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KINETIC STUDY ON PHOTOISOMERIZATION OF SOME TETRA- AND HEXASUBSTITUTED 4H-THIOPYRANS

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The effects of phenyl and methyl groups at 3,5-positions of tetrasubstituted 4H-thiopyrans **1a** and **1b** on photoisomerization are investigated from a kinetic point of view using ¹H-NMR spectroscopy. On irradiation of **1a-1d** in benzene-d₆ solution the hexasubstituted 4H-thiopyrans **1c** and **1d**, unlike those of the tetrasubstituted analogues **1a** and **1b**, give the isomeric 2H-thiopyrans **3c** and **3d** with no detectable signals for intermediates in ¹H-NMR spectra. The photoisomerization of hexasubstituted 4H-thiopyrans **1c** and **1d** occur with relative rate constants lower than the corresponding tetrasubstituted model compounds **1a** and **1b**. Moreover, the kinetic comparison of **1a** with **1b** reveal that the presence of two phenyl groups at 4-position of tetrasubstituted 4H-thiopyran increases the relative rate constant of photoisomerization.

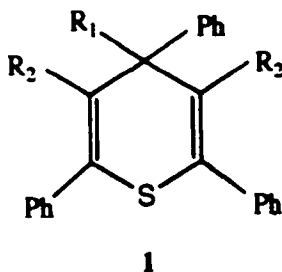
Keywords: 4H-Thiopyrans; 2H-thiopyrans; photoisomerization; kinetic study

INTRODUCTION

Previously we reported on the photochemistry of tetrasubstituted 4H-thiopyran derivatives which upon irradiation in the solid state or solution undergo an intramolecular photoisomerization to yield the corresponding 2H-thiopyrans¹. It was found that, when 2,4,4,6-tetraaryl-4H-thiopyrans or 4-alkyl-2,4,6-triphenyl-4H-thiopyrans are irradiated with UV light at room temperature under nitrogen, only aryl groups rearrange to form 2H-thiopyran isomers and no alkyl group rearrangement could be observed^{1,2}. The formation of bicyclic intermediates in these photorearrangements was successfully proved in our and other laboratories²⁻⁵. It is also shown that

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the electron donating or electron withdrawing groups on the para position of the migratory 4-aryl group of tetrasubstituted 4H-thiopyrans affect the relative rates of photoisomerization⁵. As reported earlier, substituents at 3,5-positions of the sulfur ring in 4H-thiopyrans alter the photoisomerization and photochromism behaviour⁶. In the present study the effects of phenyl and methyl groups at 3,5-positions on the relative rate constants of photoisomerization are investigated. Accordingly tetra- and hexasubstituted 4H-thiopyrans **1a-1d** are selected for study.

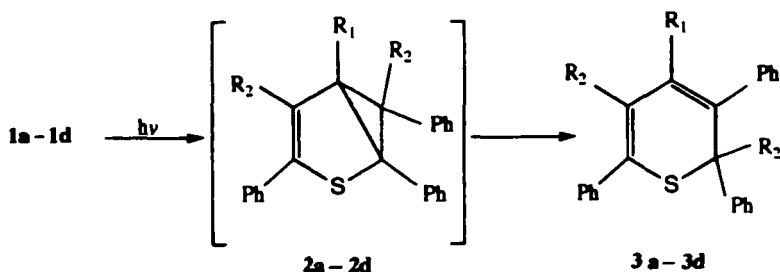


a) $R_1 = \text{Me}$, $R_2 = \text{H}$; **b)** $R_1 = \text{Ph}$, $R_2 = \text{H}$; **c)** $R_1 = \text{Ph}$, $R_2 = \text{Me}$; **d)** $R_1 = \text{Me}$, $R_2 = \text{Ph}$

RESULTS AND DISCUSSION

In order to study the effects of 3,5-substitutions on the relative rate constants of 4-phenyl group migration, the 3×10^{-2} M solutions of 4H-thiopyrans **1a-1d** were prepared in benzene- d_6 . Irradiations were carried out in sealed NMR tubes with a monochromatic low-pressure mercury lamp at $\lambda = 254$ nm under an argon atmosphere at room temperature. The reactions were followed by ^1H -NMR and the spectra recorded at different time intervals. In ^1H -NMR spectra, the singlets of **1a-1b** at 5.88–6.33 (H-3,-5) ppm gradually decreased, while new sets of singlets appeared at 2.55–3.60 (H-6) and 5.75–5.98 (H-4) ppm for intermediates **2a-2b**, and at 4.60–4.74 (H-2) and 6.49–6.92 (H-5) ppm for products **3a-3b**. In the case of **1c-1d** the singlets of **1c** at $\delta = 1.52$ (Me-3,-5) ppm and of **1d** at $\delta = 1.92$ (Me-4) ppm decreased with the appearance of two singlets at 1.63 (Me-2) and 1.65 (Me-5) ppm for product **3c** and one singlet at 1.98 (Me-4) ppm for

product **3d** (Table I), where no signals for intermediates could be observed. The lower yields of photoproducts **3c-3d** (Table II) and the disappearance of intermediates for hexasubstituted **1c-1d** contrast sharply with those of the corresponding 3,5-unsubstituted model compounds **1a-1b** which are consistent with the unfavourable steric interactions and increasing energy contents of bicyclic intermediates **2c-2d**; thus, the intermediates may be changed to undetectable transition states leading to photoproducts.



