

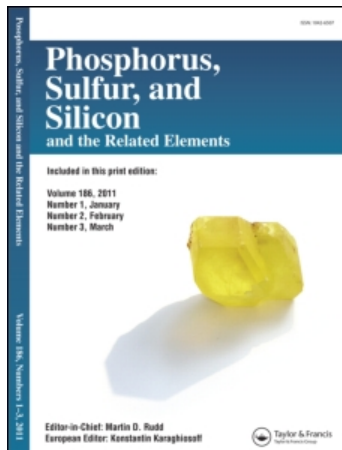
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## Synthesis of Photochromic Thieno-2H-Chromenes

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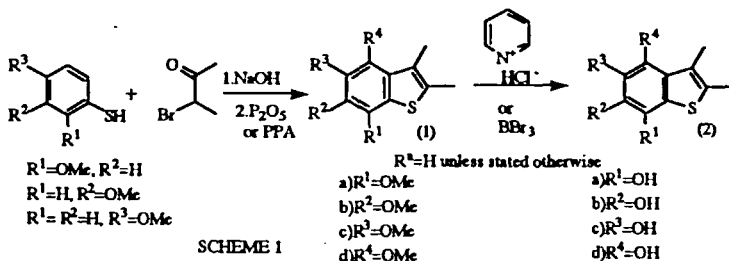
The synthesis of photochromic thieno-2H-Chromenes from hydroxybenzo[b]thiophenes and 1,1-diphenyl-2-propyn-1-ol in presence of an acidic catalyst is discussed

### INTRODUCTION

Some classes of heteroannellated 2H-Chromenes are already known for their photochromic properties and for their application in ophthalmic lenses<sup>1</sup> (coloured in the sun and bleach in the dark). The photochromic properties are based on the reversible reaction of the colourless pyran form to the coloured opened forms, when liquid solutions or polymer matrices containing the closed form are exposed to UV light or sunlight.

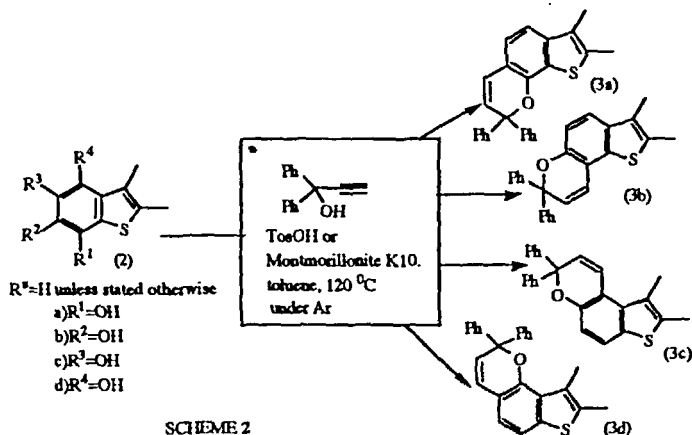
### RESULTS AND DISCUSSION

It was decided to synthesise hydroxybenzo[b]thiophenes (SCHEME 1) as precursors of the required thieno-2H-Chromenes, starting from methoxythiophenols.



In the obtention of the methoxybenzo[b]thiophenes (1) the use of PPA<sup>2</sup> as cyclising agent gave better yields. The compounds (1b) and (1d) were obtained in the same cyclisation reaction. Two methods for the demethylation of compounds (1) were used to obtain the hydroxybenzo[b]thiophenes (2) but it was only possible to evaluate which method was the best for each compound and not to generalize.

The thieno-2*H*-Chromenes (3) were isolated in their closed *leuco* forms in 9 to 11% yield after chromatography, from the reaction between the corresponding compounds (2) and 1,1-diphenyl-2-propyn-1-ol in presence of an acidic catalyst (SCHEME 2).



The compounds (3) were fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, UV spectroscopy, mass spectrometry and HRMS or elemental analysis. Comparing with other heteroannellated chromenes<sup>3</sup> we have also observed in the  $^1\text{H}$  NMR spectra a doublet centred around 6.2 ppm with  $J$  10Hz which is typical for the  $\alpha$  proton to the quaternary carbon of the pyran ring. The doublets of the benzenic rings have a coupling constant of 8Hz. In the  $^{13}\text{C}$  NMR spectra the chemical shift around 82 ppm is also characteristic of the  $\text{sp}^3$  carbon atom.

Spectrokinetic studies in (3a) and (3b) were evaluated in terms of the  $\lambda_{\text{max}}$  of the opened coloured forms, of the colourability ( $A_{\text{max}}$ ) and of the thermal bleaching rate ( $K_d$ ), which are the parameters used for the quantification of the photochromic behaviour.

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