheme 5).

Finally, photolysis of 3,3-bis-(o-iodobenzyl)indolinone 37 under continuous flow induced sequential 6- and 5-membered ring formation to give azapropellane 38 in a remarkable 72% isolated yield (Scheme 6). The structure of the product was confirmed by X-ray crystallography (CCDC-2334898).

In conclusion, photocyclisations of *o*-iodobenzylindanones and tetralones in acetonitrile give markedly different outcomes to analogous reactions conducted under radical forming conditions. Thus, while radical reactions respectively promote ring expansion to dibenzo-cyclooctanes and cyclononanes *via* a

Scheme 3 The influence of C5 indanone substituents of the course of the reaction.

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Scheme 4 Photocyclisations of 1-(o-iodobenzyl)-2-tetralones give benzoanthracenones in moderate to good yield

21j, 43%

5-exo-trig ipso-cyclisation and ring expansion, photochemical reactions induce ortho-cyclisation implicating the intermediacy of triplet aryl cations. Cyclisations to 2-indanones and 2-tetralones differ in that the former produce acephenanthrylenones that react further by photo-extrusion of carbon monoxide to give dibenzoisochromenones,10 while the latter produce the homologous benzo[a]phenalenones which are not prone to photo-extrusion of carbon monoxide. We are currently examining further intramolecular photocyclisation reactions of aryl iodides to better understand the opportunities triplet aryl cation intermediates present in the context of synthetic chemistry.

Marian Powderly and Toby Lindup conducted the bulk of the experimental work with support from Edward Jackman.

Extension to related fused heterocycles Scheme 5

Scheme 6 A tandem cyclisation leading to an azapropellane

X-ray analyses were conducted by Mark Light. The project was conceived by the corresponding author, Julien Legros and Isabelle Chataigner. The authors thank Xl-Chem (ANR-18-EURE-0020 XL-CHEM) by Region Normandie; the European Regional Development Fund [ERDF Interreg Va programme (Project 121)]; the EPSRC [EP/P013341/1 and EP/K039466/1]; the Universities of Rouen, Normandy and Southampton, and CNRS INSA Rouen for their financial support.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article has been included in the main text and/or the accompanying supplementary information (SI). Supplementary information: full experimental accounts for the preparation of starting materials and products along with characterisation data [where appropriate, MP, IR, UV, LRMS,

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HRMS, ¹H NMR, ¹³C NMR and ¹⁹F NMR data]. Copies of NMR spectra accompany each account and include expansions of key regions. X-ray data is provided for 7 representative products. See DOI: https://doi.org/10.1039/d5cc05185a.

CCDC 2334898, 2334954, 2339960, 2339968, 2339972, 2352648 and 2355891 contain the supplementary crystallographic data for this paper. 14

Notes and references

- 1 For reviews covering the photochemistry of aryl iodides see: R. K. Sharma and N. Kharasch, Angew. Chem., Int. Ed. Engl., 1968, 7, 36; R. S. Davidson, J. W. Goodin and G. Kemp, Adv. Phys. Org. Chem., 1984, 20, 191; G. Lodder, in Halides, Pseudo-Halides and Azides: Part 2, ed., S. Patai and Z. Rappoport, Wiley, New York, 1983, Ch 29, p. 1605; G. Lodder and J. Cornelisse, in The Chemistry of Halides, Pseudo-halides and Azides, ed., S. Patai and Z. Rappoport, Wiley, New York, 1995, Suppl. D2, p. 861; J. Grimshaw and A. P. de Silva, Chem. Soc. Rev., 1981, 10, 181; N. J. Bunce, in Handbook of Photochemistry and Photobiology, ed., W. M. Horspool and P. S. Song, CRC Press, Boca Raton FL, 1995, p. 1181.
- 2 For evidence that C-I bond homolysis of aryl iodides occurs via a triplet excited state see: A. Marchetti and D. R. Kearns, J. Am. Chem. Soc., 1967, 89, 5335.
- 3 M. Freccero, M. Fagnoni and A. Albini, J. Am. Chem. Soc., 2003, 125, 13182.
- 4 M. Winkler and W. Sander, Angew. Chem., Int. Ed., 2000, 39, 2014; C. Raviola, F. Chiesa, S. Protti, A. Albini and M. Fagnoni, J. Org. Chem., 2016, 81, 6336-6342.
- 5 W. Sun, L. Wilding-Steele, R. C. D. Brown and D. C. Harrowven, Chem. Commun., 2023, 59, 10797; D. C. Harrowven, M. I. T. Nunn, N. A. Newman and D. R. Fenwick, Tetrahedron Lett., 2001, 42, 961.
- 6 A shift from homolytic to heterolytic cleavage as solvent polarity increase has been noted in the photolysis of aryl chlorides ref. 3 and J. P. Soumillion and B. De Wolf, Chem. Commun., 1981, 436; G. C. Miller, M. J. Mille, D. G. Crosby, S. Sontum and R. G. Zepp, Tetrahedron, 1979, 35, 1797; L. O. Ruzo, N. J. Bunce and S. Safe, Can. J. Chem., 1975, 53, 688.
- 7 D. C. Harrowven, N. L'Helias, J. D. Moseley, N. J. Blumire and S. R. Flanagan, Chem. Commun., 2003, 2658Photolysis of 1a with

