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Kinetic study on photoisomerization of some tetrasubstituted 4-aryl-4-methyl-2,6-diphenyl-4*H*-thiopyrans

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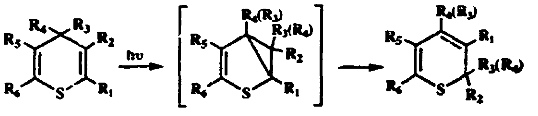
Abstract

The selective photoisomerization of tetrasubstituted 4-aryl-4-methyl-2,6-diphenyl-4*H*-thiopyrans (**4a–4f**) are investigated from a kinetic point of view using ^{1}H-NMR spectroscopy. On exposure to a monochromatic UV light at $\lambda = 254$ nm, these compounds rearrange to 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0] hex-3-en intermediates (**5a–5f**), then convert to thermodynamically more stable isomers, 2-aryl-4-methyl-3,6-diphenyl-2*H*-thiopyrans (**6a–6f**) in quantitative yields. In the course of photoisomerization, only the intermediates **5a–5f** and unreacted 4*H*-thiopyrans **4a–4f** are present in the reaction media. It is found that the electron donating or electron withdrawing groups on the para position of the migratory 4-aryl group increase the relative rates of photoisomerizations in methanol-d$_4$ solutions. The efficiencies of photoisomerizations in methanol-d$_4$ are greater than in benzene-d$_6$ solutions, depending upon the substituents used. On the basis of the observed intermediates, the effects of substituents and the polarity of solvents, a mechanism is proposed for the photoisomerization of 4*H*-thiopyrans **4a–4f** to bicyclic intermediates **5a–4f**.

Keywords: 4*H*-thiopyrans; 2*H*-thiopyrans; Photoisomerization; Di-π-methane rearrangement; Kinetic study

1. Introduction

Our previous studies and other reports on the photochemical reactions of 4*H*-thiopyran derivatives **1** in the solid state and solution revealed that, on exposure to UV light, some of these compounds rearrange to their thermodynamically more stable isomeric 2*H*-thiopyrans **3** through an intramolecular photoisomerization. When 2,4,4,6-tetraaryl-4*H*-thiopyrans **1** ($R_1 = R_3 = R_4 = R_6 =$ aryl; $R_2 = R_5 = H$) were irradiated with a monochromatic low-pressure mercury lamp at $\lambda = 254$ nm in methanol at room temperature, an isomerization took place in the system and a mixture of two isomeric 2*H*-thiopyrans **3** ($R_1 = R_3 = R_4 = R_6 =$ aryl; $R_2 = R_5 = H$) were obtained [1,2]. In the case of 4-alkyl-2,4,6-triphenyl-4*H*-thiopyrans **1** ($R_1 = R_3 = R_6 =$ phenyl; $R_4 =$ alkyl; $R_2 = R_5 = H$), only the 4-phenyl group migrated to give 2*H*-thiopyran **3** ($R_1 = R_3 = R_6 =$ phenyl; $R_4 =$ alkyl; $R_2 = R_5 = H$) selectively [1,3]. The yields of these photoproducts in the solid state were lower than in solution [1].



1 2 3

Substituents at the 3,5-positions of the sulfur ring in 4*H*-thiopyrans alter the photoisomerization behaviour, where only some of the hexasubstituted 4*H*-thiopyran derivatives, such as 4-aryl-2,4,6-triphenyl-3,5-dimethyl-4*H*-thiopyrans **1** ($R_1 = R_4 = R_6 =$ phenyl; $R_3 =$ aryl; $R_2 = R_5 =$ methyl) and 3,4,5-trimethyl-2,4,6-triphenyl-4*H*-thiopyran **1** ($R_2 = R_4 = R_5 =$ methyl; $R_1 = R_3 = R_6 =$ phenyl), could isomerize to their isomeric 2*H*-thiopyrans **3** with lower yields [4].

