Intermediates Formed in the Reaction of Benzenethiol or *t*-Butylthiobenzene with Ethyl Benzoylacetate in Polyphosphoric Acid

Hiroyuki NAKAZUMI,* Shigeru WATANABE, Tohru KITAGUCHI, and Teijiro KITAO
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591
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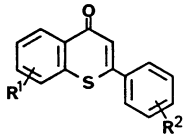
The reaction of benzenethiol with ethyl benzoylacetate in polyphosphoric acid (PPA) at low temperature gave mainly ethyl 3-phenyl-3,3-bis(phenylthio)propionate **8** as an intermediate in the synthesis of thioflavones, while that from *t*-butylthiobenzene under similar conditions gave ethyl 3-(phenylthio)cinnamate **7** as a major product and many by-products. The reaction constant for intramolecular cyclic condensation of **7** in 98% sulfuric acid was −0.46 and −0.54 using Hammett substituent constants, σ_m and σ_m^+, respectively. It is suggested that the increase of electron density at the ring closure site of the benzenethiol moiety of **7** promotes this ring closure reaction.

We have prepared some 2-phenyl-4*H*-1-benzothiopyran-4-ones (thioflavones) **1** and their 1,1-dioxides which exhibit antimicrobial activity.[1-4] Thioflavone **1** has been prepared by cyclic condensation of benzenethiol **5** with ethyl benzoylacetate **6**.[2,5] Poly-



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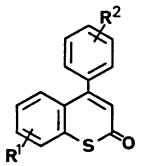

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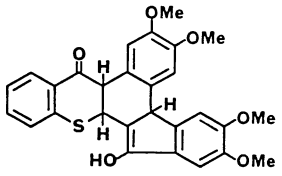

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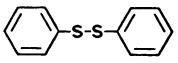

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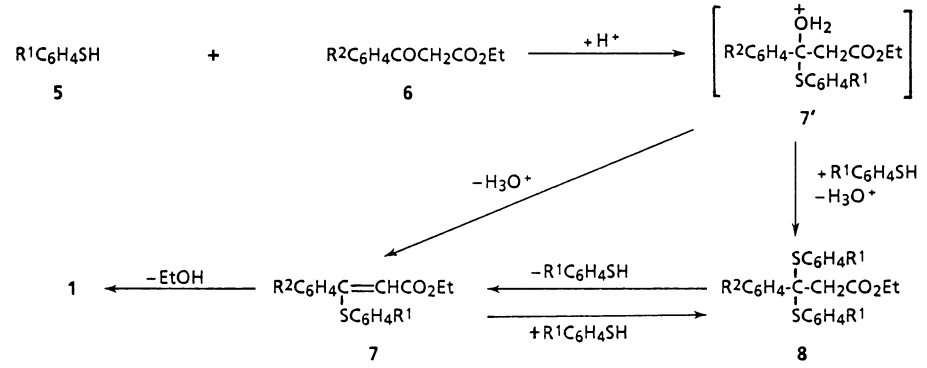
phosphoric acid (PPA), as a dehydrating agent, promotes this cyclization. Although it is well known that this method using PPA affords thioflavone free from the isomeric 4-phenylthiocoumarins, in some reactions of benzenethiol with dimethoxy-substituted ethyl benzoylacetate, thiocoumarin derivative **2**[6] is isolated. When malonic acid was reacted with 2-*t*-butylthiobenzaldehyde, instead of unstable 2-mercaptobenzaldehyde, benzothiopyran derivatives are produced in high yield.[7] We also have reported that condensation of *t*-butylthiobenzene **9**, which is an *S*-protected benzenethiol, with **6** gives the corresponding thioflavone in a suitable yield.[6]

We have attempted to examine reaction intermediates from benzenethiol and *t*-butylthiobenzene in order to find a more advantageous method to obtain thioflavone. Though only 3-(phenylthio)crotonic acids[8,9] are reported as intermediates in a similar preparation of 4*H*-1-benzothiopyran-4-ones having the same heterocyclic ring to thioflavone, these reaction mechanisms are not known in detail.

In this paper, we report on the distributions of intermediates in the reactions of **5** and **9**, respectively, with **6** in PPA or diluted PPA at low temperature. The kinetics of the formation of thioflavones from an intermediate to examine the substituent effect in cyclic condensation is also discussed.

