Elimination, ring-contraction, and fragmentation reactions of 1-thioflavanone 1-oxides

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Abstract: Epimeric thioflavanone sulfoxides (**2b**) were selectively transformed into thioflavone (**1a**), thioaurone (**3a**), and di(2-cinnamoylphenyl) disulfide (**4**). Disulfide **4** can be recyclized into thioaurones (**3a**–**c**) and thioflavanones (**2a**, **5**) with heterolysis of the S—S bond. The 3-*p*-anisylidene sulfoxide analog of **2b** (**6**) transforms, with fragmentation, into 4′-methoxythioaurone **3b**.

Key words: chalcone, ring contraction, sulfoxides, thioaurones, thioflavonoids.

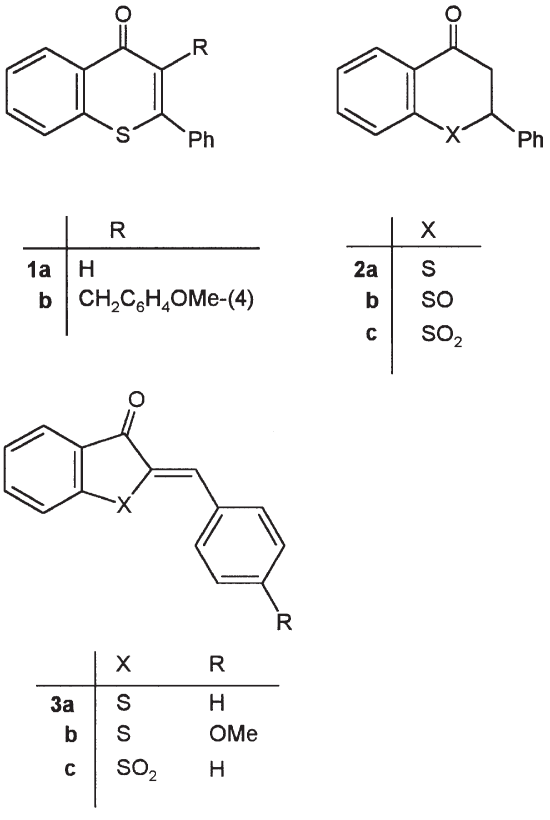
Résumé : On a réalisé la transformation sélective des sulfoxydes épimères de la thioflavanone (**2b**) en thioflavone (**1a**), thioaurone (**3a**) et en disulfure de di(2-cinnamoylphényle) (**4**). Le disulfure **4** peut être recyclisé en thioaurones (**3a**–**b**) et en thioflavanones (**2a**, **5**) avec hétérolyse de la liaison S—S. Le sulfoxyde de 3-*p*-anisylidène analogue de **2b** (**6**) subit une fragmentation et se transforme en 4′-méthoxythioaurone (**3b**).

Mots clés : chalcone, contraction de cycle, sulfoxydes, thioaurones, thioflavonoïdes.

[Traduit par la Rédaction]

Introduction

In the course of our efforts for the synthesis of 1-thioflavone derivatives, dehydrogenation of the dihydrobenzothiopyran (thioflavan) ring became necessary. Several methods useful in flavonoid chemistry have been successfully adopted (1, 3*c*) for thioflavanones, however, in some cases these methods were found either ineffective or, just the opposite; destructively drastic. Due to the greater variability of the electronic states of sulfur as compared to that of oxygen, additional methods, e.g., treatment (2) with PCl_5, or ceric ammonium nitrate (CAN) oxidation (3*a*–*c*) of thioflavanone (**2a**), and also alkali-mediated (2, 3*b*) or Pummerer-type transformation (3*b*) of sulfoxides (e.g., **2b**, in ca. 50% yield) have been successfully applied for the dehydrogenation. The PCl_5, CAN, or alkali-mediated transformations may have severe limitations when sensitive functional groups are present. As to the Pummerer-type transformation, 2-methyl-1-thiochroman 1-oxides (**7a**, **b**) have been transformed (3*d*) into the corresponding thiochromenes (**8a**, **b**) in nearly quantitative yields by treatment with acetic anhydride. However, due to the different electronic properties of the Me and Ph groups, the sulfoxides **2b** and 6-Me-**2b** undergo also ring-contraction reaction photochemically (4*b*, 4*d*), thermally (1), or upon treatment with I_2–DMSO (1) to give thioaurones (**3a**, 5-Me-**3a**) merely in 14–70% yields. Because of the relatively poor yields and the competing formation of **1a** and **3a**, we decided to find a selective conversion of thioflavanone 1-oxide (**2b**) into **1a** or **3a**.



