A Mechanistic Approach to Photochemical Behavior of 4-Anisyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide
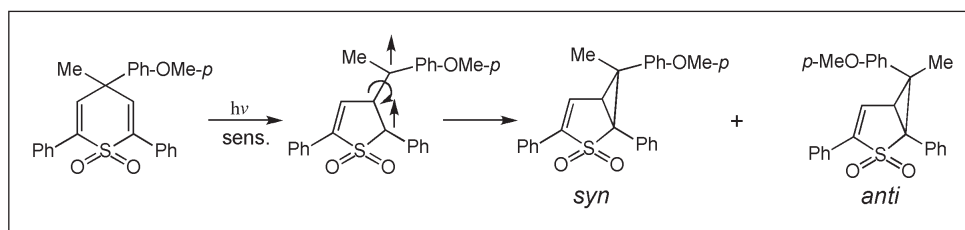
Ghasem Rezanejadebardajee, Farnaz Jafarpour and Hooshang Pirelahi*

Department of Chemistry, University of Tehran, PO Box 13145-143, Tehran, Iran
Received January 31, 2005

Photoisomerization of 4-anisyl-4-methyl-2,6-diphenyl-4*H*-thiopyran-1,1-dioxide is described in the presence of a sensitizer and new mechanistic features are proposed. The relative molar ratios of the stereoselective photoproducts compared in the presence and the absence of sensitizer in different concentrations of the starting material using hplc. The results observed are discussed on the basis of a triplet excited state thia-di-π-methane rearrangement.

Introduction.

Enormous efforts have been expended on the photochemical behavior of 4*H*-thiopyrans [1-4] and their sulfone derivatives [5,6]. 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 **1** [7], which unlike those of the previously reported tetraaryl analogs [8], upon irradiation with low-pressure mercury lamp underwent a thia-di-π-methane rearrangement in high regioselectivity to form two bicyclic stereoisomers *anti*-**2** and *syn*-**2** without SO₂ extruded byproducts. Due to the lack of reports on the mechanistic features of this rearrangement in 4*H*-thiopyran-1,1-dioxides, the present investigation was undertaken to determine the effect of sensitizer on the efficiencies of the stereoselective photoproducts.
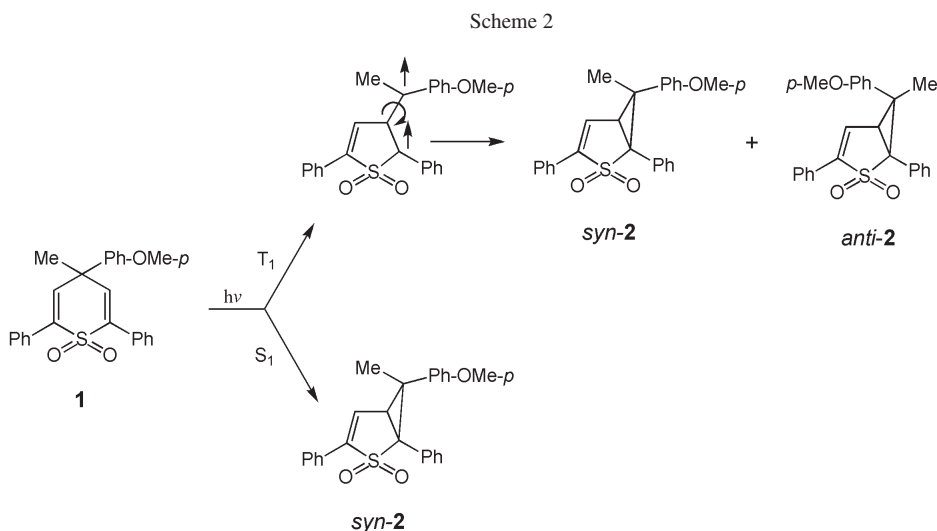
Scheme 1
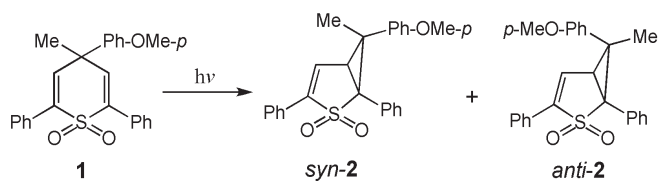
Results and Discussion.

In order to select the suitable solvent for photoisomerization, the photolyses of the compound **1** were performed in different solvents such as acetone, acetonitrile, methanol and chloroform, where the highest yields of the photoproducts obtained in chloroform. Then, to select the most efficient sensitizer, irradiation of the 4*H*-thiopyran was carried out in the presence of catalytic amounts (high enough that all of the light is absorbed by the sensitizer and not by the starting material) of various sensitizers such as acetone, acetophenone, anthraquinone, benzene, benzophenone and hydroquinone were investigated in chloroform solutions, where the best results were obtained with anthraquinone. Therefore, the photolyses of degassed 3.7×10^{-4} *M* solutions of **1** in chloroform in the presence and the absence of catalytic amount of anthraquinone were performed and the results compared with each other.