Results and Discussion

Intermediates from Reaction of Benzenethiols or *t*-Butylthiobenzenes with Ethyl Benzoylacetate. The reaction of **5** with **6** in PPA (phosphorus pentaoxide 85%) at 90 °C generally gives thioflavone in high yield, except for some methoxy-substituted derivatives. In the reaction of benzenethiol **5a** with ethyl 3,4-dimethoxybenzoylacetate, disulfide **4**[8] and compound **3** together with thioflavone derivative were isolated. We have now found that the same reaction of **5a** (R^1=H) with **6a** (R^2=H) in diluted PPA (phosphorus pentaoxide 75%), which has low viscosity even at 5—15 °C, selectively gave ethyl 3-phenyl-3,3-bis(phenylthio)propionate **8a** isolated by crystallization. Its structure was assigned on the basis of the ^{1}H NMR spectra and a comparison of the reported melting point of **8a** prepared by a similar reaction using hydrogen chloride and zinc chloride.[10] From other benzenethiol derivatives the corresponding thioacetals **8** were mainly isolated under the same conditions (Table 1). The by-products were a mixture of ethyl (*E*)- and (*Z*)-3-(phenylthio)cinnamates. Thus, this method is useful for the selective preparation of **8**. A singlet resonance corresponding to the resonances for methylene protons characteristically appeared at δ ca. 3.00 ppm in the ^{1}H NMR spectrum of **8** (Table 2). In the mass spectra **8**, a fragmentation of $M^+-SC_6H_4R^1$ was characteristic, but their molecular ion was not observed. The configura-



For 7 and 8
a; R1 = H, R2 = H
b; R1 = 4-Me, R2 = H
c; R1 = 4-MeO, R2 = H
d; R1 = 4-Cl, R2 = H
e; R1 = 4-MeO, R2 = 4-MeO
f; R1 = 2,5-(MeO)2, R2 = H

Scheme 1.

Table 1. Products Obtained by Reaction of Benzenethiols **5** or **9** with Ethyl Benzoylacetate **6** in PPA at low Temperature

Run	Benzenethiol			Products[a]/%				Conversion/%
	5 or **9**	R^1	R^2	**8**	(*E*)-**7**	(*Z*)-**7**	**1**	
1	**5a**	H	H	82	1.6	1.1	—	99
2	**5b**	4-Me	H	50	12	5.5	—	91
3	**5c**	4-OMe	H	70	18	3.4	—	84
4	**5d**	4-Cl	H	48	0.3	1.8	—	32
5	**5e**	4-OMe	4-OMe	61	17	5.6	—	92
6	**5f**	2,5-$(OMe)_2$	H	—	27	9.9	—	39
7	**9a**	H	H	—	18	26	22	86
8	**9b**	4-Me	H	—	22	16	11	40
9	**9c**	4-OMe	H	—	37	20	1.8	84
10	**9d**	4-Cl	H	—	9.8	10	8.3	27
11	**9e**	4-OMe	4-OMe	—	19	9.0	—	35

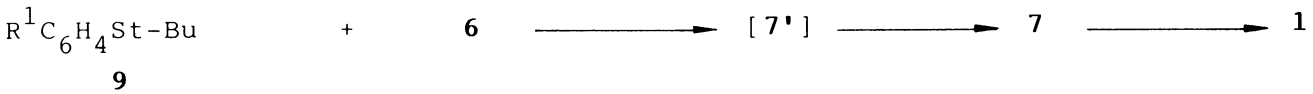
a) Isolated yield based on the converted benzenethiol. Compound **5** (0.5—3.0%) was observed in runs 8—10 and other by-products existed in runs 7, 9, 10, and 11.

Table 2. Ethyl 3-Phenyl-3,3-bis(phenylthio)propionate **8**

Compound	^{1}H NMR ($CDCl_3$) δ/ppm	MS *m/z* (relative intensities)
8b	1.08 (3H, t, *J*=7.7 Hz), 2.20 (6H, s), 3.04 (2H, s), 3.90 (2H, q, *J*=7.7), 6.84—7.48 (13H, m)	299 (30), 253 (18), 225 (100), 210 (18), 121 (43)
8c	1.16 (3H, t, *J*=7.5 Hz), 3.04 (2H, s), 3.76 (6H, s) 4.10 (2H, q, *J*=7.5 Hz), 6.64—6.80 (4H, m), 7.12—7.52 (9H, m)	315 (25), 314 (41), 269 (14), 242 (48), 140 (100), 139 (36), 121 (53)
8d	1.08 (3H, t, *J*=7.6 Hz), 3.06 (2H, s), 3.96 (2H, q, *J*=7.6 Hz), 7.00—7.48 (13H, m)	321 (23), 319 (55), 245 (29), 185 (33), 149 (30), 144 (100), 143 (51), 109 (82)
8e	1.12 (3H, t, *J*=7.5 Hz), 3.00 (2H, s), 3.68 (9H, s), 4.00 (2H, q, *J*=7.5 Hz), 6.56—6.76 (6H, m), 7.04—7.32 (6H, m)	345 (1.3), 289 (1.4), 278 (5.3), 271 (2.3), 246 (4.1), 140 (100)

