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#### Short communication

# The synthesis and photochromism of a 2,2-diaryl-6-styryl-2*H*-[1]benzopyran: Unexpected palladium-mediated ring-contraction of a 6-bromo-2, 2-diaryl-2*H*-[1]benzopyran

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#### 1. Introduction

The phenomenon of photochromism has attracted considerable interest over the last three decades [1]. A considerable proportion of this attention has been directed towards the highly commercially successful naphthopyrans [2] and related pyran-derived systems [3] where the excellent photochromic response is due to the photochemical electrocyclic ring-opening of the pyran ring to afford intensely coloured photo-merocyanines; a subsequent thermal cyclisation with concomitant fading of the colour completes the process. With the ever increasing structural complexity of the naphthopyran unit resulting from the need for superior photochromic performance it comes as no surprise to note that transition metal-mediated chemistry has been applied in this area [4]. In a recent study the Pd-mediated cyanation, carboxylation and trimethylsilylethynylation of the 2-bromo-3.3-diaryl-3Hnaphtho[2,1-b]pyran 1 was described leading to new substituted naphthopyrans which displayed modified photochromic properties [5]. Of particular interest and of relevance to our studies on naphthopyrans [6,7] was the observation that upon attempted cyanation

#### ABSTRACT

The ligand-free Pd-mediated reaction between styrene and a 6-bromo-2,2-diaryl-2*H*-[1]benzopyran proceeded anomalously to give a 2-(diarylmethyl)-5-styrylbenzofuran *via* a tandem Heck coupling — ring-contraction process; none of the styryl substituted 2,2-diaryl-2*H*-[1]benzopyran was observed. A 2,2-diaryl-6-styryl-2*H*-[1]benzopyran resulted from the condensation between 4-hydroxystilbene and a 1,1-diarylpropynol and which exhibited photochromism through the reversible electrocyclisation of the pyran unit; no isomerisation — electrocyclisation of the stilbene moiety was detected.

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mediated by  $Pd(OAc)_2$  an appreciable yield of the ring-contracted naphthofuran **2** resulted (Scheme 1) [5]. Whilst ring-contractions of naphthopyrans e.g. **3** [7], **4** [8] and dihydronaphthopyrans **5** [9] to naphthofurans are known (Scheme 1) we were interested by the Pd-mediated ring-contraction and now report our observations on attempts to access the photochromic styrylbenzopyran **6** by a Pd-mediated Heck reaction.

#### 2. Experimental

#### 2.1. Equipment

Unless otherwise stated, reagents were used as supplied by the major chemical catalogue companies. NMR spectra were recorded on a Bruker Avance 400 MHz spectrophotometer (<sup>1</sup>H NMR 400 MHz, <sup>13</sup>C NMR 100 MHz) for sample solutions in CDCl<sub>3</sub> with tetramethylsilane as an internal reference. The crystal structure determination was carried out at 150 K on a Bruker-Nonius Apex X8 diffractometer equipped with an Apex II CCD detector and using graphite monochromated Mo-K $\alpha$  radiation from an FR591 rotating anode generator. The structure was solved by direct methods and refined using SHELXL-97. FT-IR spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer system equipped with a golden gate ATR attachment (neat sample). UV–visible spectra

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Scheme 1. Ring-contractions of naphthopyrans to naphthofurans.

were recorded for spectroscopic grade CH<sub>2</sub>Cl<sub>2</sub> solutions of the samples (10 mm path length quartz cuvette, PTFE capped, ca.  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>) using a Cary 50 Probe spectrophotometer equipped with a single cell Peltier temperature controlled (20 °C) stirred cell attachment with activating irradiation provided by an Oriel 150 Watt xenon arc lamp source (Newport 66906), xenon ozone free arc lamp (Newport 6255), distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) and liquid light guide (Newport 77557). All compounds were homogeneous by TLC (Merck TLC aluminium sheets, silica gel 60 F<sub>254</sub>) using a range of eluent systems of differing polarity and flash column chromatography was performed on chromatography silica gel (Fluorochem, 40-63 micron particle size distribution). Mass spectra were recorded at the National EPSRC Mass Spectrometry Service Centre, Swansea.

