Heteroatom Chemistry
Volume 17, Number 2, 2006

# Conformational Analysis of 2-Alkyl-4-methyl-2,6-diphenyl-2*H*-thiopyran Derivatives: A Combined Experimental and Theoretical Study

Farnaz Jafarpour and Hooshang Pirelahi

*Department of Chemistry, University of Tehran, P.O. Box 13145-143, Tehran, Iran*

*Received 14 September 2005; revised 29 October 2005*

ABSTRACT: *Some 2-alkyl-4-methyl-2,6-diphenyl-2H-thiopyrans were synthesized, and the crystal structure of 2-tert-butyl-4-methyl-2,6-diphenyl-2H-thiopyran* **1** *was determined by single-crystal X-ray diffraction. X-ray crystallographic analysis and ab initio HF/6-31G(d) and B3LYP/6-31G(d) calculations revealed a favorable nonplanar half-chair conformation for these compounds in which two ethylene units were rotated relative to each other around the single bond. The most conspicuous feature was the orientation of alkyl and phenyl groups with respect to the S atom.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:142–147, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20192

## *INTRODUCTION*

Increasing interest has been focused on stereochemical aspects of substituted tetrahydro-2*H*-thiopyrans and their conformational analysis is an area of attraction for many groups [1–8]. It is confirmed that there is a preference by most substituents to occupy the equatorial positions on the chair conformers of these compounds. However, there are fewer reports on their unsaturated derivatives [9]. We are especially interested in the investigation of unsaturated 2*H*-thiopyran derivatives as a product of thermal rearrangement of the corresponding thiabenzens or a four-electron [1,3]-sigmatropic rearrangement in photoisomerization of 4*H*-thiopyrans (Scheme 1) [10]. The formation of such products could be explained by analytical or spectroscopical data, but arrangement of the groups required an additional confirmation by X-ray crystal structure analysis, since it is considered that there are two possible paths of migration for alkyl moiety in thermal and photochemical rearrangement.

The X-ray study reported in the present work assigns the structure **1a** to the mentioned 2*H*-thiopyran which adopts a half-chair conformation of the cyclohexadiene moiety with the more bulky group and S atom in the same side. In order to ascertain a rationale for the apparent stability of this conformer and to compare the results with the other possible derivatives of the compound (Scheme 2), we synthesized two more 2*H*-thiopyran derivatives **3, 5** and performed computer modelling studies on the both conformers of mentioned 2*H*-thiopyrans **1**, **3**, and **5** as well as some other hypothetical derivatives **2, 4**, and **6** using ab initio calculations utilizing the GAMMES programs [11]. The equilibrium geometries and zero-point energies of the two conformers were computed using the restricted Hartree–Fock functional as well as density functional theory in conjunction with the 6-31G(d) basis set.

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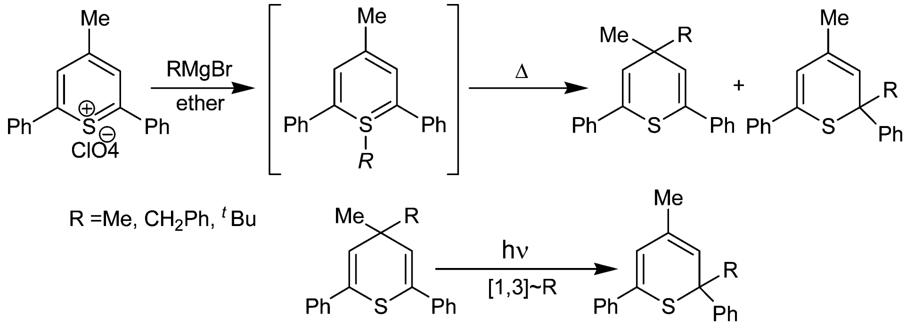
*Correspondence to:* Hooshang Pirelahi; e-mail: pirelahi@khayam.ut.ac.ir.

Contract grant sponsor: Research Council at the University of Tehran.
Contract grant number: 6102020/6d/02.