Table 3. Ethyl (*Z*)- and (*E*)-3-(Phenylthio)cinnamates (*Z*)-**7** and (*E*)-**7**

Compound	^{1}H NMR ($CDCl_3$) δ/ppm	MS *m/z* (relative intensities)
(*Z*)-**7d**	1.36 (3H, t, *J*=7.8 Hz), 4.28 (2H, q, *J*=7.8 Hz), 6.08 (1H, s), 6.92—7.52 (9H, m)	320 (M^++2; 26), 318 (M^+, 73), 273 (46), 245 (100), 210 (46), 147 (64), 144 (36), 121 (100)
(*Z*)-**7e**	1.28 (3H, t, *J*=7.5 Hz), 376 (6H, s), 4.16 (2H, q, *J*=7.5 Hz), 5.88 (1H, s), 6.40—7.52 (8H, m)	344 (M^+; 78), 299 (21), 271 (21), 236 (23), 205 (78), 177 (100), 161 (23), 151 (66), 140 (32)
(*Z*)-**7f**	1.28 (3H, t, *J*=7.5 Hz), 3.48 (3H, s), 3.52 (3H, s), 3.72 (2H, q, *J*=7.5 Hz), 5.92 (1H, s), 7.08—7.80 (8H, m)	344 (M^+; 100), 299 (18), 272 (65), 257 (23), 241 (33), 121 (77)
(*E*)-**7d**	0.96 (3H, t, *J*=7.8 Hz), 3.84 (2H, q, *J*=7.8 Hz), 5.36 (1H, s), 6.92—7.44 (9H, m)	320 (M^++2; 28), 318 (M^+, 70), 273 (44), 245 (100), 210 (48), 147 (63), 144 (96), 121 (78)
(*E*)-**7e**	1.00 (3H, t, *J*=7.5 Hz), 3.60 (3H, s), 3.68 (3H, s), 3.84 (2H, q, *J*=7.5 Hz), 5.12 (1H, s), 6.40—7.52 (8H, m)	344 (M^+; 66), 299 (24), 271 (24), 252 (34), 236 (26), 205 (84), 177 (100), 151 (66), 140 (74)
(*E*)-**7f**	1.00 (3H, t, *J*=7.5 Hz), 3.68 (3H, s), 3.76 (3H, s), 3.84 (2H, q *J*=7.5 Hz), 5.36 (1H, s), 6.68—7.52 (8H, m)	344 (M^+; 100), 299 (17), 272 (75), 257 (25), 240 (35), 121 (94)



Scheme 2.

tion of ethyl (*Z*)-3-(phenylthio)cinnamates was established on the basis of the ^{1}H NMR spectra, from an analogy of the assignment for the reported methyl (*Z*)- and (*E*)-2-chlorocinnamates.[11] The resonances of the vinylic proton and the ethoxycarbonyl group appeared constantly at lower field (ca. 0.3—0.7 ppm) for the (*Z*)-isomer than those for the (*E*)-isomer, as shown in Table 3. Reaction of chloro-substituted benzenethiol with **6** (run 4) leads to a significantly low conversion, due to the low nucleophilicity of the thiol. In the case of 2,5-dimethoxy-substituted benzenethiol (run 6), no thioacetal **8** was obtained, though **7f** was isolated as the main product, together with an unidentified product of *m/z*=372 (2.0%). This shows that the formation of thioacetal **8** may be inhibited by a steric hindrance of the 2-substituent group of benzenethiol.

When the reaction temperature increased to 60 °C in a reaction of **5** with **6**, the formation of thioflavone **1** together with intermediate **8** was observed. Intermediate **8** was also obtained from a reaction of **7** with **5** in dilute PPA at 20 °C.