The variations in molar ratios of each species are measured by the integration of characteristic signals; the percentage of each species in the reaction mixture of **1a-1d** during the 90 minutes of the reaction are shown in Table II. In all cases, the reactions continued until the complete conversion of **1a-1d** and **2a-2b** to **3a-3d** in nearly quantitative yields. At the end of irradiations only the signals assigned to sole photoproducts **3a-3d** are observable in the $^1\text{H-NMR}$ spectra with no signs of byproducts.

The relative rate constants of photoisomerization of **1a-1d** were determined using absorption and fluorescence data according to the following equation^{7b,8}, where k_R is the rate constant for formation of photoproducts and ϕ_R the quantum yield for formation of photoproducts,

$$\frac{k_R}{k_R \cdot \phi_R} = \frac{\phi_R \phi_F \cdot k_F}{\phi_R \cdot \phi_F k_F}$$

where k_F is rate constant for fluorescence and ϕ_F the quantum yield of fluorescence.

The experimental values of these determinations in benzene- d_6 are listed in Table III. Comparison of the relative rate constants of **1d** with **1a** reveal that in spite of larger k_F for **1d**, the smaller ϕ_R and larger ϕ_F lower the relative rate constant of **1d**. In the case of **1c** to **1b** the intensive decrease in ϕ_R and smaller k_F reduce the relative rate constant of **1c**. However, due to increasing ϕ_R and k_F in **1b**, the relative rate constant of **1b** is greater than **1a**.

TABLE I The characteristic chemical shifts for 4H-thiopyrans **1a-1d**, bicyclic intermediates **2a-2b** and photoproducts **3a-3d** in benzene- d_6

Compound	Chemical shifts (ppm)				
	Benzene- d_6				
	Me-4	H-3,-5	Me-3,-5		
1a	1.53	5.88	—		
1b	—	6.33	—		
1c	—	—	1.52		
1d	1.92	—	—		
	H-4	H-6			
2a	5.75	2.55			
2b	5.98	3.60			
	Me-2	Me-4	Me-5	H-2	H-5
3a	—	1.9	—	4.60	6.49
3b	—	—	—	4.74	6.92
3c	1.63	—	1.65	—	—
3d	—	1.98	—	—	—

These results reveal that, the presence of phenyl or methyl groups in 3,5-positions of sulfur ring in hexasubstituted 4H-thiopyrans **1c-1d** decrease the relative rates of migrations of 4-phenyl groups by losing the energy in excited states. Considering the ϕ_R , ϕ_F and k_F in **1c-1d** and the disappearance of intermediates **2c-2d**, this behaviour could be due to the steric as well as the electronic effects of 3,5-substituents in the photochemical pathway to the intermediates.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-80 spectrometer using tetramethylsilane as the internal standard. UV spectra were taken on a Shimadzu 265-FW spectrometer. Fluorescence spectra were taken on a Shimadzu RF 5000 spectrofluorophotometer. Photolyses were performed using a low-pressure mercury lamp.

TABLE II The variations (%) of **1a-1d**, **2a-2b** and **3a-3d** during the 90 minutes of photoisomerization under identical experimental conditions. The values are an average for two different runs measured by integration of the $^1\text{H-NMR}$ characteristic signals in the reaction mixtures*

Compound	Variations (%)								
	Time (min), benzene- d_6								
	5	10	15	20	30	45	60	75	90
1a	93.9	91.4	89.5	85.2	75.7	62.2	53.2	45.9	38.9
1b	89.9	69.8	57	44.3	32.1	21.1	13.8	13.3	9.1
1c	~100	~100	~100	~100	98.3	95.6	93.4	92.7	90.0
1d	97.5	94.4	92	88.3	83.9	82.2	76.4	75.7	73.4
2a	4.7	6.1	7.5	9.3	13.2	16.3	16.5	15.9	14.8
2b	10.1	25.1	33.5	39.3	42.6	49.1	38.5	31.0	24.8
3a	1.4	2.5	3.0	5.5	11.1	21.5	30.3	38.2	46.3
3b	~0.0	5.1	9.5	16.4	25.3	29.8	47.7	55.7	66.1
3c	~0.0	~0.0	~0.0	~0.0	1.7	4.4	6.6	7.3	10.0
3d	2.5	5.6	8.0	11.7	16.1	17.8	23.6	24.3	26.6

* The more sensitive UV spectroscopy could not be used for these determinations since the UV absorption of the reaction intermediates interfere with those of the photoproducts.

