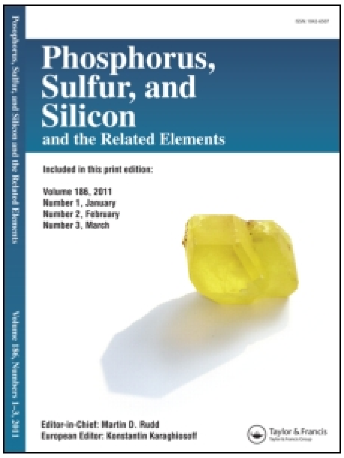

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The Effects of Electron Donating Methoxy Group on the Photoisomerization Kinetic of Some Tetrasubstituted 2,4,4,6-Tetraaryl-4*H*-Thiopyrans

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THE EFFECTS OF ELECTRON DONATING METHOXY GROUP ON THE PHOTOISOMERIZATION KINETIC OF SOME TETRASUBSTITUTED 2,4,4,6-TETRAARYL-4*H*-THIOPYRANS

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*Irradiation of 2,4,4,6-tetraaryl-4*H*-thiopyrans* ***4a–4c*** *in methanol solutions led to a mixture of 1,3,5,6-tetraaryl-2-thiabicyclo[3.1.0]hex-3-ene intermediates* ***5a–5c*** *and the thermodynamically more stable 2,3,4,6-tetraaryl-2*H*-thiopyran isomers* ***6a–6c*** *with no signs of by-products. The intermediates* ***5a–5c*** *were separated and the photoisomerization of* ***4a–4c*** *investigated from a kinetic point of view using HPLC. The relative rate constants reveal that the formation of the intermediate is the rate-determining step in the photoisomerization of tetraarylsubstituted 4*H*-thiopyrans. It is also found that the electron donating paramethoxy substituents on 2,6-aryl groups, unlike those of the migratory 4,4-aryl groups, decrease both the formation and conversion relative rate constants of the corresponding intermediates.*

Keywords: 2*H*-thiopyrans; 4*H*-thiopyrans; intermediates; kinetic study; photoisomerization

INTRODUCTION

Recently, we reported the isolation and kinetic study of intermediates in photoisomerization of tetrasubstituted 4-aryl-4-methyl-2,6-diphenyl-4*H*-thiopyrans **1** to their isomeric 2*H*-thiopyrans **3**, where the relative rate constants of formation and conversion steps of the 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene intermediates **2** were investigated.[1,2]

The formation of bicyclic intermediates in photoisomerization of tetraarylsubstituted 4*H*-thiopyran analogues has been investigated

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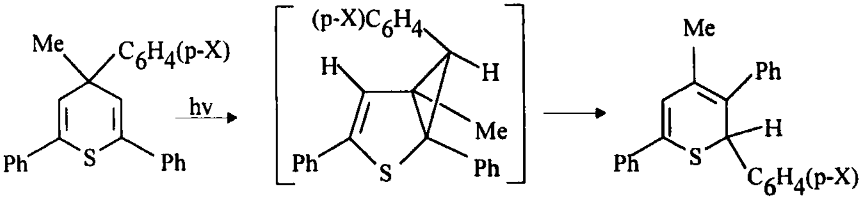
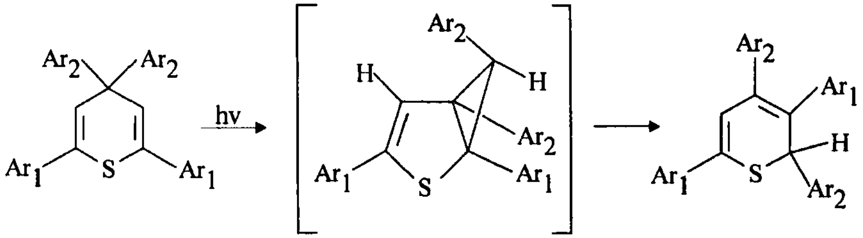


1 2 3

SCHEME 1

in our and other laboratories,[3–5] however, no kinetic behavior of the corresponding intermediates have been studied previously. Here, we report on the isolation of 1,3,5,6-tetraaryl-2-thiabicyclo[3.1.0]hex-3-ene intermediates **5a–5c** and the results of a kinetic study on their selective formation and conversion to the 2*H*-thiopyran isomers **6a–6c** using HPLC. Moreover, the effect of electron donating p-methoxy substituents at 4-positions of **4b** on the relative rate constants of photoisomerization were also compared with those of 2,6-positions of **4c**.