The formation of bicyclic intermediates **2**, previously proposed only by NMR spectroscopy in photoisomerizations of 4,4-diphenyl-4*H*-thiopyran **1** ($R_1 = R_2 = R_5 = R_6 = H$; $R_3 = R_4 =$ phenyl) [5] and 2,4,4,6-tetraphenyl-4*H*-thiopyran **1** ($R_1 = R_3 = R_4 = R_6 =$ phenyl; $R_2 = R_5 = H$) [3], was successfully confirmed by isolation of a pure sample of 1,3,5,6-tetraphenyl-2-thiabicyclo[3.1.0]hex-3-en **2** ($R_1 = R_3 = R_4 = R_6 =$ phenyl; $R_2 = R_5 = H$) as non-photochromic compound with λ_{max}(MeCN) = 322 nm [2]. However, previous attempts were unsuccessful to monitor such an inter-

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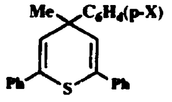
mediate in 4-methyl-2,4,6-triphenyl-4*H*-thiopyran **1** ($R_1 = R_3 = R_6$ = phenyl; R_4 = methyl; $R_2 = R_5 = H$) [3].

The present study was carried out to compare the effects of electron donating and electron withdrawing groups on the para positions of the migratory 4-aryl group on the efficiencies and relative rates of photoisomerizations of tetrasubstituted 4*H*-thiopyrans **4a–4f** in methanol and benzene solutions.



4a-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

Melting points (m.p.) were measured on a Gallenkamp apparatus and are uncorrected. 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. Mass spectra were recorded on a Finningan MAT-TSQ 70 mass spectrometer. Fluorescence spectra were taken on a Shimadzu RF5000 spectrofluorophotometer. Photolyses were performed using a low-pressure mercury lamp.

2.1. Syntheses

The new 4*H*-thiopyrans **4b–4f** and the model compound **4a** were synthesized by reactions of MeMgBr with the corresponding equimolar 4-aryl-2,6-diphenyl-thiopyrylium perchlorates in dry ether at an argon atmosphere according to the reported method [6]. The products were isolated by PLC on neutral alumina (petroleum ether 40–60°C:diethyl ether = 95:5–80:20) and purified by recrystallization from ethanol.

2.1.1. 4-Methyl-2,4,6-tripheyl-4H-thiopyran (**4a**)

Colourless crystals, m.p. 102–103°C (from EtOH). *m/z* 340 ($M^{\cdot +}$ 28.60%), 325 (100), 289 (2.40), 263 (23.33), 247 (7.14), 215 (3.33), 77(6.66). UV, λ_{max}(MeOH) nm (logϵ): 236 (4.41). ^{1}H-NMR (C_6D_6), δ:1.53 (3H, s, Me-4), 5.89 (2H, s, H-3, -5), 7.04–7.54 (15H, m, ArH).

2.1.2. 4-Methyl-4-(4-bromophenyl)-2,6-diphenyl-4H-thiopyran (**4b**)

Colourless crystals, m.p. 75–76°C (from EtOH). *m/z*, 418 ($M^{\cdot +}$ 25.74%), 405 (67.33), 403 (72.28), 263 (100), 215 (18.32), 165 (11.88), 121 (65.84), 77(31.68). UV, λ_{max}(MeOH) nm (logϵ): 234 (4.74). ^{1}H-NMR ($CDCl_3$), δ: 1.74 (3H, s, Me-4), 5.97 (2H, s, H-3, -5), 7.36–7.72 (14H, m, ArH).

2.1.3. 4-Methyl-4-(4-trifluoromethylphenyl)-2,6-diphenyl-4H-thiopyran (**4c**)

Colourless crystals, m.p. 119–120°C (from EtOH). *m/z* 408 ($M^{\cdot +}$ 5.71%), 393 (100), 263 (74.76), 247 (6.19). UV, λ_{max}(MeOH) nm (logϵ): 236 (4.58). ^{1}H-NMR ($CDCl_3$), δ: 1.72 (3H, s, Me-4), 5.91 (2H, s, H-3, -5), 7.30–7.60 (14H, m, ArH).

2.1.4. 4-Methyl-4-(4-methylphenyl)-2,6-diphenyl-4H-thiopyran (**4d**)

Colourless crystals, m.p. 86–87°C (from EtOH). *m/z* 354 ($M^{\cdot +}$ 11.43%), 339 (100), 263 (24.76), 231 (3.33). UV, λ_{max}(MeOH) nm (logϵ): 236 (4.74). ^{1}H-NMR($CDCl_3$), δ: 1.80 (3H, s, Me-4), 2.45 (3H, s, Me), 6.06 (2H, s, H-3, -5), 7.39–7.67 (14H, m, ArH).

