Oxidative Rearrangement of Chalcones without a Hydroxy Group by Thallium(III) Nitrate in Methanol

Tokunaru Horie,* Yasuhiko Kawamura, Chikako Sakai, Ayako Akita and Masafumi Kuramoto
Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima-cho, Tokushima 770, Japan

Oxidative rearrangement of chalcones with no free hydroxy group with thallium(III) nitrate (TTN) in methanol was studied in detail and the following results were found. The reactions were greatly accelerated when there were methoxy groups at the 2-, 4-, and/or 6-position on the B ring and formed the corresponding 1,2-diaryl-3,3-dimethoxypropan-1-one (acetal) only. The methoxy groups on the A ring also had a tendency to accelerate the reaction, but the 2',6'-dimethoxy groups greatly retarded the reaction. The 2'-methoxy group in the chalcones with no substituent at the 6'-position apparently accelerated the reaction, although other 2'-substituents retarded it. In the reaction of the 2',4'-dimethoxychalcones (3a and 3g) with no electron-donating group on the B ring, a mixture of the acetal, methyl 2,3-diaryl-3-methoxypropanoate, and thallium compounds were obtained. The three thallium compounds obtained from compound 3h were assigned as cyclic complexes of thallium(I) chloride with two molecules of the acetal and/or propanoate. Based on these results, the mechanism of the oxidative rearrangement was proposed as shown in Schemes 3 and 4.

Thallium(III) compounds have been widely used as unique reagents in synthetic chemistry.[1] For example, oxidative rearrangement of 2'-hydroxychalcones with thallium(III) nitrate (TTN)[2] has been utilized with advantage in a convenient isoflavone synthesis, since the corresponding 1,2-diaryl-3,3-dimethoxypropan-1-ones (acetals) are formed as immediate precursors.[3,4] The major drawback of the method is that the reaction is susceptible to the nature of the substituents and the reaction does not always proceed in a desirable manner.[5-7] For example, TTN oxidation of a 2'-hydroxy-4',5',6'-trioxygenated chalcone in methanol gives the quinone monoacetals by A-ring oxidation.[5,8] The 2'-hydroxychalcones with a chloro or nitro group afford the corresponding α-methoxybenzylcoumaran-ones.[7] In the reaction of the chalcones without a free hydroxy group, the A ring migrates to give methyl 2,3-diaryl-3-methoxypropanoates when the chalcone has a B ring with low migrating ability.[6] These notable substituent effects on the reaction have not been clearly elucidated so far in spite of numerous studies.[1] Therefore, as part of our work to establish a method for the synthesis of isoflavonoids,[9] we first studied the oxidation of 2'-hydroxyacetophenones with TTN and reported the mechanism and unique features of the products.[8] As an extension of this study, we report here the reactivity and mechanism in the oxidative rearrangement of 2'-methoxychalcones with TTN. The reaction was markedly influenced by the presence of 2'- and/or 6'-methoxy groups, and thallium complexes which were very relevant to the reaction were obtained from the reaction mixture in some specific cases.

Results and Discussion

Preliminary experiments showed that the oxidative rearrangement of all 2'-methoxychalcones with methoxy groups on the B ring proceeded smoothly to give only the corresponding acetal, as expected from previous papers.[1-6] In the UV spectra of the chalcones and corresponding acetals, the absorption band at longer wavelength (Band I) for the chalcones appears at appreciably longer wavelength than that for the acetal and its intensity is larger than that for the acetal at the requisite wavelength. Also, Band I does not overlap with the absorption
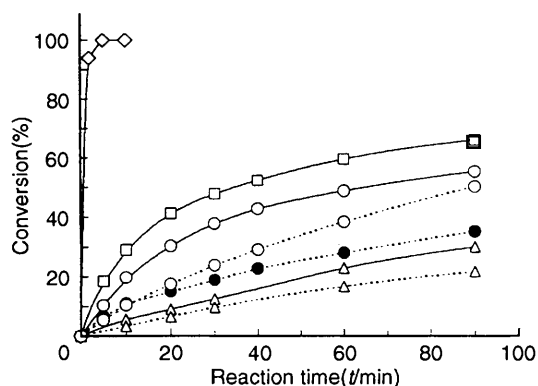