#### 2.2. Preparation of (E)-4-hydroxystilbene (11)

n-Butyllithium (1.6 M in hexanes, 56.25, mL, 90 mmol) was added portionwise by syringe over 1 h to a cold  $(-10 \circ C)$  stirred suspension of benzyltriphenylphosphonium chloride (35.0 g, 90 mmol) in anhydrous THF (150 mL). Upon completion of the addition the mixture was stirred for 30 min at -10 °C and a solution of 4-hydroxybenzaldehyde (5.0 g, 41 mmol) in THF (80 mL), was added drop wise over 20 min and the resulting solution was stirred for 3 h at room temperature. The mixture was poured into water (200 mL), neutralised with aqueous saturated ammonium chloride solution (150 mL) and extracted with ethyl acetate ( $3 \times 70$  mL). The combined organic layers were washed with water (100 mL) and dried (anhyd. Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent gave a pale brown semi-solid that was eluted from silica (30% EtOAc/hexane) to afford the crude product as a mixture of the *cis-* and *trans-* isomers. Heating a solution the foregoing crude isomer mixture in hexane (100 mL) containing a catalytic amount of iodine (20 mg) gave the title product 11 as an off-white solid 5.78 g, 72%, mp 184–186 °C (lit. mp = 186 °C [10]),  $\delta_{\rm H}$  4.76 (1H, s, -OH), 6.83 (2H, m, Ar-H), 6.94 (1H, d, *J* = 16.3 Hz, styryl), 7.03 (1H, d, *J* = 16.3 Hz, styryl),7.34 (2H, m, Ar-H), 7.42 (2H, m, Ar-H), 7.49 (2H, m, Ar-H).

## 2.3. Preparation of 6-bromo-2,2-bis-(4-methoxyphenyl)-2H-[1] benzopyran (8)

Aluminium oxide (activated, acidic, Brockmann 1, ~150 #) (3.0 g) was added in a single portion to a warm (ca. 50 °C) stirred solution of the 4-bromophenol (2.0 g, 11.6 mmol) and 1,1-bis-(4methoxyphenyl)prop-2-yn-1-ol 7 (3.1 g, 11.6 mmol) in toluene (60 mL). The resulting suspension was heated under reflux until no propynol remained by TLC (ca. 2 h). The solution was cooled  $(\sim 30 \ ^{\circ}C)$  and filtered and the spent alumina catalyst was washed with warm toluene (2  $\times$  30 mL). Evaporation of the toluene from the combined washings and filtrate afforded the crude product which was eluted from silica using 10% EtOAc in PhMe, to afford the title benzopyran 8 as colourless microcrystals 1.32 g, 27%, mp = 100-101 °C,  $v_{max}$  1608.2, 1506.1, 1470.7, 1301.8, 1252.5, 1240.6, 1175.3, 1029.1, 983.5, 946.3, 817.0, 702.1, 586.6, 556.9 cm<sup>-1</sup>,  $\delta_{\rm H}$  3.79 (6H, s, [OMe]<sub>2</sub>), 6.13 (1H, d, J = 9.8 Hz, 3–H), 6.50 (1H, d, *J* = 9.8 Hz, 4–H), 6.73 (1H, d, *J* = 8.3 Hz, 8–H), 6.82 (4H, m, Ar–H), 7.11 (1H, d, J = 2.3 Hz, 5–H), 7.18 (1H, dd, J = 8.3, 2.3 Hz, 7–H), 7.28 (4H, m, Ar–H); δ<sub>C</sub> 55.26, 82.58, 113.04, 113.50, 118.29, 122.00, 123.04, 128.31, 128.95, 130.57, 131.96, 136.77, 151.66, 159.02. Found C, 65.20; H, 4.55; [M + H<sup>+</sup>] 423.0591 (Br<sup>79</sup>). C<sub>23</sub>H<sub>19</sub>BrO<sub>3</sub> requires C, 65.26; H, 4.52;  $[M + H^+]$  423.0590 (Br<sup>79</sup>).