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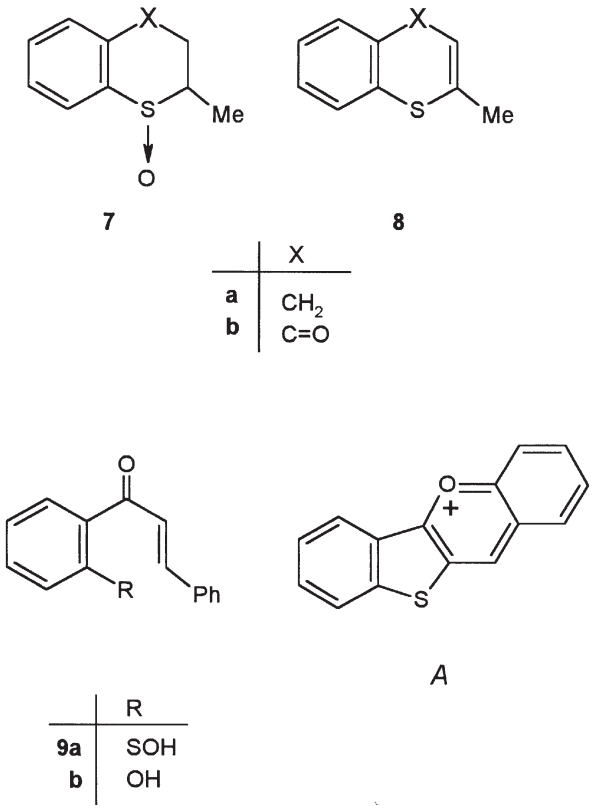
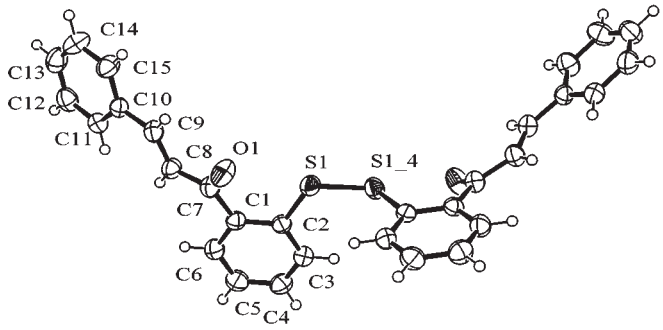


Results and discussion

The conversions of thioflavanone 1-oxide (**2b**) into either thioflavone (**1a**) or thioaurone (**3a**) proceed with loss of the elements of water, which are consumed by Ac_2O. The initial steps of these elimination reactions are, however, different. The Pummerer-type reactions of sulfoxides involve (3*e*, 3*f*) transient formation of sulfur and sulfur-stabilized carbonium cations. Accordingly, reaction conditions favouring the activation of the acyl moiety of the anhydrides may be advantageous for the formation of thioflavone, which starts with an electrophilic attack at the sulfoxide group exerted by the proton of the acid catalyst, or by the acetyl cation generated from Ac_2O by protonolysis or by the electrophilic acetyl moiety of Ac_2O being activated by the strong nucleophile (15) 4-dimethylaminopyridine (DMAP) (see Scheme 1). Thus, treatment of sulfoxide **2b** with Ac_2O–(TsOH), Ac_2O–DMPA, or TFAA–Et_3N afforded **1a** in excellent yields (>80% for the pure product, see Table 1).