On the other hand, the same reaction of **9** at 20—30 °C in PPA (phosphoric pentaoxide 85%) gave **7** as the main product; the formation of **8** was not observed. No reaction of **9** using diluted PPA (phosphoric pentaoxide 75%) occurred under the same conditions for the preparation of **8**. The chloro derivative of **9** also leads to a low conversion. From the reaction of **9**, many by-products were observed by GC-mass analysis, though not isolated.

Cyclization of intermediates **7** and **8** both in PPA (phosphoric pentaoxide 85%) or 98% sulfuric acid gave thioflavone **1** in high yield. Thus, intermediates **7** and **8** are important precursors of thioflavones. The reaction from **5** is favored for the preparation of thioflavones over that from **9**, since oxidation and a side reaction of **5** are less than those of **9**.

In conclusion, in a reaction using benzenethiol **5**, thioflavone **1** would be formed through **7'**→**7**, **7'**→**8**→**7**, and **7'**→**7**→**8**→(**7**); however in a reaction using **9**, thioflavone **1** would be produced only through intermediates **7'** and **7**, not through **8** (Scheme 2). This is because a direct attack of **9** on **7'** may be difficult and deprotection of **9** accompanies the oxidation of **9** and **5**.

Kinetics of Formation of Thioflavone from Intermediate 7. The rate of formation of **1** from **7** in 98% sulfuric acid at 20 °C was determined spectrophotometrically so as to investigate the substituent effect in cyclic condensation. There was an isosbestic point at 380 nm in this reaction, as shown in Fig. 1, and absorbances of the two maxima at 280 and 370 nm increased with time, the final spectrum being in good agreement with that of **1**. The reaction from (*Z*)-**7**- obeyed first-order kinetics; results are shown in Table 4. The reaction from the (*E*)-form of **7** gave similar

Table 4. First-Order Rate Constants for Formation of **1** from **7** at 20 °C in 98% Sulfuric Acid

Starting compound No.	R^1	$k\times10^3$ s^{-1}	Average deviation[a] $\times10^3$ s^{-1}
7a	H	2.39	±0.16
7b	4-Me	2.35	±0.07
7c	4-OMe	1.90	±0.10
7d	4-Cl	1.46	±0.09

a) Average from two results.

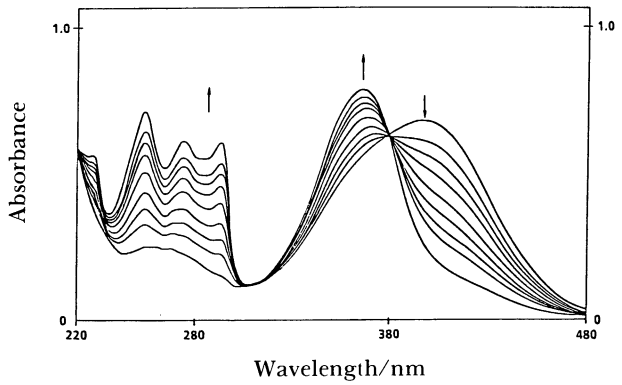


Fig. 1. Cyclic condensation of **7a** in 98% sulfuric acid at 20 °C.

rate constants. When $\log(k_x/k_H)$ was plotted against the Hammett substituent constant, σ_m or σ_m^+, a good linear correlation was observed; however, plotting against σ_p or σ_p^+ did not give any correlation. The reaction constants using σ_m and σ_m^+ are −0.51 and −0.46, respectively, much lower than that obtained for various forms of electrophilic substitution.

The rate-determining step may be a ring closure step of **7** in this reaction. This substituent effect suggests that an increase of the electron density of the ring closure site (at the position ortho to the sulfur) or benzenethiol moiety of **7** promotes this intramolecular cyclization.

An electron-withdrawing substituent, such as a chlorine atom, leads to a decrease in the rate of formation of **1**. Though acetyl derivative **7g** (R^1=4-Ac, R^2=H) having a stronger electron-withdrawing substituent group gave no thioflavone, it afforded **5g** (R^1=4-Ac), **6** (R^2=H), and 3-hydroxy-1-indenone[12] at a yield of 73, 53, and 31%, respectively. The decomposition of **7g** also obeyed first-order kinetics and its rate (k=8.31×10^{-5} s^{-1}) is slower than the observed rate of cyclic condensation.

Although small reaction constants show that substituent participation is not highly significant in determining the reaction rate, an aromatic ring of benzenethiol moiety of **7** is deactivating by electron-withdrawing substituent. This result suggests that a mechanistic change occurs for an acetyl-substituted compound.

