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Competitive Photochemical Pathways in the Rearrangement of Tetrasubstituted 4*H*-Thiopyrans

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Summary. The photoisomerization of 4,4-dialkyl-2,6-diphenyl-4*H*-thiopyrans and 4-benzyl-2,4,6-triphenyl-4*H*-thiopyran was investigated and compared with those of the 2,4,4,6-tetraaryl- and 4-alkyl-2,4,6-triaryl-4*H*-thiopyran analogues reported earlier. Obviously, the alkyl groups at the 4-positions of the 4*H*-thiopyrans strongly diminish the efficiency of the di-π-methane rearrangement and, contrastingly, a four-electron suprafacial [1,3]-sigmatropic rearrangement is found to be highly efficient.

Keywords. Di-π-methane rearrangement; Photoisomerization; [1,3]-Sigmatropic rearrangement; 2*H*-Thiopyran; 4*H*-Thiopyran.

Introduction

The photochemistry of 4*H*-thiopyrans has been the subject of study in our and other laboratories [1–4]. The previous investigations revealed that, under the influence of ultraviolet light, 2,4,4,6-tetraaryl- or 4-alkyl-2,4,6-triaryl-4*H*-thiopyrans **1** undergo isomerization to give only aryl migrated 2*H*-thiopyrans **3** through the bicyclic intermediates **2** (Scheme 1) with no alkyl group migration [2, 3]. Furthermore, in the latter work, the detailed mechanism of the photoisomerization behavior was also discussed with respect to the aryl-vinyl bonding interactions *via* di-π-methane rearrangement [5].

Considering the lack of alkyl migration in 4*H*-thiopyrans **1**, it seemed of considerable interest to study systems where the 4-substituents were both alkyl rather than aryl or aryl-alkyl groups. Accordingly, new tetrasubstituted 4,4-dimethyl-2,6-diphenyl-4*H*-thiopyran (**4a**), 4-*tert*-butyl-4-methyl-2,6-diphenyl-4*H*-thiopyran (**4b**), and 4-benzyl-4-methyl-2,6-diphenyl-4*H*-thiopyran (**4c**) (Scheme 2) were selected for synthesis and study.

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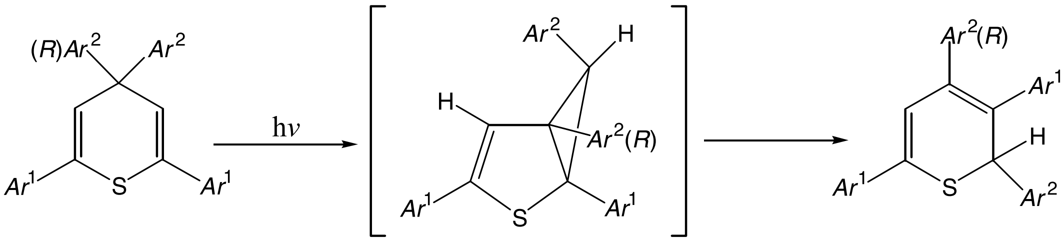
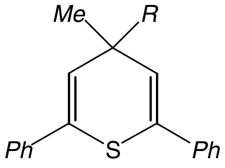


1 **2** **3**

Scheme 1



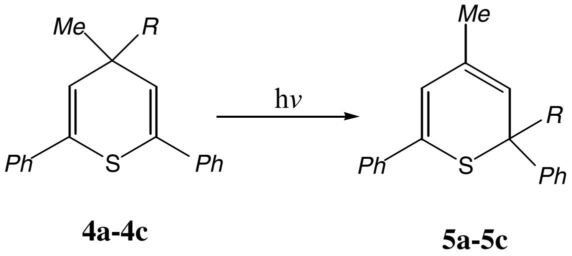
	R
4a:	*Me*
4b:	*tBu*
4c:	CH$_2$*Ph*

Scheme 2

Results and Discussion

To study the effects of 4,4-dialkyl substituents on the photoisomerization of tetrasubstituted 4*H*-thiopyrans, irradiation of degassed solutions of 4-alkyl-4-methyl-2,6-diphenyl-4*H*-thiopyrans **4a**–**4c** in benzene-d$_6$ was performed in sealed pyrex or quartz NMR tubes by an unfiltered low-pressure mercury lamp with a transmission maximum at 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.