- UVA and UVB under analogous conditions principally returned the starting material.
- 8 For reviews on aryl cation chemistry see: V. Dichiarante, S. Protti and M. Fagnoni, J. Photochem. Photobiol., A, 2017, 339, 103; Dicoordinated Carbocations, ed., Z. Rappaport and P. J. Stang, Wiley, New York, 1997; H. Zollinger, Angew. Chem., Int. Ed. Engl., 1978, 17, 141; M. Fagnoni and A. Albini, Acc. Chem. Res., 2005, 38, 713; H. B. Ambroz and T. Kemp, Chem. Soc. Rev., 1979, 8, 353.
- 9 Support for the intermediacy of acephenanthrylenone 8 was provided by the isolation of 8b in 35% yield and 8c in 33% yield on irradiation of 1b and 1c for shortened residence times with a lower powered UVC lamp, see SI.
- 10 K. K. De Fonseka, J. J. McCullough and J. Yarwood, J. Am. Chem. Soc., 1979, 101, 3277; D. Leinweber, M. Schnebel, R. Wartchow, H. G. Wey and H. Butenschoen, Eur. J. Org. Chem., 2002, 2385; D. Leinweber and H. Butenschoen, Tetrahedron Lett., 1997, 38, 6385; D. Ng, Z. Yang and M. A. Garcia-Garibay, Tetrahedron Lett., 2002, 43, 7063; W. Sun, S. Kayal, W. A. T. Raimbach, X.-Z. Sun, M. E. Light, M. W. D. Hanson-Heine, M. W. George and D. C. Harrowven, Chem. Commun., 2022, 58, 1546.
- 11 For a related C-C bond homolysis involving a 5,7-methanobenzo[7]annulen-10-one see: D. C. Harrowven, D. D. Pascoe and I. L. Guy, Angew. Chem., Int. Ed., 2007, 46, 425.
- 12 We presume that formation of 15 occurs by photo-extrusion of CO from the corresponding cyclopropanone: S. Kulyk, B. B. Khatri and S. Mc. N. Sieburth, Angew. Chem., Int. Ed., 2017, 56, 319.
- 13 For related radical cyclisations of o-iodobenzylquinolinones induced by the photochemical generation of carbon dioxide radical anion see: V. K. Simhadri, R. Sur and V. R. Yatham, J. Org. Chem., 2025, 90, 3557.
- 14 (a) CCDC 2334898: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2jcn9w; (b) CCDC 2334954: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ ccdc.csd.cc2jcq3r; (c) CCDC 2339960: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2jjxll; (d) CCDC 2339968: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2jjxvv; (e) CCDC 2339972: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2jjxzz; (f) CCDC 2352648: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2jz3wj; (g) CCDC 2355891: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc. csd.cc2k2hhn.