Oxidative rearrangement of 2'-hydroxychalcones having no substituent at the 3'- and 5'-positions with thallium(III) nitrate in methanol

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Oxidation of 2'-hydroxychalcones with no substituents at the 3'- and 5'-positions with thallium(III) nitrate (TTN) in methanol has been studied in detail and the following results obtained. (1) 2'-Hydroxy-4,6'-dimethoxychalcones (1b and 2b) have increased reactivity over their methyl ethers as a result of participation of the 6'-methoxy oxygen atom; the reactivity of 2'-hydroxy-4,4'-dimethoxychalcone 3b however was decreased. (2) The reactions were greatly affected by the substituents on the A and B rings and formed the corresponding 1,2-diaryl-3,3-dimethoxypropan-1-ones (acetal) and/or 2-(α-methoxybenzyl)coumaranones (coumaranone): the oxidative rearrangement was greatly accelerated by methoxy groups at the 4- and/or 2-positions to give an acetal as a main product. (3) Formation of the coumaranone was observed only when the 2'-hydroxychalcones had a methoxy group at the 6'-position and a B ring with weaker electron-donating nature. (4) The ratio of the coumaranones formed in the reaction of 2 with no substituent at the 4'-position was lower than that of 1 which formed quickly a cyclic TTN complex between the 2'-hydroxy and the neighbouring carbonyl groups. Only the reaction of 2'-hydroxy-6'-methoxychalcone 2a afforded the acetal and coumaranone together with a large amount of thallium compounds which were converted into a mixture of the corresponding isoflavone and aurone by treatment with hydrochloric acid. From these results, the mechanism of the reaction was proposed as shown in Schemes 2 and 3.

Introduction

Earlier,[1] we reported that the oxidative rearrangement by thallium(III) nitrate (TTN) of chalcones with no hydroxy group was studied in order to elucidate the effects of the substituents and a likely mechanism was proposed for the reactions. In connection with this study, oxidative rearrangement of 2'-hydroxychalcones 1–3 with no substituent at the 3'- and 5'-positions was examined in detail. It was found that the reactions were greatly affected by substituents on the A and B rings and formed the corresponding 1,2-diaryl-3,3-dimethoxypropan-1-ones (acetal; **A**) and/or 2-(α-methoxybenzyl)coumaranones (**C**). In particular, the 6'-methoxy group did not accelerate the oxidative rearrangement, but was much involved in coumaranone formation. As an extension of the previous study, we report here the substituent effect and mechanism in the reaction of 2'-hydroxychalcones with TTN.

Results and discussion

In a previous paper on the oxidation of 2'-hydroxyacetophenones with TTN in methanol, we reported the following results.[2] (1) The acetophenones with methoxy groups at the 3'- and/or 5'-positions are oxidized to the corresponding quinone monoacetals, the reactivity of the compounds being greatly increased with increasing numbers of methoxy groups. (2) The acetophenones with no substituent at the 3'- and 5'-positions are scarcely oxidized. (3) Only 2'-hydroxy-4',6'-dimethoxyacetophenone failed to oxidize, instead it rapidly formed a thallium complex. The results suggest that the oxidative rearrangement of 2'-hydroxychalcones having no substituent at the 3'- and 5'-positions proceeds without oxidation of the A-ring skeleton, although the 2'-hydroxy-4',6'-
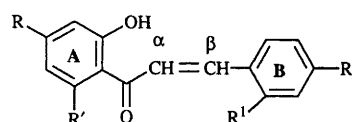
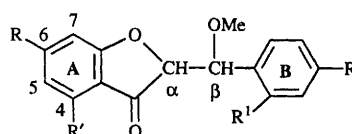1a,b,c,d R=R'=OMe
2a,b R=H, R'=OMe
3a,b R=OMe, R'=H
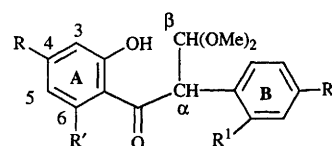
A1a,b,c R=R'=OMe
A2a,b R=H, R'=OMe
A3b R=OMe, R'=H

C1a,b R=R'=OMe
C2a,b R=H, R'=OMe

a; R¹=R²=H   b; R¹=H, R²=OMe   c; R¹=R²=OMe   d; R¹=H, R²=NO₂

dimethoxychalcones 1 form their thallium complexes prior to the oxidative rearrangement. Therefore, the reactions of 1, 2'-

hydroxy-6'-methoxychalcones **2** and 2'-hydroxy-4'-methoxy-chalcones **3** were examined in detail.

Bands I in the UV spectra for the 2'-hydroxychalcones (**1b**, **1c**, **2b**, **3a** and **3b**) were unaffected by the addition of TTN, making it possible to determine the chalcone content of the reaction mixture as with the reactions of chalcones with no hydroxy group.[1] However, the UV spectra of 2'-hydroxychalcones **1a** and **2a** were affected by the addition of TTN as follows. The intensity of band I in **1a** increased by *ca.* 10% without a shift in the wavelength of the band; the intensity of the band I in **2a** did not vary, but its wavelength was shifted hypsochromically by 10–15 nm as the reaction proceeded. This result shows that UV spectroscopy is analytically useful for a qualitative determination of chalcone reactivity.[1] In view of this, the reaction of seven chalcones together with their methyl ethers[1] was examined in order to elucidate the effect of the 2'-hydroxy group and their relative rates of reaction (see Fig. 1).

