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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 dibenzisochromenones by sequential cyclisation, CO extrusion and electrocyclicisation. 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)<sup>1,2</sup> 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.<sup>3–6</sup> Indeed, we recently observed such a phenomena in the photocyclisations of benzyl *ortho*-iodoaryl ethers and related compounds, where regiochemical outcomes differed from those given by analogous reactions *via* radical intermediates.<sup>5,7</sup>

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 <sup>3</sup>[3].<sup>8</sup> Thus, while radical reactions mediated by tributyltin hydride for the most part gave dibenzocyclooctanes **7** in high yield *via* a ubiquitous 5-*exo*-trig cyclisation to **4** and fragmentation,<sup>7</sup> related photocyclisations gave dibenzisochromenones **11**. The dichotomy can be attributed to formation of a triplet aryl cation <sup>3</sup>[3] that undergoes a ‘carbene like’ closure to phenonium ion **6**.<sup>8</sup> 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

## Photocyclisations of *o*-iodobenzyl-indanones and tetralones infer the intermediacy of triplet aryl cations

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cases (*e.g.* **5b** Fig. 1 and **5g**, *vide infra*).<sup>9</sup> Attempts to optimise for this product proved unrewarding due to a facile Norrish type 1 cleavage of its 2-indanone core to biradical <sup>3</sup>[9].<sup>10</sup> Decarbonylation to quinodimethane **8**,<sup>10</sup> cyclisation to keteneacetal **10**, and oxidation then gives dibenzisochromenone **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 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 <sup>3</sup>[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**,<sup>11</sup> giving access to dibenzocyclooctane **7** and dibenzocycloheptane **16** through relaxation to a cyclopropanone and decarbonylation.<sup>12</sup>

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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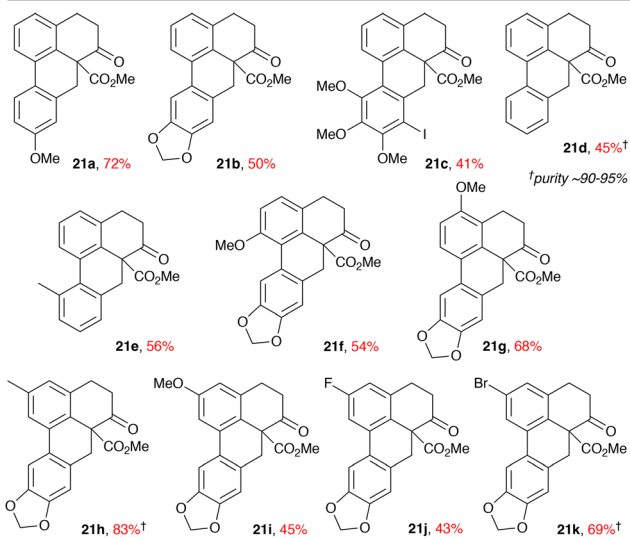
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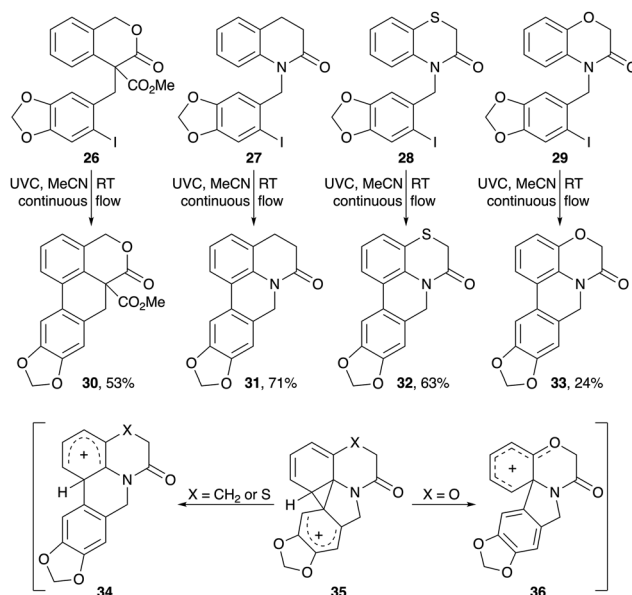




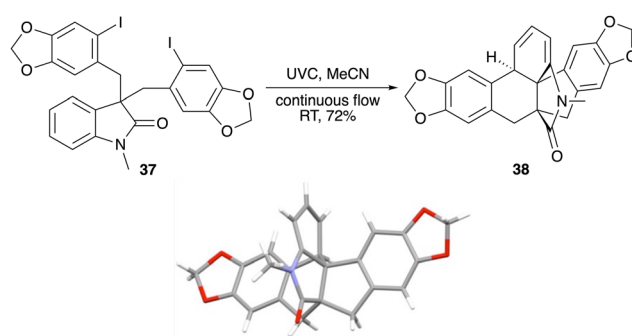
**Scheme 4** Photocyclisations of 1-(*o*-iodobenzyl)-2-tetralones give benzoanthracenones in moderate to good yield.

5-*exo*-trig *ipso*-cyclisation and ring expansion,<sup>7</sup> 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,<sup>10</sup> 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.

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## 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,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  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.<sup>14</sup>

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