**SCHEME 1** Two possible mechanisms for the synthesis of 2*H*-thiopyran derivatives.

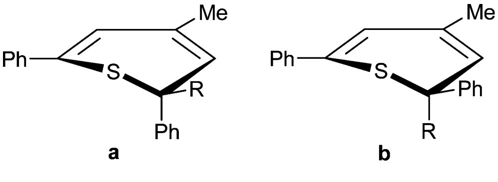
## *EXPERIMENTAL AND CALCULATIONS*

2*H*-thiopyrans **1, 3**, and **5** were prepared as a product of thermal rearrangement of the corresponding 1-alkyl-4-methyl-2,6-diphenylthiabenzene, obtained by the reaction of RMgBr (1 mmol) and 4-methyl-2,6-diphenylthiopyrylium perchlorate (1 mmol) in diethyl ether in room temperature as well as photochemical rearrangement of 4-alkyl-4-methyl-2,6-diphenyl-4*H*-thiopyran as a consequence of irradiation with a low pressure mercury lamp at $\lambda = 254$ nm (85% transmission of 254 nm and 15% transmission of light from 254 to 579 nm) under an argon atmosphere at room temperature.

### *Crystal Structure Analysis*

Suitable crystals for X-ray analysis were grown from the ethanolic solution by slow evaporation at room temperature. The X-ray diffraction measurements were carried out on a Bruker SMART 1000 CCD area detector diffractometer at 280(2) K employing graphite-monochromatized Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) with a colorless prism 0.8 mm × 0.6 mm × 0.3 mm specimen of the 2*H*-thiopyran **1a**. Accurate unit cell parameters were obtained by a least-squares fit to $2.47° < \theta < 29.97°$. Data were collected in the $\omega/\varphi$ scan mode. Structure solutions were performed by direct methods and refinements by full-matrix least-squares methods on $F^2$. The data collection and processing were performed using program SMART and SAINTPlus [12a]. The structure solution, refinement, and geometrical calculations were carried out through SHELXTL-98 [12b].

All other relevant information regarding crystal data, data collection, and refinements are given in Table 1. Bond distances and bond angles for **1a** are listed in Table 2, and an ORTEP plot of the molecular structure is given in Fig. 1. CCDC 277898



**1**) R = $^t$Bu **3**) R = $CH_2Ph$ **5**) R = Me
**2**) R = $^i$Pr **4**) R = Et **6**) R = H

**SCHEME 2** Derivatives of 2,2-disubstituted 2*H*-thiopyrans.

**TABLE 1** Crystal Data and Structure Refinement

| | |
|---|---|
| Empirical formula | $C_{22}H_{24}S$ |
| Formula weight | 320.47 |
| *T* (K) | 280 (2) |
| Crystal system | Triclinic |
| Space group | $P1^{-}$ |
| *a* (Å) | 8.987(4) |
| *b* (Å) | 9.048(4) |
| *c* (Å) | 12.698(5) |
| $\alpha$ (°) | 84.653(10) |
| $\beta$ (°) | 69.666(11) |
| $\gamma$ (°) | 76.499(12) |
| *V* (Å$^3$) | 941.4(7) |
| *Z* | 2 |
| $D_{\text{calcd}}$ (mg m$^{-3}$) | 1.131 |
| Absorption coefficient, $\mu$(cm$^{-1}$) | 1.70 |
| $\lambda$ (Å) | 0.71073 |
| *F*(0 0 0) | 344 |
| $\theta$ range for data collection (°) | $2.47 \le \theta \le 29.97$ |
| Index ranges | $-12 \le h \le 12$<br>$-11 \le k \le 12$<br>$-17 \le l \le 17$ |
| Reflection collected | 9683 |
| Independent reflections | 5127 |
| Data/restraints/parameters | 5127/0/208 |
| Goodness-of-fit on $F^2$ (S) | 1.030 |
| *R* | 0.049 |
| $R_w$ | 0.097 |
| $\Delta(\rho)_{\max,\min}$ (e Å$^{-3}$) | 0.277, −0.296 |

