Effects of Electron-Withdrawing Group on the Photoisomerization of Tetraaryl-4*H*-thiopyran-1,1-dioxides

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ABSTRACT: *Syntheses and photoisomerization of the new sulfone derivatives, 4,4-di (p-trifluoromethylphenyl)-2,6-diphenyl-4H-thiopyran-1, 1-dioxide and 4-(p-trifluoromethylphenyl)-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide, have been investigated. The relative molar ratios of the photoproducts are compared with those of 2,4,4,6-tetraphenyl-4H-thiopyran-1,1-dioxide as well as electron-donating substituted 4-methyl-2,4,6-triaryl-4H-thiopyran-1,1-dioxides as model compounds under identical experimental conditions using ^{1}H NMR spectroscopy. The results observed are discussed on the basis of a triplet excited state di-π-methane rearrangement.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:557–561, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20455

INTRODUCTION

The di-π-methane rearrangement has attracted much attention from organic chemists because of its importance in organic synthesis and its interesting mechanistic aspects, which today still continues to be an active field of research [1]. This type of

photochemical transformations has been widely described in several heterocyclic substrates. Enormous efforts have also been made on the photochemical behavior of tetrasubstituted 4*H*-thiopyrans and their sulfone derivatives in our laboratory as well as in other laboratories [2–12]. In the course of our studies on photoisomerization of 2,4,4,6-tetrasubstituted 4*H*-thiopyran-1,1-dioxides, recently we reported on the synthesis and photochemical transformations of 4-anisyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide **1a** and 2,6-dianisyl-4-methyl-4-phenyl-4*H*-thiopyran-1,1-dioxide **1b** [13,14], which upon irradiation with low-pressure mercury lamp underwent a di-π-methane rearrangement in high regioselectivity to form two *syn*-**2a–2b** and *anti*-**2a–2b** bicyclic stereoisomers (Scheme 1). The electron-donating *p*-methoxy group on the 4-phenyl ring of the sulfone increased the efficiency of formation of *anti*-**2a** stereoisomer, whereas on the 2,6-diphenyls the efficiencies increased for both *syn*-**2b** and *anti*-**2b** stereoisomers.
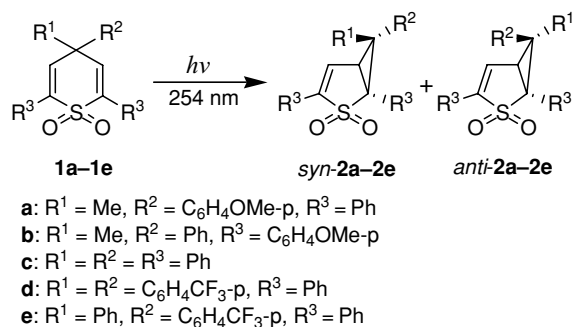
To investigate the effects of electron-withdrawing substituents on the photoisomerization of 4*H*-thiopyran-1,1-dioxides and provide further insight into mechanistic aspects of this reaction, it seemed of considerable interest to investigate some 4,4-diaryl derivatives of the system bearing electron-withdrawing groups. Accordingly, two new compounds, 4,4-di(*p*-trifluoromethylphenyl)-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide **1d** and 4-(*p*-trifluoromethylphenyl)-2,4,6-triphenyl-4*H*-thiopyran-1,1-dioxide **1e** were selected for synthesis

SCHEME 1

a: R^1 = Me, R^2 = C_6H_4OMe-p, R^3 = Ph
b: R^1 = Me, R^2 = Ph, R^3 = C_6H_4OMe-p
c: R^1 = R^2 = R^3 = Ph
d: R^1 = R^2 = $C_6H_4CF_3$-p, R^3 = Ph
e: R^1 = Ph, R^2 = $C_6H_4CF_3$-p, R^3 = Ph

and photochemical studies (Scheme 1). The results were compared with those of the model compounds 2,4,4,6-tetraphenyl-4H-thiopyran-1,1-dioxide **1c** and electron-donating substituted 4-methyl-2,4,6-triaryl-4H-thiopyran-1,1-dioxides **1a** and **1b** under the same experimental conditions. The molar ratios of the compounds during the photochemical transformations are determined using ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