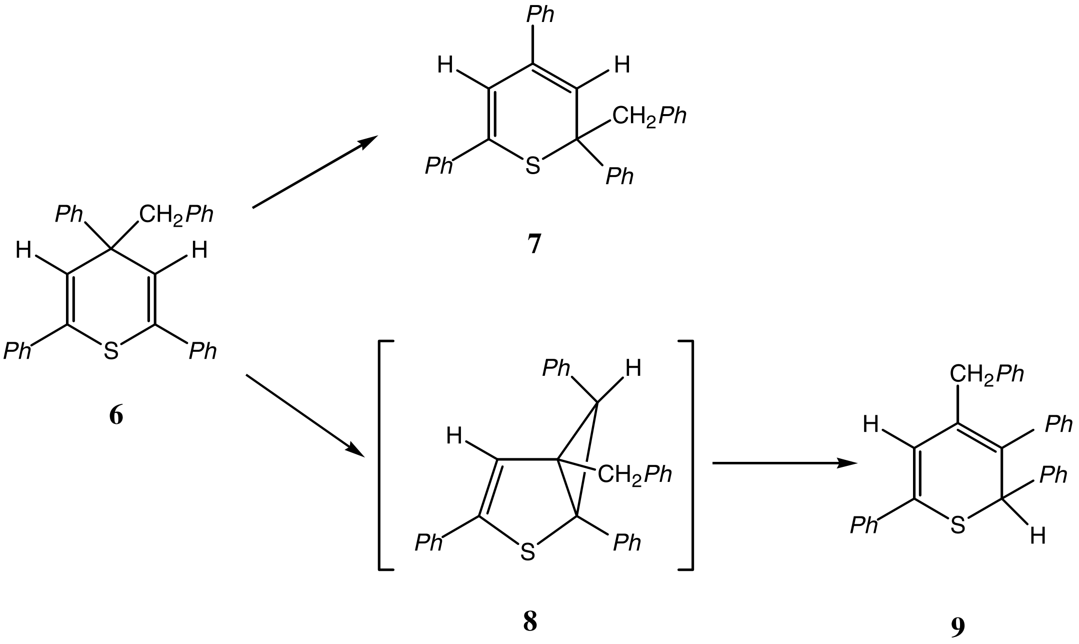
Irradiation through pyrex of **4a** in bezene-d$_6$ under experimental conditions identical to those used with the previously reported 2,4,4,6-tetraaryl- or 4-alkyl-2,4,6-triaryl-4*H*-thiopyrans **1** [2, 4–5] failed to give any photoproduct, even on prolonged time of 7 h, whereas under vigorous conditions irradiation through quartz of **4a** in benzene-d$_6$ after 1 h gave 13% of the photoisomer **5a**, 43% of unchanged **4a**, and 44% of unidentifiable decomposition products. However, on irradiation of **4b**–**4c** (Scheme 3) in pyrex NMR tubes in benzene-d$_6$ under identical experimental conditions as those of **4a** singlets at $\delta = 0.99$ (CMe$_3$), 1.10 (Me), and 5.79 (H-3, H-5) ppm for **4b** and 1.18 (Me), 2.73 (CH$_2$), and 5.64 (H-3, H-5) ppm for **4c** gradually decreased, while two new sets of signals appeared at $\delta = 1.09$ (s, CMe$_3$), 1.80 (d, Me), 5.92 (br q, H-3), and 6.09 (s, H-5) ppm for **5b** and 1.77 (d, Me), 3.42 (s, CH$_2$), 6.21 (br q, H-3), and 6.92 (s, H-5) ppm for **5c**. At the end of irradiations only the



Scheme 3

signals assigned to the photoproducts **5b**–**5c** are observable in the ^{1}H NMR spectra with no signs of byproducts, which indicated a selective and nearly quantitative transformation of 4*H*-thiopyrans **4b**–**4c** to 2*H*-thiopyrans **5b**–**5c**. The structural difference between the photoproducts **5a**–**5c** with those of a di-π-methane one are pretty evident from the allylic coupling between H-3 and the CH_3 groups.

In another experiment, irradiation of 4-benzyl-2,4,6-triphenyl-4*H*-thiopyran (**6**) was performed in benzene-d_6 under conditions identical to those of **4a** using a pyrex NMR tube. In the ^{1}H NMR spectrum of **6**, the singlets at $\delta = 3.19$ (CH_2) and 5.96 (H-3, H-5) ppm gradually decreased, while three new sets of signals appeared at $\delta = 3.49$ (s, CH_2), 6.14 (d, H-3), and 6.78 (d, H-5) ppm for **7**, at $\delta = 2.18$ (s, H-6), 3.46 (s, CH_2), and 5.44 (s, H-4) ppm for intermediate **8**, and at $\delta = 3.72$ (s, CH_2), 4.64 (s, H-2), and 6.6 (s, H-5) ppm for **9** (Scheme 4). The signals characteristic of intermediate **8** appear in the spectrum at an early stage of photoisomerization, then the signals of product **9** become detectable on progress of



Scheme 4

the reaction. At the end of irradiation only the signals assigned to photoproducts **7** and **9** are observable in a ratio of 5.5 to 1.0 with no signs of byproducts.