The reaction of **1c** proceeded rapidly because of the electronic effect of the 2- and 4-methoxy groups.[1] The reactivities of **1b** and **2b** with 4- and 6'-methoxy groups are greater than that of their methyl ethers **Me-1b** and **Me-2b**, respectively, and that of **3b** with no 6'-substituent is lower. The reactivities of the 2'-hydroxy-4-methoxychalcones are in the order **2b** > **1b** > **3b**, in contrast to that of their methyl ethers (**Me-3b** > **Me-1b** > **Me-2b**). In the reactions of the chalcones (**1a**, **2a** and **3a**) with no substituent on the B ring, similar results were also obtained, but their reactivities were lower than those of the corresponding methyl ethers[1] (**3a** did not react).

This difference in the reactivity of 2'-hydroxy-4-methoxychalcones **1b**, **2b** and **3b** and their methyl ethers is explained as follows on the basis of our previous study on the oxidative rearrangement of the 2'-methoxychalcones.[1] The reaction of 6'-methoxychalcones (**1b** and **2b**) is accelerated by the participation of the neighbouring 6'-methoxy oxygen atom because of the coplanarity between the A-ring and carbonyl group (see Schemes 2 and 3): The reactivity of each is then higher than that of its corresponding methyl ether since the latter lack coplanarity.[1] The reactivity of the chalcone (**3b**) with no 6'-substituent is lower than that of its methyl ether because of its lack of a 6'-methoxy group. Although the reaction of the chalcones (**1a** and **2a**) with no substituent on the B ring is explained by a similar participation of the 6'-methoxy group, that the reactivities are lower than those of the corresponding methyl ethers[1] suggests that reactions other than the oxidative rearrangement proceed simultaneously.

Furthermore, the reactivities of **2a** and **2b** are slightly higher than those of **1a** and **1b**, respectively, although the latter has an extra methoxy group at the 4'-position. These results may be explained by a difference in the complexation ability between the two kinds of chalcones **1** and **2**, as deduced from the fact that although 2'-hydroxy-4',6'-dimethoxyacetophenone quickly forms a thallium complex with TTN, the complexation of 2'-hydroxy-6'-methoxyacetophenone is slow.[2] That is, the chalcones **1** react rapidly with an equimolar amount of TTN to form a cyclic thallium complex between the carbonyl and hydroxy oxygen atoms after which the reaction proceeds with the excess of TTN; with the chalcones **2** the oxidation reaction and the formation of the cyclic thallium complex proceed simultaneously. In fact, in a TLC test of the reactions of **1a** and **1b**, the starting material spot disappeared within a few minutes and reappeared without the formation of products when the mixture was treated with dilute hydrochloric acid. Furthermore, the UV spectra of the mixture of **1b** and an equimolar quantity of TTN did not change with increasing reaction time. The results show that 2 molar equivalents of TTN are needed at least for the completion of the reaction of **1**. The highly reactive 2,4-dimethoxychalcone **1c** reacted with an equimolar amount of TTN, but stopped after *ca.* 50% conversion. In these reactions of **1**, all the products existed as thallium complexes which were
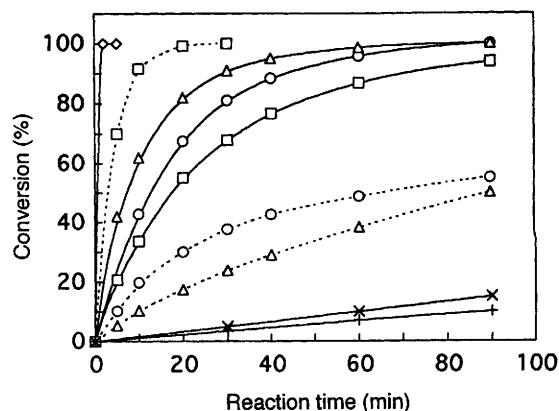

Fig. 1 Time conversion of the reaction of 2'-hydroxychalcones with TTN at 30 °C. **1c**, $-\Diamond-$; **1b**, $-\bigcirc-$; **Me-1b**, $\cdots\bigcirc\cdots$; **2b**, $-\triangle-$; **Me-2b**, $\cdots\triangle\cdots$; **3b**, $-\square-$; **Me-3b**, $\cdots\square\cdots$; **1a**, $-+-$; **2a**, $-\times-$.

obtained as pale yellow powders by extraction with chloroform after the mixture had been treated with sodium hydrogen sulfite. The structures were not established because of purification difficulties. Gradual decomposition of these complexes with dilute hydrochloric acid at 0 °C gave the thallium-free products.

