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Isolation and kinetic study of intermediates in photoisomerization of some tetrasubstituted 4-aryl-4-methyl-2,6-diphenyl-4H-thiopyrans

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Abstract

On irradiation of 4-aryl-4-methyl-2,6-diphenyl-4H-thiopyrans **4a–4f** in methanol solutions with a low-pressure mercury lamp under mild conditions for short time, only aryl groups rearrange selectively to form 2H-thiopyran isomers **6a–6f** through their 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene intermediates **5a–5f** in quantitative yields. The intermediates **5a–5f** were separated by HPLC from the mixtures of unreacted **4a–4f** and photoproducts **6a–6f**. Both steps of unimolecular photoisomerization of **4a–4f** are investigated from a kinetic point of view using HPLC. The relative rate constants reveal that the formation of intermediate is the rate-determining step in photoisomerization of 4H-thiopyrans **4a–4f** to the corresponding 2H-thiopyrans **6a–6f** in methanol-d_4 solution. Moreover, comparison of the relative rate constants for the faster step show that the electron withdrawing groups on the para position of the migratory 4-aryl group, unlike those of the electron donating, decrease the conversion relative rates of intermediates to their 2H-thiopyran isomers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 4H-thiopyrans; 2H-thiopyrans; Photoisomerization; Intermediates; Kinetic study

1. Introduction

The possibility of formation of bicyclic intermediates in photoisomerization of 4H-thiopyrans to the corresponding 2H-thiopyrans was first proposed by Gravel and his co-workers in 1982 [1]. Upon irradiation of a solution of 4,4-diphenyl-4H-thiopyran **1a**, they could isolate an unstable mixture, the resemblance of ^{1}H-NMR spectrum with that of the photoisomerization of 4,4-diphenyl-4H-pyran analogue led them to anticipate the existence of intermediate, 5,6-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene **2a**, along with 2,4-diphenyl-2H-thiopyran **3a** in the mixture [2]. The formation of tetrasubstituted intermediate, 1,3,5,6-tetraphenyl-2-thiabicyclo[3.1.0]hex-3-ene **2b**, in photoisomerization of 2,4,4,6-tetraphenyl-4H-thiopyran **1b–3b** was studied with ^{1}H-NMR spectroscopy in the reaction mixture by Mori and his co-workers [3] which was then separated and identified by Sebek et al. [4]. Despite unsuccessful previous attempts to identify the methyl analogue intermediate in the photoisomerization of 4-methyl-2,4,6-triphenyl-4H-thiopyran **4a–6a** with high-pressure mercury lamp in identical conditions [3], the formation of 5-alkyl-1,3,6-triphenyl-2-thiabicyclo [3.1.0] hex-3-ene **2c–d** and **5a** intermediates were studied by ^{1}H-NMR spectroscopy in photoisomerization of 4-alkyl-2,4,6-triphenyl-4H-thiopyran analogues **1c–d** and **4a** to **3c–d** and **6a** with low-pressure mercury lamp under mild conditions [5]. Recently we reported the selective photoisomerization of tetrasubstituted 4-aryl-4-methyl- 2,6-diphenyl-4H-thiopyrans **4a–4f** to their thermodynamically more stable isomers 2-aryl-4-methyl-3,6-diphenyl-2H-thiopyrans **6a–6f** from a kinetic point of view by ^{1}H-NMR spectroscopy in the solution [6] along with the effect of electron donating or electron withdrawing groups on para position of the migratory 4-aryl group on the overall relative rate of the photoisomerization.

The stereochemistry of intermediates involved in the photoisomerization is unspecified and the question is open to experiments, however, considering that the photorearrangements of constrained six-membered dienes [7] and the 4H-pyran analogue [2] proceed only via a regiospecific phenyl-vinyl di-π-methane pathway to the corresponding *trans-endo*-bicyclic primary photoproducts, the photoisomerization of 4H-thiopyrans should also lead to formations of the predominant stereoisomers as shown.

