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An approach to the novel stereoselectivity in photorearrangement of 4,4-dialkyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxides

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Abstract

The photochemical behaviour of 4,4-dimethyl-, 4-*tert*-butyl-4-methyl- and 4-benzyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxides has been investigated and compared with those of 4-methyl-2,4,6-triphenyl-4*H*-thiopyran-1,1-dioxide and 2,4,4,6-tetraphenyl-4*H*-thiopyran-1,1-dioxide as model compounds under identical experimental conditions followed by ^{1}H NMR spectroscopy. The high yields of the stereoisomeric bicyclic photoproducts of dialkyl analogues in the absence of SO_2 extruded byproducts are discussed on the basis of a vinyl–vinyl di-π-methane (DPM) rearrangement.

Keywords: 4*H*-thiopyran-1,1-dioxides; Photoisomerization; Stereoselectivity; Di-π-methane rearrangements

1. Introduction

The di-π-methane (DPM) rearrangement has attracted much attention from organic chemists because of its importance in organic synthesis as well as its interesting mechanistic aspects, which today still continues to be an active field of research [1]. The very broad spectrum of types of organic molecules obtainable by the DPM rearrangement is remarkable and makes it particularly synthetically useful. More often than not, the photoproducts are not available by alternative routs. This type of photochemical transformations has widely described on several heterocyclic substrates containing oxygen and nitrogen [1]. Enormous efforts have also been expended on the photochemical behaviour of tetrasubstituted 4*H*-thiopyrans **1** in our and other laboratories [2–10], which upon irradiations undergo a phenyl-vinyl DPM rearrangement to yield the corresponding 2*H*-thiopyran isomers **3** via their 2-thiabicyclo[3.1.0]hex-3-ene intermediates **2** (Scheme 1).

However, on the interesting sulfone derivatives studies are limited to some tetraaryl-substituted 4*H*-thiopyran-1,1-dioxides which upon direct photolysis at 254 nm, the corresponding 1,2,4,5-tetrasubstituted cyclopentadienes **6** were obtained as the main products through SO_2 extrusion along with the minor bicyclic photoproduct **5** (Scheme 2) [11,12].

Recently, we reported on the photoisomerizations of 4-methyl-2,4,6-triphenyl-4*H*-thiopyran-1,1-dioxide **7d** [13]. The interesting mechanistic aspect contributed by our original study on this compound was the observation of an absolute chemoselectivity in the reaction, where rearrangement takes place solely through vinyl–vinyl bonding to yield the corresponding thiabicylo[3.1.0]hex-3-ene-2,2-dioxides **10d** (Scheme 3). Unlike those of the other previously reported sulfones [12], none of the alternative phenyl–vinyl thiabicyclo[3.1.0] analogues of **2** could be found, which shows that phenyl–vinyl bonding does not take place, at least to any significant extent. To investigate substituent effects on the carbon bearing two π-moieties, provide further insight into mechanistic aspects, and get access to a novel stereoselectivity in formation of new thiabicyclic dioxides, it seemed of considerable interest to investigate some 4,4-dialkyl derivatives of the system. Accordingly three new compounds, 4,4-dimethyl-, 4-*tert*-butyl-4-methyl- and 4-benzyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxides **7a**–**7c** (Scheme 3) were selected for synthesis and photochemical studies. The biradical species are drawn since they help to understand and predict the reaction courses, stereoselectivity, and general reaction trends, although such biradical entities are the real reaction intermediates and play role in the transition states. In order to give further evidence for the

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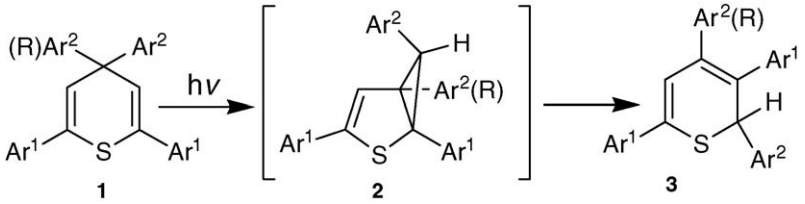
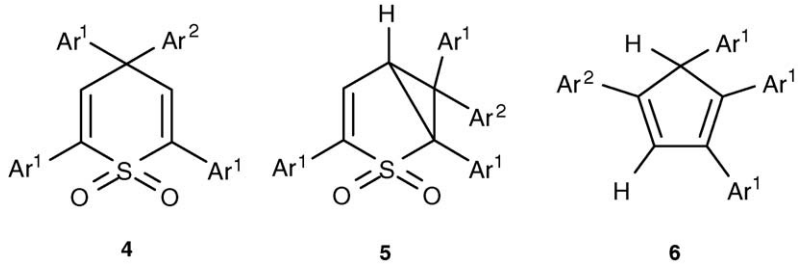


Scheme 1.