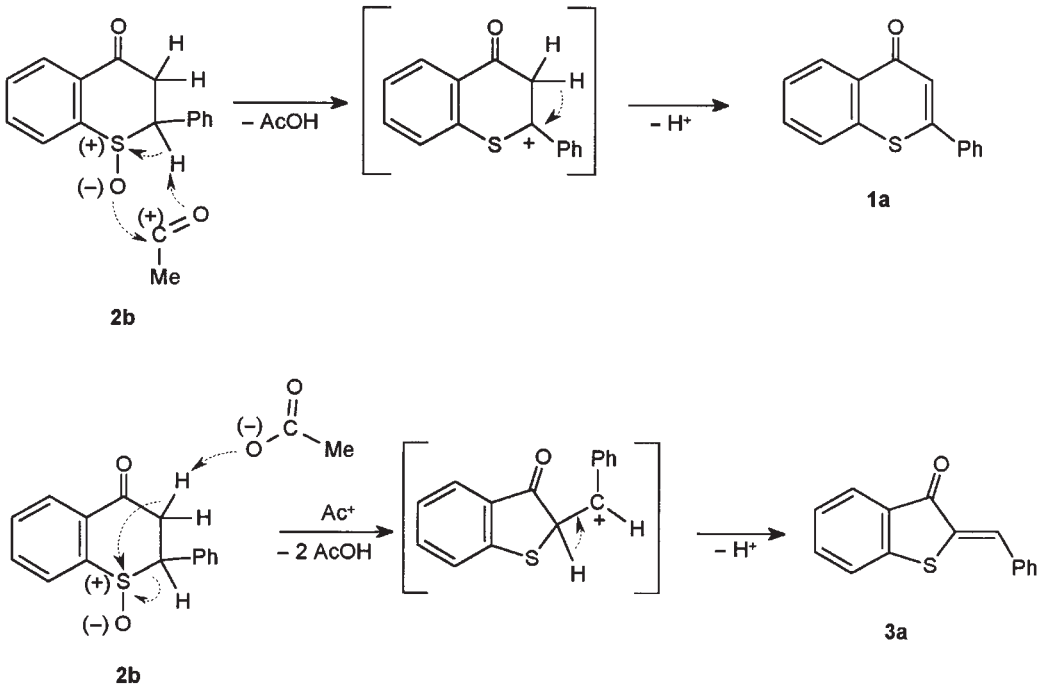
The methylene group of 1-(thio)benzopyran-4-ones is activated by the neighboring carbonyl and -XCH(Ph)- groups (X = O, S, SO, SO_2), so this is the reactive site of the molecule when treated with bases. Thus, the deprotonated C-3 creates a bond to the electron-deficient sulfur, and then the transiently generated thiiranium (4) species is stabilized by ring contraction and loss of proton to give 2-benzylidenebenzo[*b*]thiophen-3(2*H*)-one (thioaurone **3a**, see Scheme 1). Accordingly, treatment of sulfoxide **2b** with Ac_2O in the presence of NaOAc, which behaved as a strong base in this medium, afforded thioaurone (**3a**) almost quantitatively (see Table 1).

Fig. 1. ORTEP drawing of compound **4** with 50% of the thermal ellipsoids.



On varying the acid or base character of the additives, treatment of sulfoxide **2b** with Ac_2O–Et_3N or $(EtCO)_2O$–Et_3N, and also with 1,3-diisopropylcarbodiimide (DIC, see Table 1), gave a new high-melting yellow product sparingly soluble in most of the common organic solvents. (In the reaction of **2b** with DIC a considerable amount of thioflavanone 1,1-dioxide **2c** was also produced, see Table 1). At room temperature, the Ac_2O–Et_3N-mediated transformation of the *equatorial* (1,2-*trans*) sulfoxide epimer (5) **2b** afforded this product in a yield half times higher than the *axial* (1,2-*cis*) (3*c*, 5) compound (see Table 1). One the basis of C, H, and S analyses (see footnotes of Table 1) and the nonanalyzable 200 MHz ^{1}H NMR spectrum, a $C_{15}H_{11}OS$ (FW = 239.31) elemental composition was first suggested for the new compound with some uncertainty, as the hydrogen content was concerned. The product was, however, quite different in all respects (color, mp, TLC, solubility, IR, ^{1}H NMR and EI-mass spectra, etc.) from **1a** and **3a**, respectively, ($C_{15}H_{10}OS$, FW = 238.3) or **2a** ($C_{15}H_{12}OS$, FW = 240.3). Eventually, the MALDI-TOF spectrometry (see also Table 1, footnotes) indicated a $C_{30}H_{22}O_2S_2$ (FW = 478.61) composition. X-Ray diffraction analysis of this new compound revealed the open-chain disulfide structure **4** (see Fig. 1) with an S—S bond distance of 2.053 Å. (Previously, photolysis of thiochroman-4-one 1-oxides has been reported (4*d*) to give o-hydroxyaralkyl disulfides in 6–8% yields via thiyl radicals). The *trans*-chalcone structure of compound **4** was corroborated by the J = 15.77 Hz coupling of the vinylene hydrogens at δ = 7.90 and 7.77 ppm in the 500 MHz ^{1}H NMR spectrum. Disulfide **4** was presumably produced from sulfoxide **2b** via a 2-cinnamoylbenzenesulfenic acid intermediate (**9a**). This step of the ring-opening of **2b** seems to be similar to the well-known base-mediated formation of 2′-hydroxychalcones (e.g., **9b**) from flavanones, however, sulfenic acids (3*g*) are generally highly unstable. Decomposition of pseudopeptidic sulfoxides via β-elimination to sulfenic acids (followed by bimolecular recombination to thiolsulfinates RS(O)SR) and the corresponding alkene has been reported most recently (16). Upon treatment with trihaloacetic anhydride [$(CX_3CO)_2O$, X = F, Cl] in a Pummerer-like reaction, thiolsulfinates are known (17) to transform into disulfides and sulfinyl carboxylates [$RS(O)OCOCX_3$] which latter gives adducts readily with olefins.

