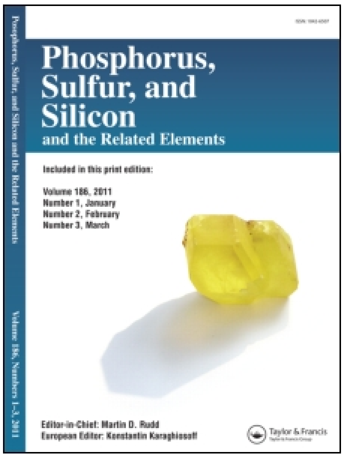

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PHOTOCHROMISM STUDY IN SOME 4-THIOPYRAN DERIVATIVES

Hooshang Pirelahi[a]; Iraj Parchamazad[a]; Mohammed Saiid Abaii[a]; Sekineh Sheikhebrahimi[a]
[a] Department of Chemistry, University of Tehran, Tehran, Iran

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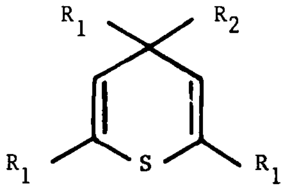
PHOTOCHROMISM STUDY IN SOME 4-THIOPYRAN DERIVATIVES

HOOSHANG PIRELAHI, IRAJ PARCHAMAZAD, MOHAMMED SAIID ABAII,
AND SEKINEH SHEIKHEBRAHIMI
Department of Chemistry, University of Tehran, P.O.Box
13145-143, Tehran, Iran

Abstract A novel photochromism observed in some 4-thiopyran derivatives is described.

INTRODUCTION

We have recently published several articles on the chemistry and the synthesis of some thiopyran derivatives[1]. Although photochromism phenomena have been studied in different heterocyclic systems, there are limited reports on the photochromic properties of thiopyrans[2]. The present investigation consists of some informations on the nature of the observed photochromism in the 4-thiopyran system. The thiopyrans studied are:



1, R_1 = phenyl, R_2 = p-trifluoromethylphenyl
2, R_1 = phenyl, R_2 = methyl
3, R_1 = p-methoxyphenyl, R_2 = phenyl
4, R_1 = p-methoxyphenyl, R_2 = p-trifluoromethylphenyl
5, R_1 = p-dimethylaminophenyl, R_2 = p-trifluoromethylphenyl

RESULTS AND DISCUSSION

On exposures to sunlight or ultraviolet radiations, the thiopyrans 1, 2, 3, 4, and 5 undergo the reversible and the irreversible color changes in crystalline states as follows:

1, white $\xrightleftharpoons{h\nu}$ violet $\longrightarrow$ yellow

2, white $\xrightleftharpoons{h\nu}$ no observable color changes

3, white $\xrightleftharpoons{h\nu}$ greenish-blue $\longrightarrow$ orange

4, white $\xrightleftharpoons{h\nu}$ reddish-violet $\longrightarrow$ orange

5, greenish white $\xrightleftharpoons{h\nu}$ dark green $\longrightarrow$ brown

These color reversibilities are limited and after several runs the samples would exhibit the fatigue phenomena and be converted to the final stable colored compounds.

The solubility of the initial unstable violet compound resulting from irradiations of 1 was examined in different solvents. It dissolved rapidly in acetone, chloroform, carbontetrachloride, and methanol while loosing the color immediately. However, the disappearance of the color and its dissolution in methanol was somewhat slower. The solubility tests were also repeated at relatively low temperatures. At - 50^{0C} in acetone or chloroform as solvent the initial unstable violet compound of 1 dissolved and lost its color rapidly, while in methanol at the same conditions the dissolution was slower and the color remained for a few minutes. At - 80^{0C} the color was such stable that 5 mg of the sample in methanol lost its color after 15 minutes.