Scheme 2.

proposed mechanism, the steps which are responsible for the stereoselection were theoretically studied. As shown below, the theoretical efforts show that the triplet biradicals are intermediates.

Here, the results are compared with those of the model compounds **7d** and **7e** under the same experimental conditions. The molar ratios of the compounds during the photochemical transformations are determined using ^{1}H NMR spectroscopy.

2. Experimental details

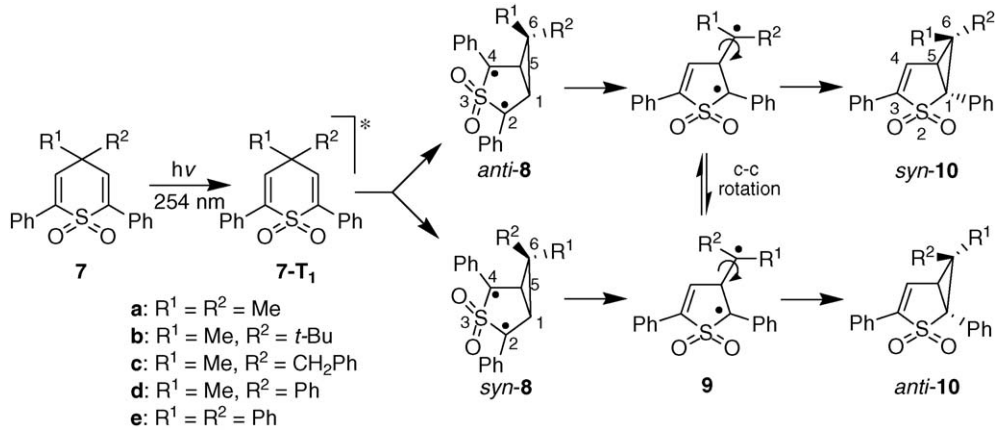
Melting points were determined on a Gallenkamp melting point apparatus. UV spectra were taken on a Shimadzu 256-FW spectrophotometer. Infrared spectra were measured in KBr with a Shimadzu 4300 FT-IR. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer using TMS or DMSO as internal standards. Mass spectra were recorded on a Finningan MAT-TSQ 70 mass spectrometer. High resolution mass spectra were recorded on a Karatos MS 25 RFA, ion source energy 70 eV. All photolyses were carried out using a low pressure mercury lamp with a transition maximum at $\lambda = 254$ nm (85% transmission) and transmitted light from 254–579 nm (15% transmission).

2.1. Syntheses

The new 4*H*-thiopyran-1,1-dioxides **7a**–**7c** were synthesized by reaction of the corresponding 4*H*-thiopyrans [14] (0.5 mmol) with hydrogen peroxide 30% (0.8 ml) in acetic acid (10 ml) at 60 °C. The reactions were followed by TLC until the transitionally formed 4*H*-thiopyran-1-oxides disappeared and the transformations completed. Then they were cooled and poured on ice (20 g). White precipitates were collected and recrystallized from ethanol to the corresponding sulfones. The model compounds **7d** and **7e** were synthesized by the methods previously described [12,13].

2.1.1. 4,4-Dimethyl-2,6-diphenyl-4H-thiopyran-1,1-dioxide (7a)

Eighty percentages yield. Colourless crystals, m.p. 130–131 °C (from EtOH). UV (EtOH) λ_{max} (log ε): 233 nm (4.29).



Scheme 3.

FT-IR (KBr): 1280, 1124 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 1.45 (6H, s, 2Me), 6.28 (2H, s, H-3, H-5), 7.39–7.67 (10H, m, Ar). MS (70 eV) *m/z*: 310 (35.1, $M^{+\bullet}$), 246 (75.7, $[M - SO_2]^+$), 231 (100.0, $[M - SO_2–Me]^+$). HR-MS (M^+) calcd for $C_{19}H_{18}O_2S$ 310.1027, found 310.1032.

