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L. Somogyi [a]

[a] Research Group for Antibiotics, Hungarian Academy of Sciences, P.O. Box 70, H-4010, Debrecen, Hungary

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TRANSFORMATION OF 1-THIOFLAVONOIDS BY OXIDATION AND DEHYDROGENATION

L. Somogyi

Research Group for Antibiotics, Hungarian Academy of Sciences,
P.O. Box 70, H-4010 Debrecen, Hungary

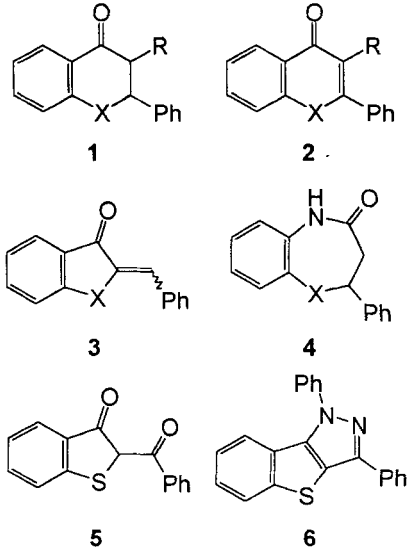
Abstract: *Simple, efficient and selective new one-step transformations with DDQ, IBDA and I_2/DMSO are presented for the dehydrogenation of thioflavanone (**1a**), as well as the oxidized (**1c**) and halogenated (**1d**) derivatives. Ring-contraction reactions of the 1-oxide **1b** and **1d** leading to the formation of the benzothiophen derivatives **3a** and **5**, respectively, are also described.*

Dehydrogenation of flavanones to flavones has been comprehensively studied. A plethora of methods and reagents, with various modes of action and sites of attack is known, including halogenation at position 3 followed by dehydrohalogenation with a base;[1,2] photochemical transformations in the presence

of NBS,[3] heterocyclic N-oxides,[4] or pyrylium salts;[5] enzymatic or microbiological methods;[6,7] Tl(III)-salts;[8-11] $Pb(OAc)_4$;[12,13] NiO_2;[14,15] iodanes [iodine(III) derivatives];[16-22] iodine or I_2/DMSO;[23-27] SeO_2;[28-30] and the "organic selenium dioxide", DDQ.[31-37] Applicability of the individual methods may be limited by the sensitivity of substituents, or by the substitution pattern of the molecule, and also by certain side-reactions (such as ring-contraction,[13,21] and the formation of isoflavones *via* 2,3-aryl shift[9,10,18,20]).

The reactivity of the carbonyl group of flavones toward oxo reagents is diminished in comparison with that of flavanones. Moreover, owing to the different electronic interactions between the carbonyl group and the heteroatom (S) of the ring along the –S–CH(Ph)–CH_2–C(O)– or the –S–C(Ph)=CH–C(O)– sequence, 1-oxides and 1,1-dioxides may even resist such condensation reactions [these structural features of (thio)flavonoids may afford possibilities for a (transient) formation of quasiaromatic intermediary forms[38-40]]. Hence, with the aim of finding more mild and selective methods, we decided to study the scope and limitations of the subsequent oxidation and dehydrogenation reactions of the carbonyl-condensation products of thioflavonoids possessing various oxidation levels. A recent publication[41] on the dehydrogenation of substituted chromanones, thiochromanone and thioflavanone by iodine-dimethylsulfoxide prompted us to present our results on the dehydrogenation of the parent thioflavanone and its oxidized derivatives using DDQ, $PhI(OAc)_2$ (PIDA, IBDA), I_2/DMSO, and nickel peroxide hydrate which complement our previous investigations[42] carried out with $(NH_4)_2Ce(NO_3)_6$ [CAN], and $NaIO_4$.

The structural characteristics outlined above are reflected in the reactivities and the type of transformations. Thioflavanone (**1a**) undergoes dehydrogenation[42,43] with CAN which may proceed *via* the formation of sulfur-stabilized carbocations,[44,45] thus we found flavanone (**1g**) to be resistant to this reagent under identical conditions. Moreover, contrary to the transformation of thioflavanone (**1a**) into thioflavone 1,1-dioxide (**2c**) in an oxidation/dehydrogenation process[42] upon treatment with $NaIO_4$, flavanone (**1g**) was shown to react unsatisfactorily under the same conditions and produced a complex mixture of unchanged **1g**, flavone (**2g**) and 3–4 unidentified minor products. Furthermore, dihydrobenzothiazepinone **4a**, also comprising the –S–CH(Ph)–CH_2–C(O)– sequence, trans-



	X	R
a	S	H
b	SO	H
c	SO_2	H
d	S	Br
e	SO	Br
f	SO_2	Br
g	O	H

formed into the corresponding sulfoxide **4b** and was neither overoxidized to a sulfone nor dehydrogenated (see Experimental).