Scheme 2. Proposed modes of photochromism of styrylbenzopyran 6.



Reagents and conditions: (i) acidic  $Al_2O_3$ , PhMe, heat; (ii) styrene, Pd(OAc)<sub>2</sub> (0.05 mol%), K<sub>3</sub>PO<sub>4</sub>, *N*,*N*-dimethylacetamide, N<sub>2</sub>, rt 1h then 140 °C for 20 h

Scheme 3. Tandem Heck reaction — ring-contraction.

## 2.4. Preparation of 2,2-bis-(4-methoxyphenyl)-6-styryl-2H-[1] benzopyran (6)

The title naphthopyran **6** was obtained in a similar manner to that described for the foregoing bromobenzopyran **8**, from 4-hydroxystilbene **11** (2.0 g, 10 mmol) and 1,1-bis-(4-methox-yphenyl)prop-2-yn-1-ol **7** (2.7 g, 10 mmol) after elution from silica with 20% EtOAc in PhMe, as colourless microcrystals, 1.1 g, 24%, mp = 142–143 °C,  $v_{max}$  1609.7, 1507.8, 1488.7, 1301.0, 1247.7, 1173.7, 1030.5, 961.4, 948.8, 828.6, 816.6, 707.1, 566.8 cm<sup>-1</sup>,  $\delta_{\rm H}$  3.79 (6H, s, [OMe]<sub>2</sub>), 6.14 (1H, d, *J* = 9.8 Hz, 3–H), 6.61 (1H, d, *J* = 9.8 Hz, 4–H), 6.86 (5H, m, Ar–H), 6.91 (1H, d, *J* = 16.3 Hz, styryl-H), 7.01 (1H, d, *J* = 16.3 Hz, styryl-H), 7.16 (1H, d, *J* = 2.1 Hz, 5–H), 7.22 (1H, m, Ar–H),7.28 (1H, dd, *J* = 8.3, 2.1 Hz, Ar–H), 7.33 (6H, m, Ar–H), 7.46 (2H, m, Ar–H);  $\delta_{\rm C}$  55.26, 82.57, 113.47, 121.21, 122.90, 124.50, 126.26, 126.75, 127.22, 127.82, 128.20, 128.33, 128.64, 129.69, 130.58, 137.19, 137.64, 152.48, 158.94. Found C, 83.35; H, 5.80; [M + H<sup>+</sup>] 447.1955.