2.1.2. 4-tert-Butyl-4-methyl-2,6-diphenyl-4H-thiopyran-1,1-dioxide (**7b**)

Eighty-five percentages yield. Colourless crystals, m.p. 144–145 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 235 nm (4.25). FT-IR (KBr): 1130, 1286 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 1.13 (9H, s, *t*-Bu), 1.39 (3H, s, Me); 6.40 (2H, s, H-3, H-5), 7.40–7.67 (10H, m, Ar). MS (70 eV) *m/z*: 352 (17.5, $M^{+\bullet}$), 295 (63.1, $[M - t\text{-Bu}]^+$), 231 (42.2, $[M - SO_2–t\text{-Bu}]^+$), 57 (100.0, *t*-Bu^+). HR-MS ($[M - t\text{-Bu}]^+$) calcd for $C_{18}H_{16}O_2S$ 296.0871, found 296.0864.

2.1.3. 4-Benzyl-4-methyl-2,6-diphenyl-4H-thiopyran-1,1-dioxide (**7c**)

Ninety-five percentages yield. Colourless crystals. m.p. 130–132 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 236 nm (4.35). FT-IR (KBr): 1126, 1284 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 1.48 (3H, s, Me), 3.01 (2H, s, CH_2), 6.25 (2H, s, H-3, H-5), 7.17–7.59 (15H, m, Ar). MS (70 eV) *m/z*: 386 (7.5, $M^{+\bullet}$), 322 (11.5, $[M - SO_2]^+$), 295 (22.1, $[M - CH_2Ph]^+$), 91 (100.0, CH_2Ph^+). HR-MS (M^+) calcd for $C_{25}H_{22}O_2S$ 386.1340, found 386.1347.

2.2. General procedure for photolysis

3×10^{-2} M solutions of sulfones **7a**–**7e**, were prepared in chloroform-d_1 and irradiated with a low pressure mercury lamp at 254 nm under an argon atmosphere at room temperature and the reactions were followed by ^1H NMR at different time intervals. The photoproducts were isolated by PLC.

2.3. Photoproducts

2.3.1. 6,6-Dimethyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (**10a**)

Seventy percentages yield. Colourless crystals. m.p. 151–152 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 266 nm (4.24). FT-IR (KBr): 1134, 1288 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 1.05 (3H, s, Me), 1.53 (3H, s, Me), 2.73 (1H, d, $J = 3.77$ Hz, H-5), 6.87 (1H, d, $J = 3.77$ Hz, H-4), 7.25–7.65 (10H, m, Ar). MS (70 eV) *m/z*: 310 (30.9, $M^{+\bullet}$), 246 (100.0, $[M - SO_2]^+$), 231(79.1, $[M - SO_2–Me]^+$). HR-MS (M^+) calcd for $C_{19}H_{18}O_2S$ 310.1027, found 310.1018.

2.3.2. anti-6-tert-Butyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (anti-**10b**)

Thirty-one percentages yield. Colourless crystals. m.p. 225–226 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 267 nm (4.35). FT-IR (KBr): 1139, 1288 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 0.94 (3H, s, Me), 1.29 (9H, s, *t*-Bu), 2.83 (1H, d, $J = 3.68$ Hz, H-5), 6.83 (1H, d, $J = 3.68$ Hz, H-4); 7.25–7.58 (10H, m, Ar). MS (70 eV) *m/z*: 352 (3.6, $M^{+\bullet}$), 295 (21.9, $[M - t\text{-Bu}]^+$), 231 (21.3, $[M - SO_2–t\text{-Bu}]^+$), 57 (76.0, *t*-Bu^+), 220 (100.0, $[M - t\text{-Bu–Ph} + 2H]^+$). HR-MS ($M^+$) calcd for $C_{22}H_{24}O_2S$ 352.1497, found 352.1487.

2.3.3. syn-6-tert-Butyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (syn-**10b**)

Thirty-seven percentages yield. Colourless crystals. m.p. 196–197 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 268 nm (3.85). FT-IR (KBr): 1145, 1292 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 0.82 (9H, s, *t*-Bu), 1.55(3H, s, Me), 3.12 (1H, d, $J = 3.98$ Hz, H-5), 6.87 (1H, d, $J = 3.98$ Hz, H-4), 7.24–7.67 (10H, m, Ar). MS (70 eV) *m/z*: 352 (2.5, $M^{+\bullet}$), 295 (25.7, $[M - t\text{-Bu}]^+$), 231 (11.8, $[M - SO_2–t\text{-Bu}]^+$), 57 (60.9, *t*-Bu^+), 220 (100.0, $[M - t\text{-Bu–Ph} + 2H]^+$). HR-MS ($M^+$) calcd for $C_{22}H_{24}O_2S$ 352.1497, found 352.1491.