To study the photochemical transformation behavior of compounds **1d** and **1e** in comparison with the model compounds **1a–1c**, 3×10^{-2} M solutions of these compounds in chloroform-d_1 were irradiated in sealed NMR tubes with a low-pressure mercury lamp at 254 nm (85% transmission of 254 nm and 15% transmission of light from 254 to 579 nm) under an argon atmosphere at room temperature. The time dependence of the transformations was studied by ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectra, the singlet signals of **1d** and **1e** at δ 6.63 and 6.67 (H-3, H-5) ppm gradually decreased, whereas three new sets of signals appeared at 4.10 (H-5), and 6.96 (H-4) ppm for **2d**, 3.94 (H-5), and 6.92 (H-4) ppm for *syn*-**2e**, and 3.98 (H-5), and 6.90 (H-4) ppm for *anti*-**2e** (Table 1). Under prolonged irradiation, the signals of the bicyclic photoproducts **2d** and **2e** began to decrease. In the model compounds **1a–1c** [13,14], the singlets of **1a–1c** gradually decreased, whereas five new characteristic sets of signals appeared for *syn*- and *anti*-**2a–2c**. 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 variations of 4H-thiopyran-1,1-dioxides and bicyclic photoproducts during 480 min of irradiation under identical experimental conditions are summarized in Table 2.

Because of the stability of the photoproducts at room temperature, we could isolate and identify the bicyclic photoproducts in pure forms. Distinction of the syn- and anti-stereoisomers established on the basis of ^{1}H NMR spectroscopy. In the bicyclic photoproducts *anti*- and *syn*-**2e**, H-5 and H-4 protons appear as doublets with $J = 3.5$ Hz, where H-5 for *syn*-**2e** is shifted upfield relative to that of *anti*-**2e** (Table 1) due to less anisotropic shielding effect of the phenyl ring with an electron-withdrawing CF_3-substituted group. Moreover, the H-4 in *syn*-**2e** is more shifted downfield relative to that of *anti*-**2e** due to anisotropic effect of two phenyl groups at 3- and 6-positions.

As shown in Table 2, the presence of electron-withdrawing groups at C-4 of the sulfone ring (**1d** and **1e**) diminishes the yields of the bicyclic photoproducts. The lower yields might be due to the phenyl migration side reactions that result in

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

4H-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	1.84	3.82	6.30	*syn*-**2a**	1.83	3.68	7.07	3.58	3.9
				anti-**2a**	1.26	3.76	6.82	3.02	3.5
1b	1.85	3.81	6.25	*syn*-**2b**	1.61	3.68	6.88	3.53	3.9
						3.82			
				anti-**2b**	1.31	3.73	6.71	2.95	3.4
						3.85			
1c			6.71	**2c**			6.91	3.96	3.8
1d			6.63	**2d**			6.96	4.10	3.4
1e			6.67	*syn*-**2e**			6.92	3.94	3.5
				anti-**2e**			6.90	3.98	3.5

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

Compound	Time (min)								
	15	30	45	60	120	180	240	360	480
1a	85.6	74.8	67.4	59.9	32.5	21.6	12.1	4.0	2.1
1b	77.4	56.3	44.7	29.3	0.0	0.0	0.0	0.0	0.0
1c	84.3	76.5	61.4	55.6	48.0	43.0	22.8	19.6	13.7
1d	79.0	61.6	48.1	35.8	16.3	8.6	4.8	0.0	0.0
1e	90.7	77.2	76.9	64.9	52.9	35.9	31.1	22.7	21.5
syn-**2a**	1.4	3.5	4.9	5.9	14.7	17.9	21.2	18.0	16.2
anti-**2a**	2.0	4.6	5.8	7.1	17.5	22.7	26.5	24.6	22.4
syn-**2b**	10.4	16.3	22.5	31.0	42.6	47.0	45.6	39.4	30.3
anti-**2b**	5.9	10.2	13.6	19.4	25.2	28.4	27.5	23.4	18.4
2c	3.8	7.2	10.5	13.2	22.6	27.9	35.0	26.6	19.5
2d	4.3	8.2	9.2	13.0	17.6	20.8	19.6	15.1	10.5
syn-**2e**	0.6	1.2	1.6	2.0	4.3	5.9	7.1	8.1	7.8
anti-**2e**	0.8	1.7	2.6	3.0	6.0	8.2	10.1	12.0	10.0

