Novel regioselective photochemical transformation of 4-methyl-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide

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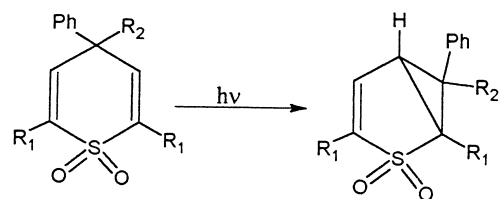*Department of Chemistry, University of Tehran, PO Box 13145-143, Tehran, Iran*

Abstract

On photolysis of 4-methyl-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide (**1d**) in chloroform solution with a low-pressure mercury lamp at $\lambda = 254$ nm under an argon atmosphere, a high regioselective rearrangement takes place via a *gem*-methylphenyl migration to yield two bicyclic stereoisomers *anti*-6-methyl-1,3,6-triphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (*anti*-**2d**) and *syn*-6-methyl-1,3,6-triphenyl-2-thiabicyclo[3.1.0]hex-3-ene-2,2-dioxide (*syn*-**2d**). The results observed are discussed in the light of a thia-di-π-methane rearrangement through a vinyl–vinyl bonding *interaction*. © 2001 Published by Elsevier Science B.V.

Keywords: 4H-thiopyrane-1,1-dioxide; Photoisomerization; Regioselectivity; Di-π-methane rearrangement

1. Introduction

In comparison with the enormous efforts expended in the photochemical behaviour of 4H-thiopyrans [1–8], relatively little attention has been paid to the subject of the photochemical transformation of interesting sulfone derivatives. According to our knowledge, this study is limited to few aryl derivatives only [9–11]. The thorough photochemical investigation of 4,4-diphenyl-4H-thiopyran-1,1-dioxide (**1a**) by Gravel and Leboeuf [9] showed that, upon direct photolysis or sensitized (acetone) condition, 6,6-diphenyl-2-thiabicyclo [3.1.0]hex-3-ene-2,2-dioxide (**2a**) along with a solvent addition photoproduct are formed in low yields. Recently, we reported on the synthesis and photoisomerization of 4,4-diphenyl-2,6-di(*p*-methoxyphenyl)-4H-thiopyran-1,1-dioxide (**1c**) which, unlike those of the other 2,4,6,6-tetraaryl-substituted sulfone derivatives [10], underwent rearrangement in high regioselectivity to the bicyclic photoproduct **2c** with no SO₂ extruded byproducts [11]. Here, in an extention of our work, we undertake the photolysis of 4-methyl-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide (**1d**) as a model of 4-alkyl sulfone derivatives. This investigation should provide further evidence of the generality of the regioselective photorearrangement in 4H-thiopyran-1,1-dioxide system as well as more insight into its detailed mechanism and also give access to novel stereoselective thiabicyclo-[3.1.0]hex-3-ene-2,2-dioxides.

1a-d   **2a-d**

a) R₁=H, R₂=Ph; b) R₁=R₂=Ph;
c) R₁=(p-MeO)C₆H₄, R₂=Ph; d) R₁=Ph, R₂=CH₃

2. Experimental details

Melting points were determined on a Gallenkamp melting point apparatus. UV and visible spectra were taken on a Shimadzu 265-FW spectrophotometer. Infrared spectra were measured in KBr with a Shimadzu FTIR-4300. The reactions were followed by HPLC using the SGX C18 column in the methanol–water system. NMR spectra were recorded with a Bruker AC-80 spectrometer; tetramethylsilane served as an internal standard. All photolyses were carried out using a low pressure mercury lamp.

2.1. Syntheses

The 4H-thiopyran-1,1-dioxide (**1d**) was synthesized by reaction of the corresponding 4H-thiopyran with hydrogen

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peroxide in hot acetic acid according to the method previously described [12].

2.1.1. 4-Methyl-2,4,6-triphenyl-4H-thiopyran (1d)

Colourless crystals, m.p. 198–198.5°C (from EtOH). UV, λ_{max} (MeOH) (nm) (log ε): 233 (4.32). IR: 1136, 1290 cm^{-1} (SO$_2$). ^{1}H NMR (CDCl$_3$), δ: 1.81 (3H, s, CH$_3$), 6.32 (2H, s, H-3, H-5), 7.25–7.74 (15H, m, Ar).