In conclusion, in dramatic contrast to the photoisomerization of 2,4, 4,6-tetraaryl- and 4-alkyl-2,4,6-triaryl-4*H*-thiopyrans **1**, photolysis of the 4,4-dialkyl-2,6-diphenyl-4*H*-thiopyrans **4a**–**4c** failed to produce any di-π-methane photorearrangement products but, instead, led to efficient four-electron suprafacial [1,3]-sigmatropic isomerization. Moreover, in 4-benzyl-2,4,6-triphenyl-4*H*-thiopyran (**6**) the benzyl-phenyl competition at the 4-position is highly in favor of the [1,3]-sigmatropic photorearrangement product **7**, which may indicate the operation of favorable interactions of the benzyl group in the transition state that leads to the photorearranged product.

Experimental

Melting points were measured on a Gallenkamp apparatus and are uncorrected. ^{1}H NMR sepectra were recorded on a Bruker AC-80 MHz FT-NMR spectrometer using *TMS* as internal strandard. UV spectra were taken on a Shimadzu 265-FW spectrometer. 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 tetrasubstituted 4*H*-thiopyrans **4a**–**4c** were synthesized by reactions of the corresponding organomagnesium salts (*R*Mg*X*; *R* = *M*e, *tBu*, CH$_2$*Ph*; *X* = Br, Cl) with 4-methyl-2,6-diphenylthiopyrylium perchlorate [6] according to the reported method [7]. The products were isolated by PLC on neutral alumina (petroleum ether 40–60°C:diethyl ether = 95:5) and purified by recrystallization from ethanol. Alternatively, **4a** was also synthesized by heating 3,3-dimethyl-1,5-diphenyl-1,5-pentanedione [8] with P$_4$S$_{10}$ in xylene at a bath temperature of 135–140°C [4c]. The 4*H*-thiopyran **6** was synthesized by reaction of benzyl magnesium bromide with 2,4,6-triphenylthiopyrylium perchlorate according to the method reported earlier [9].

4,4-Dimethyl-2,6-diphenyl-4H-thiopyran (**4a**, C$_{19}$H$_{18}$S)

Colorless crystals, mp 90°C; MS: m/z (%) = 278 (M$^{\bullet+}$, 22), 264 (M–CH$_2$, 64), 262 (M–CH$_4$, 100); UV (*Me*OH): λ_{max} (log ε) = 234 (4.27), 275 (sh) nm; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.16$ (s, 2Me), 5.70 (s, H-3, H-5), 7.02–7.65 (m, 10H, Ph) ppm.

4-tert-Butyl-4-methyl-2,6-diphenyl-4H-thiopyran (**4b**, C$_{22}$H$_{24}$S)

Colorless crystals, mp 72–73°C; MS: m/z (100) = 320 (M$^{\bullet+}$, 5), 262 (M–C$_4$H$_{10}$, 100), 246 (35); UV (*Et*OH): λ_{max} (log ε) = 255 (4.04), 275 (sh) nm; ^{1}H NMR (C$_6$O$_6$): $\delta = 0.99$ (s, CMe$_3$), 1.10 (s, Me), 5.79 (s, H-3, H-5), 7.07–7.65 (m, 10H, Ph) ppm.

4-Benzyl-4-methyl-2,6-diphenyl-4H-thiopyran (**4c**, C$_{25}$H$_{22}$S)

Colorless crystals, mp 82.5–83.5°C; MS: m/z (%) = 354 (M$^{\bullet+}$, 19), 263 (M–CH$_2$Ph, 100), 262 (M–MePh, 20); UV (*Et*OH): λ_{max} (log ε) = 237 (4.32), 275 (sh) nm; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.18$ (s, Me), 2.73 (s, CH$_2$), 5.64 (s, H-3, H-5), 7.03–7.63 (m, 15H, Ph) ppm.

4-Benzyl-2,4,6-triphenyl-4H-thiopyran (**6**, $C_{30}H_{24}S$)

Colorless crystals, mp 111–112°C; MS: m/z (%) = 416 ($M^{\bullet +}$, 17), 325 ($M–CH_2Ph$, 100); UV (*Et*OH): λ_{max} (log ε) = 234 (4.58) nm; ^{1}H NMR (C_6D_6): δ = 3.19 (s, CH_2), 5.96 (s, H-3, H-5), 6.84–7.53 (m, 20H, Ph) ppm.