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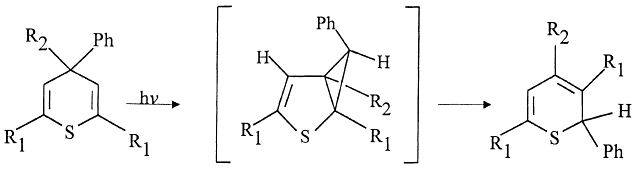
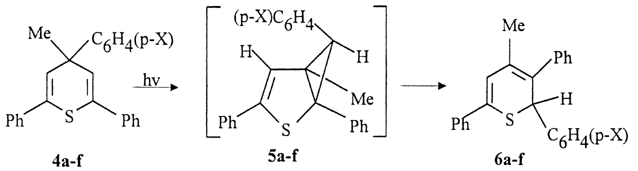


1a-d **2a-d** **3a-d**

a) R_1= H, R_2= Ph ; b) R_1= R_2= Ph ;

c) R_1= Ph, R_2= Et ; d) R_1= Ph, R_2= n-Bu ;

In the present study we wish to report the isolation of the previously proposed intermediates 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene **5a–5f** and the results of a kinetic study on their selective photoconversion relative rates to the 2H-thiopyran isomers **6a–6f** using HPLC. Here, the effects of electron donating or electron withdrawing groups on para position of the migratory 4-aryl group on the relative rate constants of formation as well as the conversion steps of the intermediates **5a–5f** were also investigated.



4a-f **5a-f** **6a-f**

a) X= H ; b) X= Br ; c) X= CF_3 ;

d) X= CH_3 ; e) X= OCH_3 ; f) X= NMe_2 ;

2. Experimental details

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.

2.1. Syntheses

The 4H-thiopyrans **4a–4f** were synthesized by reactions of MeMgBr with the corresponding 4-aryl-2,6-diphenylthiopyrylium perchlorates according to the reported method [8–10].

2.2. General procedure for isolation of intermediates

Due to the quantitative dependence of intermediates to the concentrations of reactants in accordance with steady-state approximation, concentrate solutions used for isolation of intermediates. 1.66×10^{-2} M solutions of 4H-thiopyrans **4a–4f** 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–5f** were separated by semipreparative HPLC (C_{18} bonded stationary phase, eluent gradient from methanol–water 64:36 for **5a** and 85:15 for **5b–5f**) from the mixtures of unreacted **4a–4f** and the photoproducts **6a–6f** with no byproducts.

2.2.1. 5-Methyl-1,3,6-triphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*a*

Pale yellow powder, UV, λ_{max} (MeOH) 205, 230 (sh), 304 nm. ^{1}H-NMR (C_6D_6), δ: 1.16 (3H, s, Me-5), 2.55 (1H, s, H-6), 5.75 (1H, s, H-4), 6.49–7.49 (15H, m, ArH).

2.2.2. 5-Methyl-6-(4-bromophenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*b*

Pale yellow powder, UV, λ_{max} (MeOH) 205, 229, 298 nm. ^{1}H-NMR (C_6D_6), δ: 1.12 (3H, s, Me-5), 2.34 (1H, s, H-6), 5.64 (1H, s, H-4), 6.84–7.51 (14H, m, ArH).

2.2.3. 5-Methyl-6-(4-trifluoromethylphenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*c*

Pale yellow powder, UV, λ_{max} (MeOH) 210, 228, 300 nm. ^{1}H-NMR (C_6D_6), δ: 1.10 (3H, s, Me-5), 2.35 (1H, s, H-6), 5.65 (1H, s, H-4), 6.82–7.51 (14H, m, ArH).

2.2.4. 5-Methyl-6-(4-methylphenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*d*

Pale yellow powder, UV, λ_{max} (MeOH) 205, 222, 300 nm. ^{1}H-NMR (C_6D_6), δ: 1.18 (3H, s, Me-5), 2.03 (3H, s, *p*-Me), 2.58 (1H, s, H-6), 5.82 (1H, s, H-4), 6.63–7.32 (14H, m, ArH).

2.2.5. 5-Methyl-6-(4-methoxyphenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*e*

Pale yellow powder, UV, λ_{max} (MeOH) 209, 229, 305 nm. ^{1}H-NMR (C_6D_6), δ: 1.17 (3H, s, Me-5), 2.53 (1H, s, H-6), 3.27 (3H, s, OMe), 5.77 (1H, s, H-4), 6.83–7.72 (14H, m, ArH).