TABLE 2 Bond Distances, Valence Angles, and Dihedral Angles for Compound **1** (the numbering is shown in Fig. 1)

| | *X-ray* | *HF/6-31G** | *B3LYP/6-31G** |
|---|---|---|---|
| Bond distances | | | |
| S1—C1 | 1.854 (2) | 1.853 | 1.881 |
| S1—C5 | 1.766 (2) | 1.768 | 1.773 |
| C1—C2 | 1.527 (2) | 1.525 | 1.520 |
| C1—C11 | 1.548 (2) | 1.549 | 1.549 |
| C1—C7 | 1.596 (2) | 1.595 | 1.601 |
| C2—C3 | 1.352 (2) | 1.327 | 1.350 |
| C3—C4 | 1.456 (2) | 1.467 | 1.454 |
| C3—C6 | 1.521 (2) | 1.509 | 1.512 |
| C4—C5 | 1.357 (2) | 1.330 | 1.356 |
| C5—C17 | 1.486 (2) | 1.488 | 1.479 |
| C7—C8 | 1.543 (2) | 1.540 | 1.543 |
| C7—C9 | 1.547 (3) | 1.542 | 1.546 |
| C7—C10 | 1.546 (3) | 1.542 | 1.546 |
| Valence angles | | | |
| C5—S1—C1 | 101.06 (7) | 101.58 | 101.253 |
| C2—C1—C11 | 110.74 (12) | 110.302 | 111.081 |
| C2—C1—C7 | 111.20 (13) | 110.00 | 110.439 |
| C11—C1—C7 | 111.62 (12) | 111.72 | 111.643 |
| C2—C1—S1 | 106.71 (10) | 107.09 | 106.633 |
| C11—C1—S1 | 109.78 (11) | 110.19 | 109.919 |
| C7—C1—S1 | 106.57 (10) | 107.40 | 106.916 |
| C3—C2—C1 | 124.38 (15) | 125.29 | 124.81 |
| C2—C3—C4 | 121.51 (14) | 121.99 | 121.901 |
| C2—C3—C6 | 121.77 (15) | 121.83 | 121.321 |
| C4—C3—C6 | 116.69 (14) | 116.17 | 116.757 |
| C5—C4—C3 | 123.61 (15) | 123.52 | 123.764 |
| C4—C5—C17 | 124.10 (15) | 123.00 | 123.328 |
| C4—C5—S1 | 120.70 (13) | 120.83 | 120.711 |
| C17—C5—S1 | 115.00 (11) | 116.11 | 115.836 |
| C8—C7—C10 | 108.37 (16) | 107.71 | 108.142 |
| C8—C7—C9 | 107.66 (16) | 106.87 | 107.264 |
| C10—C7—C9 | 108.51 (17) | 108.03 | 108.353 |
| C8—C7—C1 | 111.62 (14) | 112.45 | 112.22 |
| C10—C7—C1 | 110.44 (14) | 111.13 | 110.869 |
| C9—C7—C1 | 110.15 (14) | 110.45 | 109.848 |
| C12—C11—C1 | 122.52 (14) | 122.26 | 122.314 |
| C22—C17—C5 | 121.09 (15) | 121.44 | 121.725 |
| Torsion angles | | | |
| C5—S1—C1—C2 | −47.55 (12) | −44.97 | −45.863 |
| C5—S1—C1—C11 | 72.51 (11) | 75.02 | 74.638 |
| C5—S1—C1—C7 | −166.45 (10) | −163.077 | −164.014 |
| C11—C1—C2—C3 | −76.02 (19) | −80.735 | −77.149 |
| C7—C1—C2—C3 | 159.26 (15) | 155.594 | 158.414 |
| S1—C1—C2—C3 | 43.42 (18) | 39.19 | 42.602 |
| C1—C2—C3—C4 | −8.5 (2) | −5.00 | −8.491 |
| C1—C2—C3—C6 | 173.51 (14) | 175.91 | 173.218 |
| C2—C3—C4—C5 | −20.1 (2) | −21.42 | −21.121 |
| C6—C3—C4—C5 | 157.95 (16) | 157.75 | 157.243 |
| C3—C4—C5—C17 | −171.04 (15) | −173.18 | −170.273 |
| C3—C4—C5—S1 | 3.6 (2) | 3.50 | 5.488 |
| C1—S1—C5—C4 | 29.17 (15) | 28.40 | 26.826 |
| C1—S1—C5—C17 | −155.77 (12) | −154.7 | −157.108 |
| C2—C1—C7—C8 | −173.77 (14) | −172.135 | −173.21 |
| C2—C1—C7—C9 | 66.70 (18) | 68.58 | 67.562 |
| C2—C1—C7—C10 | −53.14 (18) | −51.31 | −52.165 |
| C11—C1—C7—C8 | 62.02 (18) | 65.02 | 62.675 |
| C11—C1—C7—C9 | −57.52 (18) | −54.26 | −56.552 |
| C11—C1—C7—C10 | −177.36 (14) | −174.15 | −176.28 |
| S1—C1—C7—C8 | −57.84 (16) | −55.92 | −57.575 |
| S1—C1—C7—C9 | −177.38 (13) | −175.21 | −176.803 |
| S1—C1—C7—C10 | 62.79 (16) | 64.90 | 63.469 |
| S1—C1—C11—C12 | 32.60 (18) | 37.49 | 36.864 |
| S1—C1—C11—C16 | −148.38 (14) | −144.07 | −144.876 |
| S1—C5—C17—C22 | 43.8 (2) | 49.32 | 39.217 |
| S1—C5—C17—C18 | −135.62 (14) | −131.05 | −140.712 |
| C4—C5—C17—C18 | 39.3 (2) | 45.78 | 35.240 |
| C4—C5—C17—C22 | −141.31 (18) | −133.85 | −144.832 |

