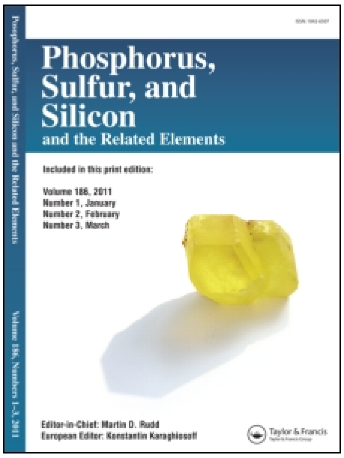

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The Effects of the Electron-Donating Methoxy Group on the Photoisomerization of 4-Methyl-2,4,6-triaryl-4*H*-thiopyran-1,1-dioxides

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The Effects of the Electron-Donating Methoxy Group on the Photoisomerization of 4-Methyl-2,4,6-triaryl-4*H*-thiopyran-1,1-dioxides

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*Syntheses and photoisomerization of the new sulfone derivatives, 4-anisyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide and 2,6-dianisyl-4-methyl-4-phenyl-4*H*-thiopyran-1,1-dioxide, are described. The relative molar ratios of the regioselective photoproducts were compared with those of the unsubstituted model compound under identical experimental conditions using ^1H NMR spectroscopy. The results that were observed are discussed on the basis of a vinyl-vinyl thia-di-π-methane rearrangement.*

Keywords 4*H*-Thiopyran-1,1-dioxides; Di-π-methane rearrangement; photoisomerization; regioselectivity

INTRODUCTION

In the course of our studies on photoisomerization of 2,4,4,6-tetrasubstituted 4*H*-thiopyrans,[1,2] recently we reported on the synthesis and photochemical transformation of 4-methyl-2,4,6-triphenyl-4*H*-thiopyran-1,1-dioxide **1a** which, unlike those of the previously reported tetraaryl analogues,[3] upon irradiation with a low-pressure mercury lamp, underwent rearrangement in high regioselectivity to form two bicyclic stereoisomers, *anti*-**2a** and *syn*-**2a**, without SO_2 extruded byproducts.[4]

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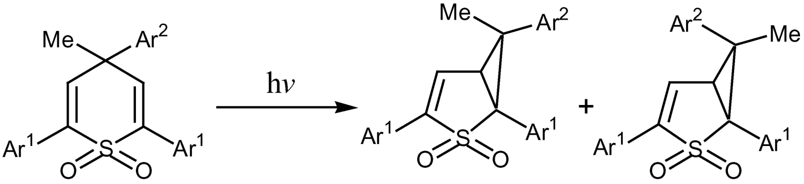
To gain further information on this topic, the present investigation was undertaken to determine the effects of electron-donating *p*-methoxy group on the phenyl substituents attached to 4- and 2,6-positions of the sulfur ring. Accordingly, new tetrasubstituted 4-anisyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide **1b** and 2,6-dianisyl-4-methyl-4-phenyl-4*H*-thiopyran-1,1-dioxide **1c** (Scheme 1) were selected for synthesis and study.



1a–1c *syn*-**2a–2c** *anti*-**2a–2c**

	Ar^1	*Ar*^{2}
a:	*Ph*	*Ph*
b:	*Ph*	C_6H_4OMe
c:	C_6H_4OMe	*Ph*

SCHEME 1

RESULTS AND DISCUSSION

In order to compare the effects of the electron-donating *p*-methoxy group on the efficiencies of *anti*- and *syn*-bicyclic stereoisomers **2b–2c**, photolyses of degassed 3×10^{-2} M solutions of **1a–1c** in chloroform-d_1 were performed under identical experimental conditions and the results were compared with those of the model compound **1a**. Irradiations were carried out in sealed NMR tubes by an unfiltered low-pressure mercury lamp with a transmission maximum of 254 nm under an argon atmosphere at room temperature. The reactions were followed by ^{1}H NMR and the spectra were recorded at different time intervals.

In the ^{1}H NMR spectra, the corresponding signals of **1a–1c** gradually decreased, while six new characteristic sets of signals appeared for *anti*- and *syn*-**2a–2c** isomers (Table I). Under prolonged irradiation, the signals of **1a–1c** disappeared and those of the bicyclic photoproducts **2a–2c** began to decrease.

