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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.

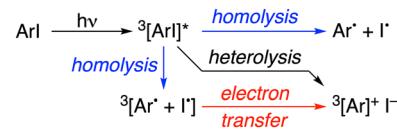
The homolytic cleavage of aryl iodides by photolysis has a long history and is usually attributed to the formation of an excited triplet state that collapses to give an iodine atom and an aryl radical intermediate (Scheme 1)^{1,2} Rarely, favourable solvent and substituent effects can combine to switch 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*-idoaryl 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

cases (e.g. **5b** Fig. 1 and **5g**, *vide infra*).⁹ 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]}.¹⁰ Decarbonylation to quinodimethane **8**,¹⁰ cyclisation to keteneacetal **10**, and oxidation then gives dibenzoisochromenone **11** as the major product.

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 C5-methyl 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 indenoindenes **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 dihydroindenoindene **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



Scheme 1 Aryl iodide photolysis leading to radical and triplet aryl cation intermediates.

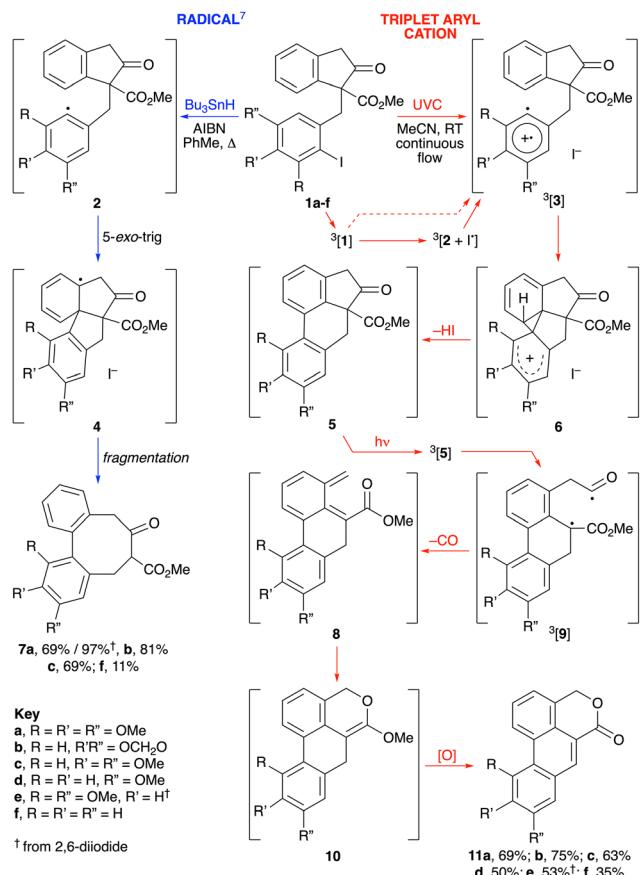
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Scheme 2 Dichotomous reactivity of iodoarenes **1** under photolysis and radical-forming conditions implicates the intermediacy of triplet aryl cation ³[3].

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 Norrish 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 7a,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**.

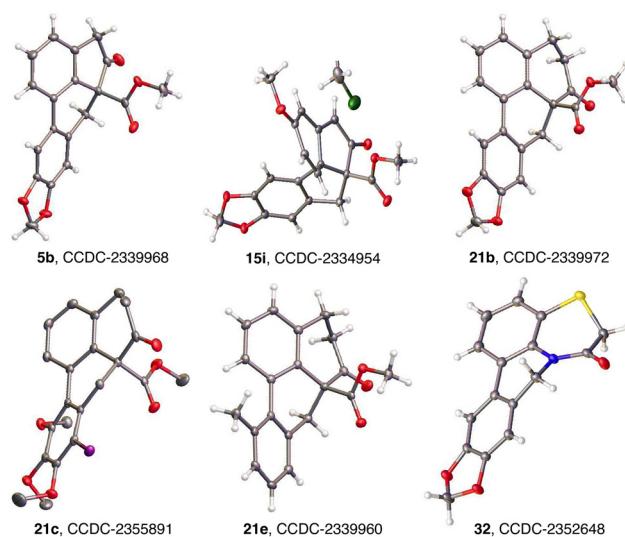
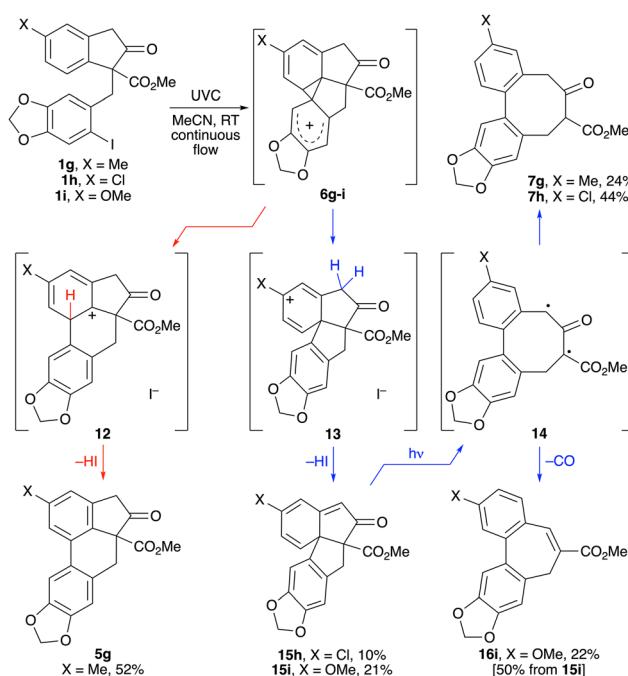


Fig. 1 X-ray crystal structures for **5b** (Scheme 2), **15i** (Scheme 3), **21b**, **c** and **e** (Scheme 4), and **32** (Scheme 5).