## 2.5. Heck coupling reaction between styrene and 6-bromo-2,2-bis-(4-methoxyphenyl)-2H-[1]benzopyran (9)

Pd(OAc)<sub>2</sub> (0.05 mol %) was added to a stirred suspension of 6-bromo-2,2-bis-(4-methoxyphenyl)-2H-[1]benzopyran (1.0 g, 2.4 mmol), styrene (0.3 g, 2.9 mmol) and K<sub>3</sub>PO<sub>4</sub> (0.7 g, 3.3 mmol) in N,N-dimethylacetamide (15 mL) under a nitrogen atmosphere and the mixture was stirred for 20 h at 140 °C. The cooled mixture was poured in to water (70 mL) and extracted with ethyl acetate  $(3 \times 40 \text{ mL})$ . The combined organic layers were washed well with water (5  $\times$  50 mL), dried (Na<sub>2</sub>SO<sub>4</sub> anhyd.) and evaporated to afford a dark brown gum which was eluted from silica using 20% EtOAc in hexane to afford 2-[1,1-bis-(4-methoxyphenyl)methyl]-5-styrylbenzo[b]furan **9** as off-white microcrystals 0.31 g, 30%, mp = 122–124 °C,  $\nu_{max}$  1608.3, 1583.8, 1507.0, 1467.1, 1450.9, 1242.8, 1173.8, 1028.7, 960.7, 830.0, 806.2, 742.5, 689.6, 609.8, 582.0, 499.3 cm<sup>-1</sup>,  $\delta_{\rm H}$  3.80 (6H, s, [OMe]<sub>2</sub>), 5.48 (1H, s, methine-H), 6.25 (1H, s, 3–H), 6.85 (4H, m, Ar–H), 7.05 (1H, d, J = 16.3 Hz, styryl-H), 7.14 (4H, m, Ar–H),7.18 (1H, d, J = 16.3 Hz, styryl-H), 7.22 (1H, m, Ar-H), 7.36 (3H, m, Ar-H), 7.42 (1H, dd, J 8.5, 1.7 Hz, 6-H), 7.51 (2H, m, Ar–H), 7.57 (1H, d, J 1.7 Hz, Ar–H); δ<sub>C</sub> 49.68, 55.27, 105.39, 110.83, 111.30, 113.92, 120.85, 125.00, 126.95, 128.22, 128.67, 129.30, 129.58, 130.53, 131.86, 133.46, 137.47, 154.64, 158.54, 160.99. Found C, 83.25; H, 5.80 [M<sup>+</sup>] 446.1876. C<sub>31</sub>H<sub>26</sub>O<sub>3</sub> requires C, 83.38; H, 5.87; [M<sup>+</sup>] 446.1876.

#### 3. Discussion

The Heck reaction [11] offers an efficient route to vinyl substituted aromatic and heteroaromatic compounds from either the bromo- or iodo- substituted precursors using a range of Pd-complexes and associated ligands [12]. One modification of the Heck reaction is the use of Pd(OAc)<sub>2</sub> without the need of a typically

expensive phosphine ligand [13]. This latter approach appeared attractive for the synthesis of the styryl substituted benzopyran **6** from the bromo- precursor **8** which is available from bromophenol and a prop-2-yn-1-ol using established methodology [14]. Styrylbenzopyran **6** was expected to display photochromism through cycling of the pyran ring – photomerocyanine and may also undergo the alternative photochemically induced process involving *E*- to *Z*- photoisomerisation of the stilbene unit followed by an electrocyclisation ultimately leading to a phenanthrene system (Scheme 2). The photocyclisation of a series of 6-phenylvinyl and 6-(2-naphthyl)vinyl substituted benzopyran-2-ones (coumarins) has been reported and the resulting helical phenanthropyranone derivatives were treated with phenylmagnesium bromide to afford diaryl substituted photochromic phenanthropyrans [15].

The 6-bromobenzopyran **8** was accessed in surprisingly low yield (27%), albeit from relatively inexpensive starting materials, by the acid-catalysed condensation between 4-bromophenol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol **7** to afford an intermediate propargylic ether which readily rearranges *in situ* to the benzopyran (Scheme 3). The formation of **8** was confirmed by <sup>1</sup>H NMR spectroscopy which displayed a key AB system with a doublet at  $\delta$  6.13 (3-H) and at  $\delta$  6.50 (4-H) with J = 9.8 Hz and a signal at  $\delta$  82.5 in the <sup>13</sup>C NMR spectrum assigned to C-2; these chemical shifts and coupling constants are typical for 2*H*-[1]benzopyrans [16].

Heating a solution of **8** with styrene in *N*,*N*-dimethylacetamide containing  $K_3PO_4$  and palladium acetate according to the procedure



Fig. 1. X-Ray crystal structure of styrylbenzofuran 9.