4a-4c 5a-5c 6a-6c

SCHEME 2

RESULTS AND DISCUSSION

In order to study the effects of electron donating p-methoxy substituents at 4-positions of the aryl groups on the conversion relative rate constants of bicyclic intermediates, solutions of 1,3,5,6-tetraaryl-2-thiabicyclo[3.1.0]hex-3-enes **5a–5c** in methanol were irradiated by UV light and followed by HPLC at different intervals. The resulting chromatograms showed gradual decreases in the peaks of bicyclic intermediates **5a–5c** as new peaks appeared for the corresponding 2*H*-thiopyrans **6a–6c**. At the end of irradiations only the 2*H*-thiopyrans were observed in the chromatograms with no signs of

TABLE I The Yields of **5a–5c** and **6a–6c** During Irradiations under Identical Experimental Conditions[a]

	Yields (%) Time (min)					
Compound	0.5	1	2	3	4	5
5a	95.3	91.4	83.9	76.7	70.1	64.4
5b	94.6	89.1	80.2	71.9	64.4	57.7
5c	95.8	93.0	86.5	80.6	74.8	69.7
6a	4.7	8.6	16.1	23.3	29.9	35.6
6b	5.4	10.9	19.8	28.1	35.6	42.3
6c	4.2	7.0	13.5	19.4	25.2	30.3

[a] The values are an average of three different runs measured by the corresponding peaks in chromatograms.

by-products. The stability of 2*H*-thiopyran solutions, irradiated under the similar conditions, highlights the selective and quantitative photoconversion of the bicyclic intermediates to 2*H*-thiopyrans **6a–6c**. The variations in molar ratios of the bicyclic intermediates shown in Table I indicate that the conversions of **5a–5c** to **6a–6c** proceed through the unimolecular first order reactions (Figure 1). To test the thermal stability, sample solutions of intermediates **5a–5c** were placed in a water bath at various temperatures. Considering the short period of time required for irradiations, the study revealed that temperatures below 60°C are insignificant in the conversions of **5a–5c**. To compare the formation relative rate constants of bicyclic intermediates, solutions of **4a–4c** were irradiated in methanol under identical experimental conditions as those of the conversions in **5a–5c** and monitored by HPLC at different intervals. The characteristic peaks in the chromatograms of **4a–4c** decreased concurrently with appearance of two new sets of peak for **5a–5c** and **6a–6c**. The variations in molar ratios of the reaction mixtures presented in Table II show that the formation of **5a–5c** from **4a–4c** also proceed through the unimolecular first order reaction (Figure 2).

The relative rate constants of conversions or formations of **5a–5c** were determined using absorption and fluorescence data according to the following equation:[6,7]

$$\frac{k_R}{k_{R'}} = \frac{\phi_R \phi_{F'} k_F}{\phi_{R'} \phi_F k_{F'}}$$

where k_R is the rate constant for conversion (k_R^c) or formation (k_R^f) of bicyclic intermediates, ϕ_R is the quantum yield for conversion (ϕ_R^c) or

TABLE II The Yields of **4a–4c**, **5a–5c**, and **6a–6c** During Irradiations under Identical Experimental Conditions[a]

	Yields (%) Time (min)					
Compound	0.5	1	2	3	4	5
4a	95.5	92.3	84.7	78.3	72.6	67.0
4b	94.3	90.5	82.0	74.4	67.7	61.5
4c	96.4	93.5	87.3	81.8	76.7	71.9
5a	4.5	7.1	13.3	19.4	22.5	26.6
5b	5.7	8.6	15.5	20.7	25.8	28.6
5c	3.6	6.5	12.3	16.7	20.9	24.2
6a	—	0.6	2.0	2.3	4.9	6.4
6b	—	0.9	2.5	4.9	6.5	9.9
6c	—	—	0.4	1.5	2.4	3.9

[a]The values are an average of three different runs measured by the corresponding peaks in chromatograms.