2.2.6. 5-Methyl-6-(4-dimethylaminophenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene 5*f*

Yellow powder, UV, λ_{max} (MeOH) 206, 231, 343 nm. ^{1}H-NMR (C_6D_6), δ: 1.22 (3H, s, Me-5), 2.46 (6H, s, NMe_2), 2.63 (1H, s, H-6), 5.86 (1H, s, H-4), 6.56–7.56 (14H, m, ArH).

2.3. General procedure for kinetic study

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

2.4. Quantum yields and fluorescence data

The incident light intensity on the samples was measured by ferrioxalate actinometry developed by Parker and Hatchard [11,12]. The preparation of solutions and the experimental details concerning the use of the chemical actinometer are well described in [13]. 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 [14]. 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.

2.5. Thermal stability

The intermediate solutions prepared for kinetic study were also examined for thermal stability. An amount of 1 ml of these solutions in the pyrex NMR tubes were degassed and sealed under argon atmosphere, then heated in darkness using a water bath at different temperatures.

3. Results and discussion

To study the effects of electron donating and electron withdrawing groups on the conversion relative rate constants of bicyclic intermediates **5a–5f** to the corresponding 2H-thiopyrans **6a–6f**, irradiations of degassed 10^{-4} M solutions of 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]

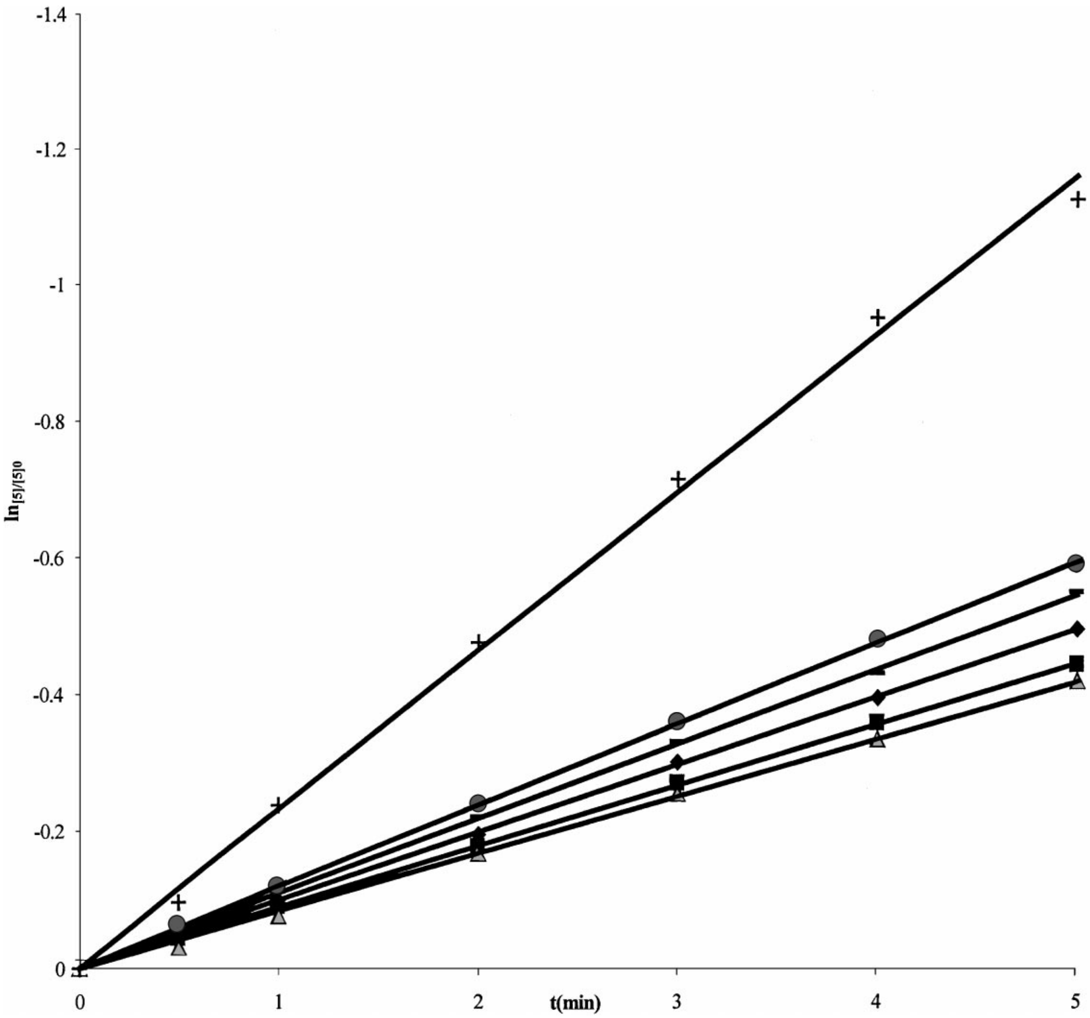


Fig. 1. The plots of ln[5]/[5]$_0$ vs. time obtained from least-squares treatments of the data for conversions of **5a–5f** (a, (◆); b, (■); c, (▲); d, (–); e, (●); f, (+)) in methanol at 20°C representing the first-order reactions.

Table 1
The yields of **5a–5f** and **6a–6f** during irradiations under identical experimental conditions[a]

Compound	Yields (%)					
	Time (min)					
	0.5	1	2	3	4	5
5a	94.5	90.6	82.3	74.1	67.4	60.9
5b	95.7	91.4	83.8	76.3	69.9	64.1
5c	96.9	92.6	84.6	77.5	71.5	65.7
5d	94.3	89.4	80.2	71.9	64.5	57.5
5e	93.9	88.9	78.6	69.7	61.8	55.4
5f	90.8	78.8	62.1	48.9	38.6	32.4