Owing to the stability of photoproducts at room temperature and the selectivity of photoisomerization, we were able to isolate and identify the photoproducts in pure forms. As shown in Table I, cyclopropyl

TABLE I The Characteristic Chemical Shifts (δ/ppm) and Coupling Constants (*J*/Hz) for 4*H*-Thiopyran-1,1-dioxides 1a–1c and Photoproducts 2a–2c in Chloroform-d$_1$ as the Solvent (25°C)

4*H*-Thiopyran-1,1-dioxide				Photoproducts					
	δ (ppm)				δ (ppm)				
Compound	Me-4	MeO	H-3, H-5	Compound	Me-6	MeO	H-4	H-5	$J_{4,5}$ (Hz)
1a[10]	1.81	—	6.32	*anti*-**2a**	1.27	—	6.86	3.04	3.8
				syn-**2a**	1.84	—	7.02	3.71	3.8
1b	1.84	3.82	6.30	*anti*-**2b**	1.26	3.76	6.82	3.02	3.5
				syn-**2b**	1.83	3.68	7.07	3.58	3.9
1c	1.85	3.81	6.25	*anti*-**2c**	1.31	3.73	6.71	2.95	3.4
				syn-**2c**	1.61	3.68 3.82	6.88	3.53	3.9

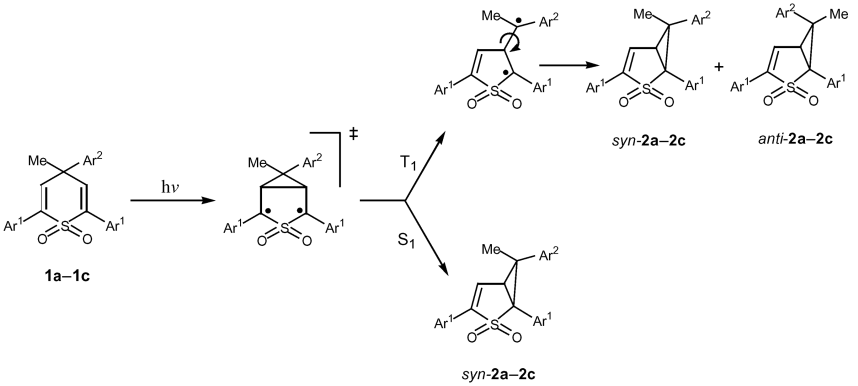
protons H-5 for the bicyclic sulfones *syn*-**2a–2c** are shifted more downfield relative to *anti*-**2a–2c** because of the stronger anisotropic deshielding effects of two syn-phenyl groups, whereas in the bicyclic sulfones *anti*-**2a–2c**, the protons of the methyl groups are more shifted upfield relative to *syn*-**2a–2c** because of the anisotropic shielding effects of the phenyl groups at 1-positions.

The variations in molar ratios of 4*H*-thiopyrans **1a–1c** and photoproducts **2a–2c** in ^{1}H NMR spectra that were recorded on repeated irradiations are presented in Table II. Unlike those of some tetraaryl-substituted sulfone derivatives reported earlier,[3] no signs of SO_2

TABLE II The Variations (%) of 4*H*-Thiopyran-1,1-dioxides 1a–1c and Bicyclic Photoproducts 2a–2c During 480 min of Irradiation Under Identical Experimental Conditions

	Time (min), chloroform								
Compound	15	30	45	60	120	180	240	360	480
1a	86.5	71.2	58.7	48.2	26.9	21.4	11.2	5.1	0.0
1b	85.6	74.8	67.4	59.9	32.5	21.6	12.1	4.0	2.1
1c	77.4	56.3	44.7	29.3	0.0	0.0	0.0	0.0	0.0
anti-**2a**	1.8	3.7	4.1	5.6	9.9	11.2	19.3	18.5	17.7
syn-**2a**	4.9	9.5	11.7	15.2	22.6	26.1	27.0	28.5	29.9
anti-**2b**	2.0	4.6	5.8	7.1	17.5	22.7	26.5	24.6	22.4
syn-**2b**	1.4	3.5	4.9	5.9	14.7	17.9	21.2	18.0	16.2
anti-**2c**	5.9	10.2	13.6	19.4	25.2	28.4	27.5	23.4	18.4
syn-**2c**	10.4	16.3	22.5	31.0	42.6	47.0	45.6	39.4	30.3