Fig. 1 Time conversion of the reaction of 2',6'-dimethoxychalcones with TTN at 30 °C. 1e, —◇—; 1d, —□—; 1b, —O—; 2b, ---O---; 1c, ---●---; 1a, —△—; 2a, ---△---. The reaction of compound 1f proceeded more rapidly than that of compound 1e and was completed within 2 min.
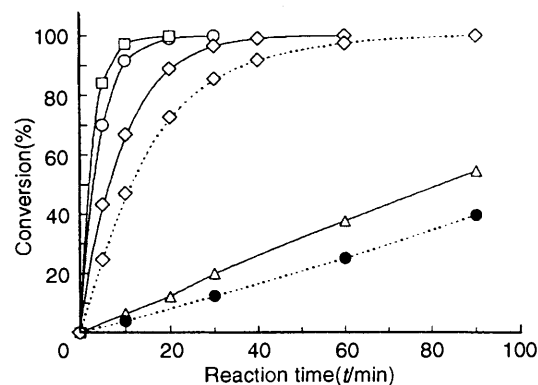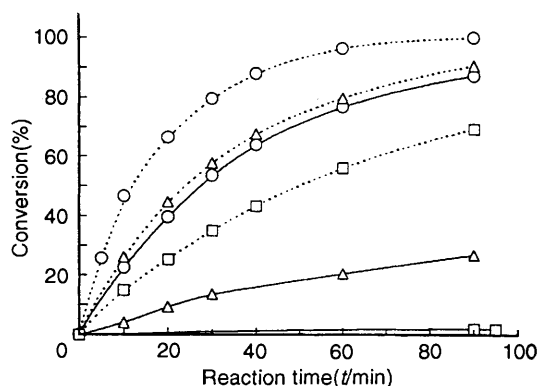

Fig. 2 Time conversion of the reaction of chalcones having no substituent at the 6'-position with TTN at 30 °C. 4b, —□—; 3b, —O—; 5b, —◇—; 6b, ---◇---; 3a, —△—; 3g, ---●---.

Table 1 Abbreviation of chalcones and the corresponding acetals

Compd.	R¹	R²	R³	R⁴	R⁵	Acetal	Compd.	R¹	R²	R³	Acetal	Compd.	R¹	R²	Acetal
1a	OMe	H	H	H	H	A1a	3a	OMe	H	H	A3a	6b	H	OMe	A6b
1b	OMe	H	H	OMe	H	A1b	3b	OMe	H	OMe	A3b	7b	Me	H	A7b
1c	OMe	OMe	H	H	H	A1c	3g	OMe	H	Cl	A3g	8b	H	Me	A8b
1d	OMe	H	OMe	OMe	H	A1d	3h	OMe	H	NO₂	a	9b	Cl	H	A9b
1e	OMe	OMe	H	OMe	H	A1e	4b	OMe	OMe	OMe	A4b	10b	H	Cl	A10b
1f	OMe	OMe	H	OMe	OMe	A1f	5b	H	H	OMe	A5b	11b	NO₂	H	A11b
2a	H	H	H	H	H	A2a						12b	H	NO₂	A12b
2b	H	H	H	OMe	H	A2b									

a No reaction.

Fig. 3 Time conversion of the reaction of 2'- or 4'-substituted 4-methoxychalcones with TTN at 30 °C. **8b**, ---O---; **10b**, ---△---; **7b**, —O—; **12b**, ---□---; **9b**, —△—; **11b**, —□—.

band for TTN. On the other hand, the intensity of Band I for a dilute solution of the chalcones decreased gradually under the influence of room light, but this phenomenon was not observed in the dark. Based on these observations, a conversion ratio of the chalcone in a reaction mixture was easily estimated from an intensity change of the UV spectra as measured by a dilution method in the dark, and the conversion curves of the chalcones served to elucidate the substituent effects. The results are shown in Figs. 1 and 2.

Reactivities in the 2',4',6'-trimethoxychalcones 1 are enhanced by an increasing number of methoxy groups on the B ring. The effect is especially significant in the substrates having 2-, 4-, and/or 6-methoxy groups, such as compounds 1e and 1f (Fig. 1; see also Table 1). In the reaction of 2',4'-dimethoxychalcones, the reactivities decrease in the order **3b** > **3a** > **3g** with a decreasing electron-donating nature of the substituent on the B ring (Fig. 2). The 2-methoxy group retards the reaction by its steric hindrance as shown in the comparison between compounds **1b** and **1c** (Fig. 1), but the effect is weaker than the electronic effect of the methoxy group at the 2- or 4-position (**1c** vs **1a** or **1e**). Although the results were expected from previous papers,[1-6] the reactivities of the chalcones (**1** and **2**) with two methoxy groups at the 2'- and 6'-position are much lower than those in the corresponding chalcones with no substituent at the 6'-position (Fig. 1 vs. Fig. 2). Furthermore, the 2'-methoxychalcone **5b** is apparently more reactive than the 4'-methoxychalcone **6b** (Fig. 2). This result suggests that the 2'-methoxy group adjacent to the
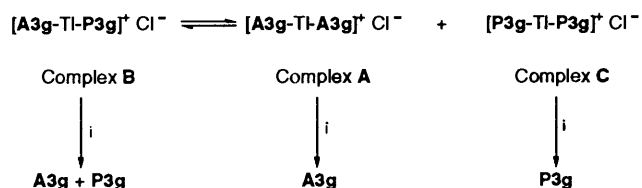
carbonyl group participates in the reaction. In order to elucidate this phenomenon, the reaction of some 2'- and 4'-substituted chalcones was additionally examined and the results are shown in Fig. 3.