General Procedure for Photolysis

Sample solutions were prepared by dissolving 2×10^{-5} mol of **4a**–**4c** and **6** in 0.4 cm^3 of benzene-d_6 in a pyrex or quartz NMR tube, and then they were degassed and sealed under Ar. Irradiations were carried out by a low-pressure mercury lamp with a transmission maximum of $\lambda = 254$ nm at room temperature. The progress of the photochemical reactions was followed by ^{1}H NMR spectroscopy and TLC at different time intervals. The variations of 4*H*-thiopyrans **4a**–**4c** and **6** mol fractions during the photolysis procedure were measured by integration of the characteristic H-3 and H-5 signals in the ^{1}H NMR spectra of the reaction mixtures.

Photoproducts

At the end of irradiations in benzene-d_6 solutions, the 4*H*-thiopyrans **4b**–**4c** and **6** were converted selectively to their isomeric 2*H*-thiopyrans with over 90% yield as evidenced by ^{1}H NMR spectra. However, in transformation of **4a** to **5a** only about 13% of photoproduct **5a** could be detected. The photoproducts were isolated by PLC on neutral alumina with petroleum ether 40–60°C as eluent and purified by recrystallization from ethanol.

2,4-Dimethyl-2,6-diphenyl-2H-thiopyran (**5a**, $C_{19}H_{18}S$)

Pale yellow crystals, mp 70–71°C; MS: m/z (%) = 278 ($M^{\bullet +}$, 17), 263 (M–Me, 78), 262 ($M–CH_4$, 100); UV (*Me*OH): λ_{max} (log ε) = 243 (4.29), 328 (4.48) nm; ^{1}H NMR ($CDCl_3$): δ = 1.79 (s, Me-2), 2.02 (d, J = 1.45 Hz, Me-4), 5.50 (br q, J = 1.45 Hz, H-3), 6.4 (s, H-5), 7.21–7.70 (m, 10H, Ph) ppm.

2-tert-Butyl-4-methyl-2,6-diphenyl-2H-thiopyran (**5b**, $C_{22}H_{24}S$)

Pale yellow crystals, mp 109–110°C; MS: m/z (%) = 320 ($M^{\bullet +}$, 7), 262 ($M–C_4H_{10}$, 100); UV (*Et*OH): λ_{max} (log ε) = 238 (3.76), 253 (4.24), 336 (3.32) nm; ^{1}H NMR ($CDCl_3$): δ = 1.07 (s, CMe_3), 2.02 (d, J = 1.45 Hz, Me), 5.98 (br q, J = 1.45 Hz, H-3), 6.24 (s, H-5), 7.10–7.70 (m, 10H, Ph) ppm.

2-Benzyl-4-methyl-2,6-diphenyl-2H-thiopyran (**5c**, $C_{25}H_{22}S$)

Pale yellow crystals, mp 107–108°C; MS: m/z (%) = 354 ($M^{\bullet +}$, 7), 263 ($M–CH_2Ph$, 100) 262 (M–MePh, 33); UV (*Et*OH): λ_{max} (log ε) = 250 (3.91), 265 (sh), 340 (3.73) nm; ^{1}H NMR ($CDCl_3$): δ = 2.0 (d, J = 1.8 Hz, Me), 3.41 (s, CH_2), 5.66 (br q, J = 1.8 Hz, H-3), 6.35 (s, H-5), 6.80–7.58 (m, 15H, Ph) ppm.

2-Benzyl-2,4,6-triphenyl-2H-thiopyran (**7**, $C_{30}H_{24}S$)

Pale yellow crystals, mp 156.5–157.5°C; MS: m/z = 416 ($M^{\bullet +}$, 3), 325 ($M–CH_2Ph$, 100), 248 ($M–CH_2Ph–Ph$, 53); UV (*Et*OH): λ_{max} (log ε) = 259 (4.34), 348 (3.74) nm; ^{1}H NMR ($CDCl_3$): δ = 3.53 (s, CH_2), 6.09 (d, J = 1 Hz, H-3), 6.81 (d, J = 1 Hz, H-5), 7.10–7.59 (m, 20H, Ph) ppm.

The structures of photoproducts **5a**–**5c** and **7** were also confirmed by authentic syntheses [7a]. Attempts failed to isolate photoproduct **9** from the reaction mixture.

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