Scheme 1.



Before performing the MALDI-TOF MS and X-ray measurements discussed above to lead to the identification of the disulfide-structure for **4**, EI-MS (see footnotes of Table 1) and HR-MS experiments were carried out with the *m*/*z* = 240 ion (M = 240.0599 Da). However, neither these mass spectral studies nor the 200 and 360 MHz ^{1}H NMR spectra (each containing superimposed signals in the "aromatic" region; δ = 8.16–7.42 ppm) gave convincing evidence for the structure of the new compound. The fragment *m*/*z* = 237 (base peak in the EI-MS) could be attributed to the formation of the benzo[*b*]thieno-[3,2-*b*]pyrylium ion (*A*), whose perchlorate has been previously prepared (7) by the condensation of 1-thia-3-indanone with salicylic aldehyde in AcOH–$HClO_4$. The same fragment was observed in the EI-MS of 1,2-*cis*-**2b** (3*c*, 5) and **3a** as a base peak, but with lesser intensity for the 1,2-*trans*-**2b**, (5) and not at all in the spectrum of thioflavone (**1a**) where *m*/*z* = 238 [$M^{+\cdot}$] was the base peak (5).

Since the reaction of other sulfoxides with active methylene compounds in the presence of dehydrating agents (Ac_2O, P_4O_{10}, DCC) has been reported (6) to furnish sulfonium ylides, a possible formation of 1,2- or 1,3-sulfur ylides similar to the thiiranium intermediate mentioned above was considered. Therefore, the reactivity of the sparingly soluble new compound **4** (at that time with uncertain structure) was also examined (see Table 2). Thus, treatment with Ac_2O–H_2SO_4 afforded thioflavone (**1a**) and thioaurone (**3a**) in poor yields. Similarly, when reacted with the I_2–DMSO couple or (in contrast to the transformation of **2b** in acid medium) with hot AcOH or cold sulfuric acid again **3a** was formed, and the reaction with CAN resulted in thioaurone 1,1-dioxide (**3c**). Interestingly, upon treatment with 4-methoxybenzaldehyde–piperidine (which is known to transform **2a** into **5**), compound **4** underwent transformation into 4′-methoxythioaurone (**3b**) and 3-(4-methoxybenzylidene)thioflavanone (**5**, see Scheme 2). Cleavage of the S—S bond, exhibiting acid–base properties can be effected by both nucleophiles or bases and electrophiles (3*g*).

The aforementioned anisaldehyde–piperidine-mediated recyclization of **4** into the thiaindanone and thiobenzopyranone derivatives **3b** and **5** can be explained by the heterolysis of the S—S bond followed by cyclization into **3a** and **2a** (see Scheme 3), and their subsequent transformation with the aldehyde into **3b** and **5**, respectively. Indeed, treatment of thioaurone **3a** with 4-anisaldehyde in piperidine at 150°C for 1.5 h afforded ca. 65% of **3b**. Compound **3b** was also formed in good yield in a fragmentation reaction upon treatment of 3-(4-methoxybenzylidene)thioflavanone 1-oxide (**6**) with Ac_2O–TsOH (see Table 1). Recently, deprotection–cyclization of 4-methoxybenzyl-protected 2′-mercaptochalcones into thioflavanones has been reported (14).