Bond distances are given in Å and angles in degrees (standard deviations are in parentheses).

contains the supplementary crystallographic data for this paper. These can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

### *Computational Methodology*

To rationalize the apparent stability of the observed conformation of **1**, we performed computer modelling studies on the half-chair conformers of 2*H*-thiopyrans **1**, and as a result of good agreement between the experimental and theoretical results, it is extended to the other derivatives **2–6** utilizing the GAMMES programs. The equilibrium geometries and zero-point energies of the compounds were computed using the restricted Hartree–Fock functional in conjunction with the 6-31G(d) basis set. The relative energies were recomputed at the B3LYP/6-31G(d) level of theory (at the HF/6-31G(d) geometries). The geometrical features predicted by ab initio calculations and those determined by X-ray are listed in Table 2. The energetics is summarized in Table 3.

## *RESULTS AND DISCUSSION*

The ORTEP plot of **1a** is shown in Fig. 1, and the perspective view of its conformation is depicted in Fig. 2. The crystal structure of the molecule consists of one independent molecule. Comparison of the selected bond lengths and bond angles of the crystallographic structure with those of the calculated ones for conformer **1a** in Table 2 shows a good agreement between the experimental and theoretical values. The orientation of the groups substituted at C-2 position with respect to the sulfur ring is obvious from the torsion angles listed in Table 2. The