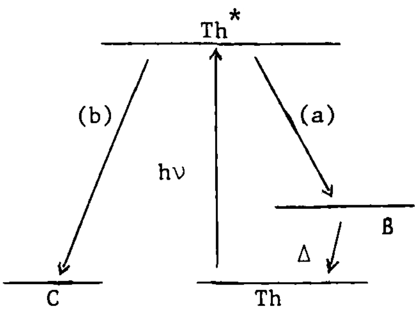
In other experiments equal amounts of the initial unstable violet compound of 1 at the same temperature were separately placed in air, in vacuum, and in helium atmosphere. The results showed that the rate of fading is somewhat slower in vacuum than air but it is the same in oxygen and helium atmosphere, while it is faster under higher oxygen pressure.

It seems that for this reversible coloration a special solid state and crystal form is required, since the cold melted crystals of 1 did not show any photochromism, however, when the melted solid was recrystalized in ethanol the resulting crystals exhibited photochromic properties again.

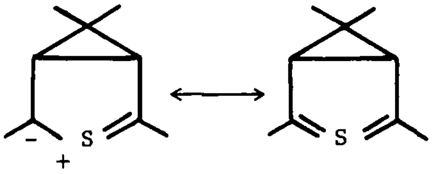
Considering the above mentioned experimental results, the general mechanism for the observed photochromism could be suggested as follows:

$$\mathrm{Th} + h\nu \longrightarrow \mathrm{Th}^{*}$$
$$\mathrm{Th}^{*} \xrightarrow{(a)} \mathrm{B}$$
$$\mathrm{B} \xrightarrow{\Delta} \mathrm{Th}$$
$$\mathrm{Th}^{*} \xrightarrow{(b)} \mathrm{C}$$

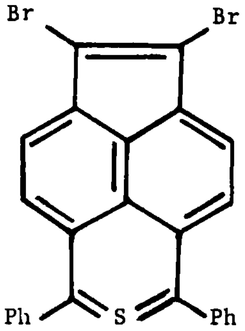
(Th = Thiopyran)



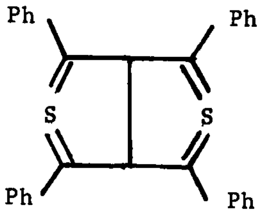
On irradiations, the photochromic Th will first be excited to Th*, then produces a new colored species B through the pathway (a). The colored B regenerates Th via a thermal process, since the color fading is temperature dependent. In these processes some of the excited Th* will produce a stable compound C through a side reaction, pathway (b), irreversibly. Gradual formation of C will finaly cease the photochromic process. The following structures may be suggested for the colored species B :



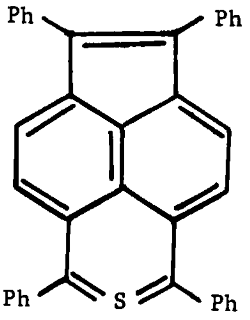
This suggestion is also in agreement with the previous reports relavant to the syntheses of the following stable colored tetravalent sulfur heterocycles using 3d orbitals[3]:



dark blue

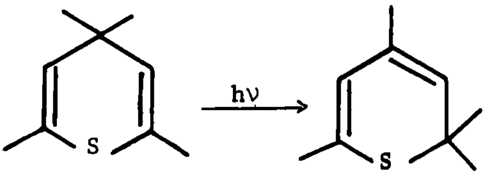


purple



blue-black

The MS, ^{13}C-NMR, ^{1}H-NMR, UV, IR spectra, and the elemental analyses of the stable compound C reveal the possibility of the following photochemical reaction:



Studies on the structure of the compound C are being continued.

ACKNOWLEDGMENT

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REFERENCES

1. H. Pirelahi et al, J. Heterocyclic Chem., 13, 237(1976); ibid., 14, 199(1977); ibid., 16, 917(1979).
2. I. Parchamazad, H. Pirelahi, and S. Sheikhebrahimi, Abstracts of Xth IUPAC Symposium on Photochemistry, Switzerland, 377(1984).
3. I.S. Ponticello and R.H. Schlessinger, J. Am. Chem. Soc., 90, 4190(1968); M.P. Cava and G.E.M. Husbands, ibid., 91, 3952(1969); J.M. Hoffman, Jr. and R.H. Schlessinger, ibid., 3953(1969).