Although the reaction of **1c** afforded only the acetal **A1c**, **1b** gave two compounds, the acetal **A1b** and (α-methoxybenzyl)coumaranone **C1b**. The result suggests that the substituents in the chalcones influence not only the reaction rate but also the type products. The products obtained from the seven chalcones are compared in Table 1. In the reaction of the 2'-hydroxy-4',6'-dimethoxychalcones **1a-c**, the ratio of the coumaranones to acetal increased with decreasing number of methoxy groups on the B-ring: the reaction of **1a** afforded the coumaranone **C1a-I** together with a little of the acetal **A1a**. The reaction of the 2'-hydroxy-6'-methoxychalcones **2a** and **2b** showed a similar tendency with that of the chalcones **1** and produced the coumaranones **C2a** and **C2b**; however, the ratio of coumaranone to acetal was lower and the reaction behaviour was also different. As a special case, the reaction of **2a** produced a mixture of two diastereoisomers of the coumaranones **C2a-I** and **C2a-II** and an acetal **A2a**, together with a large quantity of thallium compounds which were converted into a mixture of an isoflavone **4a** and aurone **5a** in refluxing aqueous methanolic hydrochloric acid. The reaction of **3b** with no 6'-substituent afforded the acetal **A3b** without the formation of coumaranone and the chalcone **3a** did not react.


4a

5a R=R'=H
6a R=OMe, R'=H
6d R=OMe, R'=NO$_2$
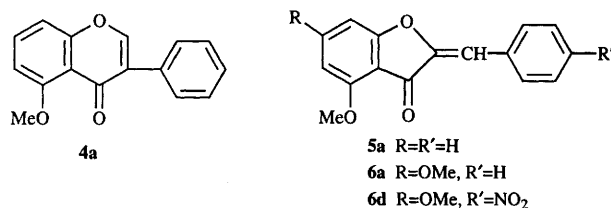
Mechanism of the reactions

The mechanism for coumaranone formation as illustrated in Scheme 1 was proposed by Lévai and Tökés[3] and explains reasonably our results in which the formation ratio of the coumaranones becomes large with the decreasing migratory aptitude of the B ring. The following results, however, can be explained only with difficulty. (1) Coumaranones are formed only when the 2'-hydroxychalcones have a 6'-methoxy group. (2) The formation ratio of the coumaranone from **2** is lower than that from **1** with the 4'-methoxy group. (3) Only the reaction of **2a** afforded the acetal **A2a** and two diastereomeric coumaranones, **C2a-I** and **C2a-II**, together with a large amount of thallium compounds.

Table 1 Conditions for the reaction of 2'-hydroxychalcones with TTN and the products

Starting material	Reaction conditions			Product yield (%)		
	TTN Mol ratio	Temp./ °C	Time/ h	Acetal	Coumara.-I	Coumara.-II
1a	2.5	50	24.0	Trace[a]	75	0
1b	2.5	30	3.0	57	25	0
1c	2.5	30	0.1	80	0	0
2a	2.5	40	24.0	11	7	7
				7 (**4a**)[b]	31 (**5a**)[b]	
2b	2.5	30	2.5	73	*ca.* 1.5[c]	*ca.* 1[c]
3b	2.0	30	3.0	63	0	0

[a] The compound was identified by ^{1}H NMR spectra for the recovered product, obtained from recrystallization of **C1a-I**. [b] The thallium compounds obtained from the reaction of **2a** were treated with boiling methanolic hydrochloric acid and the the product yields were estimated from the ^{1}H NMR spectra. [c] The coumaranones **C2b-I** and **C2b-II** were not isolated in a pure form.
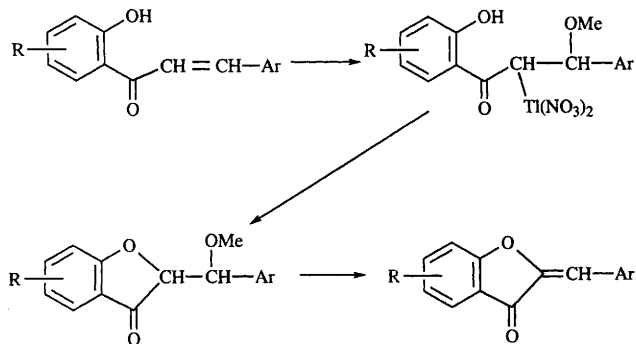
Scheme 1

These results suggest that the existence of the 6'-methoxy group and cyclic thallium complex between the 2'-hydroxy and carbonyl groups has a significant role for coumaranone formation. In this, coumaranone formation proceeds after the formation of the cyclic thallium complex. Thus, a new mechanism for the reaction is proposed as shown in Schemes 2 and 3.

That is, the 2'-hydroxychalcones **1** with 4'- and 6'-methoxy groups are converted into a complex **7** with TTN *via* the cyclic thallium complex between the 2'-hydroxy and carbonyl groups [Scheme 2; path (a)]. When the chalcones have 4- and/or 2-methoxy groups, the β-carbon in complex **7** is attacked by a methoxide ion to give a thallium compound **8** [path (b)]. Complex **8** is converted into a thallium complex **9** of the acetal (A1) by elimination of the thallium moiety and simultaneous migration of the B ring. The bonding ability of the bulky thallium atom to the α-carbon in complex **7**, however, decreases as a result of steric hindrance of the 6'-methoxy group but increases with a decrease in the electron-releasing nature of the B ring. As the result, the thallium complex **7a** formed from **1a** with no substituent at the B ring is isomerized into a complex **10a** [path (c)] and then stereospecifically cyclized to a thallium compound **11a** by attack of the 2'-hydroxy oxygen atom. Compound **11a** is converted into a thallium complex **12a** of the coumaranone **C1a-I** by solvolysis with methanol. The ratio between the paths (b) and (c) is dependent on the electronic effect of the substituents at the B ring: the reaction of **1b** with a methoxy group at the 4-position affords the two products **9b** and **12b** by paths (b) and (c), and that of **1c** with 2- and 4-methoxy groups affords an acetal **9c** only.