First, we carried out the experiments in quartz sealed nmr tubes by a low-pressure mercury lamp with a transmission maximum at 254 nm (85% transmission and 15% transmitted light from 254-579 nm) under an argon atmosphere at room temperature, which led to reaction mixtures with very little or no desired bicyclic photoproducts. Due to this unexpected result, we concluded that the bicyclic photoproducts might be particularly susceptible to secondary photolysis at higher energy wavelengths, as both of them have large absorption extinction coefficients at wavelengths approximately 265 nm. Then, to avoid the secondary photolysis problem, all the irradiations were carried out in sealed pyrex nmr tubes in the same conditions. The reactions were followed by hplc and the chromatograms recorded at different time intervals.

Upon irradiation of **1** in the presence and the absence of sensitizer the characteristic ^{1}H nmr signals of the compound at δ 1.84 (s, CH₃), 3.82 (s, CH₃O), and 6.30 (s, H-3, H-5) gradually decreased while the two characteristic signals appeared at δ 1.26 (s, CH₃), 3.02 (d, J = 3.5 Hz, H-5), 3.76 (s, CH₃O), and 6.82 (d, J = 3.5 Hz, H-4) ppm for *anti*-**2** and 1.83 (s, CH₃), 3.58 (d, J = 3.9 Hz, H-5), 3.68 (s,

CH$_3$O), and 7.07 (d, J = 3.9 Hz, H-4) ppm for *syn*-**2**. The variations in molar ratios of each photoproduct during the irradiation were determined by the area of characteristic peaks in hplc using calibration curves of the isolated photoproducts *anti*-**2** and *syn*-**2**. The results are summarized in Tables 1 and 2. As it is obvious, in the absence of sensitizer the yields of two bicyclic photoproducts were low and after 10 minutes of irradiation they reach to a maximum yield with approximately the same amounts which is consistent with an inefficient intersystem crossing to proceed through T$_1$ for direct photoexcitation. As triplet-triplet energy transfer might allow for the efficient indirect production of such triplets, therefore sensitization was needed for optimum yields. So, the irradiation was repeated in the presence of sensitizer, where it was found that the yield increases and the ratio of the *anti*-isomer is more than 20 times of the corresponding *syn*-isomer. In addition, the reaction was clearly quenched in the presence of oxygen and hydroquinone. Hence, we concluded that the reaction takes place from the excited triplet state of the photosensitizer and proceeds *via* a radical pathway. Use of a sensitizer, which normally produces a triplet excited state, gives the triplet biradical. In the photosensitized decomposition the triplet biradical has a longer lifetime, and therefore more chance for bond rotation and loss of stereochemistry, since it must undergo a spin inversion before the ring can close. Therefore the formation of anti stereoisomer is rationalized by considering rotation around the C-C bond in the triplet intermediate as shown below.

Table 1

The yields (%) of photoproducts *anti*-**2** and *syn*-**2** on irradiation of 3.7×10^{-4} *M* solution of compound **1** in the absence of sensitizer.

Compounds/Time(min)	0	5	10	20	30
anti-**2** [a]	0	2.57	10.57	6.1	4.2
syn-**2** [b]	0	5.4	9.9	5.5	1.3

[a] The retention time of *syn*-**2** was 9.11min in a mixture of methanol-water; [b] The retention time of *anti*-**2** was 10.93 min in a mixture of methanol-water.

Table 2

The yields (%) of photoproducts *anti*-**2** and *syn*-**2** on irradiation of 3.7×10^{-4} *M* solution of compound **1** in the presence of anthraquinone.

Compound/Time (min)	0	5	10	20	30	45	60	90
anti-**2**	0	6	18.2	22	34.1	44	43	40.9
syn-**2**	0	0	1.8	1.7	1.7	1.8	2	2

interfering intermolecular side reactions, while increasing the concentration of compound **1** (Table 3) leads to decreasing the photoproducts. In high concentrations of the reactant the singlet excited state of the sensitizer formed by irradiation has not enough time to convert itself to triplet state through collision with reactant, so the yields of the photoproducts decrease. The results are in accordance with the intramolecular nature of the di-π-methane rearrangement.

Scheme 2

Moreover, the effect of concentration of the starting material on the ratios of photoproducts was investigated and the results are summarized in Tables 1, 3 and 4. As is evident from the Tables, by decreasing the concentration of compound **1** (Table 4) the yields of bicyclic photoproducts considerably increases due to the decreasing of

Table 3

The yields (%) of photoproducts *anti*-**2** and *syn*-**2** on irradiation of 5.0×10^{-4} *M* solution of compound **1**.

Compounds/Time(min)	0	5	10	20	30
anti-**2**	0	4.6	7.9	5.6	3.9
syn-**2**	0	4.3	7.4	4.7	2.9

Table 4

The yields (%) of photoproducts *anti*-**2** and *syn*-**2** on irradiation of
1.0×10⁻⁴ *M* solution of compound **1**.