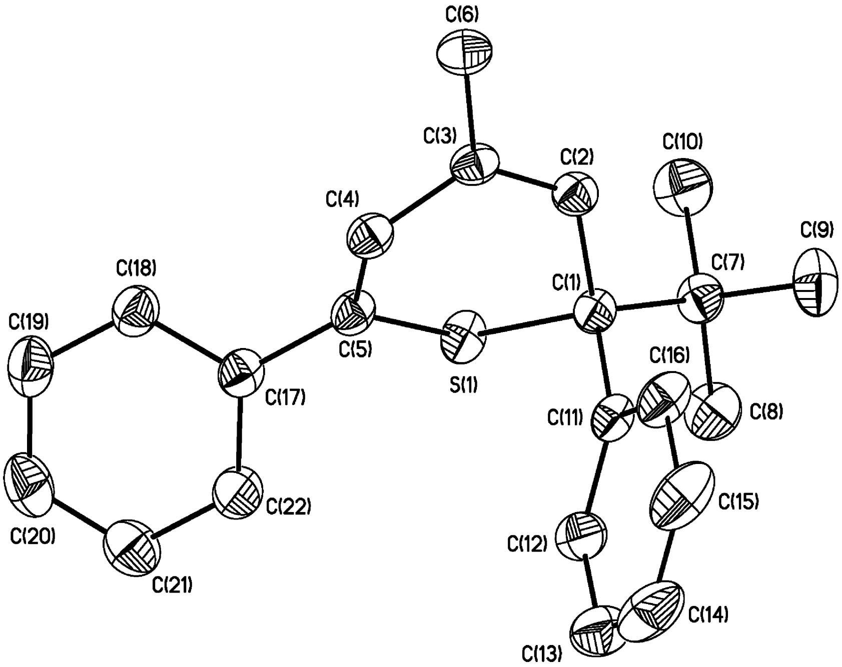


**FIGURE 1** ORTEP plot of compound **1** with atom labeling.

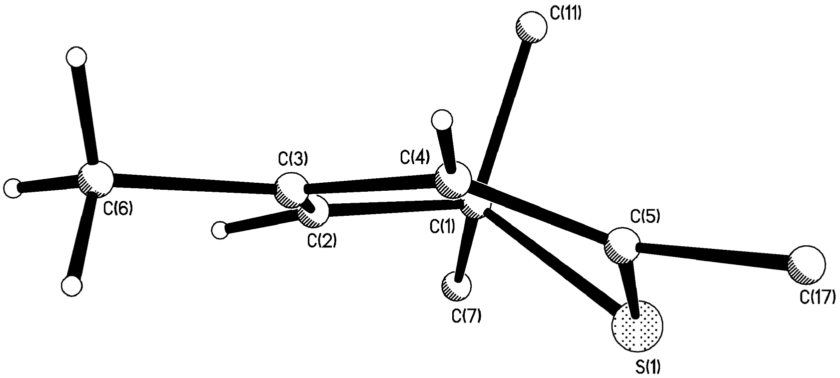


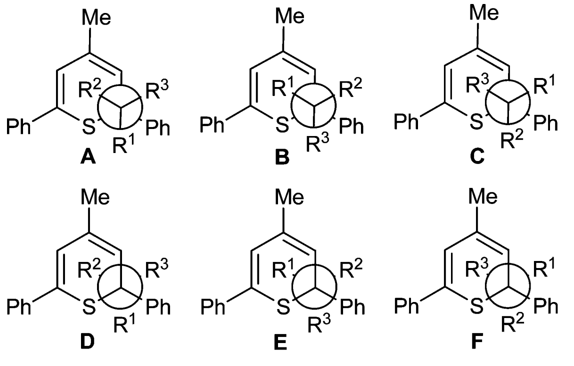
**FIGURE 2** Perspective view of conformer **1a**.

**TABLE 3** Total Energies and Relative Energies Obtained from the Hartree–Fock as well as Density Functional Theory Calculations

| | *HF/6-31G** | | *B3LYP/6-31G** | |
|---|---|---|---|---|
| | *E (a.u.)* | *ΔE (kcal mol$^{-1}$)* | *E (a.u.)* | *ΔE (kcal mol$^{-1}$)* |
| **1a** | −1244.556280 | – | −1250.962696 | – |
| **2a** | −1205.529910 | 0.0 | −1211.654804 | 0.0 |
| **2b** | −1205.526830 | 1.9 | −1211.652570 | 1.4 |
| **3a** | −1357.011428 | 0.0 | −1364.080531 | 0.0 |
| **3b** | −1357.007212 | 2.7 | −1364.077761 | 1.7 |
| **4a** | −1166.498684 | 2.3 | −1172.341687 | 2.9 |
| **4b** | −1166.502272 | 0.0 | −1172.346362 | 0.0 |
| **5a** | −1127.469763 | 0.7 | −1133.033590 | 0.7 |
| **5b** | −1127.470821 | 0.0 | −1133.034753 | 0.0 |
| **6b** | −1088.440547 | – | −1093.722674 | – |