The I_2/DMSO couple dehydrogenated thioflavanone (**1a**) and the 1,1-dioxide (**1c**) in almost quantitative yield. Thioflavanone 1-oxide (**1b**), however,

was transformed into 2-(phenylmethylene)benzo[*b*]thiophen-3(2*H*)-one [thioaurone, **3a**, (80%)] under the same conditions (see the Table). Photochemical transformation of the sulfoxide 6-Me-**1b** into the corresponding thioaurone (5-Me-**3a**) in a 14% yield has been reported[46] previously. We found that sulfoxide **1b** is also transformed thermally to **3a** to some extent when refluxed in benzene for 1 day. I_2/DMSO was however, unsuitable for the dehydrogenation of 3-bromothioflavanone (**1d**), giving a multicomponent mixture in which thioflavone (**2a**) and thioaurone (**3a**) were the major components.

In boiling methanol, iodobenzene diacetate (IBDA) dehydrogenated thioflavanone **1a** and the dioxide **1c** to the thioflavones **2a** (86%) and **2c** (50%), respectively. Under the same conditions sulfoxide **1b** transformed into the thioaurone **3a** (32%; see the Table and Experimental). The moderate yield of the 1,1-dioxide **2c** may be attributed to the diminished electron density at C-3 of **1c** effected by the sulfone moiety. Dehydrogenation of thiochroman-4-ol to thiochromanone with *o*-iodosobenzoic acid,[47] C-3-hydroxylation of thiochromanone by treatment with IBDA,[48] and selective oxidation of alkyl- and aryl sulfides to sulfoxides with IBDA,[49] [hydroxy(tosyloxy)iodo]benzene[50] and *tert*-butylperoxy iodanes[51] have been reported as characteristic transformations of related sulfur compounds with iodanes.

On treatment with IBDA in glacial acetic acid at room temperature, 3-bromothioflavanone (**1d**) gave a complex mixture containing thioflavone (**2a**), 3-bromothioflavone (**2d**), thioflavone 1-oxide (**2b**), and 3-bromothioflavone 1-oxide (**2e**) as the major products. Similar treatment in MeOH in the presence or absence

Table DDQ[a], IBDA[b] and I_2/DMSO dehydrogenation of thioflavonoids **1a-d**[c]

Sub-strate (mmol)	Solvent (ml)	Agent (mmol)	Reaction temp. [°C] (time [h])	Prod-uct	% Yield crude (pure)[d]	M.p. [°C] (solvent)	Lit. m.p. [°C] (solvent)
1a (3)	PhH (25)	DDQ[e] (3.3)	b.p. (22)	**2a**	94.4 (85.2)	125 (2-PrOH/hexane)	125 (EtOH)[f]
1a (3)	MeOH (10)	IBDA (4.5)	b.p. (48)	**2a**	(86.2)	124 (MeOH)	124.5–125.5 (abs. EtOH)[g]
1a (10)	DMSO (5)	I_2 (0.25)	100[h] (18)	**2a**	97.6 (92.7)	125 (2-PrOH/heptane)	125 (EtOH)[f]
1b (0.25)	PhH (4)	DDQ[i] (0.275)	b.p. (23)	**3a**	(37.8)	132 (MeOH/EtOAc)	134–134.5 (EtOH)[j]
1b (0.5)	MeOH (4)	IBDA (0.75)	b.p. (41)	**3a**	(32.3)	134 (MeOH)	134–134.5 (EtOH)[j]
1b (1.5)	DMSO (1.5)	I_2 (0.038)	100[h] (18)	**3a**	83.7 (66)	133 (2-PrOH/hexane)	134–134.5 (EtOH)[j]
1c (20)	MeOH (60)	IBDA (30)	b.p. (48)	**2c**	(49.8)	135 (MeOH)	135–136 (EtOH)[k] 135 (2-PrOH)[l]
1c (10)	DMSO (5)	I_2 (0.25)	100[h] (42)	**2c**	99.1 (90.8)	134.5 (2-PrOH)	135–136 (EtOH)[k] 135 (2-PrOH)[l]
1d (3)	PhH (10)	DDQ[e] (5)	b.p. (48)	**2d**	85.6 (66.8)	136 (2-PrOH)	136 (EtOH)[m]

