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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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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.

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-3*H*-naphtho[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 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 (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) for sample solutions in $CDCl_3$ 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-Kα 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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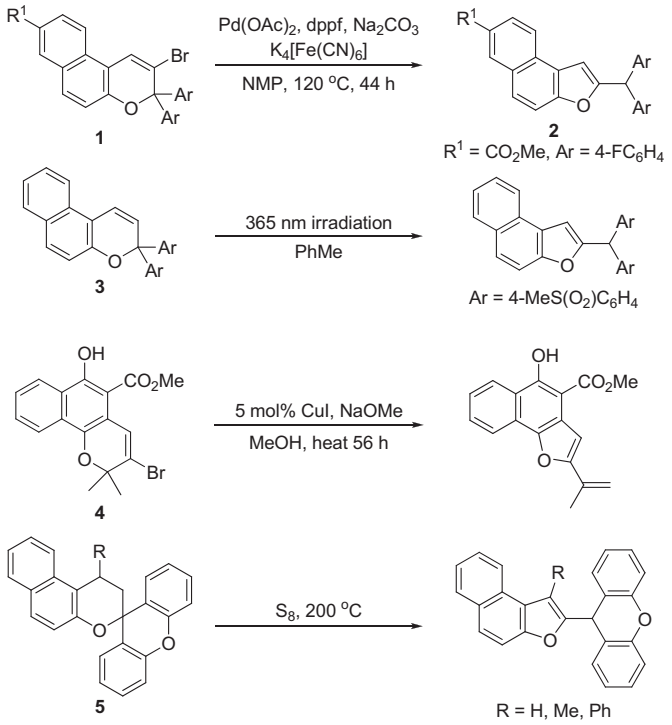


Scheme 1. Ring-contractions of naphthopyrans to naphthofurans.

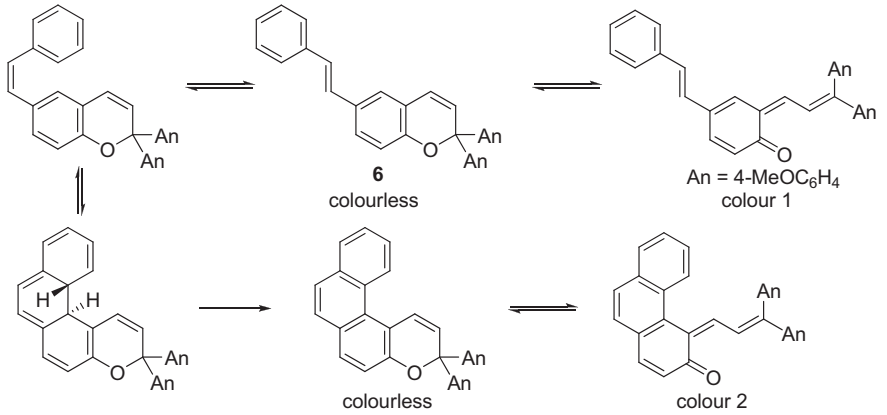
were recorded for spectroscopic grade CH_2Cl_2 solutions of the samples (10 mm path length quartz cuvette, PTFE capped, *ca.* 2.5×10^{-4} mol dm^{-3}) using a Cary 50 Probe spectrophotometer equipped with a single cell Peltier temperature controlled (20 °C) stirred cell attachment with activating irradiation 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_{254}) 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 °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 × 70 mL). The combined organic layers were washed with water (100 mL) and dried (anhyd. Na_2SO_4). 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]), δ_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-(4-methoxyphenyl)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 (~30 °C) and filtered and the spent alumina catalyst was washed with warm toluene (2 × 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, ν_{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^{-1}, δ_H 3.79 (6H, s, $[OMe]_2$), 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_C 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; $[M + H^+]$ 423.0591 (Br^{79}). $C_{23}H_{19}BrO_3$ requires C, 65.26; H, 4.52; $[M + H^+]$ 423.0590 (Br^{79}).



Scheme 2. Proposed modes of photochromism of styrylbenzopyran **6**.