6a	5.5	9.4	17.7	25.9	32.6	39.1
6b	4.3	8.6	16.2	23.7	30.1	35.9
6c	3.1	7.4	15.4	22.5	28.5	34.3
6d	5.7	10.6	19.8	28.1	35.5	42.5
6e	6.1	11.1	21.4	30.3	38.2	44.6
6f	9.2	21.2	37.9	51.1	61.4	67.6

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

hex-3-ene **5a–5f** in methanol were performed in sealed pyrex NMR tubes by a low-pressure mercury lamp with $\lambda = 254$ nm under argon atmosphere at 20°C. The reactions were followed by HPLC with UV detector and the chromatograms were recorded at different intervals. The chromatograms showed gradual decreases in the peaks of bicyclic intermediates **5a–5f** as new peaks appeared for the corresponding 2H-thiopyrans **6a–6f**. The areas of new peaks increased on progress of the reactions. At the end of irradiations only the corresponding peaks of 2H-thiopyrans **6a–6f** were observed in the chromatograms with no signs of byproducts indicating a selective and quantitative photoconversion of bicyclic intermediates **5a–5f** to 2H-thiopyrans **6a–6f**. This was further highlighted by the stability of 2H-thiopyran solutions that had been irradiated under similar conditions. Our observation is consistent with what would be expected for such a structure, since the anticipated thiodienone photoproduct is only stable at 77K and reverses to the 2H-thiopyran system by warming up to room temperature [16]. The variations in molar ratios of bicyclic intermediates **5a–5f** were measured by the integration of the corresponding peaks in chromatograms. The results shown in Table 1 indicate that the conversions of **5a–5f** to **6a–6f** proceed through the unimolecular first-order reactions (Fig. 1).

To examine the thermal stability, sample solutions of intermediates **5a–5f** were placed in water bath at various temperatures of 20, 30, 40 and 50°C for 30 min. Considering the short period of time required for irradiations of **5a–5f**, the study revealed that temperatures below 40°C are insignificant in the conversions, since the intermediates begin to convert to their 2H-thiopyran isomers at 50°C.