Compounds/Time(min)	0	5	10	20	30
anti-**2**	0	29.7	35.6	15.8	12.1
syn-**2**	0	27	30.8	11.9	6.4

To gain a better picture of the conformational profile of the given compound and to determine the most stable conformation of the photoproducts, *ab initio* calculations performed at Hartree-Fock level using the 6-31G* basis set with full geometry optimization. We used the GAMESS program in the present *ab initio* calculations [9]. Results of *ab initio* calculations gave a rather flattened boat conformation for compound **1** in which the anisyl group rather than the methyl group is preferentially oriented toward the S atom. Furthermore, the calculated heats of formation revealed that the *anti*-**2** isomer is 1.46 Kcal/mol more stable than the *syn*-**2** isomer. These results are consistent with the results of experimental section. The full geometry optimized structures of the compounds **1** and **2** are presented in Figures 1 and 2 respectively.
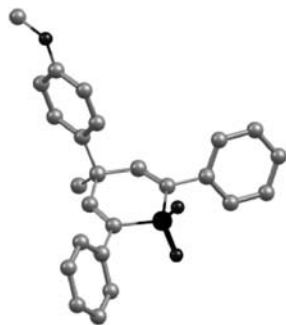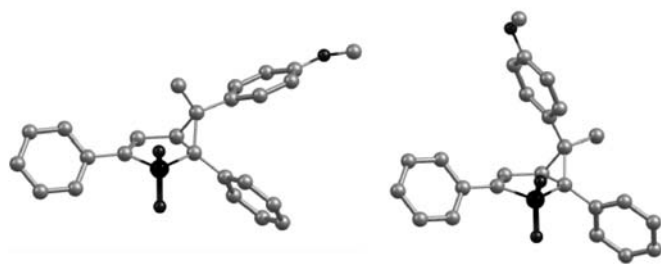

1

Figure 1

syn-**2**　　　　　　　　　*anti*-**2**

Figure 2

In conclusion the results showed that the thia-di-π-methane rearrangement in 4*H*-thiopyran-1,1-dioxides proceeds *via* an intramolecular non-concerted triplet excited state. Also, here we presented a route for the selective synthesis of bicyclic heterocycles not as readily constructed by other means.

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Uv and visible spectra were taken on a Shimadzu 265-FW spectrophotometer. Ir spectra were obtained on a Shimadzu ft-ir 4300 spectrophotometer in KBr disks. ¹H nmr spectra were recorded on Bruker Ac-500 MHz FT-nmr spectrometers relative to internal standard tetramethylsilane. Mass spectra were determined with a Finningan MAT-TSQ 70 mass spectrometer. The reactions followed by hplc using the SGX C18 column in the methanol-water system. Photolysis performed using a low- pressure mercury lamp with a transmission maximum at λ = 254 nm (85% transmission) and transmitted light from 254-579 nm (15% transmission).

Synthesis.

The 4*H*-thiopyran-1,1-dioxide **1** was synthesized by the reaction of the corresponding 4*H*-thiopyran with hydrogen peroxide in acetic acid according to the procedure reported earlier [5,10].

General Procedure for Photolysis.

Different solutions of 4*H*-thiopyran-1,1-dioxide **1** with a catalytic amount of various sensitizers were prepared in chloroform in nmr tubes, then degassed and sealed under argon atmosphere. Irradiations were carried out by a low-pressure mercury lamp at room temperature. The progress of the photochemical reactions was followed by hplc at different time intervals.

anti-6-Anisyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (anti-**2**).

Colorless crystals, mp 261-262°; ir (potassium bromide): 1139 and 1292 (SO₂) cm⁻¹; uv: λmax 267 nm (logε 2.9), 221 nm (logε 3.1); ¹H nmr (deuteriochloroform): δ 1.26 (s, 3H), 3.02 (d, 1H, 5-H, J = 3.5 Hz), 3.76 (s, 3H), 6.82 (d, 1H, 4-H, J = 3.5 Hz), 6.84-7.80 (m, 14H); ms: m/z 402 (6.6), 338 (100), 323 (98).

Anal. Calcld. for $C_{25}H_{22}O_3S$ (402.51): C, 74.58; H, 5.51; S, 7.97. Found: C, 74.73; H, 5.58; S, 7.87.

syn-6-Anisyl-6-methyl-1,3-diphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (syn-**2**).

Colorless crystals, mp 172-173°; ir (potassium bromide): 1139 and 1294 (SO₂) cm⁻¹; uv: λmax 265 nm (logε 3.2), 220 nm (logε 3.3); ¹H nmr (deuteriochloroform): δ 1.83 (s, 3H), 3.58 (d, 1H, 5-H, J = 3.9 Hz), 3.68 (s, 3H), 7.07 (d, 1H, 4-H, J = 3.9 Hz), 6.68-7.47 (m, 14H); ms: m/z 402 (5.7), 338 (100), 323 (98).

Anal. Calcld. for $C_{25}H_{22}O_3S$ (402.51): C, 74.58; H, 5.51; S, 7.97. Found: C, 74.71; H, 5.53; S, 8.11.

Acknowledgement.

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*　Corresponding author. E-mail: pirelahi@khayam.ut.ac.ir

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