2.1.5. 4-Methyl-4-(4-methoxyphenyl)-2,6-diphenyl-4H-thiopyran (**4e**)

Colourless crystals, m.p. 86–87°C (from EtOH). *m/z* 370 ($M^{\cdot +}$ 28.50%), 355 (100), 312 (7.00), 263 (11.00), 247 (2.50). UV, λ_{max}(MeOH) nm (logϵ): 236 (4.35). ^{1}H-NMR ($CDCl_3$), δ: 1.88 (3H, s, Me-4), 3.89 (3H, s, OMe), 6.15 (2H, s, H-3, -5), 7.05–7.86 (14H, m, ArH).

2.1.6. 4-Methyl-4-(4-N,N-dimethylaminophenyl)-2,6-diphenyl-4H-thiopyran (**4f**)

Colourless crystals, m.p. 138–139°C (from EtOH). *m/z* 383 ($M^{\cdot +}$ 28.57%), 368(100), 306 (12.67), 263 (9.52), 247 (3.81), 184 (3.62). UV, λ_{max}(MeOH) nm (logϵ): 236 (4.68), 275 (shoulder). ^{1}H-NMR ($CDCl_3$), δ: 1.65 (3H, s, Me-4), 2.93 (6H, s, NMe_2), 5.90 (2H, s, H-3, -5), 6.67–6.78 (2H, ArH), 7.24–7.54 (12H, m, ArH).

2.2. General procedure for photolysis

Sample solutions were prepared by dissolving 1.47×10^{-5} mol of **4a–4f** in 0.4 ml methanol-d_4 or benzene-d_6 in a pyrex NMR tube, then were degassed and sealed under an argon atmosphere. Irradiations 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 monitored by ^{1}H-NMR spectroscopy. The variations of 4*H*-thiopyrans **4a–4f** mole fractions during the photolysis procedure were measured by integrations of the characteristic methyl singlets in the spectra of reaction mixtures.

2.3. Quantum yields and fluorescence data

The incident light intensity on the samples was measured by ferrioxalate actinometry developed by Parker and Hatchard [7]. The preparation of solutions and the experimental details concerning the use of the chemical actinometer are well described in the literature [8]. 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 [9]a. 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 or benzene solutions.

2.4. Photoproducts

At the end of irradiations in methanol-d_4 or benzene-d_6 solutions, the 4*H*-thiopyrans **4a–4f** were converted selectively to their isomeric 2*H*-thiopyrans **6a–6f** with over 98% of yields.

2.4.1. 4-Methyl-2,3,6-triphenyl-2H-thiopyran (6a)

m/z 340 ($M^{\cdot+}$ 35.00%), 325 (16.30), 263 (100), 215 (17.60), 128 (18.70), 121 (29.00), 77 (19.90), 51 (7.43). UV, λ_{max}(MeOH) nm (logϵ): 352 (3.86), 250 (shoulder), 275 (shoulder). ^{1}H-NMR (C_6D_6), δ: 1.94 (3H, s, Me-4), 4.60 (1H, s, H-2), 6.49 (1H, s, H-5), 6.97–7.47 (15H, m, ArH).

2.4.2. 4-Methyl-2-(4-bromophenyl)-3,6-diphenyl-2H-thiopyran (6b)

m/z, 418 ($M^{\cdot+}$ 15.84%), 403 (22.77), 389 (4.95), 263 (42.28), 215 (5.94), 165 (4.95), 115 (9.41), 105 (44.06), 91 (54.75), 86 (60.89), 77 (100), 51 (57.43). UV, λ_{max}(MeOH) nm (logϵ): 354 (3.77), 278 (shoulder), 232 (shoulder). ^{1}H-NMR (C_6D_6), δ: 1.89 (3H, s, Me-4), 4.41 (1H, s, H-2), 6.45 (1H, s, H-5), 6.99–7.52 (14H, m, ArH).

2.4.3. 4-Methyl-2-(4-trifluoromethylphenyl)-3,6-diphenyl-2H-thiopyran (6c)

m/z 408 ($M^{\cdot+}$ 47.03%), 393 (19.80), 331 (8.91), 263 (100), 215 (7.43), 128 (5.94), 121 (17.82), 91 (6.93), 77 (20.79), 51 (6.44). UV, λ_{max}(MeOH) nm (logϵ): 357 (3.87), 277 (shoulder), 228 (shoulder). ^{1}H-NMR (C_6D_6), δ: 1.90 (3H, s, Me-4), 4.46 (1H, s, H-2), 6.46 (1H, s, H-5), 6.98–7.50 (14H, m, ArH).