After all, even if intermediates **7** having electron-withdrawing substituent groups are formed in the reaction of **5** or **9** with **6**, they are not converted into thioflavone. Thus, the selection of benzenethiol having a donor-substituent group may be favorable to the prepare thioflavone.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were taken on a JEOL JNM-MH-100 spectrometer with tetramethylsilane as an internal standard. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. Mass spectra were recorded on a Shimadzu LKB 9000 GC-Mass spectrometer operating at 70 eV with glass capillary column SE-54 (0.3 mm×25 m, column temperature 130 °C).

Reaction of Benzenethiol with Ethyl 3,4-Dimethoxybenzoylacetate. A mixture of benzenethiol (0.029 mol) and ethyl 3,4-dimethoxybenzoylacetate (0.036 mol) was added to PPA (62 g) and then stirred for 1 h at 90—100 °C. The mixture was poured into ice-water and filtered. The crude products were purified by column chromatography on silica gel using benzene as the eluent. The corresponding thioflavone **1**[4] (0.7%), **3** (2.5%), and **4**[8] (6.1%) were isolated.

3: mp 194—195 °C; IR 3400 cm^{-1} (OH) and 1680 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ=1.96 (1H, s), 2.88 (1H, d, J=18 Hz), 3.48 (1H, d, J=18 Hz), 3.56 (3H, s), 3.72 (3H, s), 3.84 (3H, s), 3.92 (3H, s), 5.96 (1H, s), 6.52 (1H, s), 7.08 (1H, s), 7.24 (1H, s), 7.32—7.68 (3H, m), and 8.28—8.52 (1H, m), the OH proton being overlapped in the range of 3.5—3.92 ppm; MS m/z 488 (M^+; 100), 459 (50), 458 (46), and 444 (24).

Found: C, 68.35; H, 4.55%. Calcd for $C_{28}H_{24}O_6S$: C, 68.84; H, 4.95%.

Reaction of Benzenethiol or *t*-Butylthiobenzene with Ethyl Benzoylacetate at low Temperature. A mixture of benzenethiol **5** (0.018 mol) and ethyl benzoylacetate **6** (0.023 mol) was added to PPA (phosphoric pentaoxide 75%, 16 g), which was the grade of commercial origin, at 5—15 °C with stirring and kept for 1 h at 15 °C.

The reaction mixture was poured into ice-water (100 ml) and extracted with ether (3×30 ml). The ethereal layer was dried over magnesium sulfate and concentrated. The products were purified by column chromatography on silica gel using benzene–hexane (1 : 1) as eluent, and were assigned on the basis of their ^{1}H NMR and mass spectra. The ratio of the (*Z*)-and (*E*)-forms of ethyl 3-(phenylthio)cinnamate **7** was determined from ratio of integrations for the vinyl proton in ^{1}H NMR spectra. These compounds did not crystallize, except for **7a**,[13] **7b**,[14] **7c**,[14] and **8a**.[10] Spectral data and elemental analyses of new derivatives of **7** and **8** are

Table 5. Elemental Analyses of **7** and **8**

Compound	Formula	Analyses/% Calcd (Found)	
		C	H
(*Z*)-**7d**	$C_{17}H_{15}O_2SCl$	64.05 (63.84)	4.74 (4.95)
(*Z*)-**7e**	$C_{19}H_{20}O_4S$	62.26 (66.48)	5.85 (5.62)
(*Z*)-**7f**	$C_{19}H_{20}O_4S$	66.26 (66.05)	5.85 (6.08)
(*E*)-**7d**	$C_{17}H_{15}O_2SCl$	64.05 (63.72)	4.74 (4.50)
(*E*)-**7e**	$C_{19}H_{20}O_4S$	66.26 (65.98)	5.85 (5.56)
(*E*)-**7f**	$C_{19}H_{20}O_4S$	66.26 (66.50)	5.85 (6.12)
8b	$C_{25}H_{26}O_2S_2$	71.05 (71.32)	6.20 (6.48)
8c	$C_{25}H_{26}O_4S_2$	66.05 (65.81)	5.77 (6.02)
8d	$C_{23}H_{20}O_2Cl_2S_2$	59.61 (59.88)	4.35 (4.62)
8e	$C_{26}H_{28}O_5S_2$	64.44 (64.18)	5.82 (5.60)

summarized in Tables 1—3.