Scheme 4. Proposed mechanism for the ring-contraction process.

reported by Yao et al. [13], resulted in a complex multi-component mixture from which the major product, a non-photochromic compound **9** was isolated in 30% yield after elution from silica (Scheme 3). No photochromic compound was detected by routine TLC examination of the reaction mixture. The <sup>1</sup>H NMR spectrum of **9** displayed signals for a *trans*-styryl function (with J = 16.4 Hz), confirming the success of the Heck process, but did not show any expected doublets that could be attributed to the benzopyran ring and instead displayed a singlet at  $\delta$  5.95 and at  $\delta$  7.25. The structure of this compound was elucidated as the styrylbenzofuran **9** by X-ray crystallography (Fig. 1) [17].

The precise mechanism for the ring-contraction leading to 9 is at present unknown, however in the presence of dimethylacetamide at high temperature it is probable that nanoparticulate Pd<sup>0</sup> is generated in situ [18–20]. Addition of nucleophilic Pd<sup>0</sup> to C-4 of the benzopyran 8, a process comparable with the many examples of addition of Pd<sup>0</sup> to allylic acetates with displacement of acetate ion leading to a  $\pi$ -allyl Pd species [21], proceeds with ring-opening and subsequent capture of the palladium to generate the palladacycle **10**. Deprotonation with either added base (K<sub>3</sub>PO<sub>4</sub>) or acetate ion regenerates Pd<sup>0</sup> and an allenylphenol, which presumably undergoes a 5-exo-dig cyclisation to the benzofuran 9 (Scheme 4). The ring-contraction sequence operates in tandem with the expected Heck reaction resulting in the overall conversion of  $\mathbf{8} \rightarrow \mathbf{9}$ . Further exploration of the nature of the Pd species and the generality of the tandem ring-contraction - Heck sequence is under investigation.

In an effort to synthesise the target benzopyran **6** we returned to more traditional chemistry and prepared (E)-4-hydroxystilbene **11** in 72% yield by a Wittig reaction between an excess of the ylide derived from deprotonation of benzyltriphenylphosphonium

chloride and 4-hydroxybenzaldehyde with subsequent isomerisation achieved upon heating the crude isomer mixture in hexane containing a catalytic amount of iodine [22]. Heating **11** with propynol **7** (An = 4-MeOC<sub>6</sub>H<sub>4</sub>) resulted in a mediocre yield of **6** (24%) after column chromatography (Scheme 5). <sup>1</sup>H NMR spectroscopy was used to confirm the structure of **6** which displayed two AB systems; the former with doublets at  $\delta$  6.14 (J = 9.8 Hz) and  $\delta$  6.61 attributed to the pyran ring protons and the latter system at lower field ( $\delta$  6.91 and 7.01) with a larger vicinal coupling constant of 16.3 Hz confirming the *E*-geometry of the styryl unit.

The photochromic response of the new benzopyrans **6** and **8** in  $CH_2Cl_2$  solution (ca.  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>) was next investigated. The bromobenzopyran 8 displayed photochromism when subjected to irradiation with light of wavelength 270-380 nm (150 Watt, 5 min) and generated a maroon shade ( $\lambda_{max}$  522 nm) associated with the photomerocyanine tautomer. However, the photogenerated colour was transient and faded almost instantaneously upon cessation of irradiation indicating the strong preference of 8 to remain in the ring-closed state. The weak photochromism of other simple diaryl substituted 2H-[1]benzopyrans has been noted [23] and more recently the photochromism of 6- and 7- aryl substituted 2H-[1]benzopyrans has been explored [24]. Similar treatment of the styryl substituted isomer 6 resulted in the generation of a far longer lived green-blue colour, the absorption at longer wavelength and persistence being in accord with the extended chromophore. The absorption spectrum of 6 is presented in Fig. 2 and shows a typical photochromic response with maxima at 580 nm (broad band) and at 446 nm. The half-life  $(t_{\frac{1}{2}}, s)$  for the persistence of the photogenerated species was determined by following the rate of decrease of the photogenerated colour at each of these wavelength maxima over 1 min period after excitation to



Reagents and conditions: (i)  $Ph_3P^+CH_2Ph CI^-$ , *n*-BuLi, THF, N<sub>2</sub>, -10 °C - rt, then cat. I<sub>2</sub>, hexane, reflux; (ii) acidic AI<sub>2</sub>O<sub>3</sub>, PhMe, heat

Scheme 5. Preparation of styrylbenzopyran 6.