2.2. General procedure for photolysis

A 1×10^{-3} M sulfone solution of 1d was prepared in chloroform-d$_1$ in an NMR tube then was degassed and sealed under an argon atmosphere. Irradiation was carried out with a low pressure mercury lamp using an UV light with $\lambda = 254$ nm at room temperature. The progress of the photochemical reaction was followed by ^{1}H NMR and HPLC at different time intervals.

2.3. Photoproducts

Irradiation at 254 nm in chloroform led to a mixture of two photoproducts anti-2d and syn-2d accompanied by the starting material 1d as evidenced by HPLC. Separation of the mixture was carried out using preparative scale TLC on alumina by increasing the order of polarity of the eluent (petroleum-ether–ether).

2.3.1. anti-6-Methyl-1,3,6-triphenyl-2-thiabicyclo[3.1.0]-hex-3-ene-2,2-dioxide (anti-2d)

Colourless crystals, m.p. 209–210°C (from EtOH). UV, λ_{max} (MeOH) (nm) (log ε): 264 (3.72). IR: 1140, 1298 cm^{-1} (SO$_2$). ^{1}H NMR (CDCl$_3$), δ: 1.27 (3H, s, CH$_3$), 3.04 (1H, d, H-5; $J = 3.8$ Hz), 6.86 (1H, d, H-4; $J = 3.8$ Hz), 7.23–7.46 (15H, m, Ar).

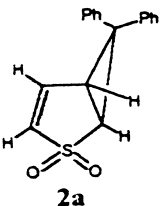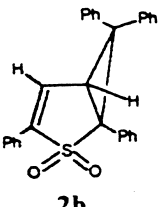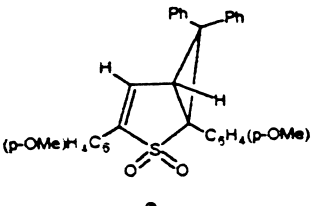### 2.3.2. syn-6-Methyl-1,3,6-triphenyl-2-thiabicyclo[3.1.0]-hex-3-ene-2,2-dioxide (syn-2d)

Colourless crystals, m.p. 168–169°C (from EtOH). UV, λ_{max} (MeOH) (nm) (log ε): 265 (3.29). IR: 1138, 1296 cm^{-1} (SO$_2$). ^{1}H NMR (CDCl$_3$), δ: 1.84 (3H, s, CH$_3$), 3.71 (1H, d, H-5; $J = 3.8$ Hz), 7.02 (1H, d, H-4; $J = 3.8$ Hz), 6.99–7.46 (15H, m, Ar).
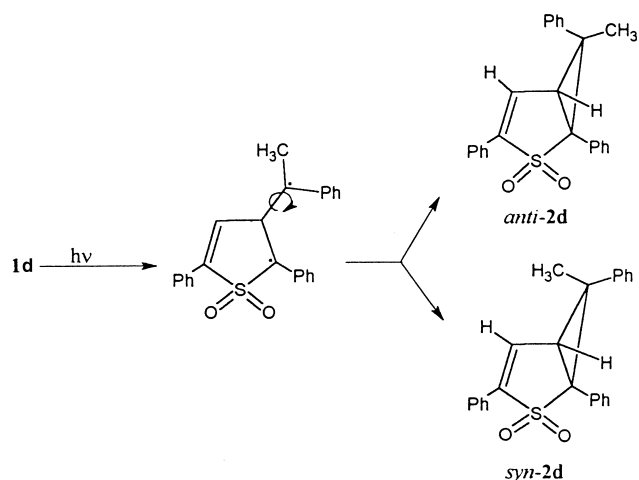
3. Results and discussion

To study the photochemical rearrangement, irradiation of a degassed 1×10^{-3} M solution of 4-methyl-2,4,6-triphenyl-4H-thiopyran-1,1-dioxide (1d) was performed in a sealed NMR tube by a low pressure mercury lamp at $\lambda = 254$ nm under an argon atmosphere at room temperature. The reaction was followed by ^{1}H NMR and quantitative analysis was performed by HPLC at different time intervals.