Experimental

Melting points (uncorrected): Kofler block. Solutions were concentrated under reduced pressure in a rotary evaporator (<50°C, bath). TLC: Kieselgel 60 F_{254} (Merck, Alurolle). IR(KBr discs): PerkinElmer 16 PC-FT spectrometer. ^{1}H NMR: 200 MHz, Bruker WP 200 SY and 500 MHz, Bruker DRX 500 spectrometers. MS: VG-7035 GC–MS–DS (EI, 70 eV, direct insertion technique); high-resolution spectrometry (EI, 70 eV, resolution 10 000, accuracy ±5 ppm, direct insertion), AEI MS-902; MALDI-TOF measurements, Bruker BIFLEX III^{TM} mass spectrometer (19 kV acceleration voltage with pulsed ion extraction (PIE^{TM}); detection of the positive ions, reflection mode (20 kV); laser desorption, nitrogen laser (337 nm, 1 ns pulse width) operating at 4 Hz, 100–120 shots were summed; external linear calibration, with poly(ethylene glycol) (M_n = 1450, MWD = 1.02). Solu-

Table 1. Transformation of sulfoxides **2b** and **6**.[a]

Substrate (mmol)	Agents (mmol)		Reaction temperature (°C)[b] (time (h))	Work-up[c]	Product	% Yield crude (pure)[d]	Mp (°C) (solvent)	Lit. mp (°C) (solvent)
2b (1)	Ac_2O (53)	TsOH[e]	100 (24)	B, C	**1a**	95.3 (76.9)	125 (2-PrOH–hexane)	125[f] (EtOH)
2b[g] (5.5)	Ac_2O (148)	DMAP[h] (8.25)	Room temp. (72)	B, D	**1a**	(80)[i]	125 (2-PrOH)	125[f] (EtOH)
2b[g] (3)	TFAA[j,k] (63)	Et_3N[k,l] (14.4)	Room temp. (2)	A	**1a**	85[d]	124.5[m]	125[f] (EtOH)
2b[n] (2)	Ac_2O (53)	NaOAc[o] (10)	105 (4)	E, F	**3a**	99.5[p] (75)	132 (MeOH)	134 to 134.5 [q] (EtOH)
2b[r] (6)	Ac_2O (159)	Et_3N[l] (29)	Room temp. (22)	A	**4**[s]	41[d] (39.4)	229–230[m], 238–240[t]	
2b[u] (6)	Ac_2O (159)	Et_3N[l] (29)	Room temp. (19)	A	**4**[s]	65.3[d] (53)	228–230[m], 238[v]	
2b[u] (2)	$(EtCO)_2O$ (55)	Et_3N[l] (7.2)	Room temp. (24)	A	**4**[s]	52.6[d] (41)	226–227[m], 236–237[t]	
2b[r] (3)	DIC[w,x] (7)		Room temp. (24)	B, G, H	**4**[s]	26[d]	238[m]	
				I	**2c**[y]	(40)	155.5 (2-PrOH)	155 to 156[z] (2-PrOH)
6[aa] (2)	Ac_2O (74)	TsOH[e]	100 (24)	B, C, D, F	**3b**	80 (68)	158 to 159 (2-PrOH)	158 to 159[q] (EtOH)