2.4.4. 4-Methyl-2-(4-methylphenyl)-3,6-diphenyl-2H-thiopyran (6d)

m/z 354 ($M^{\cdot+}$ 68.32%), 339 (52.47), 277 (21.58), 263 (100), 247 (11.88), 174 (14.85), 121 (37.13), 91 (54.45), 77 (99), 51 (29.70). UV, λ_{max}(MeOH) nm (logϵ): 355 (3.90), 275 (shoulder). ^{1}H-NMR (C_6D_6), δ: 1.95 (3H, s, Me-4), 2.05 (3H, s, Me), 4.62 (1H, s, H-2), 6.52 (1H, s, H-5), 6.98–7.57 (14H, m, ArH).

2.4.5. 4-Methyl-2-(4-methoxyphenyl)-3,6-diphenyl-2H-thiopyran (6e)

m/z 370 ($M^{\cdot+}$ 9.41%), 355 (11.88), 222 (7.43), 189 (3.96), 148 (8.42), 121 (19.80), 89 (9.41), 77 (100), 51 (8.91). UV, λ_{max}(MeOH) nm (logϵ): 355 (3.92), 276 (4.08). ^{1}H-NMR (C_6D_6), δ: 1.97 (3H, s, Me-4), 3.25 (3H, s, OMe), 4.61 (1H, s, H-2), 6.54 (1H, s, H-5), 6.68–7.54 (14H, m, ArH).

2.4.6. 4-Methyl-2-(4-N,N-dimethylaminophenyl)-3,6-diphenyl-2H-thiopyran (6f)

m/z 383 ($M^{\cdot+}$ 72.77%), 368 (100), 306 (32.18), 263 (19.80), 247 (12.38), 209 (26.73), 165 (7.92), 132 (12.38), 121 (21.78), 77 (18.51), 51 (3.46). UV, λ_{max}(MeOH) nm (logϵ): 342 (4.00), 260 (4.31). ^{1}H-NMR (C_6D_6), δ: 2.00 (3H, s, Me-4), 2.43 (6H, s, NMe_2), 4.66 (1H, s, H-2), 6.51 (1H, s, H-5), 6.59–6.62 (2H, ArH), 6.98–7.57 (12H, m, ArH).

3. Results and discussion

To study the effects of electron donating and electron withdrawing para substituents on the efficiencies and relative rates of migration of 4-aryl groups, irradiation of degassed 3×10^{-2} M solutions of 4-aryl-4-methyl-2,6-diphenyl-4*H*-thiopyrans (**4a–4f**) in methanol-d_4 were performed in sealed pyrex 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 ^{1}H-NMR, and the spectra recorded at different time intervals. In the ^{1}H-NMR spectra, the singlets of **4a–4f** at 1.63–1.73 (Me-4) and 5.89–6.00 (H-3, -5) ppm gradually decreased, while two new sets of singlets appeared at 1.29–1.34 (Me-5), 2.63–2.80 (H-4) and 6.00–6.06 (H-6) ppm for intermediates **5a–5f**, and at 2.04–2.08 (Me-4), 4.63–4.88 (H-2) and 6.61–6.69 (H-5) ppm for products **6a–6f** (Table 1). In spite of the previous attempts to detect the intermediate **5a** [3], the signals characteristic of intermediates **5a–5f** appear in the spectra at early stage of photoisomerization, then the signals of products **6a–6f** become detectable on progress of the reactions. At the end of irradiations only the signals assigned to sole photoproducts **6a–6f** are observable in the ^{1}H-NMR spectra with no signs of byproducts, which indicate a selective and quantitative transformation of 4*H*-thiopyrans **4a–4f** to 2*H*-thiopyrans **6a–6f** through the bicyclic intermediates **5a–5f** (Fig. 1) under our experimental conditions. The variations in molar ratios of each species are measured by the integration of the characteristic methyl singlets; the percentages of each species in the reaction mixture of **4a–4f** during the first hour of the reactions are shown in Table 2. In all cases, the reactions continued until the complete conversion of **4a–4f** and **5a–5f** to **6a–6f** in nearly quantitative yields.