In the ^{1}H NMR, the singlet of 1d at 6.32 ppm (H-3, H-5) gradually decreased, while new sets of doublets appeared at

Table 1
^{1}H NMR parameters of bicyclo[3.1.0]hex-3-ene-2,2-dioxide derivatives

Compound	Proton	Multiplicities, J (Hz)	δ (ppm)	Ref.
2a	H$_1$ H$_3$ H$_4$ H$_5$	dd, $J_{1,5} = 6.5$; $J_{1,3} = 1.5$ dd, $J_{3,4} = 6.5$; $J_{3,1} = 1.5$ dd, $J_{4,3} = 6.5$; $J_{4,5} = 3.0$ dd, $J_{5,1} = 6.5$; $J_{5,4} = 3.0$	3.49 6.16 6.88 3.29	[9]
2b	H$_4$ H$_5$	d, 3.6 d, 3.6	6.91 3.96	[10]
2c	H$_4$ H$_5$	d, 3.6 d, 3.6	6.77 3.85	[11]

Scheme 1. Odd-electron representation of the reaction pathways for the formation of two stereoisomers *anti*-**2d** and *syn*-**2d**.

3.04, 3.71 (H-5) and 6.86, 7.02 ppm (H-4) for *anti*-**2d** and *syn*-**2d** with no signs of other protons for SO_2 extrusions of **1d** to the tetrasubstituted cyclopentadiene byproducts which were reported earlier for some tetraarylsubstituted sulfone derivatives [10]. Although the vinyl proton H-4 and cyclopropyl proton H-5 data are consistent with the bicyclo[3.1.0]hex-3-ene-2,2-dioxide structures proposed, we present in Table 1 a series of pertinent NMR values taken from our and other works. Using these data, it is readily apparent that bicyclic sulfones *anti*-**2d** and *syn*-**2d** have NMR spectra which are related to structures originating from vinyl migration; indeed, in these structures, H-4 and H-5 appear as doublets with $J = 3.8$ Hz centred in the range of 6.7–6.9 and 3.2–3.9 ppm, respectively, where H-5 for *syn*-**2d** is shifted more downfield relative to *anti*-**2d** because of the stronger anisotropic deshielding effects of two *syn*-phenyl groups.

The formation of two stereoisomers is rationalized by considering rotation around the C–C bond as depicted in Scheme 1. Such a mixture of photoproducts and absence of phenyl migrated products through a phenyl–vinyl pathway or SO_2 extruded byproducts are consistent with the regioselectivity in favour of a vinyl–vinyl thia-di-π-methane mechanism proposed earlier for the sulfone derivatives [9,13].

Due to the stability of photoproducts at room temperature and the selectivity of photochemical transformation, we were able to separate and isolate *anti*-**2d** from *syn*-**2d**. Isolation of photoproducts in a pure form let us determine the variation in molar ratios of each bicyclic stereoisomer species during the reaction by the area of characteristic peaks in HPLC using the corresponding calibration curves of the isolated photoproducts *anti*-**2d** and *syn*-**2d** (Table 2). Because of the conversion of the primary bicyclic photoproducts to other unidentified products during the reaction, the isolation of *anti*-**2d** and *syn*-**2d** in high yields was unsuccessful.

Table 2
The yield (%) of *anti*-**2d** and *syn*-**2d** during 90 min of photoisomerization. The values are an average for two different runs measured by the area of HPLC characteristic peaks in the reaction mixture

Compound	Time (min), chloroform						
	5	10	20	30	45	60	90
anti-**2d**[a]	4.0	17.0	16.8	3.2	3.0	2.1	2.0
syn-**2d**[b]	25.0	69.0	62.0	21.2	18.9	18.6	16.0

[a] The retention time of *anti*-**2d** was 4.37 min in a mixture of methanol–water (80:20).

[b] The retention time of *syn*-**2d** was 4.17 min in a mixture of methanol–water (80:20).

4. Conclusions

The selective stereochemistry in *gem*-methylphenyl migration of **1d** is fully in accordance with a non-concerted process involving rotation around the C–C bond. Considering the photoinduced regioselectivity in the formation of *anti*-**2d** and *syn*-**2d**, the thia-di-π-methane rearrangement observed should proceed efficiently from the excited triplet state as proposed by Zimmerman and Diehl [13], Gravel and Leboeuf [9] for vinyl moieties bonded by a heteroatom with no unshared electrons.

Acknowledgements

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