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Photochromic Naphthopyrans Containing a Latent Carbene Unit

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Photochromic Naphthopyrans Containing a Latent Carbene Unit

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3-(Hydroxyalkyl)-1-naphthols 12 have been accessed in two steps from an isoquinolinium salt. The naphthopyrans 15, derived from 12, were readily diazoacylated with ethyl diazomalonyl chloride. The carbenoid generated from 16 failed to undergo any cycloaddition and was instead intercepted by water to afford 18.

Keywords: carbenes; naphthopyrans; photochromism

INTRODUCTION

The reversible ring – chain tautomerism (or valence isomerisation) of the 2*H*-pyran system [1] has attracted considerable attention from academic and industrial research groups, particularly when this system is fused to a naphthalene moiety to afford the naphthopyran isomers **1** and **2** [2] which change from colourless (pyran) to coloured (merocyanine) (Scheme 1); a colour change phenomenon known as photochromism [3].

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SCHEME 1

Control over this dynamic ring – chain interconversion can be accomplished through choice of substituents on the naphthalene unit and *geminal* diaryl groups [2] and also by external matrix effects e.g., solvent polarity, **3** [4] pH, **4** [5] and metal ion concentration, **5** [6] with appropriately substituted naphthopyrans. More recently we have shown that carbenes can be used to irreversibly obtain merocyanine dyes, e.g., **6**, from naphthopyrans (Scheme 2) [7].

In our preliminary communication we demonstrated that the yield of a naphthopyran–carbene adduct could be markedly improved by adopting an intramolecular trapping strategy. Thus reduction of naphthopyran 7 using LiAlH₄ at rt gave the hydroxymethyl compound 8 (63%) (Scheme 3) [7]. Diazoacylation of the hydroxymethyl residue with ethyl diazomalonyl chloride gave two new compounds, 9 (45%)







Reagents: (i) LiAIH₄, THF, rt; (ii) ethyl 2-diazomalonyl chloride, 2,6-lutinine, DMAP, CH₂Cl₂; (ii) Rh₂(OAc)₄, CH₂Cl₂, rt

SCHEME 3



FIGURE 1 X-Ray crystal structure of compound 10 [8].

and an unknown solid, which has now been characterised as **10** (34%) by X-ray crystallography (Fig. 1) [8]. Treatment of a solution of **9** with $Rh_2(OAc)_4$ in CH_2Cl_2 gave the tetracyclic merocyanine dye **11** in 92% yield [7].

We now expand upon these preliminary results and describe the synthesis and behaviour of carbenoids tethered to a 2*H*-naphtho[2,1-*b*]pyran unit by either a hydroxyethyl or hydroxypropyl linkage.

RESULTS AND DISCUSSION

The required 3-(hydroxyalkyl)-1-naphthols, **12**, were obtained from the isoquinolinium salt, **13**, by a two step sequence involving a Bradsher $[4^++2]$ cycloaddition [9] to afford the 3-(hydroxyalkyl)-1naphthaldehydes **14** and a subsequent Baeyer-Villiger oxidation (~ 35% two steps) (Scheme 4). The new photochromic naphthopyrans **15** [10] were obtained by the well established propynol route [2]. The visible spectra of irradiated (365 nm) toluene solutions of these compounds (**15**) each showed two absorption bands; an intense band at ca. 498 nm with a weaker band at ca. 415 nm. The hydroxyalkyl naphthopyrans **15** were readily diazoacylated (~ 44% yield) with ethyl diazomalonyl chloride in CH₂Cl₂ containing 2,6-lutidine and a catalytic amount of 4-dimethylaminopyridine (DMAP) to afford a readily separable mixture of the desired carbenoid precursors **16** and the chloro-compounds **17**.



Reagents: (i) vinyl ether, MeOH then HCl, MeCN, heat; (i) H⁺, H₂O₂, heat;(iii) 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol, H⁺, PhMe, heat; (iv) ethyl 2-diazomalonyl chloride, 2,6-lutinine, DMAP, CH₂Cl₂; (v) Rh₂(OAc)₄, CH₂Cl₂, rt.

SCHEME 4

Generation of the carbenoid from 16, n = 2 in anhydrous CH_2Cl_2 gave a complex reaction product, which contained three new photochromic compounds. After extensive column chromatography only one pure fraction could be obtained. The ¹H NMR spectrum of this compound [11] was remarkably similar to the carbenoid precursor, but displayed an additional AB system with a doublet at δ 3.39 and at δ 4.66 ($J = 8.2 \,\text{Hz}$). A routine D₂O experiment revealed that the doublet at δ 4.66 was due to a hydroxyl group and thus suggested the structure as 18, n = 2, which was subsequently confirmed by HRMS. The ¹H NMR data for **18**, n = 2 compares favourably with that for other 2-hydroxymalonate esters where the methine proton typically resonates at ca. δ 3.9 and the hydroxyl proton at δ ca. 4.7 [12]. The interception of rhodium carbenoids by water has been previously noted [12,13]. A similar result was obtained when diazo compound 16, n = 3 was treated with $Rh_2(OAc)_4$ in CH_2Cl_2 . Unfortunately, it would appear that the carbenoids generated from 16 fail to undergo an intramolecular cyclisation comparable to that observed for 9 and are instead intercepted by water, despite the reaction being run under anhydrous conditions, to afford 18 in moderate yield.

CONCLUSIONS

Two novel 3-(hydroxyalkyl)-1-naphthols have been obtained by a two step strategy from an isoquinolinium salt employing a Bradsher cycloaddition reaction and a Baeyer-Villiger rearrangement. These naphthols have been transformed into new photochromic

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2*H*-naphtho[1,2-*b*]pyrans by an acid catalysed reaction with a prop-2yn-1-ol. Diazoacylation of the pendant hydroxyl functions and subsequent rhodium carbenoid generation failed to afford tetracyclic cycloadducts and instead the carbenoid was intercepted by water. This contrasts with our previous observations and indicates that the length of the tether dictates the mode of the carbenoid addition process. Further work in this area is ongoing.

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- [11] Characterisation data for 2,2-bis(4-methoxyphenyl)-5-[2-(3-ethoxycarbonyl-2-hydroxy-1-oxopropyloxy)-1-ethyl]-2H-naphtho[1,2-b]pyran **18**, n = 2: as a red oil, 20%, $\delta_{\rm H}$ 1.11 (3H, t, J 7.2, CH₂CH₃), 3.15 (2H, m, Ar-CH₂CH₂), 3.39 (1H, d, J 8.2, CHOH), 3.76 (6H, s, OCH₃), 4.06 (2H, m, CH₂CH₃), 4.43 (2H, m, Ar-CH₂CH₂), 4.66 (1H, d, J 8.2, CHOH), 6.19 (1H, d, J 10.0, 3-H), 6.82 (4H, m, Ar-H), 6.92 (1H, d, J 10.0, 4-H), 7.17 (1H, s, 6-H), 7.40 (6H, m, Ar-H), 7.63 (7.64)

(1H, d, J 9.4, Ar–H), 8.28 (1H, m, Ar–H). (Found: M + H^+ 569.2170. $C_{34}H_{32}O_8;$ requires M + H^+ 569.2175).

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