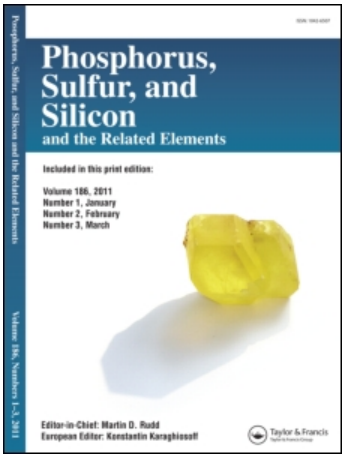

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Selective Photoisomerization of some 2,4,4,6-Tetrasubstituted 4H-Thiopyrans

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SELECTIVE PHOTOISOMERIZATION OF SOME 2,4,4,6-TETRASUBSTITUTED 4H-THIOPYRANS

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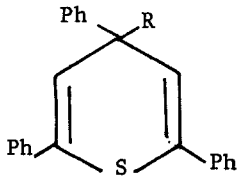
Abstract A selective photoisomerization observed in some 2,4,4,6 - tetrasubstituted 4H-thiopyrans is described.

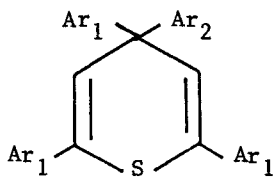
INTRODUCTION

Following our studies on the photochromism and photoisomerization of some 4H-thiopyran derivatives [1,2], the structures of the photoproducts have been studied by other research groups which shed more light on the structures of the resulting 2H-thiopyran isomers[3]. In the present study, the structures of the photoproducts from non-photochromic 4H-thiopyrans 1 and photochromic 4H-thiopyrans 2 have been investigated in solution and compared with those of the final stable coloured compounds in the solid state. Here, the rearrengement difference between alkyl and aryl groups in 4-position of the thiopyran skeleton as well as the effects of solvent polarity on the ease of photoisomerization were determined in the identical conditions.

RESULTS AND DISCUSSION

Irradiation of non-photochromic 4-alkyl-2,4,6- triphenyl-4H-thiopyrans 1 and photochromic 2,4,4,6-tetraaryl-4H-thiopyrans 2 in the solid state or in solution by a monochromatic UV light at λ= 254 nm led to the identical 2H-thiopyran isomers with much lower yields in the solid state than in solution. The progress of photoisomerizations, which monitored by ^{1}H-NMR spectroscopy, were quite fast and yields nearly quantitative in methanol.





1: R = Me, C_2H_5, n-C_4H_9 2: Ar_1 = Ph, p-$MeOC_6H_4$, p-$NMe_2C_6H_4$
Ar_2 = p-$CF_3C_6H_4$

To study the effects of solvent polarity on this photoisomerization the solutions of 4H-thiopyrans were separately irradiated in methanol or benzene in the same conditions. The ^{1}H-NMR spectra recorded at different time intervals revealed that the progress of reactions are much faster and the yields are quite higher in methanol than in benzene solution.

The formation of the sole phenyl-shifted photoproducts with almost quantitative yields in 1 clearly signify that no detectable alkyl-shifted products are formed.

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