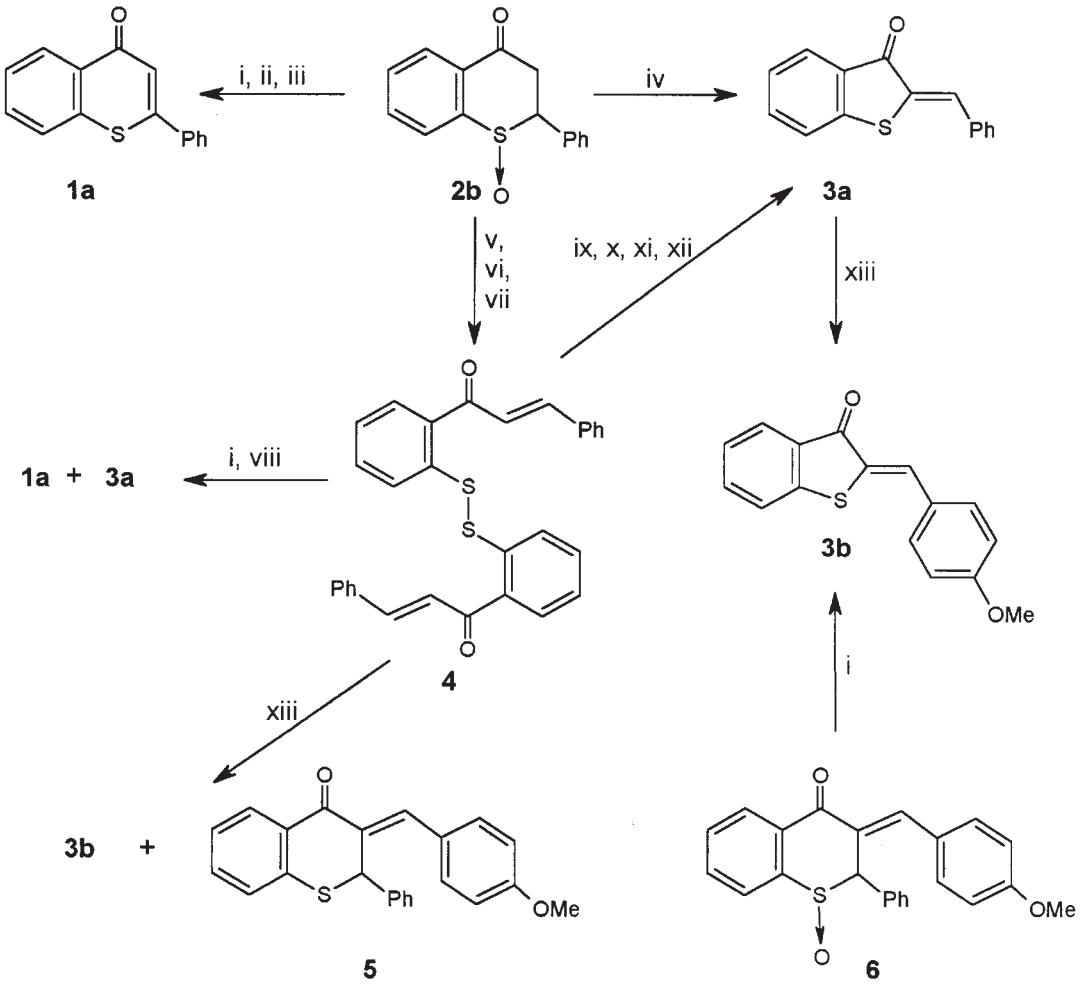
[a]For general methods see *Experimental*. [b]Bath. [c]See *Experimental*. [d]Without work-up of mother liquors. [e]4-Toluenesulfonic acid, a catalytic amount. [f]Reference 2. [g]1,2-*cis*. [h]4-Dimethylaminopyridine. [i]After purification by column chromatography (silica gel 60, 0.063–0.2 mm, 110 g, $r \sim 4.8$ cm, $l = 12$ cm, $CHCl_3$). [j]Trifluoroacetic anhydride. [k]CAUTION! The agents should be mixed carefully with ice–salt cooling. [l]Dried with and distilled from P_4O_{10}. [m]Crude product. [n]Either 1,2-*cis* or *trans*. [o]Anhydrous. [p]Contaminated by a small amount of **1a** when obtained from 1,2-*trans*-**2b** and by a somewhat larger one starting from the 1,2-*cis* diastereomer. [q]Reference 12. [r]The 1,2-*cis* isomer. [s]MALDI-TOF-MS (*m*/*z*): 584.98 [M + $^{107}Ag^+$] (calcd. 585.01). EI-MS *m*/*z* (%): 240(12), 239(20), 238(63), 237(100), 208(6), 178(3), 165(10), 149(3), 136(23), 134(16). IR (KBr) ν (cm^{-1}): 1650 (s), 1588 (s), 1574 (s), 1496 (w), 1454 (m), 1448 (m), 1338 (s). ^1H NMR ($[CD_3]_2SO$, 500.13 MHz) at 700 K δ: 7.90 and 7.77 (each d, 1H, $J = 15.77$ Hz; 2 *trans H*-vinylene). Anal. calcd. for $C_{30}H_{22}O_2S_2$ (478.61) (%): C 75.28, H 4.63, S 13.40; found (%): C 75.20, H 4.85, S 13.41. For the stereostructure of the molecule see Fig. 1. [t]From DMF with addition of some water to the hot solution. [u]The 1,2-*trans* isomer. [v]Recrystallized from Ac_2O. [w]1,3-Diisopropylcarbodiimide. [x]In the presence of anhydrous benzene (5 mL) with or without addition of anhyd Et_3N (21 mmol). [y]Identical (TLC, $CHCl_3$–EtOAc (95:5)) with an authentic specimen. [z]Reference 3*a*: 155°C or 156 to 157°C (from 2-PrOH); ref. 3*c*: 155 to 156°C (from 2-PrOH). [aa]Prepared according to ref. 13.

