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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

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Hooshang Pirelahi; Hossein Rahmani; Arash Mouradzadegun; Ali Fathi; Ali Moudjoodi

To cite this Article Pirelahi, Hooshang , Rahmani, Hossein , Mouradzadegun, Arash , Fathi, Ali and Moudjoodi, Ali(1997) 'Photochromism and Photoisomerization in Some 2,3,4,4,5,6-Hexasubstituted 4H-Thiopyrans', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 403-404

To link to this Article: DOI: 10.1080/10426509708545569 URL: http://dx.doi.org/10.1080/10426509708545569

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Photochromism and Photoisomerization in Some 2,3,4,4,5,6-Hexasubstituted 4H-Thiopyrans

HOOSHANG PIRELAHI, HOSSEIN RAHMANI, ARASH MOURADZADEGUN, ALI FATHI AND ALI MOUDJOODI Department of Chemistry, University of Tehran, P.O.Box 13145-143, Tehran, IRAN

Photochromism and photoisomerization reactions of some new 2,3,4,4,5,6-hexasubstituted 4H-thiopyrans are described.

INTRODUCTION

In the course or our studies on photochromism and photoisomerization of 2,4,4,6-tetrasubstituted 4H-thiopyrans¹, it seemed of considerable import to inspect the effects of 3,5-substitutions on these phenomena. Accordingly the new hexasubstitued 4-aryl-2,3,4,5,6-pentaphenyl-4H-thiopyrans 1a-c, 2,3,4,5,6-pentaphenyl-4-methyl-4H-thiopyran 1d, 4-aryl-2,4,6-triphenyl-3,5-dimethyl-4H-thiopyrans 2a-c and 2,4,6-triphenyl-3,4,5-trimethyl-4H-thiopyran 2d analogues were selected for synthesis and the present study.

RESULTS AND DISCUSSION

The 4H-thiopyrans 1a-c, in contrast to the photochromic 2,4,4,6-tetraarylsubstituted 4H-thiopyrans 1,2, did not exhibit any photochromic or photoisomerization behaviour in the solid state, however, in 4H-thiopyrans 2a-c the photochromic and photoisomerization properties were restored with a hypsochromic shift in the absorption maxima of the photochromic species as well as a decrease in the yields of the photorearranged products. The 4H-thiopyrans 1d and 2d in accord with non-photochromic 2,4,6-triphenyl-4-alkyl-4H-thiopyran analogues 1,2 remained colourless in the solid state.

None of the non-photochromic 4H-thiopyrans 1a-c or photochromic 2a-c exhibited any reversible photochemical colour changes in benzene solution.

On irradiation of 1a-c in benzene with UV light of λ =254 nm no absorption bands around 370 nm characteristic for the expected isomeric 2H-thiopyrans could be detected. Irradiations of 2a-c in methanol gave mixtures of the both corresponding aryl-migrated 2H-thiopyran isomers. Irradiation of 1d or 2d in benzene- d_6 in a sealed pyrex NMR tube furnished only the phenyl-migrated isomer.

The results are consistent with the operation of unfavourable steric interactions in the transition states that lead to photoproducts caused by non-bonded repulsions between the substituents of sulfur ring which lessen the ability of the aryl groups to delocalize charges.

ACKNOWLEDGMENT

Financial assistance from the Research Council at the University of Tehran through Grant No. 254/1/514 is gratefully acknowledged.

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