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Synthesis and Photoisomerization Of 4,4-Diphenyl-2,6-Di(p-Methoxyphenyl)-4H-Thiopyran-1,1-Dioxide, An Approach To The Regioselectivity in Photorearrangement of 2,4,4,6-Tetraaryl-4H-Thiopyran-1,1-Dioxides

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SYNTHESIS AND PHOTOISOMERIZATION OF 4,4-DIPHENYL-2,6-DI(p- METHOXYPHENYL)-4H-THIOPYRAN-1,1- DIOXIDE, AN APPROACH TO THE REGIOSELECTIVITY IN PHOTOREARRANGEMENT OF 2,4,4,6-TETRAARYL-4H-THIOPYRAN- 1,1-DIOXIDES

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Synthesis and photoisomerization of the new sulfone derivative **1c** is described. Upon photolysis at 254 nm the sulfone **1c**, unlike those of the model compound **1b** and the other 2,4,4,6-tetraarylsubstituted sulfone derivatives, undergoes rearrangement in high regioselectivity to the bicyclic photoproduct **2c**. The isolation of bicyclic photoproducts **2b** and **2c** under our experimental conditions led us to determine the molar ratios of these species during the transformations using HPLC.

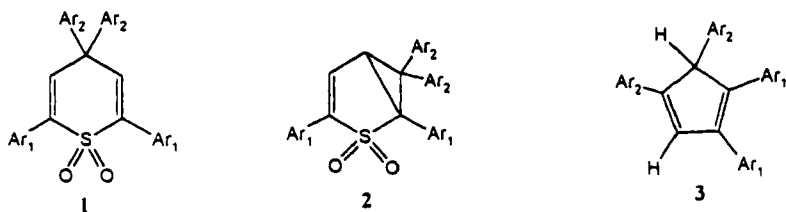
Keywords: 4H-Thiopyran-1,1-dioxide; regioselectivity; photoisomerization

INTRODUCTION

Recently, interesting photochemical behavior of 4H-thiopyrans have been studied extensively in our and other laboratories¹⁻⁶, however on sulfone derivatives these studies are limited only to 4,4-diphenyl-4H-thiopyran-1,1-dioxide and some of the tetraarylsubstituted sulfones with general structure **1**^{7,8}. Upon direct photolysis at 254 nm or sensitized (in acetone) photolysis at 350 nm the 4,4-diphenyl-4H-thiopyran-1,1-dioxide

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1a undergoes rearrangement to 6,6-diphenyl-2-thiabicyclo[3.1.0]hexen-2,2-dioxide **2a** accompanied by a solvent addition product 3-methoxy-4,4-diphenyl-2,3-dihydro-4H-thiopyran-1,1-dioxide⁷. On irradiation of some 2,4,4,6-tetraaryl-4H-thiopyran-1,1-dioxides **1** ($\text{Ar}_1=\text{C}_6\text{H}_5$, $\text{Ar}_2=\text{C}_6\text{H}_5$, 4-($t\text{-C}_4\text{H}_9$) C_6H_4 , 4- $\text{CH}_3\text{C}_6\text{H}_4$, 4- FC_6H_4 and $\text{Ar}_1=4\text{-(}t\text{-C}_4\text{H}_9\text{)-C}_6\text{H}_4$, 4- $\text{CH}_3\text{C}_6\text{H}_4$, 4- FC_6H_4 , $\text{Ar}_2=\text{C}_6\text{H}_5$) with high pressure mercury lamp the corresponding 1,2,4,5-tetrasubstituted cyclopentadienes with general structure **3** were obtained as the main photoproducts through SO_2 extrusion along with the bicyclic photoproduct **2** and the other minor components⁸.



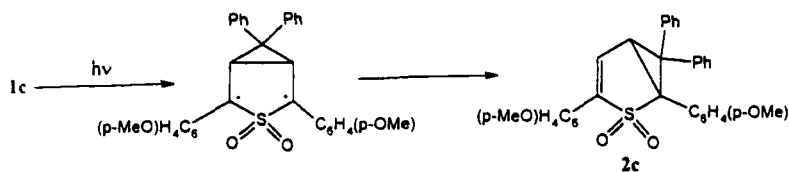
a) $\text{Ar}_1=\text{H}$, $\text{Ar}_2=\text{C}_6\text{H}_5$; b) $\text{Ar}_1=\text{Ar}_2=\text{C}_6\text{H}_5$; c) $\text{Ar}_1=4\text{-CH}_3\text{OC}_6\text{H}_4$, $\text{Ar}_2=\text{C}_6\text{H}_5$

The present study deals with the preparation and photochemistry of a new compound of general structure **1**, 4,4-diphenyl-2,6-di(*p*-methoxyphenyl)-4H-thiopyran-1,1-dioxide, having electron donating groups in para positions of 2,6-diphenyl substituents. Such a model should provide further insight into the probable photochemical mechanism in comparison with the other tetraaryl analogues and also furnishes an access to a new hetero bicyclo[3.1.0] system and its chemistry.

RESULTS AND DISCUSSION

In order to study the photochemical transformation behavior of **1c** in comparison with the model compound **1b**, $1 \times 10^{-3}\text{M}$ solutions of sulfones **1b** and **1c** were prepared in chloroform. Irradiation was carried out in sealed NMR tubes with a low pressure mercury lamp at $\lambda=254\text{ nm}$ under an argon atmosphere at room temperature. The reactions were followed by $^1\text{H-NMR}$ and the quantitative analyses were performed by HPLC at different time intervals.