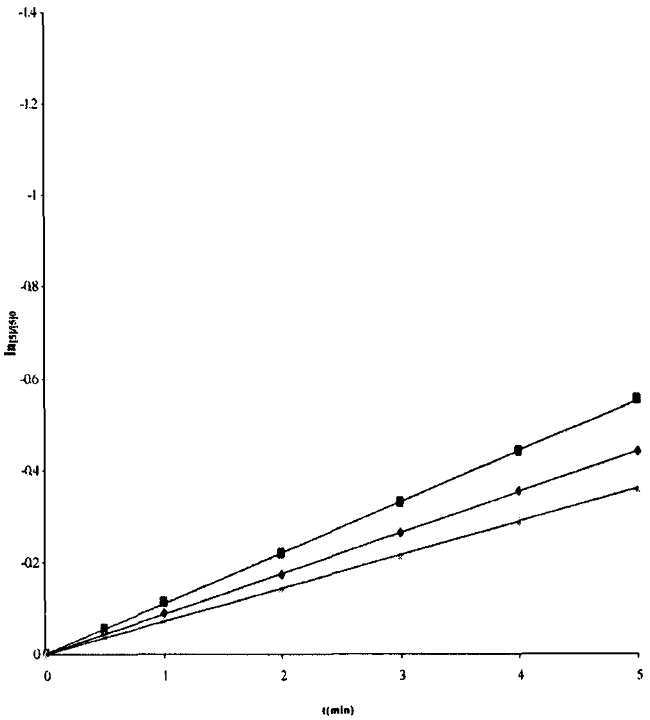


FIGURE 1 The plots of ln[5]/[5]$_0$ versus time obtained from least-squares treatments of the data for conversions of **5a–5c** (a, ♦; b, ■; c,) in methanol at 20°C representing the first-order reactions.

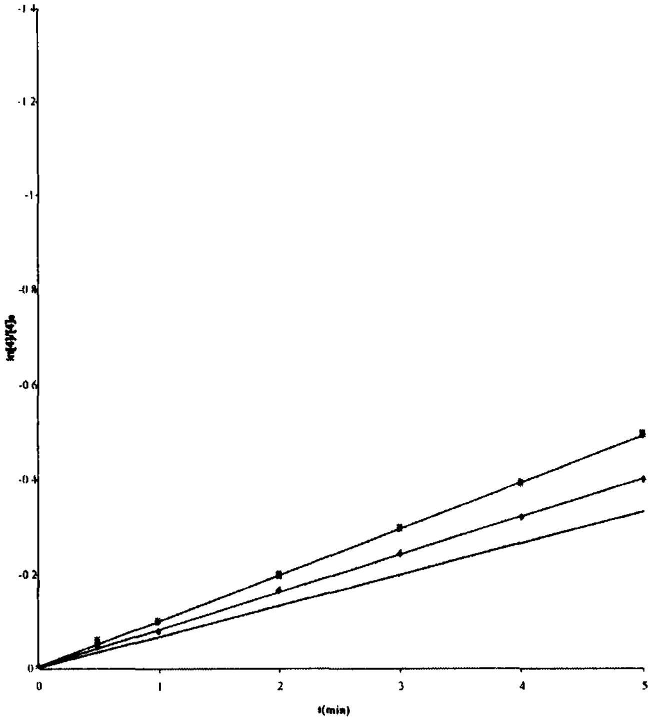


FIGURE 2 The plots of ln[4]/$[4]_0$ versus time obtained from least-squares treatments of the data for formations of **5a–5c** from **4a–4c** (a, ♦; b, ■; c,) in methanol at 20°C representing the first-order reactions.