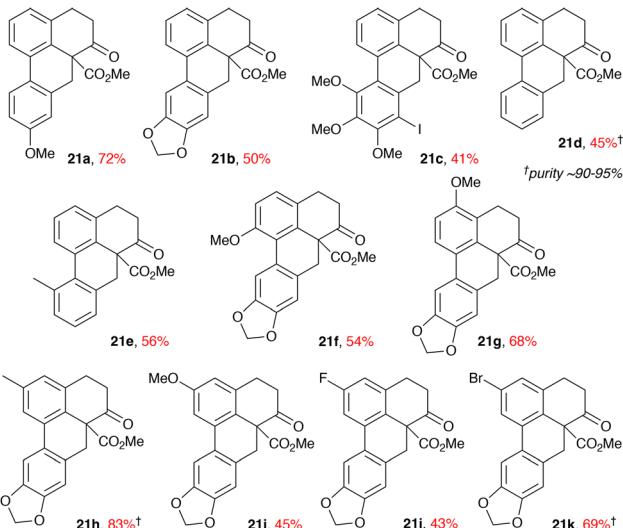
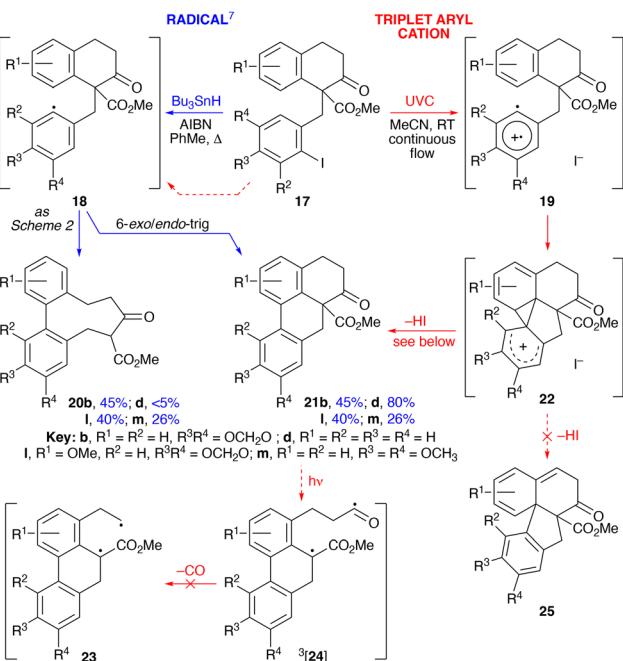
Finally, photolysis of 3,3-bis(*o*-iodobenzyl)indolinone **37** under continuous flow induced sequential 6- and 5-membered ring formation to give azapropellane **38** in a remarkable 72% isolated yield (Scheme 6). The structure of the product was confirmed by X-ray crystallography (CCDC-2334898).

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 cyclonananes *via* a



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

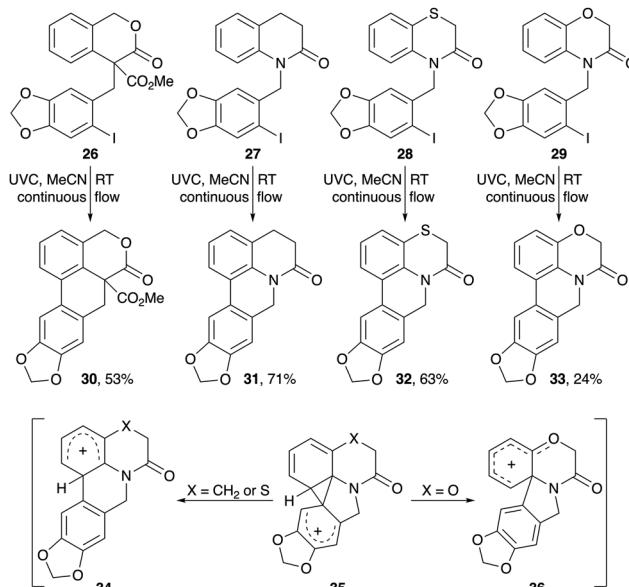




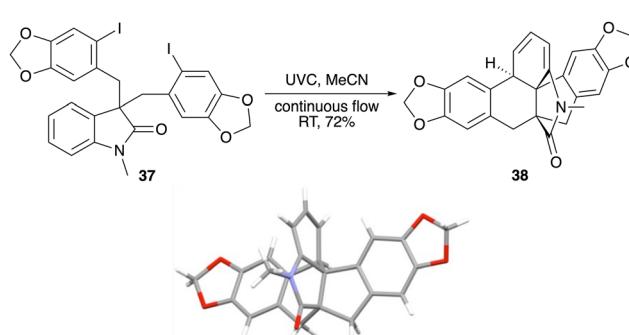
Scheme 4 Photocyclisations of 1-(o-iodobenzyl)-2-tetralones give benzoanthonenones in moderate to good yield.

5-exo-trig *ipso*-cyclisation and ring expansion,⁷ 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.



Scheme 5 Extension to related fused heterocycles.



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,

HRMS, ^1H NMR, ^{13}C NMR and ^{19}F 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

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