extruded byproducts could be observed in the ^{1}H NMR spectra. As is clear from Table II, in each case, two stereoisomers are formed in the reaction mixtures. The formation of two stereoisomers could be interpreted through vinyl-vinyl thia-di-π-methane rearrangement by considering the rotation around the C—C bond as shown in Scheme 2. The ^{1}H NMR data reveals that the transformation of **1c** is more efficient and the yields of photoproducts in **2c** are considerably higher than in **2a** and **2b**. In the case of **2b**, on the contrary to **2a** and **2c**, the *anti*-**2b** is formed in a higher yield than *syn*-**2b**. This behavior could be due to the increase in the half-life time required for the intersystem crossing of the first singlet excited state.



SCHEME 2

In conclusion, the electron-donating *p*-methoxy group attached to the 4-phenyl ring of the sulfone increases the efficiency of *anti*-stereoisomer, while on the 2,6-diphenyls, the efficiencies increase for both *syn*- and *anti*-stereoisomers **2c** relative to the stereoisomers **2a** of the model compound with no change of preference in the stereoisomers. This behavior is consistent with the operation of two different favorable electronic effects of the *p*-methoxy group on two different transition states leading to the corresponding photoproducts.

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. UV absorption spectra were taken on a Shimadzu 265-FW spectrophotometer. IR spectra were obtained on a Shimadzu FT-IR 4300 spectrophotometer in KBr disks. ^{1}H NMR spectra were recorded on Bruker Ac-80 or 500 MHz FT-NMR spectrometers relative to internal standard tetramethylsilane. Mass spectra were determined with a Finningan MAT-TSQ 70 mass spectrometer. Photolyses were performed using a low-pressure mercury lamp with a transmission maximum at $\lambda = 254$ nm (85% transmission) and transmitted light from 254–579 nm (15% transmission).

Syntheses

The new 4*H*-thiopyran-1,1-dioxides **1b–1c** were synthesized from the reaction of the corresponding 4*H*-thiopyrans (0.5 mmol) with hydrogen peroxide of 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 were completed. Then they were cooled and poured on to ice (20 g). White precipitates were collected and recrystallized from ethanol to give **1b** (96.5%) and **1c** (91%). The model compound **1a** was synthesized by the method previously described.[4,5]

4-Anisyl-4-methyl-2,6-diphenyl-4H-thiopyran-1,1-dioxide (1b)

Colorless crystals. m.p. 165–166°C. Anal. Calcd. for $C_{25}H_{22}O_3S$ (402.51): C, 74.60; H, 5.51; S, 7.97. Found: C, 74.46; H, 5.57; S, 7.83. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.84 (s, Me), 3.82 (s, MeO), 6.30 (s, H-3, H-5), 6.80–7.74 (m, 14H, Ph). EI-MS: *m/z* 402 ($M^{\cdot+}$, 5.1), 387 (M—Me, 29), 338 (M—SO_2, 100). UV (MeOH) λmax (logε) nm: 241 (4.36). IR (KBr) (ν_{max}, cm^{-1}): 1128, 1288 (SO_2).

2,6-Dianisyl-4-methyl-4-phenyl-4H-thiopyran-1,1-dioxide (1c)

Colorless crystals. m.p. 136–137°C. Anal. Calcd. for $C_{26}H_{24}O_4S$ (432.54): C, 72.20; H, 5.59; S, 7.41. Found: C, 72.04; H, 5.54; S, 7.30. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.85 (s, Me), 3.81(s, 2 MeO), 6.25 (s, H-3, H-5), 6.85–7.66 (m, 13H, Ph). EI-MS: *m/z* 432 ($M^{\cdot+}$, 44.8), 417 (M—Me, 2.1), 368 (M—SO_2, 100). UV (EtOH) λmax (logε) nm: 260 (4.4). IR (KBr) (ν_{max}, cm^{-1}): 1128, 1290 (SO_2).

General Procedure for Photolysis

3×10^{-2} M solutions of 4*H*-thiopyran-1,1-dioxides **1a–1c** were prepared in chloroform-d_1 in NMR tubes, then were degassed and sealed under Ar. Irradiations were carried out by a low-pressure mercury lamp with a transmission maximum of 254 nm at room temperature. The progress of the photochemical reactions were followed by ^{1}H NMR at different time intervals.