formation (ϕ_R^f) of bicyclic intermediates, k_F the rate constant for fluorescence of **5a–5c** (k_F^c) or **4a–4c** (k_F^f), and ϕ_F is the quantum yield for fluorescence of **5a–5c** (ϕ_F^c) or **4a–4c** (ϕ_F^f). To reduce the experimental errors in quantitative values, the relative rate constants for conversions and formations are determined under identical experimental conditions with reference to the unsubstituted model compounds **5a** and **4a** as shown in Tables III and IV respectively. To evaluate the kinetic order of

TABLE III Relative Rate Constant, Quantum Yield, and Fluorescence Data for Conversions of **5a–5c**[a]

Compound	ϕ_F^c (rel)	k_F^c (rel)	ϕ_R^c (rel)	k_R^c (rel)
5a	1	1	1	1
5b	0.953	1.347	1.149	1.624
5c	1.287	1.274	0.894	0.885

[a] The values are an average of three different runs.

TABLE IV Relative Rate Constant, Quantum Yield and Fluorescence Data for Formations of **5a–5c** from **4a–4c**[a]

Compound	ϕ_F^f (rel)	k_F^f (rel)	ϕ_R^f (rel)	k_R^f (rel)
4a	1	1	1	1
4b	1.063	1.388	1.266	1.653
4c	1.224	1.241	0.800	0.811
1(X=H)	0.906	0.885	0.666	0.650

[a] The values are an average of three different runs.

photorearrangement and put the relative rate constants for conversions and formations of intermediates on a quantitative basis, the conversion relative rate constants of **5a–5c** were determined with reference to the model compound **4a** as well. The resulting unified conversion relative rate constants k_R^{uc}(rel) are shown in Table V. In addition, the formation relative rate constant for the previously reported 4-phenyl-4-methyl-2,6-diphenyl-4*H*-thiopyran analogue **1** (X=H) is also compared with that of **4a** in Table IV.

Comparison of the unified conversion relative rate constants of **5a–5c**, k_R^{uc}(rel), given in Table V with those of the relative rate constants for their formations, k_R^f(rel), in Table IV reveal that the formation of intermediate is slow enough to be the rate-determining step in photoisomerization of tetraarylsubstituted 4*H*-thiopyrans **4a–4c** to the corresponding 2*H*-thiopyran isomers. The resulting kinetic order is in agreement with the order of slops in Figures 3 and 4. Moreover, the k_R^c(rel) values of **5a–5c** (Table III) indicate that the electron donating methoxy groups on parapositions of the 1,3-aryl groups of intermediate **5c**, unlike those of the 5,6-aryl groups of **5b**, decrease the conversion relative rate constant in the faster step.

CONCLUSIONS

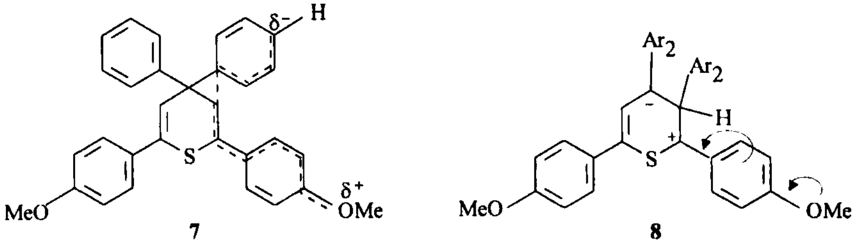
The opposite observed role of paramethoxy substituents on 2,6-aryl groups of **4c** in decreasing the formation relative rate constant of **5c**

TABLE V The Unified Relative Rate Constant, Quantum Yield and Fluorescence Data for Conversions of **5a–5c** with Reference to **4a**[a]

Compound	ϕ_F^{uc} (rel)	k_F^{uc} (rel)	ϕ_R^{uc} (rel)	k_R^{uc} (rel)
5a	0.790	0.911	1.044	1.204
5b	0.753	1.227	1.200	1.955
5c	1.017	1.161	0.933	1.065

[a] The values are an average of three different runs.

in the rate-determining step (Table IV) could be due to the unfavorable electronic effects of these groups on the transition state by increasing the electron density at the 2,6-positions through the transition state **7**. In the case of conversion relative rate constant, the decreasing effects of paramethoxy substituents on 1,3-aryl groups of **5c** (Table III) could be attributed to the relative stability of **5c** through the resonance form **8** and the resulting unfavorable transition state involved in the faster step.



