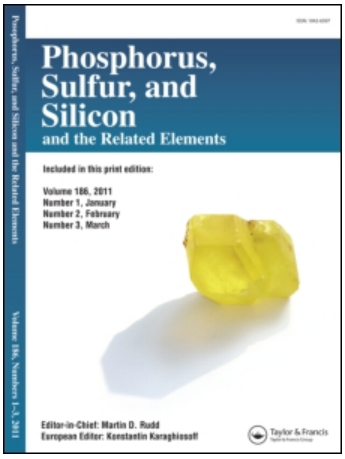


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Photochromic Thieno-2*H*-Chromenes

Maria-João Rp. Queiroz; Robert Guglielmetti

To cite this Article Queiroz, Maria-João Rp. and Guglielmetti, Robert(1999) 'Synthesis of Photochromic Thieno-2*H*-Chromenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 397 — 398
To link to this Article: DOI: 10.1080/10426509908546489
URL: http://dx.doi.org/10.1080/10426509908546489

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 397-398
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis of Photochromic Thieno-2*H*-Chromenes

MARIA-JOÃO RP. QUEIROZ* and ROBERT GUGLIELMETTI

*Departamento de Química, Universidade do Minho, 4710 Braga, Portugal
Université de la Mediterranée, Faculté des Sciences de Luminy, ERS CNRS 158, 13288 Marseille Cédex 9, France*

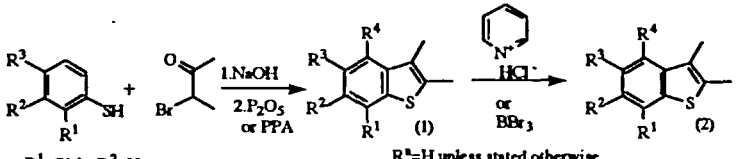
The synthesis of photochromic thieno-2*H*-Chromenes from hydroxybenzo[*b*]thiophenes and 1,1-diphenyl-2-propyn-1-ol in presence of an acidic catalyst is discussed

INTRODUCTION

Some classes of heteroannellated *2H*-Chromenes are already known for their photochromic properties and for their application in ophthalmic lenses[1] (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.



R^1=OMe, R^2=H
R^1=H, R^2=OMe
R^1= R^2=H, R^3=OMe

R^4=H unless stated otherwise

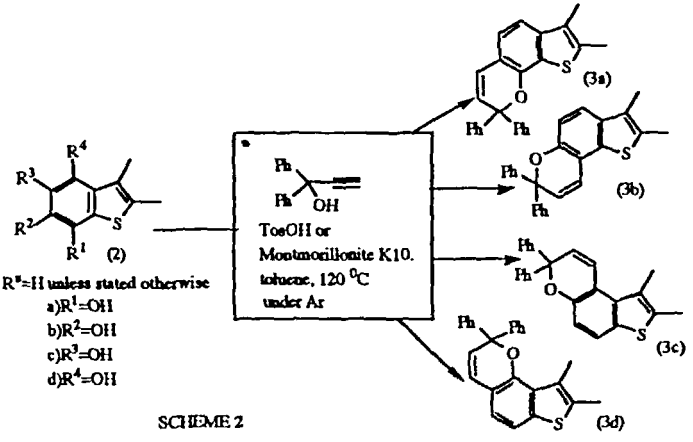
a)R^1=OMe
b)R^2=OMe
c)R^3=OMe
d)R^4=OMe

a)R^1=OH
b)R^2=OH
c)R^3=OH
d)R^4=OH

SCHEME 1

In the obtention of the methoxybenzo[*b*]thiophenes (1) the use of PPA[2] 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-*2H*-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).



SCHEME 2

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

Spectrokinetic studies in (3a) and (3b) were evaluated in terms of the λ_{max} of the opened coloured forms, of the colourability (A_0) and of the thermal bleaching rate (K_Δ), which are the parameters used for the quantification of the photochromic behaviour.

Acknowledgements: IBQF-UM/Praxis XXI for financial support. R.Dubest -Université de Paris VII- for the spectrokinetic evaluations.

References

[1] J-L. Pozzo, A. Samat et R. Guglielmetti/ ESSILOR Int, Brevet Français n°9203297, 1992 (Extension Europe, USA, Japon, 1993).

[2] R. Royer, P. Demerseman, J.-P. Lecharter, A.-M. Laval-Jeantet et A. Cheutin, *Bull. Soc. Chim. Fr.*, 1964, 315–320.

[3] J-L. Pozzo, V.A. Lokshin and R. Guglielmetti, *J. Chem. Soc. Perkin Trans 1*, 1994, 2591–2595.