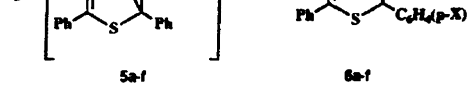


Table 1
The characteristic chemical shifts for 4*H*-thiopyrans **4a–4f**, bicyclic intermediates **5a–5f** and photoproducts **6a–6f** in methanol-d_4 and benzene-d_6

Compound	Chemical shifts (ppm)					
	Methanol-d_4			Benzene-d_6		
	Me-4	H-3, -5		Me-4	H-3, -5	
4a	1.68	5.95		1.53	5.88	
4b	1.70	5.95		1.46	5.77	
4c	1.73	6.00		1.41	5.74	
4d	1.65	5.92		1.56	5.92	
4e	1.65	5.91		1.55	5.91	
4f	1.63	5.89		1.61	5.98	
	Me-5	H-6	H-4	Me-5	H-6	H-4
5a	1.31	2.70	6.01	1.16	2.55	5.75
5b	1.32	2.68	6.06	1.12	2.33	5.64
5c	1.34	2.80	6.05	1.10	2.35	5.65
5d	1.30	2.67	6.00	1.18	2.58	5.82
5e	1.30	2.63	6.00	1.17	2.53	5.77
5f	1.29	2.67	6.00	1.21	2.63	5.86
	Me-4	H-2	H-5	Me-4	H-2	H-5
6a	2.06	4.75	6.65	1.94	4.60	6.49
6b	2.06	4.76	6.66	1.89	4.41	6.45
6c	2.08	4.88	6.69	1.90	4.46	6.46
6d	2.05	4.70	6.64	1.95	4.59	6.47
6e	2.04	4.70	6.64	1.97	4.60	6.54
6f	2.94	4.63	6.61	2.00	4.66	6.51

The relative rates of photoisomerizations of **4a–4f** were determined using absorption and fluorescence data according to the following equation [9b,10], where k_R is the rate constant for formation of photoproducts and ϕ_R the quantum

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

yield, for the formation of photoproducts, where k_F is the rate constant for fluorescence and ϕ_F the quantum yield for fluorescence. The experimental values of these determinations in methanol are listed in Table 3. The relative rate constants of para-substituted **4b–4f** to unsubstituted **4a** in methanol-d_4 revealed that both of the electron donating and electron withdrawing groups increase the relative rates of migrations of para-substituted 4-aryl migratory groups. This observation is in accordance with the effects of the electron donating and electron withdrawing groups, p-OCH_3, p-CN, on the increasing rate and efficiency of rearrangement in the 1,3-diarylpropene–di-π-methane system reported previously [10–12].

In a different experiment, irradiation of 1×10^{-5} M solution of the model compound **4a** was performed in methanol with a monochromatic low-pressure mercury lamp at $\lambda = 254$ nm in a quartz tube using a pyrex filter at room temperature. The progress of the reaction was monitored by UV spectroscopy, and the values of absorptions (A) were plotted against wavelength at periodic time intervals. In the UV spectra, the intensity of new absorption characteristic of 2*H*-thiopyran **6a** gradually appeared at $\lambda = 357$ nm, while the intensity of absorption of 4*H*-thiopyran **4a** at $\lambda = 236$ nm decreased simultaneously (Fig. 2). Although the UV spectra nicely demonstrates the gradual photoisomerization of **4a** to **6a**, the interference of the resulting intermediate **5a**, recorded in the ^{1}H-NMR spectrum (Fig. 1), with UV absorption at around $\lambda = 322$ nm [2], prevents the quantitative use of UV spectroscopy for the monitoring of photoisomerizations of **4a–4f** to **6a–6f**.

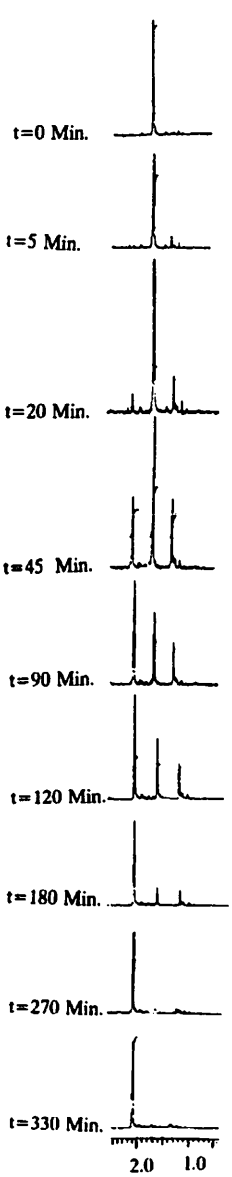


Fig. 1. The methyl region of ^{1}H-NMR spectra of **4a** in methanol-d_4 before and after irradiation at different time intervals.