[a] 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. – [b] Iodobenzene diacetate, $PhI(OAc)_2$. – [c] For general procedures see Experimental. – [d] Without workup of the mother liquor. – [e] In the presence of *p*-toluenesulfonic acid. – [f] Prepared by treatment of **1a** with PCl_5 in boiling benzene; ref. 62. – [g] Ref. 43. – [h] Bath. – [i] Similar result was obtained by treatment with chloranil. – [j] Ref. 63. – [k] Ref. 64. – [l] Ref.42. – [m] Ref. 62.

of KOH or *p*-toluenesulfonic acid led to the formation of several compounds from which the alkali-soluble 2-benzoylbenzo[*b*]thiophen-3(2*H*)one **5** (25%), and after separation by column chromatography, **2d**, **2a**, **2e**, and **2b** could be isolated.

For corroboration of structure **5** the product was transformed into 1,3-diphenyl-1*H*-[1]benzothieno[3,2-*c*]pyrazole (**6**) by a known method.[52] Ring contraction reactions of 3-halogenothiochromans and -thiochromones in the presence of bases to 2-substituted benzo[*b*]thiophen-3(2*H*)-ones have been reported[53-58] to proceed with a transient formation of thiiranium cations. Interestingly, however, diketone **5** was also formed – although in poor (3-5%) yield – also upon treatment of the 1,1-dioxide **1c** with IBDA/MeOH.

3-Bromothioflavone (**2d**) was recovered unchanged after treatment with IBDA in MeOH at room temperature for 3.5 d, or in AcOH near the b.p. for 22 h. Thus, the 1-oxide moiety of **2e** was probably introduced before the dehydrogenation step. Similarly, generation of the 1-oxide moiety of **2b** presumably precedes dehydrogenation, as thioflavone (**2a**) was found to resist transformation into sulfoxide **2b** when treated with IBDA in MeOH at room temperature (even in the presence of *p*-toluenesulfonic acid) for 12 d, or in AcOH for 13 d. However, similarly to the oxidation of thioxanthone to the sulfoxide,[49] treatment of thioflavone (**2a**) with IBDA in boiling AcOH gave the corresponding sulfoxide **2b**.

Treatment of thioflavanone (**1a**) or the 3-bromo derivative **1d** with DDQ expectedly afforded thioflavones (**2a** and **2d**) in excellent yields (see the Table), but under similar conditions dehydrogenation of **1a** with *o*-chloranil (tetrachloro-1,2-benzoquinone) failed. The synthesis of **2d** has been performed[39] by CAN oxidation

of **1d** at room temperature, or by treatment of sulfoxide **1e** with Ac_2O (in 25% and 51%, respectively). For quinone-dehydrogenation, the ring to be dehydrogenated must contain at least one benzylic or allylic hydrogen atom.[59] In addition to the dehydrogenation of 4*H*-thioflavenes with DDQ to benzothiopyrylium salts, transformation of 2-alkyl(thio)chromanones to the corresponding (thio)chromones have been performed.[33,60] The introduction of a double bond by hydride ion abstraction and proton elimination constitutes the primary reaction of DDQ.[59,61] When dehydrogenating flavonoids in this way the inductive effects are much more important than the steric and resonance ones.[34,37] In agreement with these findings thioflavanone 1,1-dioxide (**1c**) resists dehydrogenation with DDQ. Thus, after treatment with 2 mol DDQ in the presence of *p*-toluenesulfonic acid in boiling dioxane for 3 d ca. 50% of **1c** remained unchanged. Upon treatment with DDQ, sulfoxide **1b** was again transformed into thioaurone (**3a**).

The toxic and relatively expensive nickel peroxide hydrate proved to be of little value for the dehydrogenations. Treatment of thioflavanone (**1a**) with NiO_2 in benzene at ambient temperature for 17 h, afforded a very complex reaction mixture containing ca. equal amounts of thioflavone (**2a**) and thioaurone (**3a**) as the major components. Furthermore, 1,1-dioxide **1c** underwent only incomplete dehydrogenation even after treatment with a 2–3-fold excess of the reagent at 53 °C for six days.