In order to compare the formation relative rate constants of bicyclic intermediates **5a–5f**, irradiations of degassed 10^{-4} M solutions of **4a–4f** were performed in methanol under identical experimental conditions as those of the intermediates **5a–5f** at 20°C. The reactions were monitored by HPLC with UV detector and chromatograms were recorded at different intervals. In the chromatograms, the characteristic peaks of **4a–4f** decreased concurrently with appearance of two new sets of peaks for **5a–5f** and **6a–6f**. The variations in molar ratios of the reaction mixtures presented in Table 2 show that the formations of **5a–5f** from **4a–4f** also proceed through the unimolecular first-order reactions (Fig. 2).

Table 2
The yields of **4a–4f**, **5a–5f** and **6a–6f** during irradiations under identical experimental conditions[a]

Compound	Yields (%)					
	Time (min)					
	0.5	1	2	3	4	5
4a	97.0	94.1	88.6	83.5	78.6	74.0
4b	96.3	92.7	86.0	80.1	74.0	68.2
4c	96.0	92.2	85.0	78.3	72.2	66.3
4d	95.6	91.8	84.2	75.9	69.8	63.4
4e	94.8	89.9	81.8	72.9	65.6	59.1
4f	94.5	87.8	77.6	72.2	60.2	53.8
5a	3.0	4.8	9.8	13.2	16.7	18.2
5b	3.7	6.9	11.8	17.4	21.8	25.5
5c	4.0	7.6	13.1	18.2	22.9	27.7
5d	3.2	5.7	11.4	18.8	23.1	28.4
5e	3.1	5.3	10.9	13.9	15.6	17.7
5f	2.2	4.7	9.3	11.1	14.7	18.2
6a	–	1.1	1.6	3.3	4.7	7.8
6b	–	0.4	2.2	2.5	4.2	6.3
6c	–	0.2	1.9	3.5	4.9	6.0
6d	1.2	2.5	4.4	5.3	7.1	8.2
6e	2.1	4.8	7.3	13.2	18.8	23.2
6f	3.3	7.5	13.1	16.7	25.1	28.0

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

In addition, the progress of conversion and formation reactions were followed by UV spectroscopy using **5a** and **4a** as the representative model compounds. In the UV spectrum of intermediate **5a**, the intensity of new absorption characteristic of 2H-thiopyran **6a** gradually appeared at $\lambda = 357$ nm, while the intensities of absorptions for bicyclic intermediate at $\lambda = 304$ and 205 nm diminished simultaneously (Fig. 3). The UV spectrum of **4a** exhibited gradual decrease in absorption at $\lambda = 236$ nm as new absorptions appeared at $\lambda = 304$ and 357 nm for the corresponding **5a** and **6a**, respectively (Fig. 4). In both spectra the disappearance or appearance of the characteristic broad absorption of **5a** at $\lambda = 304$ nm are dominated by the more intense and broader absorption of **6a** at $\lambda = 357$ nm.

The relative rate constants of conversions or formations of **5a–5f** were determined using absorption and fluorescence data according to the following equation [15,17]:

$$\frac{k_{\mathrm{R}}}{k_{\mathrm{R}^0}} = \frac{\phi_{\mathrm{R}}\phi_{\mathrm{F}^0}k_{\mathrm{F}}}{\phi_{\mathrm{R}^0}\phi_{\mathrm{F}}k_{\mathrm{F}^0}}$$

where k_{R} is the rate constant for conversion ($k_{\mathrm{R}}^{\mathrm{c}}$) or formation