formation of 1,2,4,5-tetrasubstituted cyclopenta-1,3-dienes through SO₂ extrusion. However, no signs of SO₂ extruded by-products were observable in the model compounds **1a** and **1b** with electron-donating substituents at C4 and C2,6 positions, respectively. One can predict this on the basis of the fact that the electron-donating substituents diminish the energy content of the transition state in the vinyl–vinyl di-π-methane rearrangement pathway relative to that of phenyl–vinyl di-π-methane rearrangement. Furthermore, the inductive effect of electron-withdrawing groups results in instability of a triplet state intermediate **I-2** in vinyl-vinyl di-π-methane rearrangement pathway (Scheme 2), which in turn gives the syn- and anti-**2e** isomers as well as the bicyclic photoproduct **2d** in lower efficiency relative to model compounds **1a–1c**.

It should also be noted that anti-**2e** is formed in higher yield than the syn isomer, which contrasts with that of the model compound **2b**. The forma-

tion of antiisomer in vinyl–vinyl DPM rearrangement should proceed by rotation around the C—C bond of the intermediate **I-2** via a triplet state. The C—C bond rotation followed by bond formation produces the most stable isomer, anti-**2e**, more selectively which has been confirmed theoretically to be 0.1 kcal/mol more stable than the syn-**2e** isomer.

To gain a better picture of the conformational profile of the given compounds and to determine the most stable conformation of the photoproducts, ab initio calculations performed at the Hartree–Fock level using the 6-31G(d) basis set with full geometry optimization. We used the GAMESS program in the present ab initio calculations [15]. The calculated heats of formation revealed that the anti-**2e** isomer is 0.1 kcal/mol more stable than the syn-**2e** isomer. This result is consistent with the results of experimental section. The full geometry optimized structures of these compounds are presented in Fig 1.
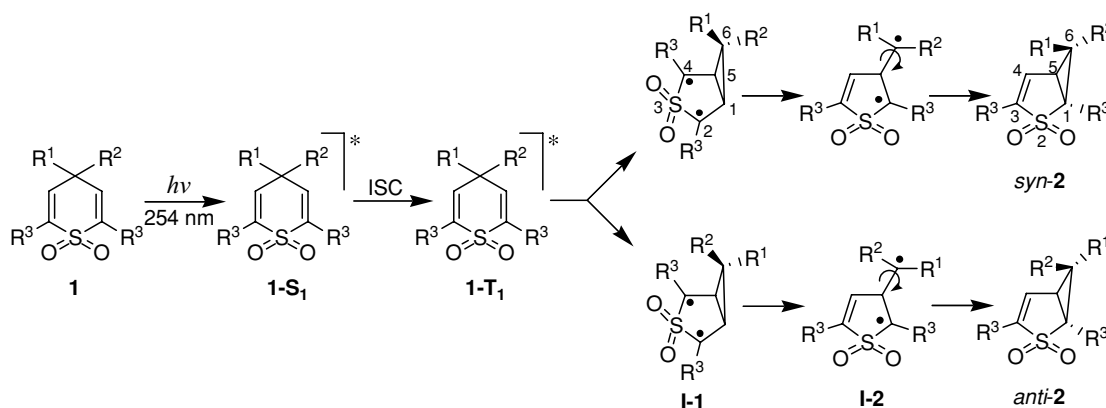
SCHEME 2 Proposed mechanism for the photochemical rearrangement of compounds **1a–1e**.
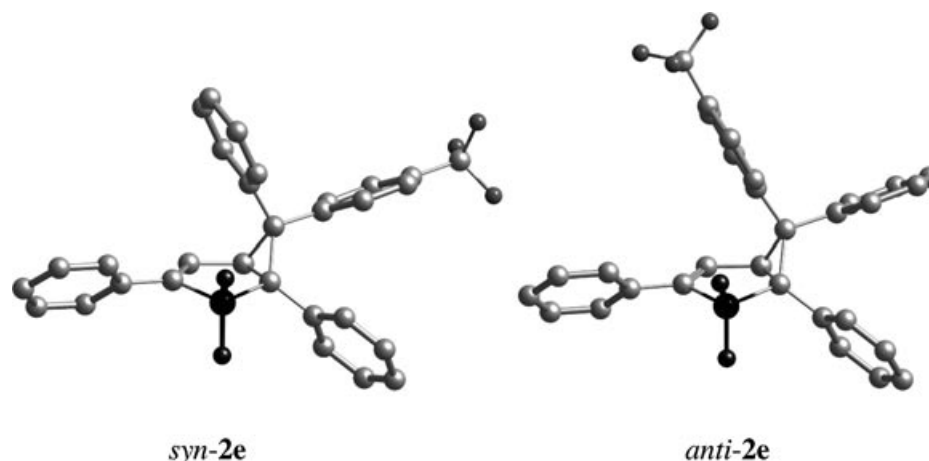
FIGURE 1 The full geometry optimized structures of the bicyclic photoproducts *syn-* and *anti-***2e**.