Photoproducts

Irradiations in chloroform gave a mixture of two photoproducts, *anti*-**2b** and *syn*-**2b** for **1b** and *anti*-**2c** and *syn*-**2c** for **1c**, accompanied by the corresponding starting materials as evidenced by ^{1}H NMR. The photoproducts were isolated by PLC on neutral alumina with n-hexane: dichloromethane (80:20) or petroleum ether 40–60°C:diethylether (35:65) as an eluent and was purified by recrystallization from ethanol.

Anti-6-Anisyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (Anti-2b)

Colorless crystals. m.p. 261–262°C. Anal. Calcd. for $C_{25}H_{22}O_3S$ (402.51): C, 74.60; H, 5.51; S, 7.97. Found: C, 74.73; H, 5.58; S, 8.06. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (3H, s, Me), 3.02 (1H, d, $^3J = 3.5$ Hz, H-5), 3.76 (3H, s, MeO), 6.82 (1H, d, $^3J = 3.5$ Hz, H-4), 6.84–7.80 (14H, m, Ph). EI-MS: m/z 402 ($M^{\cdot+}$, 6.6), 338 ($M—SO_2$, 100), 323 ($M—SO_2—Me$, 98). UV (MeOH) λmax (logε) nm: 267 (2.9), 221 (3.1). IR (KBr) (ν_{max}, cm^{-1}): 1139, 1292 (SO_2).

Syn-6-Anisyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (Syn-2b)

Colorless crystals. m.p. 172–173°C. Anal. Calcd. for $C_{25}H_{22}O_3S$ (402.51): C, 74.60; H, 5.51; S, 7.97. Found: C, 74.81; H, 5.53; S, 8.11. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.83 (3H, s, Me), 3.58 (1H, d, $^3J = 3.9$ Hz, H-5), 3.68 (3H, s, MeO), 7.07 (1H, d, $^3J = 3.9$ Hz, H-4), 6.68–7.47 (14H, m, Ph). EI-MS: m/z 402 ($M^{\cdot+}$, 5.7), 338 ($M—SO_2$, 100), 323 ($M—SO_2—Me$, 98). UV (MeOH) λmax (logε) nm: 265 (3.2), 220 (3.3). IR (KBr) (ν_{max}, cm^{-1}): 1139, 1294 (SO_2).

Anti-1,3-Dianisyl-6-methyl-6-phenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (Anti-2c)

Colorless crystals. m.p. 237–238°C. Anal. Calcd. for $C_{26}H_{24}O_4S$ (432.54): C, 72.20; H, 5.59; S, 7.41. Found: C, 72.32; H, 5.63; S, 7.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (3H, s, Me), 2.95 (1H d, $^3J = 3.4$ Hz, H-5), 3.73 (3H, s, MeO), 3.85 (3H, s, MeO), 6.71 (1H, d, $^3J = 3.4$ Hz, H-4), 6.77–7.41 (13H, m, Ph). EI-MS: m/z 432 ($M^{\cdot+}$, 1.5), 368 ($M—SO_2$, 100), 353 ($M—SO_2—Me$, 15). UV (EtOH) λmax (logε) nm: 282 (4.2), 233 (4.4). IR (KBr) (ν_{max}, cm^{-1}): 1138, 1296 (SO_2).

Syn-1,3-Dianisyl-6-methyl-6-phenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (Syn-2c)

Colorless crystals. m.p. 220–221°C. Anal. Calcd. for $C_{26}H_{24}O_4S$ (432.54): C, 72.20; H, 5.59; S, 7.41. Found: C, 72.11; H, 5.57; S, 7.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.61 (3H, s, Me), 3.53 (1H, d, $^3J = 3.9$ Hz, H-5), 3.68 (3H, s, MeO), 3.82 (3H, s, MeO), 6.88 (1H, d, $^3J= 3.9$ Hz, H-4), 6.62–7.72 (13H, m, Ph). EI-MS: m/z 432 ($M^{\cdot+}$, 21), 368 ($M—SO_2$, 100), 353 ($M—SO_2—Me$, 40). UV (EtOH) λmax ($\log\varepsilon$) nm: 282 (4.3), 228 (4.4). IR (KBr) (ν_{max}, cm^{-1}): 1137, 1300 (SO_2).

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