2.3.4. anti-6-Benzyl-6-methyl-1,3-diphenyl-2-thiabicylo[3.1.0]hex-3-ene-2,2-dioxide (anti-**10c**)

Forty-six percentages yield. Colourless crystals. m.p. 149–150 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 266 nm (3.98). FT-IR (KBr): 1130, 1294 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 0.86 (3H, s, Me), 2.87(1H, d, $J = 3.7$ Hz, H-5), 3.28 (2H, AB q, CH_2), 7.01 (1H, d, $J = 3.7$ Hz, H-4), 7.25–7.67 (15H, m, Ar). MS (70 eV) *m/z*: 386 (11.4, $M^{+\bullet}$), 322 (4.9, $[M - SO_2]^+$), 231 (40.9, $[M - SO_2–CH_2Ph]^+$), 91 (100.0, CH_2Ph^+). HR-MS (M^+) calcd for $C_{25}H_{22}O_2S$ 386.1340, found 386.1335.

2.3.5. syn-6-Benzyl-6-methyl-1,3-diphenyl-2-thiabicylo[3.1.0]hex-3-ene-2,2-dioxide (syn-**10c**)

Twenty-eight percentages yield. Colourless crystals. m.p. 256–257 °C (from EtOH). UV (EtOH) λ_{max} ($\log \varepsilon$): 233 nm (4.29). FT-IR (KBr): 1124, 1280 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$) δ: 1.43 (3H, s, Me), 2.45 (2H, AB q, CH_2), 3.13 (1H, d, $J = 3.8$ Hz, H-5), 6.86 (1H, d, $J = 3.8$ Hz, H-4); 7.39–7.63 (15H, m, Ar). MS (70 eV) *m/z*: 386 (11.3, $M^{+\bullet}$), 295 (9.3, $[M - CH_2Ph]^+$), 231 (20.7, $[M - SO_2–CH_2Ph]^+$), 91 (100.0, CH_2Ph^+). HR-MS (M^+) calcd for $C_{25}H_{22}O_2S$ 386.1340, found 386.1332.

3. Results

To study the photochemical transformation behaviour of compounds **7a**–**7c** in comparison with the model compounds **7d** and **7e**, 3×10^{-2} M solutions of the mentioned sulfones in $CDCl_3$ were irradiated in NMR tubes with a low pressure mercury lamp at 254 nm (85% transmission of 254 nm and 15% transmission of light from 254–579 nm) under an Ar atmosphere at room temperature. The time dependence of the transformations was studied by ^1H NMR spectroscopy.

In the ^1H NMR spectra, the signals of **7a**–**7c** at 1.13–3.01 ppm (Me, *t*-Bu, CH_2) and 6.25–6.40 ppm (H-3, H-5) gradually decreased, while five new sets of signals appeared at 1.05 ppm (Me), 1.53 ppm (Me), 2.73 ppm (H-5), and 6.87 ppm (H-4) for **10a**, 0.94 ppm (Me), 1.29 ppm (*t*-Bu), 2.83 ppm (H-5), and 6.83 ppm (H-4) for *anti*-**10b**, 0.82 ppm (*t*-Bu), 1.55 ppm (Me),

Table 1
The characteristic chemical shifts of 4*H*-thiopyran-1,1-dioxides **7a–7e** and bicyclic photoproducts **10a–10e**

Compound	H-3, H-5	Me	CH_2Ph	*t*-Bu	H-4	H-5
7a	6.28	1.45				
7b	6.40	1.39		1.13		
7c	6.25	1.48	3.01			
7d	6.33	1.88				
7e	6.71					
10a		1.05, 1.53			6.87	2.73
anti-**10b**		0.94		1.29	6.83	2.83
syn-**10b**		1.55		0.82	6.87	3.12
anti-**10c**		0.86	3.28		7.01	2.87
syn-**10c**		1.43	2.45		6.86	3.13
anti-**10d**		1.26			6.86	3.06
syn-**10d**		1.85			7.02	3.65
10e					6.91	3.96