CONCLUSION

In conclusion, on the contrary to electron-donating groups at C4 position of thiopyran rings, the opposite observed role of the electron-withdrawing substituents in decreasing the efficiencies of photoproducts is consistent with operation of an unfavorable electronic effect of these groups on the intermediates leading to photoproducts. The relative ratios of anti- and syn-bicyclic photoproducts are consistent with their relative stability predicted by theoretical calculations.

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. Photolysis was performed using a low-pressure mercury lamp with a transmission maximum at $\lambda = 254$ nm (85% transmission) and transmitted light from 254 to 579 nm (15% transmission).

Syntheses

The new 4H-thiopyran-1,1-dioxides **1d** and **1e** were synthesized from the reaction of the corresponding 4H-thiopyrans (0.5 mmol) with hydrogen peroxide 30% (0.8 mL) in acetic acid (10 mL) at 60°C. Once the complete disappearance of transitionally formed

4H-thiopyran-1-oxides and starting materials was apparent by TLC, the reaction mixtures were cooled and poured on ice (20 g). White precipitates were collected and recrystallized from ethanol to give **1d** (85%) and **1e** (90%).

*4,4-di(p-Trifluoromethylphenyl)-2,6-diphenyl-4H-thiopyran-1,1-dioxide (***1d***).* Colorless crystals, yield 85%; mp 220–221°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 6.63$ (s, H-3, H-5), 7.38–7.76 (m, 18H, Ar-H) ppm; EI-MS (m/z, %) = 570 [M$^+$, 12], 506 [M$^+$–SO$_2$, 100]; UV (EtOH): λ_{max} (log ε) = 242 (4.6) nm; IR: 1128, 1288 (SO$_2$) cm^{-1}; Anal. Calcd for C$_{31}$H$_{20}$F$_6$O$_2$S. (570.54): C, 65.26; H, 3.53; S, 5.62%. Found: C, 65.35; H, 3.48; S, 5.51%.