The above findings show that in addition to the known methods, DDQ, IBDA, and I_2/DMSO are new useful synthetic tools for the one-step dehydrogenation of thioflavonoids, the method of choice being dependent on the nature (reactivity, sensitivity towards various side reactions, etc.) of the substrates.

The dehydrogenation reactions of other thioflavonoid derivatives are being studied.

EXPERIMENTAL

General: Melting points (uncorrected): Kofler block. – Solutions were concentrated under reduced pressure (rotary evaporator < 40 °C, bath). – TLC: Kieselgel 60 F_{254} (Merck, Alurolle) solvents: $CHCl_3$/EtOAc *A* = (9:1) or *B* = (95:5), *C* = $CHCl_3/Et_2O$ (95:5), *D* = $CHCl_3$, and hexane/$CHCl_3$ *E* = (1:2) or *F* = (1:1). – IR(KBr discs): Perkin-Elmer 16 PC-FT. – MS(EI): VG-7035 GC/MS/DS (70 eV), ion current 0.1 mA, direct insertion technique. Except compound **2e** all of the products described in this paper are known compounds. Identification was executed by comparison with the respective authentic samples (m.p., TLC, IR).

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) Dehydrogenation:

A mixture of substrate **1**, DDQ, anhydrous benzene, and a small amount of anhydrous *p*-toluenesulfonic acid was boiled with stirring for a period indicated in the Table, then cooled. The precipitated hydroquinone ($DDQH_2$) was filtered off and the filtrate was concentrated. A $CHCl_3$ solution of the residue was washed with aq. $NaHCO_3$ and water, dried ($MgSO_4$), treated with fuller's earth and charcoal, and then concentrated. The residue was crystallized from the solvent indicated in the Table.

Iodobenzene Diacetate (IBDA) Dehydrogenation:

A mixture of substrate **1**, IBDA, and MeOH was boiled (until dissolution was

complete with stirring) for a period indicated in the Table, then cooled. The precipitated crude product was recrystallized from methanol.

Iodine/Dimethyl Sulfoxide Dehydrogenation:

A mixture of substrate **1**, iodine (conveniently as a 0.1 M I_2/DMSO solution), and DMSO was kept at 100 °C for a period indicated in the Table, then cooled and poured into water. The mixture was extracted several times with $CHCl_3$, and the $CHCl_3$ solution was washed with aq. Na_2SO_3 and water, dried ($MgSO_4$), treated with fuller's earth and charcoal, and then concentrated. The residue was crystallized from the solvent indicated in the Table.

*2,3-Dihydro-2-phenyl-1,5-benzothiazepin-4(5H)-one 1-Oxide (**4b**):*

a) A mixture of benzothiazepin **4a** (6.384 g, 25 mmol), $NaIO_4$ (8.021 g, 37.5 mmol), 2-PrOH (180 ml), and water (85 ml) was boiled until dissolution was complete (~40 min) with stirring and for an additional 6 h, and then concentrated. The residue was triturated with lukewarm water to leave undissolved crude **4b** (6.176 g, 91%), m.p. 193°C.

b) A mixture of compound **4a** (0.1276 g, 0.5 mmol), $NaIO_4$ (0.4278 g, 2 mmol), 2-PrOH (8 ml), and water (8 ml) was boiled with stirring for 3 h and then processed as above to give sulfoxide **4b** (0.1219 g, 89.9%), m.p. 196–197°C, ref.[65] 197–198°C (from MeOH).

*Attempted Dehydrogenation of Flavanone (**1g**) with $NaIO_4$:*

A mixture of **1g** (0.0561 g, 0.25 mmol), $NaIO_4$ (0.2139 g, 1 mmol), 2-PrOH (4

ml), and water (4 ml) was boiled for 24 h, and then concentrated. The residue was partitioned between $CHCl_3$ and water. In the $CHCl_3$ solution approximately equal amounts of **1g** and **2g** could be detected along three minor products (TLC, solvent *B*).