3.12 ppm (H-5), and 6.87 ppm (H-4) for *syn*-**10b** and 0.86 ppm (Me), 2.87 ppm (H-5), 3.28 ppm (CH_2), 7.01 ppm (H-4) for *anti*-**10c**, and 1.43 ppm (Me), 2.45 ppm (CH_2), 3.13 ppm (H-5), 6.86 ppm (H-4) for *syn*-**10c** (Table 1). Under prolonged irradiation, the singlets of **7a–7c** disappeared and the signals of the bicyclic photoproducts **10a–10c** began to decrease with no signs of SO_2 extruded cyclopentadiene byproducts. In the model compounds **7d** and **7e**, the singlets of **7d** at 6.33 ppm (H-3, H-5) and 1.88 ppm (Me) gradually decreased, while two new sets of doublets appeared at 6.86, 7.02 ppm (H-4) and 3.06, 3.65 ppm (H-5) accompanied by two new singlets at 1.26 and 1.85 ppm due to methyl groups for *anti*-**10d** and *syn*-**10d**, respectively. The singlet of **7e** at 6.71 ppm (H-3, H-5) gradually decreased, while two new doublets appeared at 6.91 ppm (H-4) and 3.96 ppm (H-5) due to bicyclic photoproduct **10e** as well as 7.33 ppm (H-4) and 5.08 ppm (H-5) for 1,2,4,5-tetraphenylcyclopenta-1,3-diene 6 (Ar^1=Ar^2=Ph). The molar ratios of the compounds at different time intervals were obtained from the intensities of the relative signals in the ^{1}H NMR spectra. The data reveal that in comparison to tetraaryl-substituted ones, the transformations of **7a–7c** are more efficient and the yields of the photoproducts **10a–10c** are higher than **10d** and **10e**. The variations of 4*H*-thiopyran-1,1-dioxides and bicyclic photoproducts during 480 min of irradiation under identical experimental conditions are summarized in Table 2.

Table 2
The variations (%) of 4*H*-thiopyran-1,1-dioxides **7a–7e** and bicyclic photoproducts **10a–10e** during 480 min of irradiation under identical experimental conditions

Compound	Time (min), chloroform								
	15	30	45	60	120	180	240	360	480
7a	83.2	68.2	54.0	35.9	19.8	11.4	7.2	4.1	0
7b	85.1	71.9	63.2	55.2	27.2	17.5	11.7	5.4	0
7c	81.2	64.0	54.1	44.7	20.1	10.8	6.9	3.8	0
7d	86.5	71.2	58.7	48.2	26.9	21.4	11.2	5.1	0
7e	84.3	76.5	61.4	55.6	48.0	43.0	22.8	19.6	13.7
10a	16.2	29.9	39.0	51.0	60.8	66.9	55.9	42.3	27.7
anti-**10b**	7.8	14.0	18.2	22.3	29.6	31.2	30.1	22.5	13.3
syn-**10b**	6.3	12.1	16.3	19.3	28.1	30.6	37.3	28.9	25.1
anti-**10c**	9.4	18.2	23.1	25.5	40.2	45.8	39.9	29.6	12.0
syn-**10c**	6.5	12.4	15.8	18.2	25.1	27.6	24.3	20.9	8.6
anti-**10d**	1.8	3.7	4.1	5.6	9.9	11.2	19.3	18.5	17.7
syn-**10d**	4.9	9.5	11.7	15.2	22.6	26.1	27.0	28.5	29.9
10e	3.8	7.2	10.5	13.2	22.6	27.9	35.0	26.6	19.5

4. Discussion

Photoirradiation of 4*H*-thiopyran-1,1-dioxides **7a–7c** in $CDCl_3$ resulted in the formation of highly strained bicyclic photoproducts, which is rationalized based on the DPM rearrangement including two unsaturated bonds of the thiopyran rings. The distribution of the photoproducts is discussed in terms of the radical stabilizing effect of the substituents and the destabilizing effect on the formation of the cyclopropane rings. As shown in Table 2, the presence of phenyl groups at the C-4 of the sulfone rings (**7e**) diminishes the yields of bicyclic photoproducts. Many cyclic systems have potentially available facile alternative pericyclic processes which compete all too successfully. The lower yields might be due to the phenyl migration side reactions which results in formation of 1,2,4,5-tetrasubstituted cyclopenta-1,3-dienes through SO_2 extrusion. However, no signs of SO_2 extruded byproducts were observable in 4,4-dialkyl derivatives **7a–7c**. The absence of migrating phenyl groups in **7a–7c** is consistent with the chemoselectivity in favour of a vinyl–vinyl DPM rearrangement.