Reactivities of the 2'-substituted chalcones are lower than those of the corresponding 4'-substituted ones, in contrast to the reactions of the 2'- and 4'-methoxychalcones **5b** and **6b**. The result clearly shows that the 2'-substituents generally retard the reaction by their steric hindrance and only the 2'-methoxy group accelerates the reaction, by participation of its oxygen atom. The participation of the substituent adjacent to the carbonyl group is observed in the oxidative rearrangement of o-hydroxyacetophenone, but the hydroxy group completely suppresses the reaction.[10]

2',6'-Dimethoxychalcones **1a** and **2a** with no substituent on the B ring afforded the corresponding acetal in high yield although the reactivities were low. On the other hand, the reaction of the chalcones **3a** and **3g** with no substituent at the 6'-position produced the corresponding methyl propanoates (**P3a** or **P3g**) together with the acetal (**A3a** or **A3g**), as expected from a previous paper.[6] However, appreciable amounts of thallium compounds were separated simultaneously from the reaction mixture after treatment with sodium sulfite and dil. hydrochloric acid. In the reaction of acetophenone with TTN in methanol in the presence of 70% perchloric acid, Higgins and Thomas[11] reported that an unstable organothallium intermediate was mixed with the product. In contrast to this result, the thallium compounds obtained from substrates **3a** or **3g** are relatively stable. Therefore, the reaction product obtained from compound **3g** was examined in detail in order to elucidate the structure of the thallium compounds.

On silica gel TLC of the reaction mixture from substrate **3g** after 24 h, the spot of the thallium compounds which moved with chloroform–ethyl acetate (2:1–1:2) but not with chloroform was not observed at all and the presence of only acetal **A3g** and a trace amount of the methyl propanoate **P3g** was detected. When a solution of sodium sulfite was added to this reaction mixture, the spots of the thallium compounds appeared without any increase in the amounts of products **A3g** and **P3g**. The thallium compound which was separated from the mixture after treatment with dil. hydrochloric acid consisted of three components, and two were isolated from fractions 1 (complex **C**) and 3 (complex **A**) by silica gel chromatography, but the remaining component (fraction 2; complex **B**) was not isolated. These compounds were stable under neutral conditions and could be solidified, and, in particular, complex **C** was recrystallized from methanol. Complexes **A** and **C** afforded only

compounds **A3g** and **P3g** after treatment with dil. hydrochloric acid in methanol, respectively, but complex **B** was converted into a mixture of compounds **A3g** and **P3g** (see Scheme 1).

[A3g-Tl-P3g]⁺ Cl⁻ ⇌ [A3g-Tl-A3g]⁺ Cl⁻ + [P3g-Tl-P3g]⁺ Cl⁻

Complex **B**		Complex **A**		Complex **C**
↓ i		↓ i		↓ i
A3g + **P3g**		**A3g**		**P3g**

Scheme 1 *Reagent:* i, HCl

Although the ¹H NMR spectral pattern for the propanoate **P3g** obtained here is greatly different from that for methyl 3-methoxy-2-(4-methoxyphenyl)-3-phenylpropanoate **P6a** synthesized from 4'-methoxychalcone **6a** by Taylor *et al.*,[6] but similar to that for compound **A3g** (see Table 4), the structure of compound **P3g** can be confirmed as methyl 3-(4-chlorophenyl)-2-(2,4-dimethyoxphenyl)-3-methoxypropanoate from the following facts. In a nuclear Overhauser enhancement (NOE) experiment on ester **P3g**, the NOE (11 and 20%) of the doublet at δ 4.58 and the aromatic proton signal at δ 6.14 were observed by irradiation of the singlets at δ 3.22 and 3.38, respectively, and that of the doublet at δ 4.36 was not observed by irradiation of the other methoxy signals. Furthermore, signals attributed to the ester group were observed at δ_C 173.4 in the ¹³C NMR spectrum and at 1740 cm⁻¹ in the IR spectrum.