Transformations of 3-Bromothioflavanone (1d) with PhI(OAc)$_2$ (IBDA) (See the Table):

a) To a suspension of **1d** (1.596 g, 5 mmol) in MeOH (40 ml), IBDA (3.287 g, 10 mmol, 98%) was added with stirring at room temperature over a period of 1.5 h. The mixture was stirred until dissolution was complete and kept for 2 d, and then concentrated. A $CHCl_3$ solution of the residue was washed with aq. $NaHCO_3$ and water, dried ($MgSO_4$), treated with charcoal and then concentrated. Column chromatography was performed as described in e).

b) To a solution of IBDA (4.601 g, 14 mmol, 98%) in MeOH (70 ml) were added 0.5 M KOH/MeOH (14 ml, 7 mmol) and **1d** (2.234g, 7 mmol) with stirring. After dissolution was complete (1 h), the solution was kept at room temperature for 3 d, and then concentrated. A $CHCl_3$ solution of the residue was treated with aq. HCl, aq. $NaHCO_3$ and water, dried ($MgSO_4$), treated with charcoal and then concentrated.

c) In MeOH (25 ml) were sequentially dissolved IBDA (2.629 g, 8 mmol, 98%), *p*-toluenesulfonic acid (1.553 g, 8 mmol), water (0.8 ml), and **1d** (1.277 g, 4 mmol) with stirring at room temperature. The solution was kept for 4 d and then concentrated and processed as in a).

d) IBDA (6.573 g, 20 mmol) was added to a suspension of **1d** (3.192 g, 10 mmol) in AcOH (50 ml) over a period of 1 h with stirring until dissolution was complete. The solution was kept for 3 d at room temperature and then processed as in a).

e) *p*-Toluenesulfonic acid (1.941 g, ~10 mmol) was added to a solution of IBDA (3.287 g, 10 mmol, 98%) in AcOH (25 ml) with stirring. To the thick slurry formed were added water (1 ml) and **1d** (1.596 g, 5 mmol) with stirring until dissolution was complete. The solution was kept for 3.5 d at room temperature and then processed as in a).

Prior to separation of the products by column chromatography, most of compound **5** can also be extracted from the $CHCl_3$ solution with 0.5 M aq. NaOH.

Column chromatography (Silicagel 60, solvent *D*) of the residue afforded various amounts of 2-benzoylbenzo[*b*]thiophen-3(2*H*)-one (**5**, 15–20%), m.p. 119°C (from MeOH), ref.[66] 116–117°C (from PhH or EtOH), ref.[67] 118–119°C (from EtOH), ref.[68] 120°C (from 95% EtOH); thioaurone (**3a**, 1–2%), m.p. 132–133°C (from MeOH/EtOAc), ref.[63] 134–134.5°C (from EtOH); 3-bromothioflavone (**2d**, 1–2%), m.p. 136°C (from MeOH), ref.[62] 136°C (from EtOH); thioflavone (**2a**, 1–2%), m.p. 124°C (from MeOH), ref.[43] 124.5–125.5°C (from EtOH); 3-bromothioflavone 1-oxide (**2e**, 15–25%, for further data see below); and thioflavone 1-oxide (**2b**, 20–25%), m.p. 135°C (from PhMe/hexane), ref.[43] 134°C (from PhH/petroleum ether).

Characteristic data for 3-bromothioflavone 1-oxide (**2e**): m.p. 131–131.5°C (from 2-PrOH). – IR(KBr): ν = 1662 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$) δ = 8.39–8.34 and 8.13–8.09 (both: m, 1 H; 5-H and 8-H, respectively), 7.91–7.72 (m, 2 H, 6,7-H), 7.62–7.48 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 173.88, 159.59, 143.71,

132.82, 126.92 and 126.18 (quaternary carbons), 133.88, 132.07, 130.51, 129.70, 128.90 (2 C), 128.84 (2 C), and 127.81 (aromatic *C*H). – MS: *m/z*(%): 286 (4) [$M^+ + 1 - SO$], 284 (4) [$M^+ - 1 - SO$]. – $C_{15}H_9BrO_2S$ (333.2): calcd. C 54.07, H 2.72, Br 23.98, S 9.62; found C 53.88, H 2.71, Br 24.07, S 9.66.

1,3-Diphenyl-1H-[1]benzothieno[3,2-c]pyrazole (6):

A mixture of compound **5** (0.300 g, 1.18 mmol), phenylhydrazine (0.300 g, 2.77 mmol) and EtOH (9 ml) was boiled with stirring for 10 h, and after addition of concd. H_2SO_4 (0.15 ml) for a further 2 h to give **6** (0.227 g, 76.4%), m.p. 172°C (from EtOH), ref.[52] 171°C (from EtOH), ref.[68] 170°C (from EtOH).

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