Due to the stability of photoproducts at room temperature, we could separate and isolate the pure bicyclic photoproducts. Distinction of the *syn*- and *anti*-stereoisomers established on the basis of ^{1}H NMR spectroscopy. In the bicyclic sulfone *anti*-**10b** the protons of the methyl group are upfield relative to that of *syn*-**10b** (Table 1) because of the anisotropic shielding effects of phenyl group at 1-position. Furthermore, H-5 and H-4 appear as doublets with J = 3.68 and 3.98 Hz for *anti*-**10b** and *syn*-**10b**, respectively, where, H-5 for *syn*-**10b** is shifted downfield due to the γ-effect of the *tert*-butyl group. In the bicyclic sulfone *syn*-**10c** the protons of the benzyl group are upfield relative to that of *anti*-**10c** because of the anisotropic shielding effects of phenyl group at 1-position. Moreover, the H-4 in *anti*-**10c** is more shifted downfield due to anisotropic deshielding effect of the benzyl group.

Considering the results given in Table 2, *anti*-**10c** is formed in higher yield than the *syn*-isomer, which contrasts sharply with that of **10b** and the model compound **10d**. The formation of *anti*-isomer in vinyl–vinyl DPM rearrangement should proceed by rotation around the C–C bond of the intermediate **9** via a triplet state, while that of the *syn*-isomer may proceed by the C–C bond formation of the triplet intermediate **9** or directly from singlet state. However, we assume that the di-π-methane rearrangement in our 4*H*-thiopyran-1,1-dioxides proceeds through the triplet energy surface. Then the *syn*/*anti*-photoproduct ratio is determined in the C–C bond rotation and formation of the triplet intermediate **9**. The increased yield of *anti*-**10c** could be related to higher stability of the triplet state of **9c** relative to **9b** through more sites of hyperconjugation. One can predict this on the basis that the more delocalized odd-electron center, with methyl and benzyl substitutions, is utilized in the ring opening

of **7c**. As a result of higher stability of **9c** intermediate relative to **9b**, the C–C bond rotation followed by bond formation produces the most stable isomer, *anti*-**10c**, more selectively which has been confirmed theoretically to be 0.7 kcal/mol more stable than the *syn*-**10c** isomer. However, due to the lower stability of intermediate **9b**, there is no selectivity in the formation of *anti*- and *syn*-**10b** photoproducts, resulting the both isomers approximately with the same amounts.

It should be noted that, as shown in Table 2, on the contrary to **10c**, the *syn*-**10d** stereoisomer is much higher in yield than *anti*-**10d**. This behaviour could be due to a marked increase in stability of **9d** intermediate as a result of π–π stacking between the two phenyl groups on the same side of the ring. Therefore, C–C bond rotation proceeds in a manner to form the **9d** intermediate with two phenyl groups on the same side of the ring and the *syn*-**10d** isomer is obtained in higher yield.

As an extension of our work, we examined the photochemical stability of the photoproducts **10b**–**10c**. On irradiation of 3×10^{-2} M solutions of the mentioned bicyclic photoproducts in $CDCl_3$ in NMR tubes with a low pressure mercury lamp at 254 nm, they undergo subsequent photorearrangements giving several unidentified photoproducts. Comparing the relative stability of the bicyclic photoproducts, it was revealed that the *anti*-**10b** isomer undergoes photolysis more rapidly than the *syn*-**10b** isomer which is consistent with theoretical results showing that the *syn*-isomer is 2.78 kcal/mol more stable than the *anti*-isomer. However the *anti*- and *syn*-**10c** isomers undergo photolysis approximately with the same rate. Furthermore, no *syn–anti* photoconversion was observed.