Complexes **9** and **12** are stable under the reaction conditions and dethallated to the corresponding acetal **A** and coumaranone **C** with dilute hydrochloric acid under mild conditions. The coumaranones are obtained as a single product **C1a,b-I**. The coumaranones **C1a,b-I** in solution were slowly isomerized to **C1a-II** and **C1b-II** when stored for a long period at room temperature. Racemic stereochemistry at the C_α- and C_β- positions in the coumaranone **C1a-I** or **C1b-I** is assumed with *RS* and *SR* configurations as expected for *cis*-hydroxylation of

a double bond with TTN.[4] In the ^{1}H NMR spectra for **C1a-I** and **-II**, the C_α-proton is greatly affected by anisotropy of the B ring and that in **C1a-I** is observed at δ 4.59 which is higher than that in **C1a-II** (δ 5.01). This assumption is also supported by a semiempirical molecular orbital calculation.[5] A C_α-methine proton of the energy-optimized structure of **C1a-I** is located just above the B ring, whereas the corresponding proton of **C1a-II** is apparently in the magnetically deshielding zone of the B ring.

Although the reactions of **2a** and **2b** with no substituent at the 4'-position are also explainable by a mechanism similar to that shown in Scheme 3, the reaction behaviours are different from that of **1** because of the slow complexation between the 2'-hydroxy and carbonyl groups. The reaction of the chalcone **2b** proceeds mainly *via* the complex **13b** and **14b** [paths (a') and (b')] to afford predominantly the acetal **A2b**, since the path (b') is accelerated by the 4-methoxy group in **2b**. In the reaction of the chalcone **2a** with no substituent on the B ring, the paths (b') and (c') proceed simultaneously to give a mixture of the acetal **A2a** and the coumaranone **C2a-I** *via* the intermediates **14a** and **16a**. The lack of the 4'-methoxy group in the chalcones, however, causes a decrease in the stability of the intermediates such as **14** and **16**, as evidenced by the relative ease of complexation[2] of 2',4',6'-trimethoxyacetophenone with TTN, but the difficulty of this with 2',6'-dimethoxyacetophenone. As a result, the intermediates **14a** and **16a** isomerize partly to more stable compounds **17a** and **18a**. The reaction of **2a** is alone in affording large amounts of the thallium compounds, which are converted into the isoflavone **4a** and aurone **5a**. The products exist also as thallium-free compounds and the coumaranone **C2a-I** initially formed is gradually isomerized to **C2a-II** under the reaction conditions: the coumaranone is obtained as a mixture of two diastereoisomers **C2a-I** and **C2a-II**.

In contrast, in the absence of a 6'-methoxy group, the reaction of the 2'-hydroxychalcones **3** does not form a coumaranone, an acetal instead being formed as the main product. The reactivity here, however, is greatly decreased, more so than with the corresponding methyl ethers, since there is no participation with a neighbouring oxygenated group as in **7** and **13**; further, the chalcone **3a** with no substituent on the B ring fails to react.

Recently, Thakkar and Cushman have reported the following unique reaction.[6] Oxidation of 2'-hydroxy-5'-methoxychalcones with 2.5–3 molar TTN affords the corresponding 4,5-dimethoxyaurones without any B ring substituent effect; however, 4-chloro-2'-hydroxy-4'-methoxychalcone and 4-chloro-2'-hydroxy-3'-methoxychalcone fail to afford an aurone. This result is similar to ours and suggests that 2'-hydroxy-4',6'-dimethoxy-4-nitrochalcone **1d** is also oxidized to 4,6-dimethoxy-4'-nitroaurone **6d** with TTN. In fact, the aurone **6d** was obtained by TTN oxidation of the chalcone **1d** in low yield after treatment with aqueous hydrochloric acid. This result suggests that the oxidation with TTN proceeds by a similar pathway to that proposed by us (see Scheme 4), although the