6a

P6a
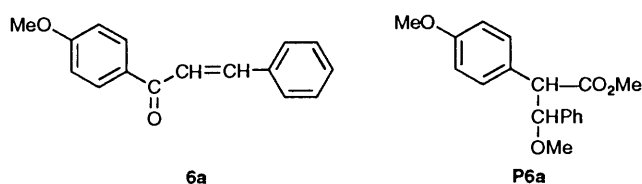
¹H NMR spectra for the three complexes show that the signals of the aromatic protons on the A ring collapse similarly to those for the cyclic thallium complexes of 2',4',6'-trioxygenated acetophenones.[8] This suggests that the complexes are cyclic thallium complexes formed by coordination of the carbonyl group and the 2-methoxy group in the A ring. The signals of the complexes **A** and **C** correspond well to those of compounds **A3g** and **P3g**, respectively, except for those of the A-ring protons. The ¹H NMR spectrum for complex **B** is complicated due to contamination with complexes **A** and **C**, but the main signals correspond to those of the two complexes **A** and **C** as shown in Table 2. On the other hand, all analytical

values (C, H, N) of the three complexes were consistent with a calculated formula (C₁₉H₂₁ClO₅)₂ TlCl and their methanolic solution afforded white precipitates on addition of aq. silver nitrate. Hydrolysis of complex **C** with dil. hydrochloric acid afforded compound **P3g** in 68 weight-percent (theoretical yield, 90%). Furthermore, TLC of a chloroform solution of complexes **A** and **C** showed the formation of an equilibrium mixture of complexes **A**, **B** and **C** within 1 h, although their methanolic solution was relatively stable. These results suggest that the complexes are consistent with the presence of one molecule of thallium(ı) chloride and two molecules of the products, the acetal **A3g** and/or propanoate **P3g**, and the relation among the complexes **A**, **B** and **C** is represented as shown in Scheme 1. Based on these results, the ¹H NMR spectral data of the complexes suggest also that complex **A** is a symmetrical molecule, complex **C** is an unsymmetrical one or a mixture of the two stereoisomers, and complex **B** exists as a mixture of four stereoisomers (Table 2).

Thallium compounds are formed only in the reaction of chalcones with a 2'-methoxy group, such as compounds **3a** and **3g**, and are not formed at all in that of chalcones with no methoxy group at both the 2'- and 6'-position, such as 4'-methoxychalcone **6a**. This shows that the methoxy-group oxygen atoms and the carbonyl group are linked to thallium as ligands in the complexes. However, the apparent difference between the complexes and the corresponding mother compounds is not seen spectroscopically: UV, IR, and ¹³C NMR spectra for complexes **A** and **C** are similar to those for the parent compounds **A3g** and **P3g**, respectively, although the signals of the aromatic protons on the A ring in the ¹³C NMR spectra collapse similar to the corresponding proton signals in the ¹H NMR spectra (see Experimental section). In the product obtained after careful treatment of the reaction mixture of compound **3g** in methanol, the quantity of ester **P3g** as the thallium-free product is very small, albeit that complex **C** is produced predominantly more than is complex **A**. The reaction of compound **3g** was affected by the solvent, and the quantity of complex **A** increased considerably when a methanol–chloroform mixture was used as the solvent, albeit that the quantity of acetal **A3g** remained unchanged as shown in Table 3. These results suggest that the acetal **A3g** is produced by two different pathways.

Mechanism of the Reaction.—In the oxidative rearrangement of chalcones with thallium(ııı) acetate in methanol, Ollis *et al.*[12] proposed two intermediates, *C*- and *O*-thallium compounds, although which intermediate was preferred is unknown. The reaction with TTN, a more efficient reagent, has also been explained by formation of a similar intermediate which is formed by oxythalliation by TTN of a carbon–carbon double bond (Scheme 2).[6,13] The mechanism also reasonably explains results in which the reaction is greatly accelerated by electron-donating substituents at the 2-, 4-, and 6-position in chalcones
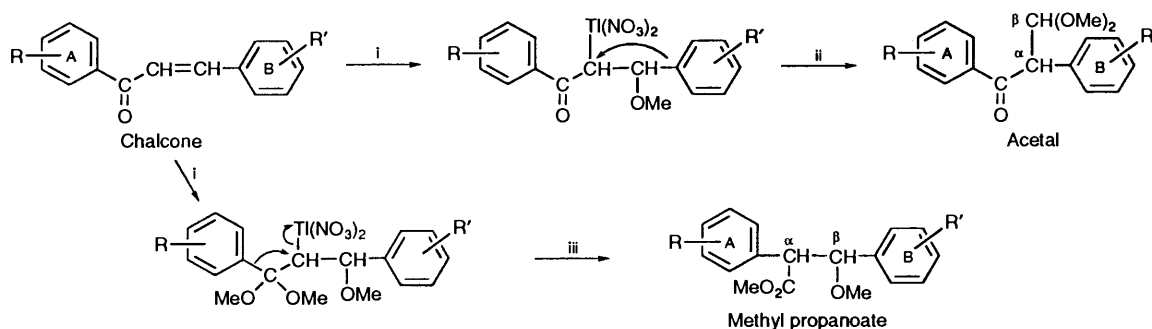
Scheme 2 *Reagents:* i, TTN, MeOH; ii, MeOH; iii, water