Table 2. Transformation of disulfide **4** into thioflavone (**1a**) and thioaurones **3a**, **b**, **c**.[a]

Substrate (mmol)	Agents (mmol)		Reaction temperature (°C)[b] (time (h))	Work-up[c]	Product	% Yield crude (pure)[d]	Mp (°C) (solvent)	Lit. mp (°C) (solvent)
4 (1.75)	Ac_2O (265)	H_2SO_4[e] (12.6)	Room temp. (20)	E, J, F	**1a**	(9)	124 (2-PrOH)	125[f] (EtOH)
					3a	(12)	133 to 134 (2-PrOH)	134 to 134.5[g] (EtOH)
4 (0.5)	AcOH[h] (873)		Bp (21)	B, D, K	**3a**	(50)	133 to 134 (2-PrOH)	134 to 134.5[g] (EtOH)
4 (0.5)	H_2SO_4[e] (18)		Room temp. (0.083)	E, J, K	**3a**	49 (43)	134 (2-PrOH)	134 to 134.5[g] (EtOH)
4 (0.125)	I_2 (0.25)	DMSO (35.2)	100 (24)	B, L, K	**3a**	(42)	132 to 133 (2-PrOH)	134 to 134.5[g] (EtOH)
4 (3)	4-MBA[i] (6.9)	$C_5H_{11}N$[j] (4.6)	152 (1.2)	B, C, K	**3b**[k]	50[d] (34)	159.5 (2-PrOH)	158 to 159[g] (EtOH)
4 (1.5)	CAN[l] (13.7)		75 (3[m] + 2.5)	B, D, F	**3c**[n]	(23)	160 (2-PrOH)	156–158 (EtOH)[o], 164 to 165 (Me_2CO–CH_2Cl_2)[p]

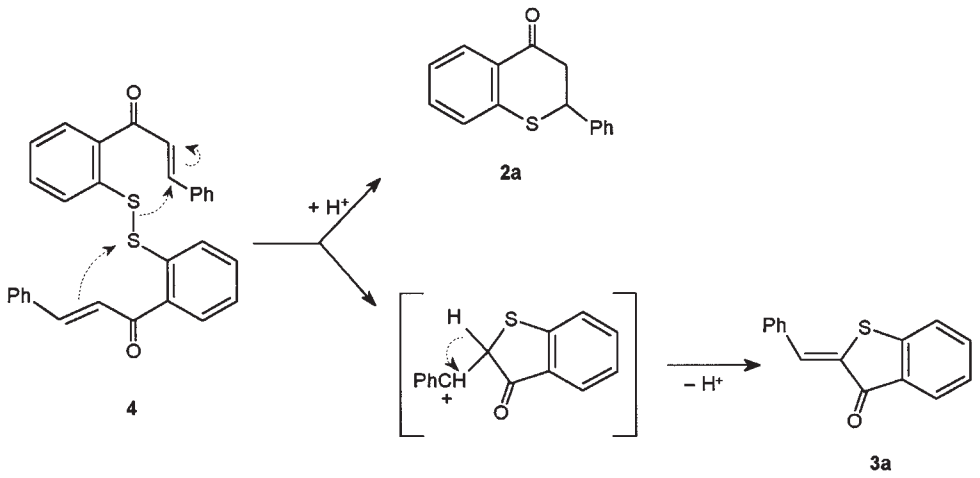
[a]For general methods see *Experimental*. [b]Bath. [c]See *Experimental*. [d]Without work-up of mother liquors. [e]Concentrated (96%). [f]Reference 2. [g]Reference 12. [h]99 to 100%. [i]4-Methoxybenzaldehyde. [j]Piperidine. [k]Besides, 3-(4-methoxybenzylidene)thioflavanone (**5**, mp 131°C (from 2-PrOH), ref. 11: 132°C (from MeOH)) could be isolated in 3% yield. [l]$(NH_4)_2Ce(NO_3)_6$, in the presence of MeCN (200 mL) and H_2O (20 mL). [m]Input. [n]IR (KBr) ν (cm^{-1}): 1708 (C=O), 1296 and 1156 (SO_2); ref. 13: 1708, 1294, and 1156 cm^{-1}. [o]Reference 3*b*. [p]Reference 13.

Scheme 2.



(i) Ac_2O/TsOH; (ii) Ac_2O/DMAP; (iii) TFAA/Et_3N; (iv) Ac_2O/NaOAc; (v) Ac_2O/Et_3N; (vi) $(EtCO)_2O$/Et_3N;(vii) 1,3-Diisopropylcarbodiimide/PhH; (viii) Ac_2O/H_2SO_4, room temp.; (ix) AcOH, reflux; (x) H_2SO_4, room temp.; (xi) I_2/DMSO; (xii) $PhI(OAc)_2$/AcOH, reflux; (xiii) 4-Methoxybenzaldehyde/piperidine (see also Tables 1 and 2).