Scheme 2

Scheme 3
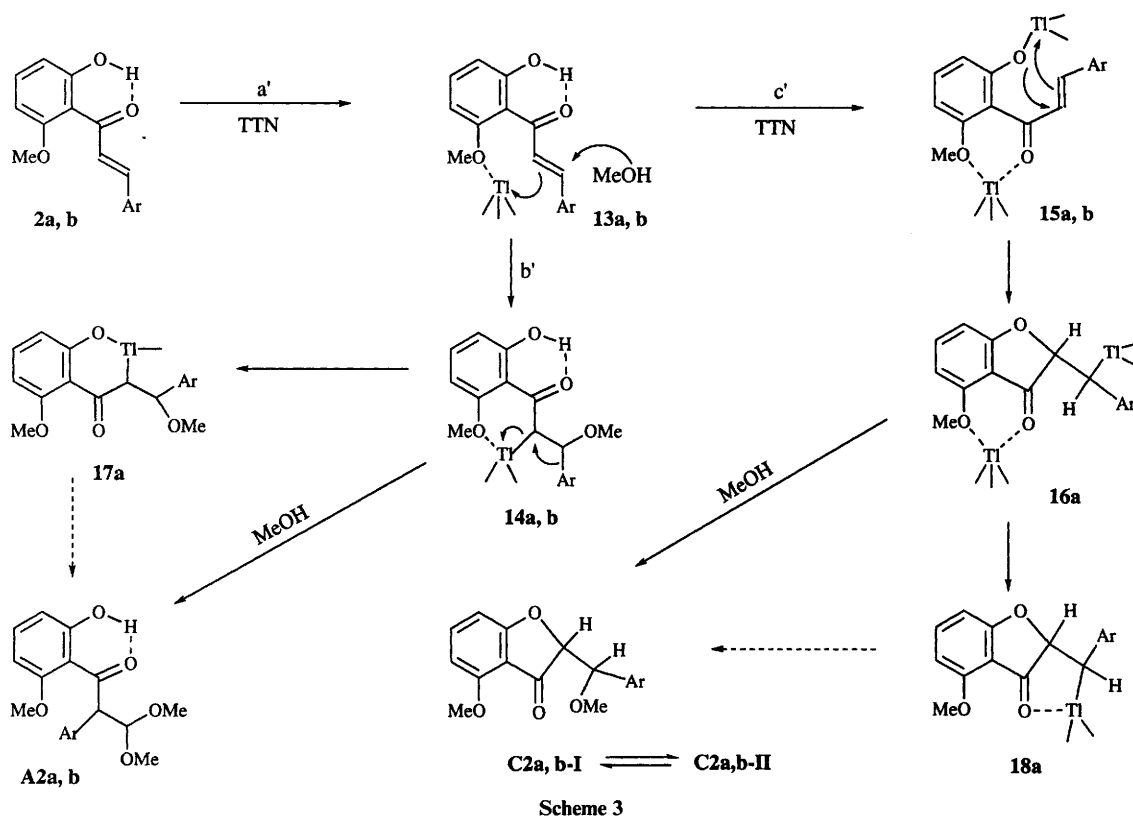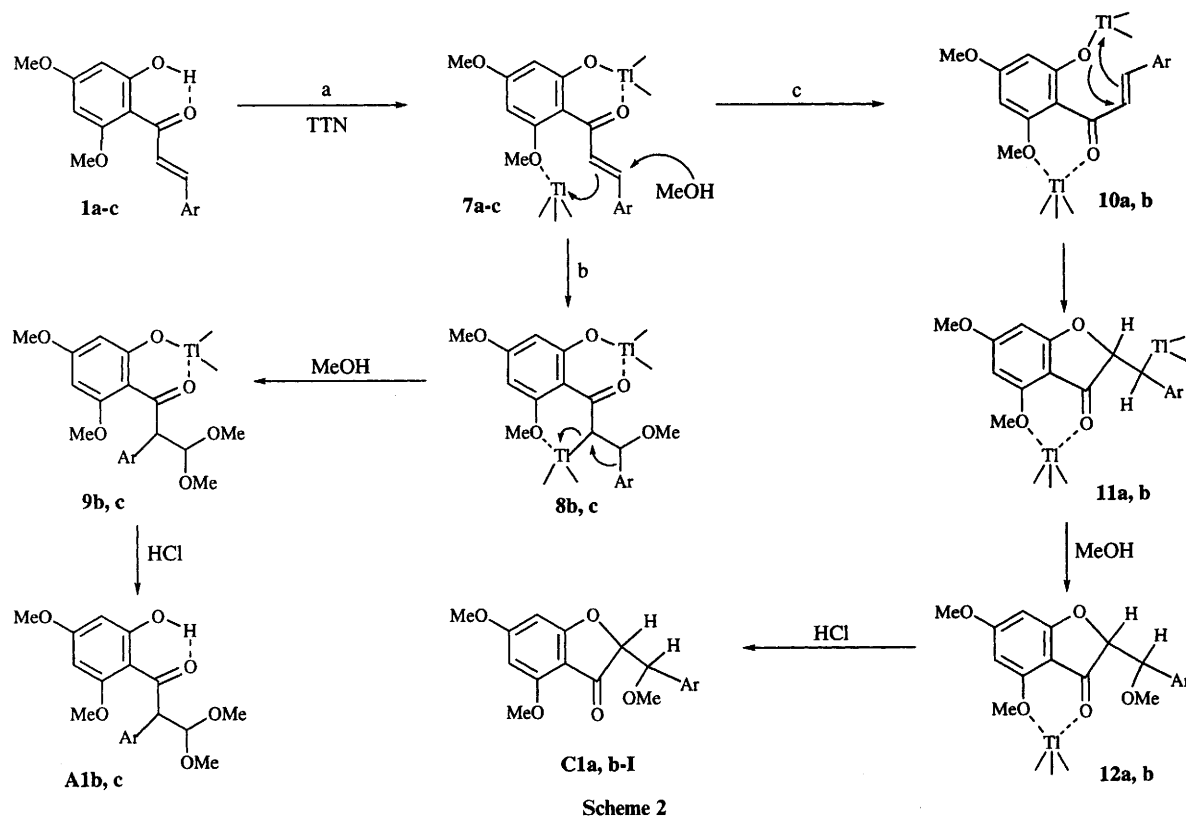
authors explain their reaction by assuming an alternative intermediate (see Fig. 2).