differences between the crystallographic structure and the calculated one concerning torsion angles arise from packing requirements. Inspection of Table 2 clearly shows that in analogy to 1,3-cyclohexadiene, the sulfur ring is nonplanar in its lowest energy conformation. In terms of ring puckering, the central ring in 2*H*-thiopyran is slightly more puckered than the analogous ring of 1,3-cyclohexadiene. The torsion angles $\alpha_1$ (C2—C3—C4—C5 in **1a**) describing the deviation from planarity of the butadiene part of the molecule is −20° versus 17–18.3° obtained from electron diffraction experiment for 1,3-cyclohexadiene ring [13]. Furthermore, as a consequence of longer C—S bond, the torsion angle $\alpha_2$ (C5—S1—C1—C2 in **1a**) is slightly higher than that in 1,3-cyclohexadiene ring (−47° vs. 46°). Apparently, the bond angles are forced to be significantly larger than the standard values in order to conform to the planar conformation of the ring. This causes an extra strain destabilizing the molecule by more than it can gain by better conjugation of the double bonds, i.e., steric considerations apparently take precedence over conjugation. The phenyl substituent at C5 is tilted by 39.3°, implying only a small conjugation with the adjacent $\pi$ orbital of the ring.

Theoretical investigations suggested two half-chair conformations for 2*H*-thiopyrans **2–5**, with the alkyl groups in pseudoequatorial (**2a–5a**) or pseudoaxial (**2b–5b**) positions, respectively. The equilibrium geometries and zero-point energies of the two conformers were computed and compared. The energetics is summarized in Table 3. As it is obvious, the more bulky groups such as *tert*-buthyl, isopropyl, and benzyl groups occupy the pseudoequatorial position. The best estimate for the energy differences are 1.4 and 1.7 kcal mol$^{-1}$ for compounds **2** and **3**, respectively, while compound **1** absolutely adopts its pseudoequatorial conformation with no evidence of its pseudoaxial one. In contrast, for ethyl, methyl, and hydrogen groups, there is a high preference of pseudoaxial orientation over pseudoequatorial one. The pseudoaxial conformer of compounds **4** and **5** is favored by 2.93 and 0.7 kcal mol$^{-1}$ respectively, while compound **6** persists on its only pseudoaxial conformer. These phenomena could be attributed to van der Waals interactions between the phenyl hydrogens, H-2 (according to X-ray crystal numerical), and alkyl hydrogens which for bulky groups are minimized in pseudoequatorial orientation. Furthermore, there are considered three staggered conformational isomers for **2a–4a** as well as **2b–4b** (Scheme 3). These conformers are generally not isolable because of the small energy barriers that separate them. Theoretical calculations showed that the most stable conformers for compounds **2a–4a** and **2b–4b** are **2B, 3C, 4A** and **2F, 3E, 4F**, respectively. Conformer **2B** is more stable than **2A** and **2C** by 0.79 and 1.35 kcal mol$^{-1}$ and conformer **3C** is more stable than **3A** and **3B** by 1.13 and 1.72 kcal mol$^{-1}$, respectively, while compound **4a** persists on its sole **4A** conformer. Furthermore, compound **2b** has the sole **2F** conformer as a stable one, while for compounds **3b–4b** two stable conformers where achieved. The best estimate for the energy difference between two conformers **3E** and **4F** relative to **3D** and **4E** were 0.66 and 1.57 kcal mol$^{-1}$, respectively.



**2** $R^1 = R^2 = Me, R^3 = H$
**3** $R^1 = Ph, R^2 = R^3 = H$
**4** $R^1 = Me, R^2 = R^3 = H$

SCHEME 3 Staggered conformational isomers of compounds **2a–4a** and **2b–4b**.

## *CONCLUSION*

In conclusion, we succeeded in the first isolation and structure determination of 2-*tert*-butyl-4-methyl-2,6-diphenyl-2*H*-thiopyran as a result of both thermal rearrangement of the corresponding thiabenzene as well as photochemical rearrangement of the corresponding 4*H*-thiopyran. A good agreement between theoretical and experimental data has been found, and it revealed that the favored conformation predicted by theoretical calculations is also found in the crystal. The only conformation ascertained for the compound (X-ray analysis as well as computational investigations) was a half-chair conformation with a pseudoequatorial arrangement of the *tert*-buthyl group. Theoretical investigations showed two probable pseudoequatorial and pseudoaxial conformations for the other analogues of 2*H*-thiopyran. Their lower energies and higher efficiencies were relative to the substituents where the bulkier alkyl groups favored the pseudoequatorial orientation.