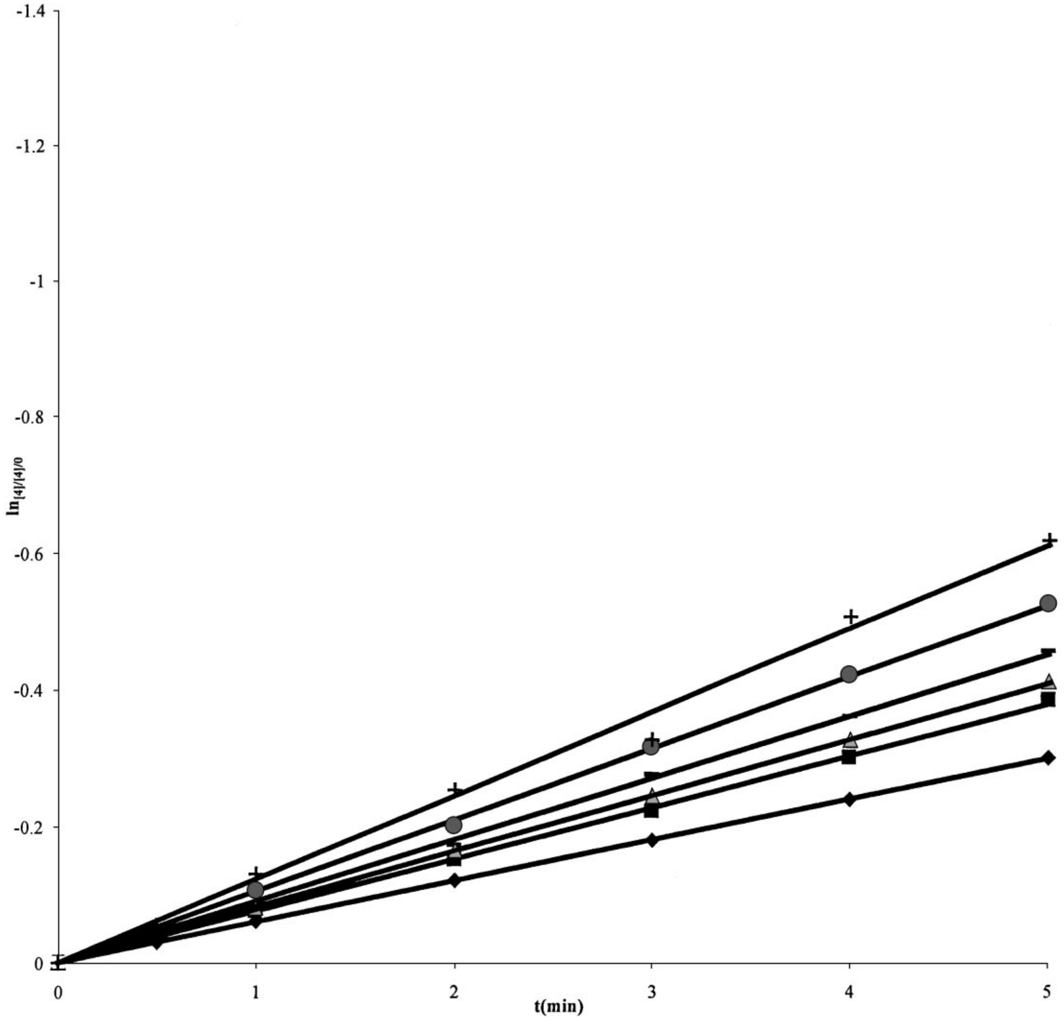


Fig. 2. The plots of $\ln[4]/[4]_0$ vs. time obtained from least-squares treatments of the data for formations of **5a–5f** from **4a–4f** (a, (◆); b, (■); c, (▲); d, (–); e, (●); f, (+)) in methanol at 20°C representing the first-order reactions.

(k_R^f) of bicyclic intermediates, ϕ_R the quantum yield for conversion (ϕ_R^c) or formation (ϕ_R^f) of bicyclic intermediates, k_F the rate constant for fluorescence of **5a–5f** (k_F^c) or **4a–4f** (k_F^f) and ϕ_F is the quantum yield for fluorescence of **5a–5f** (ϕ_F^c) or **4a–4f** (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 3 and 4, respectively. To evaluate the kinetic order of photorearrangement and put the relative rate constants for conversions and formations of intermediates on a quantitative basis, the conversion relative rate constants of **5a–5f** were determined with reference to the model compound **4a** too. The resulting unified conversion relative rate constants k_R^{uc}(rel) are shown in Table 5.