That is, the quinone monoacetal **D** formed from the 2'-hydroxy-5'-methoxychalcones by the oxidation is converted into a cyclic thallium complex **E** by attack of a methoxide ion. The complex **E** is complexated with an excess of TTN to give a complex **F** which is cyclized into a thallium compound **G** by a similar pathway [see Scheme 2, path (c)]. Compound **G** is converted into the aurone **H** *via* the corresponding

coumaranone. This seems to more plausibly explain the fact that the oxidation of 2'-hydroxychalcones with no 5'-methoxy group does not afford any aurone.

Experimental

All mps were determined in glass capillaries and are uncorrected. ¹H NMR spectra were recorded on a Bruker 400 or JEOL EX400 spectrometer, using tetramethylsilane as an

Table 2 ¹H NMR data of 1-(2-hydroxyphenyl)-2-phenyl-3,3-dimethoxypropan-1-ones, 2-(α-methoxybenzyl) coumaranones and aurones, and 6-methoxyisoflavone in CDCl₃^a

Compd.	α-H	β-H	Aromatic H in A ring				Aromatic H in B ring			–CH(OMe)₂	OMe	2-OH
			4-H or 5-H	6-H	3-H or 7-H	5-H	4'-H	2'-H 6'-H	3'-H 5'-H			
A1a	5.25d	5.07d	—	—	6.02d'	5.84d'	7.24t	7.41d (2 H)	7.31t (2 H)	3.16s (3 H) 3.44s (3 H)	3.78s (3 H) 3.83s (3 H)	14.00s
A1b	5.19d	5.02d	—	—	6.02d'	5.84d'	—	7.32d (2 H)	6.84d (2 H)	3.17s (3 H) 3.43s (3 H)	3.77s (3 H) 3.78s (3 H) 3.83s (3 H)	13.96s
A1c	5.73d	4.98d	—	—	6.00d'	5.81d'	—	— 7.30d	6.44d' 6.41dd	3.18s (3 H) 3.43s (3 H)	3.76s (3 H) 3.77s (6 H) 3.83s (3 H)	13.84s
A2a	5.27d	5.05d	7.29t	—	6.54d	6.31d	7.25t	7.41d (2 H)	7.32t (2 H)	3.16s (3 H) 3.43s (3 H)	3.86s (3 H)	13.04s
A2b	5.22d	5.02d	7.29t	—	6.53d	6.31d	—	6.85d (2 H)	7.32d (2 H)	3.18s (3 H) 3.43s (3 H)	3.78s (3 H) 3.86s (3 H)	13.07s
A3b	4.74d	5.08d	—	7.73d	6.38d'	6.40dd	—	6.85d (2 H)	7.33d (2 H)	3.22s (3 H) 3.44s (3 H)	3.77s (3 H) 3.80s (3 H)	12.82s
C1a-I	4.59d'	4.82d'	—	—	6.21d'	6.01d'	7.35t	7.49d (2 H)	7.42t (2 H)	3.22s (3 H)	3.86s (3 H) 3.92s (3 H)	—
C1a-II	5.01d'	4.79d'	—	—	6.03d'	5.83d'	7.18t	7.34dd (2 H)	7.22t (2 H)	3.36s (3 H)	3.79s (3 H) 3.80s (3 H)	—
C1b-I	4.56d'	4.75d'	—	—	6.22d'	6.01d'	—	7.41d (2 H)	6.95d (2 H)	3.19s (3 H)	3.83s (3 H) 3.86s (3 H) 3.92s (3 H)	—
C2a-I	4.57d'	4.82d'^{b}	7.52t	—	6.71d	6.47d	7.35t	7.49d (2 H)	7.42t (2 H)	3.20s (3 H)	3.97s (3 H)	—
C2a-II	4.99d'	4.79d'^{b}	7.37t	—	6.57d	6.29d	7.16t	7.33dd (2 H)	7.20t (2 H)	3.36s (3 H)	3.85s (3 H)	—
C2b-I	4.55d'	4.76d'	7.52t	—	6.72d	6.46d	—	7.42d (2 H)	6.95d (2 H)	3.17s (3 H)	3.83s (3 H) 3.97s (3 H)	—
C2b-II	4.97d'	4.64d'	7.38t	—	6.59d	6.30d	—	7.25d (2 H)	6.73d (2 H)	3.33s (3 H)	3.71s (3 H) 3.85s (3 H)	—
6a	—	6.78s^c	—	—	6.40d'	6.14d'	7.36t	7.87d (2 H)	7.43t (2 H)	—	3.92s (3 H) 3.96s (3 H)	—
5a	—	6.85s^c	7.58t	—	6.90d	6.63d	7.39t	7.91d (2 H)	7.45t (2 H)	—	4.02s (3 H)	—
6d	—	6.78s^c	—	—	6.44d	6.18d	—	8.00d (2 H)	8.28d (2 H)	—	3.95s (3 H) 3.98s (3 H)	—
4a	—	7.88s (2-H)	7.58t (7-H)	—	7.06d (8-H)	6.83d (6-H)	7.36t	7.53dd (2 H)	7.41t (2 H)	—	3.96s (3 H)	—