When the reaction temperature was raised to 60 °C in a reaction of **5a** with **6a**, thiflavone **1a**[6] (3.2%) was isolated together with **8a**.[10]

A mixture of benzenethiol **5a** (0.15 mmol) with **7a** (0.16 mmol) was added to 75% PPA (1.0 g) at 20 °C with stirring. After 1 h, the reaction mixture was worked up, as described above. Only thioacetal **8a** was isolated (48% yield).

In the reaction of *t*-butylthiobenzene, PPA of 85% phosphoric pentaoxide, which was the grade of commercial origin, was used and the reaction temperature was 20—30 °C. After 1 h, the reaction mixture was worked up, as described above. Thioflavone **1** and benzenethiol **5** were confirmed by direct comparisons of authentic samples.[4,6]

Ethyl (*Z*)-3-(4-Acetylphenylthio)cinnamate (7g). Sodium hydroxide (0.20 g) was added to a mixture of *p*-mercaptoacetophenone (0.361 g, 2.4 mmol) and ethyl 3-chlorocinnamate (0.5 g, 2.4 mmol); the mixture was then kept for 36 h at 70 °C with stirring. The reaction mixture was poured into water, and extracted with ether, the layer of which was dried over magnesium sulfate and concentrated. The residual oil was purified by column chromatography on silica gel using benzene as eluent to give the (*Z*)-form (17%) and the (*E*)-form (0.9%); (*Z*)-**7g**: ^{1}H NMR ($CDCl_3$) δ=1.32 (3H, t, J=7.5 Hz), 2.80 (3H, s), 4.24 (2H, q, J=7.5 Hz), 6.18 (1H, s), 7.00—7.40 (7H, m), and 7.60 (2H, d, J=7.5 Hz); MS m/z 326 (M^+; 100), 281 (63), 253 (29), and 239 (22); Anal. ($C_{19}H_{18}O_3S$) C, H. (*E*)-**7g**: ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, t, J=7.5 Hz), 2.60 (3H, s), 3.92 (2H, q, J=7.5 Hz), 5.60 (1H, s), and 7.08—7.84 (9H, m); MS m/z 326 (M^+; 100), 281 (46), and 253 (46); Anal. ($C_{19}H_{18}O_3S$) C, H.

Kinetics Measurements. A solution of 98% sulfuric acid was kept in a 25 ml volumetric flask at 20 °C, and 4 ml of 98% sulfuric acid was transferred to a UV cell in which the isolated ethyl (*Z*)-3-(phenylthio)cinnamate **7** (ca. 0.017 mg) was placed. A cell containing this solution of **7** (1.99×10^{-5} mol dm^{-3}) was put in cell holders thermostatted at 20 °C (±0.05 °C) during the measurement.

The absorbance was measured at an absorption maximum (293 nm) of **1** formed for ca. 6—7 min. The rate constants were determined graphically using plots of $\ln(A_t-A_o)$ vs. time (correlation coefficients 0.97—0.99). The kinetic data for the formation of thioflavones are shown in Table 4.

Preparation of Thioflavone from 7 and 8. Method A: Thioacetal **8a** (1.0 g) or ethyl (*Z*)-3-(phenylthio)cinnamate **7a** (50 mg) was added to PPA (15 g or 1 g) at 90 °C with stirring. After 1 h, the mixture was worked up, as described above. Thioflavone **1a**[6] was isolated in 95% and 98% yields, respectively.

Method B: Thioacetal **8a** (1.0 g) or ethyl (*Z*)-3-(phenylthio)cinnamate **7a** (0.5 g) was added to concd H_2SO_4 (15 ml or 4 ml) at 20 °C, with stirring. After 20 min, the mixture was worked up, as described above. Thioflavone **1a** was isolated in 85 and 90% yields, respectively.

Decomposition of Ethyl (Z)-3-(4-Acetylphenylthio)cinnamate. Compound **7g** (100 mg) was added to concd H_2SO_4 (5 ml) at 20 °C with stirring and the mixture was kept for 1 h at 20 °C. The reaction mixture was poured into ice-water (50 ml) and extracted with ether. The products were purified by column chromatography on silica gel using benzene–acetone (3:1) as eluent to give **5g** (R^1=4-Ac) (73%), **6** (53%), and 3-hydroxy-1-indenone[12] (31%).

5g: ^{1}H NMR ($CDCl_3$) δ=2.50 (3H, s), 3.65 (1H, s), 7.22 (2H, d, J=10 Hz), and 7.74 (2H, d, 10 Hz); MS m/z 152 (M^+; 58), 137 (100), 109 (42); Anal. (C_8H_8OS) C, H.

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