To gain a better picture of the conformational profile of the given compounds and to determine the most stable conformations of the photoproducts, some ab initio calculations performed using 6-31G* basis set on GAMESS [15], using HF method. The open-shell states were treated at the same level of accuracy as the closed shell states. We verified that the obtained structures were minima on the potential energy surfaces calculating the frequencies of the optimized structures. The ground and the lowest triplet states of **7b**–**7c**, the triplet biradicals **8b**–**8c** which are supposed to occur in the photoisomerization process leading to the formation of the bicyclic photoproducts **10b**–**10c** in their ground states were investigated. The compounds **7b**–**7c** in the ground state show a flattened boat conformation, while in the triplet state a half-chair conformation is ascertained. The relative energies for the above-mentioned structures are shown in Table 3. The results are consistent with the experimental section. In fact, the excited triplet state of compounds **7b**–**7c** can evolve to give the corresponding *syn*- and *anti*-biradicals **8b**–**8c** with the *anti*-**8b** isomer showing a higher energy relative to first triplet excited state (T_1) of **7b** and probably lower efficiency, which in turn gives the intermediate **9** followed by *syn*- and *anti*-bicyclic photoproducts by cleavage of the C5–C6 bond and rotation around C1–C6 bond. In contrast, *anti*- and *syn*-**8c** both could be formed since their relative energies are lower than the triplet excited state (T_1) of **7c**. The full geometry optimized structures of the compounds mentioned above are presented in Fig. 1.

Table 3
Relative energies of possible transition states and intermediates in the photochemical isomerization of **7b**–**7c**

Compound	Electr. state	Relative energy (kcal mol^{-1})
7b	S_0	0.00
7b	T_1	45.37
anti-**8b**	T_1	47.87
syn-**8b**	T_1	42.75
anti-**10b**	S_0	16.82
syn-**10b**	S_0	14.04
7c	S_0	0.00
7c	T_1	45.60
anti-**8c**	T_1	43.42
syn-**8c**	T_1	42.83
anti-**10c**	S_0	7.53
syn-**10c**	S_0	8.20

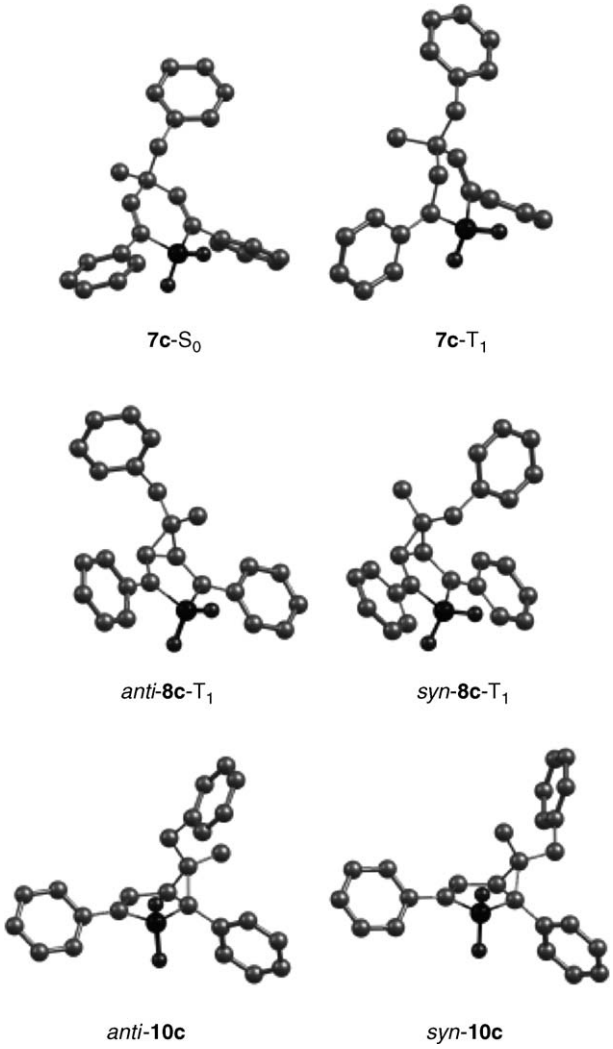


Fig. 1. Structures of stable compounds and intermediates in the photochemical isomerization of **7c**.

5. Conclusions

Here we outlined a detailed mechanism for compounds **7a**–**7c** as examples of cyclic DPM rearrangement. On expo-

sure to UV light the 4,4-dialkyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxides, unlike those of 2,4,4,6-tetraaryl-substituted analogues, underwent solely a vinyl–vinyl DPM rearrangement in higher yields without SO_2 extruded byproducts, while the distribution of the photoproducts conversed by the substituents. On the contrary to the phenyl group, the opposite observed role of the alkyl substituents in increasing the efficiencies are consistent with operation of a favourable electronic effects of these groups on the intermediates leading to photoproducts. Photochemical transformations of 4*H*-thiopyran-1,1-dioxides described here could prove to be an interesting and efficient means of obtaining bicyclic heterocycles containing sulfur atom.

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