^{a} s = singlet, d = doublet (J = 8.0–9.0 Hz), d', doublet (J = 2.0–2.5 Hz), dd, double doublet (J = 8.5, 2.0 Hz); t, triplet (J = 7.5–8.5 Hz). ^{b} The intensity of the signal increased upon the irradiation of the methoxy group signal at δ 3.20–3.36. ^{c} Methine proton.
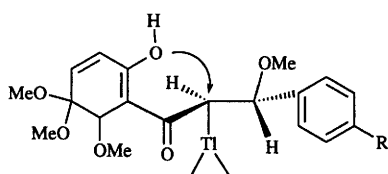

Fig. 2

internal standard in CDCl₃, and the chemical shifts are given as δ values. UV and MS spectra were recorded on a Hitachi 124 spectrophotometer in MeOH and on a Shimadzu QP1000 spectrometer, respectively. Column chromatography was carried out on Kieselgel 60 (70–230 mesh; Merck). For the preparative HPLC, a column (20 mm diam. × 600 mm) packed with Hitachi gel No. 3019 using MeOH was employed. Elemental analyses were performed with a Yanaco CHN-corder, Model MT-5. Thallium(III) nitrate trihydrate was obtained from Aldrich (the customary safety precautions should be employed). The ¹H NMR data for the products obtained here are summarized in Table 2.

Determination of the chalcone in the reaction mixture
Measurement of the reaction rates with TTN was carried out as described earlier.[1]

Oxidative rearrangement of the chalcones with TTN
The chalcone (2.0 mmol) was treated with TTN in MeOH (50–80 cm³) with stirring under the conditions indicated in Table 1 after which the reaction mixture was cooled at 0 °C. Saturated aqueous Na₂SO₃ (0.8–1.1 g, 4.0–6.5 mmol) and cooled 10% aq. HCl (15–20 cm³) were added to the reaction mixture which was then stirred at 0 °C for a further 1.5–2 h. The precipitates were filtered off and the filtrate was diluted with cold water and extracted with CHCl₃. The extract was washed with water, dried (Na₂SO₄) and then passed a short column of silica gel with CHCl₃ as eluent. The eluate was evaporated under reduced
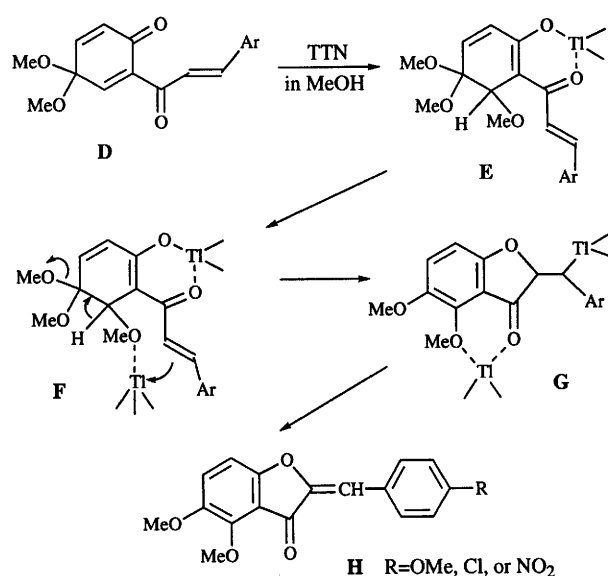
Scheme 4

pressure and the residue was purified by recrystallization and/or column chromatography with silica gel (Table 3).

Reaction of 2'-hydroxy-6'-methoxychalcone 2a with TTN
A mixture of **2a** (0.50 g) and TTN·3H₂O (1.92 g) in MeOH (40 cm³) was stirred at 40 °C for 24 h and then treated by the same method as described above. The CHCl₃ extract obtained was passed through a short column of silica gel, and eluted successively with CHCl₃ and then EtOAc (Tl-compounds). The product obtained from CHCl₃ eluate was rechromatographed over silica gel using CHCl₃ to give **A2a** (65 mg, 11%) and a mixture of the coumaranones. The mixture was separated to **C2a-II** (fraction 1; 40 mg, 7%) and **C2a-I** (fraction 2; 40 mg, 7%) by the preparative HPLC: **C2a-I**; λ_{max}/nm (log ε) 271 (4.05),