SCHEME 3

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-80 spectrometer using Me_4Si as the internal standard. UV spectra were taken on a Shimadzu 265-FW spectrometer. Fluorescence spectra were taken on a Shimadzu RF5000 spectrofluorophotometer. Photolyses were performed using a low-pressure mercury lamp. HPLC analyses were carried out on a C_{18} column.

Syntheses

The 4*H*-thiopyrans **4a–4c** were synthesized by reactions of ArMgBr with the corresponding 2,4,6-triarylthiopyrylium perchlorates according to the reported method.[8,9]

General Procedure for Isolation of Intermediates

1.66×10^{-2} M solutions of 4*H*-thiopyrans **4a–4c** in methanol were prepared in the pyrex NMR tubes then degassed and sealed under argon atmosphere. Irradiations were carried out with a low-pressure mercury lamp under mild conditions using UV light with $\lambda = 254$ nm at 20°C from 30 to 60 min. The intermediates **5a–5c** were separated by semipreparative HPLC (C_{18} bonded stationary phase, eluent gradient from methanol-water 85:15) from the mixtures of unreacted **4a–4c** and the photoproducts **6a–6c**.

1,3,5,6-Tetraphenyl-2-thiabicyclo[3.1.0]hex-3-ene (5a)

Pale yellow powder, UV, λ_{max} (MeOH) 205, 225, 250 (sh), 303 nm. ^{1}H-NMR (C_6D_6), δ: 3.60 (1H, s, H-6), 5.99 (1H, s, H-4), 6.33–7.58 (20H, m, ArH).

5,6-Bis(4-methoxyphenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene (5b)

Pale yellow powder, UV, λ_{max} (MeOH 207, 227, 302 nm. ^{1}H-NMR (C_6D_6), δ: 3.18 (3H, s, OMe), 3.23 (3H, s, OMe), 3.60 (1H, s, H-6), 6.06 (1H, s, H-4), 6.63–7.57 (18H, m, ArH).

1,3-Bis(4-methoxyphenyl)-5,6-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene (5c)

Pale yellow powder, UV, λ_{max} (MeOH) 203, 232, 261, 300(sh) nm. ^{1}H-NMR (C_6D_6), δ: 3.13 (3H, s, OMe), 3.16 (3H, s, OMe), 3.60 (1H, s, H-6), 6.65–7.28 (18H, m, ArH).

General Procedure for Kinetic Study

Sample solutions of 10^{-4} M were prepared by dissolving 4*H*-thiopyrans **4a–4c**, bicyclic intermediates **5a–5c**, or 2*H*-thiopyrans **6a–6c** in methanol. An amount of 1 ml of these solutions were degassed and sealed under argon atmosphere in the pyrex NMR tubes. Irradiations were carried out by a low-pressure mercury lamp with $\lambda = 254$ nm at 20°C under mild conditions. The progress of the photochemical reactions were monitored by HPLC using UV detector. The variations of 4*H*-thiopyrans **4a–4c** and bicyclic intermediates **5a–5c** mole fractions during the photolysis procedure were measured by integration of the characteristic peaks in the chromatograms of the reaction mixtures.

Quantum Yields and Fluorescence Data

The incident light intensity on the samples was measured by ferrioxalate actinometry developed by Parker and Hatchard.[10] The preparation of solutions and the experimental details concerning the use of the chemical actinometer as well described in Calvert and Pitts' *Photochemistry*.[11] Reaction quantum yields (ϕ_R) were determined at less than 5% conversions. 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.[6] Relative fluorescence quantum yields (ϕ_F) were computed from the relative intensities at the maximum in the fluorescence spectra (values computed from integrated areas under the emission curves); λ (excitation) = 350.4 nm, concentration = 2×10^{-5} M in methanol solutions.

Thermal Stability

An amount of 1 ml of the intermediates solutions were degassed and sealed under argon atmosphere in pyrex NMR tubes, then heated in darkness using a water bath at different temperatures for 30 min.

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