Comparison of the unified conversion relative rate constants of **5a–5f**, k_R^{uc}(rel), observed in Table 5 with those of the relative rate constants for their formations, k_R^f(rel), in Table 4 reveal that the formation of intermediate is slow enough to be the rate-determining step in photoisomerization of 4H-thiopyrans to the corresponding 2H-thiopyran isomers. The resulting kinetic order is in agreement with the order of slops in Figs. 1 and 2. Here, the increasing effects of electron donating or electron withdrawing groups on the rate-determining step are consistent with the effects of these groups on the overall relative rates of photoisomer-

Table 3
Relative rate constant, quantum yield and fluorescence data for conversions of **5a–5f**[a]

Compound	ϕ_F^c(rel)	k_F^c(rel)	ϕ_R^c(rel)	k_R^c(rel)
5a	1	1	1	1
5b	1.114	1.254	0.782	0.879
5c	1.013	1.526	0.563	0.848
5d	0.843	1.123	1.036	1.380
5e	0.917	1.175	1.109	1.420
5f	0.964	1.833	1.672	3.178

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

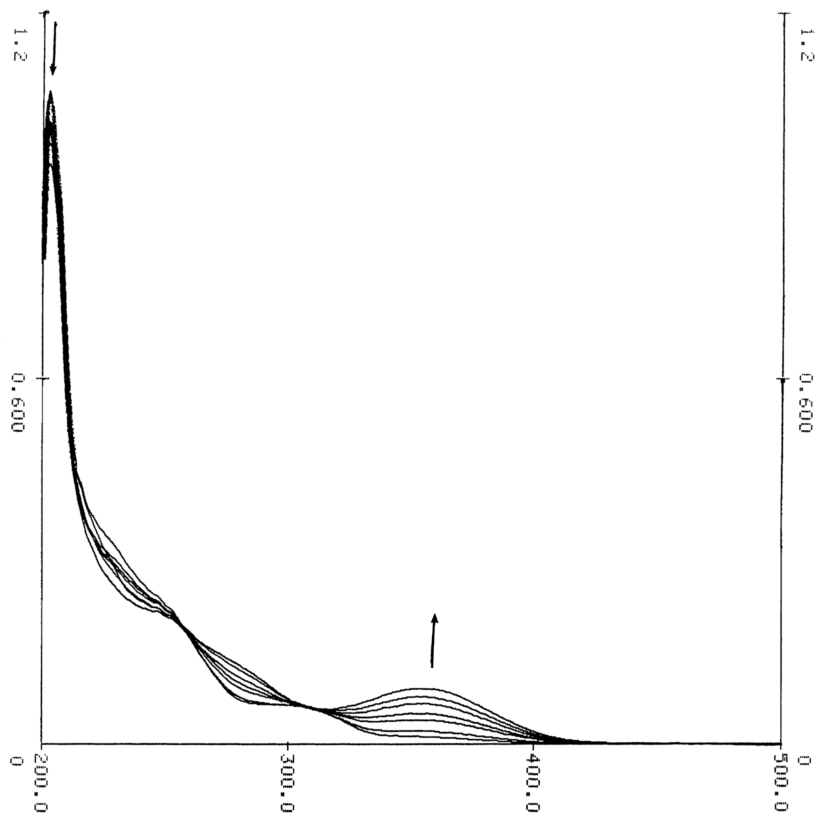


Fig. 3. UV spectra of **5a** before and after 1–6 min of illumination in methanol.