Table 3 1,2-Diaryl-3,3-dimethoxypropan-1-ones, 2-(α-methoxybenzyl) coumaranones, and related compounds

| Product | Mp/°C | Recrystn. solvent | Formula | Found | | Calcd. | |
				C (%)	H (%)	C (%)	H (%)
A1a[a]	97–99	CHCl$_3$–MeOH	C$_{19}$H$_{22}$O$_6$	65.37	6.37	65.88	6.40
A1b	90–92	MeOH	C$_{20}$H$_{24}$O$_7$	63.71	6.37	63.82	6.43
A1c	123–125	MeOH	C$_{21}$H$_{26}$O$_8$	61.81	6.39	62.06	6.45
A2a[a]	91–92	MeOH	C$_{18}$H$_{20}$O$_5$	68.29	6.38	68.34	6.37
A2b	93–95	CHCl$_3$–MeOH	C$_{19}$H$_{22}$O$_6$	66.03	6.35	65.88	6.40
A3b	66–68	CHCl$_3$–MeOH	C$_{19}$H$_{22}$O$_6$	65.70	6.36	65.88	6.40
C1a-I	143–145	CHCl$_3$–MeOH	C$_{18}$H$_{18}$O$_5$	68.72	5.70	68.78	5.77
C1a-II[b]	117–118	MeOH	C$_{18}$H$_{18}$O$_5$	68.58	5.78	68.78	5.77
C1b-I	167–169	MeOH	C$_{19}$H$_{20}$O$_6$	65.98	5.82	66.27	5.85
C2a-I	138–140	MeOH	C$_{17}$H$_{16}$O$_4$	71.67	5.59	71.82	5.67
C2a-II	153–155	MeOH	C$_{17}$H$_{16}$O$_4$	72.05	5.64	71.82	5.67
6a[c]	125–128	CHCl$_3$–MeOH	C$_{17}$H$_{14}$O$_4$·$\frac{1}{2}$H$_2$O	70.32	5.26	70.09	5.19
5a[c,3]	149–151	MeOH	C$_{16}$H$_{12}$O$_3$	76.09	4.66	76.18	4.80
4a[d,3]	88–89	Et$_2$O–hexane	C$_{16}$H$_{12}$O$_3$	75.97	4.76	76.18	4.80

[a] The acetals A1a and A2a were synthesized from the benzyl ethers of 1a and 2a by the oxidative rearrangement with TTN in methanol and the following debenzylation [7] with 10% Pd–C in a hydrogen atmosphere. [b] This was isolated from the mother liquor of the recrystallization of C1a-I by preparative HPLC. [c] These aurones were obtained by cyclization of the corresponding coumaranones with aq. HCl in MeOH. [3] [d] This was obtained by cyclization of A2a with aq. HCl in MeOH.

277i (4.01), 335 (3.67); m/z (EIMS, 70 eV), (rel. int.) 314 (M$^+$, 1.0), 283 (4.2), 282 (20.1), 281 (6.7), 253 (4.7), 251 (10.1) and 151 (100): **C2a-II**; λ_{max}/nm (log ε) 271 (4.01), 277i (3.99), 335 (3.62); m/z (EIMS, 70 eV) (rel. int.) 314 (M$^+$, 2.4), 283 (10.0), 282 (50.6), 281 (17.5), 253 (11.0), 251 (20.7) and 151 (100).

The thallium compounds (ca. 350 mg) obtained from the EtOAc eluate were refluxed with 10% aq. HCl (4 cm^3) in MeOH (20 cm^3) after which the mixture was concentrated, diluted with water, and then extracted with EtOAc to give a mixture (190 mg) of the isoflavone **4a** and aurone **5a**. The yields of the two compounds were estimated by integrating the C-2 and benzylidene protons in their ^{1}H NMR spectra (see Table 1).

Oxidation of 2′-hydroxy-4′,6′-dimethoxy-4-nitrochalcone 1d with TTN

2′,4′,6′-Trimethoxy-4-nitrochalcone [(6.68 g, 91%), mp 174–176 °C] was readily synthesized from 2′,4′,6′-trimethoxyacetophenone (4.5 g) by the condensation with p-nitrobenzaldehyde (3.5 g) in the presence of KOH (6.0 g) in EtOH (45 cm^3) at 50 °C. The chalcone (3.0 g) was dissolved in a solution of anhydrous AlBr$_3$ (7.0 g) in MeCN (35 cm^3) and set aside 30 °C for 1 h. 10% Aq. HCl (50 cm^3) and CHCl$_3$ (80 cm^3) were added to the mixture which was then stirred at 50 °C for 2 h and finally concentrated. The precipitates were collected and recrystallized from N,N-dimethylformamide to give **1d** (2.3 g, 93%), mp 231–233 °C (Found: C, 61.82; H, 4.51; N, 4.05. C$_{17}$H$_{15}$O$_6$N requires C, 62.00; H, 4.59; N, 4.25%).

A mixture of **1d** (0.50 g) and TTN·3H$_2$O (1.80 g) in MeOH (100 cm^3)–CHCl$_3$ (50 cm^3) was stirred at 40 °C for 24 h after which it was diluted with 10% aq. HCl (10 cm^3) and then

refluxed for 4.0 h. The precipitates were filtered off and the filtrate was concentrated under reduced pressure and extracted with CHCl$_3$. Concentration of the extract gave a residue which was chromatographed over silica gel using CHCl$_3$ and then recrystallized from CHCl$_3$–MeOH to afford the aurone **6d** (80 mg, 16%), mp 272–275 °C (Found: C, 60.46; H, 3.94; N, 4.34. C$_{17}$H$_{13}$O$_6$N·1/2H$_2$O requires C, 60.71; H, 4.17; N, 4.16%).

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