Fig. 2. Absorption spectrum of styrylbenzopyran 6.

a photostationary state (5 min irradiation). Multiple estimates resulted in  $t_{y_2}$  values of 1.8 s; it should be noted that this value is approaching the limit of detection using the present apparatus.

In order to firmly establish whether any isomerisation – cyclisation of the stilbene unit had occurred upon irradiation a CDCl<sub>3</sub> solution of **6** was irradiated for 30 min using the same activating light source employed for the absorption studies. Recording the <sup>1</sup>H NMR spectrum immediately after the irradiation indicated that no photocyclisation of the stilbene unit had occurred. It may be the case that the disruption of the aromatic  $\pi$ -system upon ringopening of the pyran unit of **6** inhibits the isomerisation – electrocyclisation of the stilbene unit. Further exploration of this phenomenon is warranted.

#### 4. Conclusion

The typically high yielding acidic alumina catalysed propargyl alkynol route to naphthopyrans affords benzopyrans in only moderate yield when applied to phenols. The ligand-free Heck functionalisation of a bromobenzopyran was complicated by a competing ring-contraction when Pd(OAc)<sub>2</sub> was employed as the Pd source. The Pd species involved in the contraction process is most probably nanoparticulate Pd<sup>0</sup> as a consequence of the severe applied reaction conditions. The styrylbenzopyran displays relatively weak photochromism generating a green-blue shade which fades relatively rapidly ( $t_{V_2} = 1.8$  s). Under the applied irradiation conditions neither isomerisation nor electrocyclisation of the styryl unit of **6** to afford a phenanthropyran was detected.

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- 17] X-Ray crystal structure details for styrylbenzofuran 9: Colourless plate; Crystal size = 0.19 × 0.07 × 0.01 mm; *T* = 150(2) K;  $\lambda$  = 0.71073 Å [Mo-*K<sub>a</sub>*]; Crystal system = monoclinic; Space group = *P*<sub>2</sub>; Unit cell dimensions = *a* = 8.9630(4) Å  $\alpha$  = 90°, *b* = 5.8390(2) Å *β* = 100.7150(10)°, *c* = 22.5140(12) Å  $\gamma$  = 90°; Volume = 1157.73(9) Å3; *Z* = 2; Density (calculated) = 1.281 Mg/m3; Absorption coefficient = 0.081 mm<sup>-1</sup>; *F*(000) = 472; Data collection range = 2.64  $\leq \theta \leq 27.47^{\circ}$ ; Index ranges = -11  $\leq h \leq 11$ ,  $-7 \leq k \leq 7$ ,  $-27 \leq l \leq 29$ ; Reflections collected = 9218; Independent reflections = 2897 [*R*(int) = 0.0686]; Observed reflections = 1919 [*I* > 2 $\sigma$ (*I*)]; Absorption correction = multiscan; Max. and min. transmission = 0.9992 and 0.7708; Refinement method = Full; Data/restraints/parameters = 2897/1/309; Goodness of fit = 0.999; Final *R* indices [*I* > 2 $\sigma$ (*I*)] = *R*<sub>1</sub> = 0.0495, *wR*<sub>2</sub> = 0.0908; *R* indices (all data) = *R*<sub>1</sub> = 0.0958, *wR*<sub>2</sub> = 0.1049; Largest diff. peak and hole = 0.172 and -0.201eÅ<sup>-3</sup>. Crystallographic data (excluding structure factors) for this structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC786366. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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