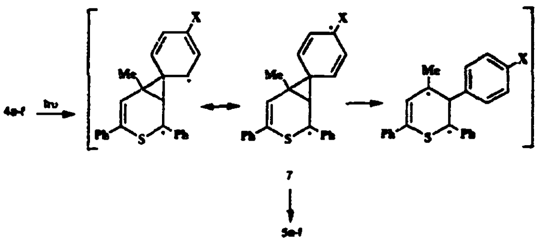
In order to compare the effects of solvent polarity on the photoisomerization rates, the 3×10^{-2} M solutions of **4a–4f**

Table 2
The variations (%) of **4a–4f**, **5a–5f** and **6a–6f** during the first hour of photoisomerization under identical experimental conditions. The values are an average for three different runs measured by the integration of characteristic methyl singlets in the reaction mixtures

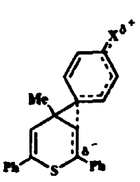
Compound	Variations (%)									
	Time (min), methanol-d_4					Time (min), benzene-d_6				
	10	20	30	45	60	10	20	30	45	60
4a	91.1	82.2	72.9	61.2	52.9	91.4	85.2	75.7	62.2	53.2
4b	89.1	79.8	68.0	56.3	47.9	93.7	84.5	80.2	70.8	57.2
4c	82.5	73.5	65.2	51.8	42.2	94.6	87.8	79.7	72.9	64.4
4d	83.6	63.3	51.0	35.8	26.9	94.0	86.5	81.0	72.2	65.5
4e	75.6	56.4	44.4	28.4	18.8	85.0	67.0	53.7	39.3	29.5
4f	73.5	55.4	41.2	25.3	16.5	81.0	60.8	45.0	29.3	17.3
5a	7.2	12.0	15.6	18.6	20.2	6.1	9.3	13.2	16.3	16.5
5b	6.7	12.9	22.0	23.7	26.1	5.3	10.2	11.4	15.9	18.5
5c	4.9	8.6	13.9	24.3	33.6	4.0	8.5	12.1	13.8	16.1
5d	6.7	12.1	21.5	35.2	50.0	4.5	9.0	10.8	13.4	14.5
5e	19.1	28.6	31.4	33.0	28.7	10.6	18.8	23.0	23.7	22.2
5f	8.0	12.6	14.6	13.1	12.2	15.6	27.8	33.5	35.7	35.4
6a	1.7	5.8	11.5	19.9	26.9	2.5	5.5	11.1	21.5	30.3
6b	4.2	7.3	10.0	20.0	26.0	1.0	5.3	8.4	13.3	24.3
6c	12.6	17.9	20.9	23.9	24.2	1.4	3.7	8.2	13.3	19.5
6d	9.7	24.6	27.5	29.0	23.1	1.5	4.5	8.2	14.4	20.0
6e	5.3	15.0	24.2	38.6	52.5	4.4	14.2	23.3	37.0	48.3
6f	18.5	32.0	44.2	61.6	71.3	3.4	11.4	21.5	35.0	47.3

were prepared in benzene-d_6. Irradiations were carried out in sealed pyrex 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 ^{1}H-NMR, and the spectra recorded at different time intervals. In the ^{1}H-NMR spectra, the characteristic signals of **4a–4f** decreased concurrently with appearance of two new sets of signals for **5a–5f** and **6a–6f** as in methanol-d_4 solutions (Table 1). The variations in percentages of each species in the reaction mixture of **4a–4f** during the first hour of the reaction are presented in Table 2. As is clear from Table 2, the efficiencies of photoisomerizations in methanol-d_4 are higher than in benzene-d_6 solutions. A similar efficiency increase was found previously for the rearrangement of 4,4-diphenyl-1-methylenecyclohexene di-π-methane system using methanol and cyclohexane as solvents [12]. The relative rate constants in benzene-d_6 are listed in Table 3. The differences in relative rates are related to a combination of substituent and solvent effects. The type of solvent in addition to the effect on the stability of transition state, can affect the energy levels of excited states involved in photoisomerization [13].