In $^1\text{H-NMR}$ spectra, the singlets of **1b** and **1c** at 6.70 and 6.62 (H-3,-5) ppm gradually decreased, while two new sets of doublets appeared at 6.91, 6.77 (H-4) ppm and 3.96, 3.85 (H-5) ppm for **2b** and **2c** respectively, as well as at 7.33 (H-3) ppm and 5.25 (H-5) ppm for cyclopentadiene **3b**, where no signals for **3c** could be detected (Table I). That the corresponding cyclopentadiene as photoproduct of **1c** is not formed contrasts sharply with that of the model compound **1b** and the other 2,4,4,6-tetraaryl-4H-thiopyran-1,1-dioxides containing $-\text{CH}_3$, $-\text{F}$ or $t\text{-C}_4\text{H}_9$ groups in para positions of the phenyl substituents. Considering that the excitation energy tends to localize in minimum MO energy and that the electronically excited species react by pathways to minimize energy as the reactions coordinates are traversed⁹, the resulting behavior reveal that by substitution of two electron donating methoxy groups at para positions of 2,6-phenyl substituents, the energy content of the transition state in the vinyl-vinyl di- π -methane pathway becomes lower than the phenyl-vinyl di- π -methane one and the rearrangement takes place with high regioselectivity to give solely **2c**.



This result is in accordance with the well documented fundamental systems that have been shown by Zimmerman, Gravel and Leboeuf^{9,7}.

TABLE I The characteristic chemical shifts for 4H-thiopyran-1,1-dioxide **1b** and **1c**, bicyclic photoproducts **2b** and **2c** and cyclopentadiene **3b** in chloroform-d

Compound	H-3,-5	OCH3	H-4	H-5	H-3	H-5
1b	6.70	—				
1c	6.62	3.81				
2b			6.91_	3.96		
2c			6.77	3.85		
3b					7.33	5.25

We could also determine molar ratios of the bicyclic species during the reaction by the area of characteristic peaks in HPLC using the corresponding calibration curves of the isolated **2b** and **2c** (Table II). Due to the transformations of the primary bicyclic photoproducts to other unidentified products during the reaction, the isolation of **2b** and **2c** in high yields was unsuccessful.

TABLE II The yields (%) of **2b** and **2c** during the 90 minutes of photoisomerization under identical experimental conditions. The values are an average of three runs measured by the area of HPLC characteristic peaks in the reaction mixtures

Compound	Time(min), chloroform							
	5	10	15	20	30	45	60	90
2b ^a	27	25	15	11	9	3	0	0
2c ^b	29	25	12.5	9.8	8	4.5	2	0

a. The retention time of **2b** was 4.5 min in a mixture of methanol-water(78:22).

b. The retention time of **2c** was 4.15 min in a mixture of methanol-water(80:20).

EXPERIMENTAL

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

Syntheses

4H-Thiopyran-1,1-dioxide **1c** was synthesized from the reaction of the corresponding 4H-thiopyran (1 mmole) with hydrogen peroxide 30% (1.6 mmole) in hot acetic acid (20 ml). The reaction mixture kept at 120°C until the transitionally formed 4H-thiopyran-1-oxide disappeared (the reaction followed by tlc), then it was cooled and poured on ice (40g). White precipitate was collected and recrystallized from ethanol to give **1c**

(90%). The model compound **1b** was synthesized by the method previously described⁸.

4,4-Diphenyl-2,6-di(*p*-methoxyphenyl)-4*H*-thiopyran-1,1-dioxide(1c)

Colorless crystals, m.p.: 198–199°C (from EtOH); UV: λ_{max} (MeOH) nm (log ϵ) 265 (3.26); IR: 1128 and 1290 cm^{-1} (SO_2); $^1\text{H-NMR}$, (CDCl_3) δ : 3.81 (3H,s,OMe), 6.62 (2H,s,H-3,5), 6.86–7.61 (18H,m,Ar₁,Ar₂).

General procedure for photolysis

$1 \times 10^{-3}\text{M}$ solutions of sulfones **1b** and **1c** were prepared in chloroform- d_1 in NMR tubes then degassed and sealed under an argon atmosphere. Irradiation was carried out with a low pressure mercury lamp using a monochromatic UV light with $\lambda=254$ nm at room temperature. The progress of the photochemical reaction was followed by $^1\text{H-NMR}$ and HPLC at different time intervals.

Photoproducts

In contrast to the model compound **1b** which converted to the main photoproduct 1,2,4,5-tetraphenylcyclopentadiene along with **2b** and the other minor photoproducts⁸, irradiation of **1c** gave the regioselective bicyclic compound **2c** as the main photoproduct which was isolated by chromatography and recrystallized from ethanol.

1,3-Di(*p*-methoxyphenyl)-6,6-diphenyl-2-thiobicyclo[3.1.0]hexen-2,2-dioxide(2c)

Colorless crystals, m.p.: 225–226°C: UV: λ_{max} (MeOH) nm (log ϵ) 290 (3.39). 225 (3.97); IR: 1138 and 1296 cm^{-1} (SO_2); $^1\text{H-NMR}$ (CDCl_3), δ : 3.74 (3H,s,OCH₃), 3.85 (1H,d,H-5), 6.77 (1H,d,H-4), 6.70–7.54 (18H,m,Ar₁,Ar₂).

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