## *EXPERIMENTAL*

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Bruker 500 MHz spectrometer using TMS as internal standard. Mass spectra were recorded on a Finningan MAT-TSQ 70 mass spectrometer. UV spectra were taken on a Shimadzu 265-FW spectrometer. TLC was performed on neutral alumina plates.

### *General Procedure for the Synthesis of 2H-thiopyrans*

Tetrasubstituted 2*H*-thiopyrans **1, 3**, and **5** were synthesized by reactions of the corresponding organomagnesium salts (RMgX; R = *t*-Bu, $CH_2Ph$, Me; X = Br) with 4-methyl-2,6-diphenylthiopyrylium perchlorate according to the reported method [10]. The products were isolated by PLC on neutral alumina (petroleum ether: diethyl ether, 95:5) and purified by recrystallization from ethanol.

*2-tert-Butyl-4-methyl-2,6-diphenyl-2H-thiopyran* **1**. Pale yellow crystals, yield 55%; mp 109–110°C; $^1$H NMR ($CDCl_3$): $\delta$ 1.07 (s, 9H, $CH_3$), 2.02 (d, $J = 1.45$ Hz, $CH_3$), 5.98 (q, $J = 1.45$ Hz, H-3), 6.24 (s, H-5), 7.10–7.70 (m, 10H, Ar-H) ppm; MS (*m/z, %*): 320 [$M^+$, 7], 262 [$M^+ - C_4H_{10}$, 100]; UV (EtOH): $\nu_{max}$ (log $\varepsilon$) 238 (3.76), 253 (4.24), 336 (3.32) nm; Anal. Calcd for $C_{22}H_{24}S$ (320.26): C, 82.43; H, 7.55; S, 10.01%. Found: C, 82.51; H, 7.60; S, 10.09%.

*2-Benzyl-4-methyl-2,6-diphenyl-2H-thiopyran* **3**. Pale yellow crystals, yield 45%, mp 107–108°C; $^1$H NMR ($CDCl_3$): $\delta$ 2.0 (d, $J = 1.8$ Hz, Me), 3.41 (s, 2H, $CH_2$), 5.66 (q, $J = 1.8$Hz, H-3), 6.35 (s, H-5), 6.80–7.58 (m, 15H, Ar-H) ppm. MS (*m/z, %*): 354 [$M^+$, 7], 263 [$M^+ - CH_2Ph$, 100], 262 [$M^+ - CH_3C_6H_4$, 33]; UV (EtOH): $\nu_{max}$ (log $\varepsilon$) 250 (3.91), 265 (sh), 340 (3.73) nm; Anal. Calcd for $C_{25}H_{22}S$ (354.24): C, 84.69; H, 6.26; S, 9.05%. Found: C, 84.61; H, 6.22; S, 9.12%.

*2,4-Dimethyl-2,6-diphenyl-2H-thiopyran* **5**. Pale yellow crystals, yield 40%; mp 70–71°C; $^1$H NMR ($CDCl_3$): $\delta$ 1.79 (s, 3H, $CH_3$), 2.02 (d, $J = 1.45$ Hz, 3H, $CH_3$), 5.50 (q, $J = 1.45$ Hz, H-3), 6.4 (s, H-5), 7.21–7.70 (m, 10H, Ar-H) ppm; MS (*m/z, %*): 278 [$M^+$, 17], 263 [$M^+ - CH_3$, 78], 262 [$M^+ - CH_4$, 100]; UV (MeOH): $\nu_{max}$ (log $\varepsilon$) 243 (4.29), 328 (4.48) nm; Anal. Calcd for $C_{19}H_{18}S$ (278.21): C, 81.95; H, 6.52; S, 11.53%. Found: C, 81.83; H, 6.57; S, 11.62%.

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