Scheme 3.



tions for preparation of samples: 1,8-dihydroxy-9(10*H*)-anthracenone matrix–THF (20 mg mL^{-1}), AgTFA–THF (5 mg mL^{-1}) to enhance the cationization; 0.5 μL of the mixture of solutions analyte (1 mg **4** mL^{-1} CH_2Cl_2) – matrix – AgTFA in 10:50:1 v/v ratio was deposited onto the sample plate (stainless steel) and allowed to air-dry). X-ray diffraction analysis (for yellow plate crystals (0.48 × 0.39 × 0.1 mm) of $C_{30}H_{22}O_2S_2$, grown from Ac_2O, M = 478.6, orthorhombic, a = 10.387(1) Å, b = 12.298(1) Å, c = 18.471(1) Å, V = 2359.7 $Å^3$, Z = 8, space group: *Pbcn*, ρ_{calc} = 1.347 g cm^{-3}): Enraf–Nonius MACH3 diffractometer; data were collected at 293(1) K, Mo Kα radiation λ = 0.71073 Å, ω-2Θ motion, Θ_{max} = 27.8°, 2222 reflections of which 1612 were unique with $I > 2\sigma(I)$; decay: 4%. The structure was solved using the SIR-92 software (8) and refined on F^2 using SHELX-97 program (9); publication material was prepared with the WINGX-97 suite (10); R(F) = 0.039 and $wR(F^2)$ = 0.094 for 2222 reflections, 154 parameters.

General method for the preparation and work-up of the reaction mixtures

The substrate was added to a mixture of the reagents and allowed to react, if necessary with stirring, as indicated in Tables 1 and 2. The reaction mixtures were processed:

(A) The product was filtered off from the cold reaction mixture; (B) The reaction mixture was concentrated; (C) The residue was triturated with MeOH and (or) water to give a crude product; (D) A $CHCl_3$ solution of the residue was washed with (when DMAP was used at first with aq. $KHSO_4$) aq. $NaHCO_3$ and water, dried ($MgSO_4$), treated with fuller's earth and charcoal and then concentrated; (E) The cold reaction mixture was poured into ice water; (F) The crude product was purified by column chromatography (eluent, $CHCl_3$); (G) The residue was triturated with hexane to give a crude product; (H) The crude product was triturated with $CHCl_3$ and the undissolved material was filtered off; (I) The material dissolved in the filtrate was purified by column chromatography (eluent, $CHCl_3$); (J) The mixture was extracted with $CHCl_3$ and processed as in (D); (K) Crystallization from the solvent indicated in Table 1 or 2; (L) A $CHCl_3$ solution of the residue was washed with a necessary amount of aq. $Na_2S_2O_3$ and water, dried ($MgSO_4$), treated with charcoal and then concentrated.

*3-(4-Methoxybenzyl)thioflavone (**1b**)*

According to the known method (11), a mixture of anisaldehyde (8.753 g, 98%, 63 mmol), thioflavanone (**2a**, 14.418 g, 60 mmol), and piperidine (2.5 mL, 25.28 mmol) was heated at 152°C (bath) for 2.5 h (instead of the 1 h reported), cooled and treated with MeOH to give crude (6.311 g, 29.3%, mp 123–126°C) or recrystallized 3-(4-methoxybenzylidene)thioflavanone (**5**, 5.572 g, 25.9%), mp 133–133.5°C (from 2-PrOH); ref. 11: 132°C (from MeOH), yield 52.2%. The mother liquor of the crude product **5** was concentrated and the residue triturated with EtOAc (10 mL) to give, after successive addition of hexane (30 mL), crude (2.623 g, 12.2%) or recrystallized colorless **1b** (2.245 g, 10.4%), mp 148.5°C (from 2-PrOH). IR (KBr) (cm^{-1}) ν: 1618 (C=O). ^{1}H NMR ($CDCl_3$, 360 MHz) δ 8.57–8.55 (m, 1 H, 5-H), 7.60–7.36 (m, 8 H, 6,7,8-H and Ph), 6.96–6.93 (d-shaped m, 2 H, 2″, 6″-H) 6.73–6.69 (m, 2 H, 3″, 5″-H), 3.94 (s, 2 H, CH_2), 3.73 (s, 3 H, OMe). Anal. calcd. for $C_{23}H_{18}O_2S$ (%): C 77.07, H 5.06; found (%): C 77.26, H 5.08.

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