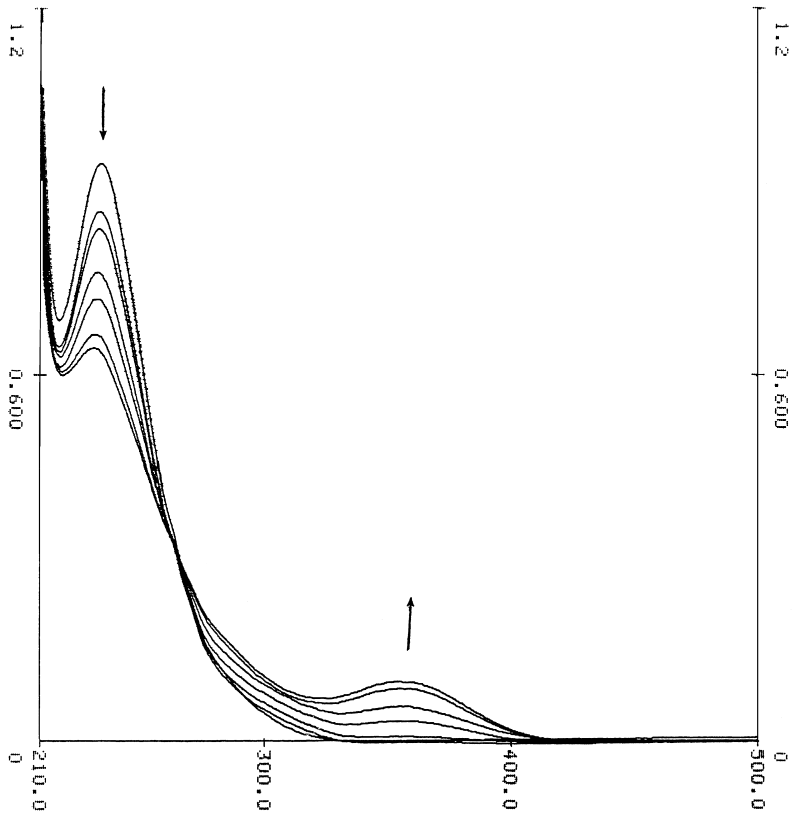


Fig. 4. UV spectra of **4a** before and after 2, 4, 6, 8, 10 and 12 min of illumination in methanol.

Table 4
Relative rate constant, quantum yield and fluorescence data for formations of **5a–5f** from **4a–4f**[a]

Compound	ϕ_F^f(rel)	k_F^f(rel)	ϕ_R^f(rel)	k_R^f(rel)
4a	1	1	1	1
4b	0.889	1.906	1.233	2.644
4c	0.885	1.747	1.333	2.631
4d	1.300	1.990	1.466	2.243
4e	0.876	1.140	1.733	2.252
4f	1.112	2.252	1.833	3.707

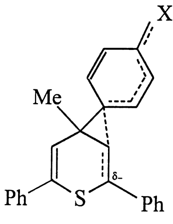
[a] The values are an average of three different runs.

Table 5
The unified relative rate constant, quantum yield and fluorescence data for conversions of **5a–5f** with reference to **4a**[a]

Compound	ϕ_F^{uc}(rel)	k_F^{uc}(rel)	ϕ_R^{uc}(rel)	k_R^{uc}(rel)
5a	0.627	1.065	1.833	3.113
5b	0.698	1.336	1.433	2.743
5c	0.635	1.626	1.033	2.645
5d	0.529	1.196	1.900	4.295
5e	0.575	1.252	2.033	4.426
5f	0.604	1.953	3.066	9.913

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

ization as well as the transition states **7** or **8** reported earlier [6], however, the k_R^c(rel) values in Table 3 or k_R^{uc}(rel) in Table 5 indicate that the electron withdrawing groups unlike those of the electron donating decrease the conversion relative rate constants of intermediates **5a–5f**. The observed role of bicyclic intermediates **5a–5f** in the reaction rate is comparable with Zimmerman study in the singlet di-π-methane rearrangement of an acyclic diene [18], where he concluded that "bridging is the major process affecting the rate".



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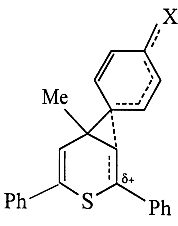

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4. Conclusions

The isolation of 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene intermediates **5a–5f** under our experimental conditions let us determine the relative rate constants for the formation and the conversion steps of these intermediates. The experimental findings reveal that the formation of intermediate is slow enough to be the rate-determining step, where both the electron donating and electron withdrawing groups on the para position of the migratory 4-aryl group could increase the relative rate constants of photoisomerization through transition states **7** or **8**, depending upon substituents used, in methanol-d_4 solutions. Concerning the bathochromic shift observed in the UV absorption of intermediate **5f** with strong electron donating group, it appears that the shift could be due to a through-space interaction between the filled 2p orbitals of the *trans-endo*-phenyl ring on carbon-6 and the empty 3d orbitals of sulfur which could be the origin of the favorable electronic interactions in the transition states leading to **6a–6f**. The fact that the electron withdrawing groups play opposite role in the conversion step is in accord with a weaker 2p–3d through-space interactions.

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