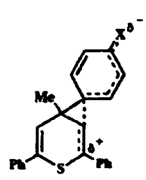
On the basis of the unimolecular nature of the whole process, the formations of bicyclic intermediates, and the similarity between the effects of electron donating and electron withdrawing substituents on the relative rates of photoisomerizations in methanol, we suggest an aryl-vinyl di-π-methane rearrangement for the conversion of **4a–4f** to **5a–5f**. In the classic form, Zimmerman proposed transition states with odd-electrons for such rearrangements [11,14]. Thus, the transition state **7** is considered for the migration of 4-aryl groups and the formation of intermediates **5a–5f**.



Considering the increasing effects of solvent polarity on the efficiencies and the resemblance of effects in electron donating and electron withdrawing substituents on the relative rates of photoisomerizations in **4a–4f** and other di-π-methane systems [6,10,11,15], the partially polar transition states **8a** or **8b** are better presentation for rearrangement of **4a–4f** to **5a–5f** in polar solvents.



8a



8b

4. Conclusions

On irradiation of 4-aryl-4-methyl-2,6-diphenyl-4*H*-thiopyrans (**4a–4f**) the formation of 6-aryl-5-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-en intermediates (**5a–**

Table 3
Relative rate, quantum yield and fluorescence data for **4a–4f**. The values are an average for three different runs

Compound	Methanol-d_4				Benzene-d_6			
	ϕ_R(rel)	$k_F \times 10^{-9}$	ϕ_F(rel)	k_R(rel)	ϕ_R(rel)	$k_F \times 10^{-8}$	ϕ_F(rel)	k_R(rel)
4a	1	1.07	1	1	1	1.23	1	1
4b	1.17	2.04	0.889	2.51	0.70	1.06	0.990	0.61
4c	1.28	1.87	0.885	2.53	0.83	0.85	0.972	0.59
4d	1.80	2.13	1.300	2.45	0.78	1.07	0.965	0.70
4e	2.04	1.22	0.876	2.65	1.91	1.04	0.927	1.74
4f	1.92	2.41	1.112	3.89	2.22	4.13	0.997	7.48

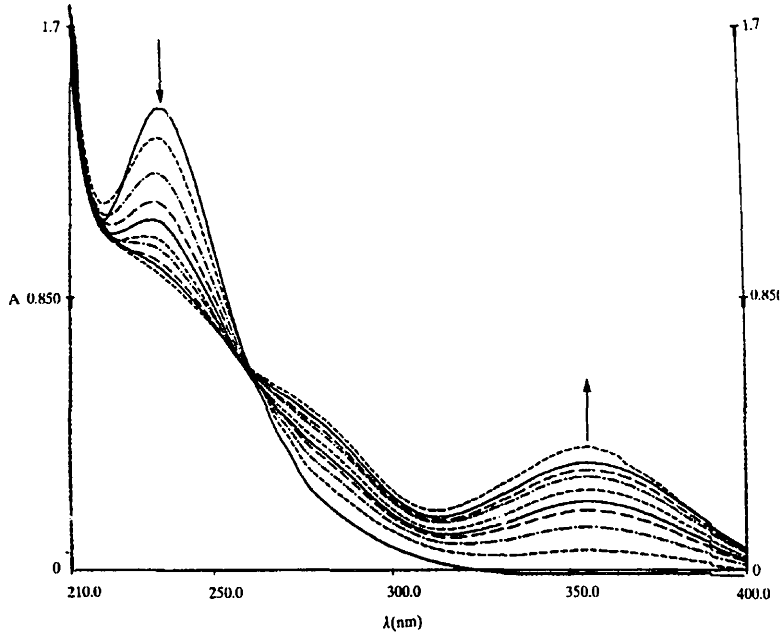


Fig. 2. UV spectra of 1×10^{-5} M solution of **4a** before and after 15, 30, 45, 60, 75, 90, 105, 120 and 135 min of UV illumination in methanol.

5f) and their selective intramolecular conversions to isomeric 2-aryl-4-methyl-3,5-diphenyl-2*H*-thiopyrans (**6a–6f**) were detected by ^{1}H-NMR spectroscopy under our experimental conditions. The relative rate constants of photoisomerization of **4a–4f** to the corresponding **6a–6f** were measured in methanol and benzene solutions. The efficiency of photoisomerization in methanol was greater than in benzene solution. The di-π-methane character of the photoisomerization is represented by the unimolecular nature of the process, by generation of bicyclic intermediates, by polarity of solvent and substituent effects on the efficiency and relative rate of photorearrangement.

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