TABLE III Relative rate, quantum yield and fluorescence data for **1a-1d**. The values are an average for two different runs

Compd.	Benzene- d_6				Compd.	Benzene- d_6			
	$\phi_R(\text{rel})$	$k_F \times 10^{-8}$	$\phi_F(\text{rel})$	$k_R(\text{rel})$		$\phi_R(\text{rel})$	$k_F \times 10^{-8}$	$\phi_F(\text{rel})$	$k_R(\text{rel})$
1a	1	1.07	1	1	1b	1	1.12	1	1
1b	1.08	1.12	1.02	1.11	1c	0.07	0.94	0.98	0.06
1d	0.30	2.34	1.13	0.57					

Syntheses

The tetra- and hexasubstituted 4H-thiopyrans **1a-1d** were synthesized from the reactions of organolithium or organomagnesium salts with the

corresponding thiopyrylium perchlorates in dry ether at an argon atmosphere by the method perviously described⁶.

General procedure for photolysis

Sample solutions were prepared by dissolving 1.47×10^{-5} mol of **1a-1d** in 0.5 ml benzene- d_6 in an NMR tube then were degassed and sealed under an argon atmosphere. Irradiation were carried out with a low-pressure mercury lamp using a monochromatic UV light with $\lambda=254$ nm at room temperature. The progress of the photochemical reactions were followed by ^1H -NMR spectroscopy. The variations of 4H-thiopyrans **1a-1d** mole fractions during the photolysis procedure were measured by integrations of the characteristic signals in the spectra of reaction mixtures.

Quantum yields and fluorescence data

The incident light intensity on the sample was measured by ferrioxalate actinometry developed by Parker and Hatchard⁹. The preparation of solutions and the experimental details concerning the use of the chemical actinometer are well described in the literature¹⁰. Radiative rate constants (k_F) were calculated from the absorption spectra, using the quantities of area under the curves of the molecular coefficients plotted against wave numbers^{7a}. Relative fluorescence quantum yields (ϕ_F) were computed from the relative intensities at the maximum in fluorescence spectra (values computed from integrated areas under the emission curves); $\lambda(\text{excitation}) = 350.4$ nm, concentration = 2×10^{-5} M in benzene solution.

Photoproducts

At the end of irradiations in benzene- d_6 solution, the 4H-thiopyrans **1a-1d** were converted selectively to their isomeric 2H-thiopyrans **3a-3d** as reported earlier^{1,5}.

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References

1. H. Pirelahi, I. Parchamazad, M.S. Abaii and S. Sheikhebrahimi, *Phosphorus, Sulfur and Silicon*, **59**, 251 (1991); H. Pirelahi, M.S. Hashtroodi, M.S. Abaii and Y.R. Shariati, *J. Photochem. Photobiol. A: Chem.* **81**, 21 (1994).
2. Y. Mori and K. Maeda, *J. Chem. Soc., Perkin Trans. 2*, 2061 (1991).
3. P. Sebek, S. Nespurek, R. Hrabal, M. Adamec and J. Kuthan, *J. Chem Soc., Perkin Trans. 2*, 1301 (1992). 4.
4. D. Gravel and C. Leboeuf, *Can. J. Chem.*, **60**, 574 (1982).
5. H. Rahmani and H. Pirelahi, *J. Photochem. Photobiol. A: Chem.*, **111**, 15 (1997); H. Pirelahi and M.S. Oskooee, *Phosphorus, Sulfur and Silicon* (in press).
6. H. Pirelahi, H. Rahmani, A. Mouradzadegan, A. Fathi and A. Moudjoodi, *J. Photochem. Photobiol A: Chem.*, **101**, 33 (1996).
7. (a) N.J. Turro, "Molecular Photochemistry", The Benjamin/Cummings Publishing Co., California, 1978, p. 87; (b) *ibid*, p. 247.
8. S.S. Hixon, *J. Am. Chem. Soc.*, **94**, 2507 (1972).
9. C.A. Parker, Proc. R. Soc. London, Ser. A, **220**, 104 (1953); C.G. Hatchard and C.A. Parker, *ibid*, **235**, 518 (1956).
10. J.G. Calvert and J.N. Pitts, *Photochemistry*, Wiley, New York, 1966, pp. 783–786.