*4-(p-Trifluoromethylphenyl)-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide (***1e***).* Colorless crystals, yield 90%; mp 171–172°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 6.67$ (s, H-3, H-5), 7.32–7.75 (m, 19H, Ar-H) ppm; EI-MS (m/z, %) = 502 [M$^+$, 23], 438 [M$^+$–SO$_2$, 100]; UV (EtOH): λ_{max} (log ε) = 233 (4.5) nm; IR: 1130, 1294 (SO$_2$) cm^{-1}; Anal. Calcd for C$_{30}$H$_{21}$F$_3$O$_2$S. (502.55):C, 71.70; H, 4.21; S, 6.38%. Found: C, 71.61; H, 4.28; S, 6.45%.

General Procedure for Photolysis

3 × 10^{-2} M solutions of 4H-thiopyran-1,1-dioxides **1d** and **1e** were prepared in chloroform-d$_1$ in NMR tubes and irradiated with a low-pressure mercury lamp at 254 nm under an argon atmosphere at room temperature. The progress of the photochemical reactions was followed by ^{1}H NMR at different time intervals.

Photoproducts

Irradiations in chloroform gave bicyclic photoproduct **2d** for **1d** and a mixture of two photoproducts *anti*-**2e** and *syn*-**2e** for **1e** accompanied by the corresponding starting materials as evidenced by ^{1}H NMR. The photoproducts were isolated by PLC on neutral alumina with petroleum ether:diethyl ether (35:65) as eluent and purified by recrystallization from ethanol.

6,6-Di(p-trifluoromethylphenyl)-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (**2d**). Colorless crystals, yield 19%; mp 214–215°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 4.10$ (d, $J = 3.4$ Hz, H-5), 6.96 (d, $J = 3.4$ Hz, H-4), 7.21–7.80 (m, 18H, Ar–H) ppm; EI-MS (m/z, %) = 570 [M$^+$, 12], 506 [M$^+$–SO$_2$, 100], 506 [M$^+$–SO$_2$–C$_6$H$_4$CF$_3$-p, 29]; UV (EtOH): λ_{max} (log ε) = 266 (4.2) nm; IR: 1140, 1296 (SO$_2$) cm^{-1}; Anal. Calcd for C$_{31}$H$_{20}$F$_6$O$_2$ S. (570.54): C, 65.26; H, 3.53; S, 5.62%. Found: C, 65.37; H, 3.60; S, 5.73%.

anti-6-(p-Trifluoromethylphenyl)-6-phenyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (*anti*-**2e**). Colorless crystals, yield 12%; mp 186–188°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 3.98$ (d, $J = 3.5$ Hz, H-5), 6.90 (d, $J = 3.5$ Hz, H-4), 7.04–7.71 (m, 19H, Ar-H) ppm; EI-MS (m/z, %) = 502 [M$^+$, 16], 438 [M$^+$–SO$_2$, 100], 293 [M$^+$–SO$_2$–C$_6$H$_4$CF$_3$-p, 10]; UV (EtOH): λ_{max} (log ε) = 217 (4.5), 262 (3.9) nm; IR: 1136, 1298 (SO$_2$) cm^{-1}; Anal. Calcd for C$_{30}$H$_{21}$F$_3$O$_2$ S. (502.55): C, 71.70; H, 4.21; S, 6.38%. Found: C, 71.82; H, 4.30; S, 6.29%.

syn-6-(p-Trifluoromethylphenyl)-6-phenyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (*syn*-**2e**). Colorless crystals, Yield 10%; mp 215–216°C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 3.94$ (d, $J = 3.5$ Hz, H-5), 6.92 (d, $J = 3.5$ Hz, H-4), 7.26–7.58 (m, 19H, Ar–H) ppm; EI-MS (m/z, %) = 502 [M$^+$, 2], 438 [M$^+$–SO$_2$, 100]; UV (EtOH): λ_{max} (log ε) = 220 (4.1), 263 (3.1) nm; IR: 1136, 1296 (SO$_2$) cm^{-1}; Anal. Calcd for C$_{30}$H$_{21}$F$_3$O$_2$ S. (502.55): C, 71.70; H, 4.21; S, 6.38%. Found: C, 71.79; H, 4.27; S, 6.48%.

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