Table 2 ¹H NMR data for the thallium compounds A, B and C^a

Compound	Cᵅ-H	Cᵝ-H	B ring 2-, 6-H	3-, 5-H	OMe on A ring		Other OMe groups	
A3g	5.03d (J 8.5)	5.00d	7.34d (J 8.5)	7.26d	3.81s	3.83s	3.19s	3.41s
Complex A	4.81d (J 8.5)	4.94d	7.34d (J 8.5)	7.22d	3.67s	3.86s	3.12s	3.36s
Complex B	4.77d (1 H) 4.81d (J 8.5)	4.94d (1 H) 4.96d	7.34d (1 H) 7.37d (J 8.5)	7.25d (1 H) 7.27d	3.54s (3 H)	3.95s (3 H)	3.12s (3 H)	3.40s (3 H) 3.41s
	4.31d (1 H) (J 9.5)	4.69d (1 H) 4.71d	6.91d (1 H) 6.93d (J 8.5)	7.05d (1 H) 7.06d	3.46s (3 H) 3.45s	3.71s (3 H)	3.16s (3 H)	3.59s (3 H) 3.60s
Complex C	4.31d 4.31d (J 9.8)	4.70d 7.72d	7.00–7.10m 7.00–7.10m		3.48s 3.50s	3.775s 3.770s	3.20s 3.21s	3.62s 3.64s
P3g	4.36d (J 10.3)	4.58d	6.98d (J 8.5)	7.10d	3.38s	3.73s	3.22s	3.71s^b

^a δ-Values in CDCl₃ (400 MHz); s, singlet; d, doublet; m, multiplet. J-Values are in Hz. ^b The ester methoxy group.

Table 3 Reaction products from compound 3g in methanol and methanol–chloroform (5:1) at 30 °C for 24 h

	Solvent	Products (%) A3g	P3g	Complex A	Complex B^a	Complex C
	MeOH	34	2	6	19	27
	MeOH–CHCl₃	32	3	18	25	17

^a The compound contained an appreciable amount of complexes A and C.

and retarded by the 2'-substituent except for the 2'-methoxy group. However, the following results can be explained only with difficulty. (1) The reactivity of 2',4-dimethoxychalcone 5b is higher than that of 4,4'-dimethoxychalcone 6b and that of 2',6'-dimethoxychalcones 1 and 2 is very much lower than that of the corresponding 2'-methoxychalcones 3 with no substituent at the 6'-position. (2) Only in the reactions of the 2'-methoxychalcones such as compounds 3a and 3g were the thallium complexes and propanoate isolated as products together with the corresponding acetal.

The former point shows that the reaction is accelerated by coordination of the 2'-methoxy-group oxygen atom when the carbonyl group is coplanar with the A ring by resonance: the reactivity of the 2',6'-dimethoxychalcones becomes much lower than that of the corresponding 2'-methoxychalcones, since the participation of 2'-methoxy group is suppressed by distortion between the carbonyl group and the A ring owing to steric hindrance of the 2',6'-dimethoxy groups. Formation of the thallium compounds in the latter suggests that the A or B ring in an initial thallium complex of the chalcone (3a or 3g) rearranges without elimination of the thallium moiety, and that the rearranged products are converted into the thallium complexes A, B and C by disproportionation under acidic reduction conditions. The structures of the rearranged products and their precursor (intermediate) are assumed to be cyclic thallium complexes such as TlX-A, TlX-C and TM-II, respectively, as shown in Scheme 3. The cyclic thallium compound linked with two oxygen atoms has already been proposed as an intermediate in the oxidation of chalcones to benzils with TTN by McKillop et al.[13,14] The fact, that the thallium complexes are obtained only in the reaction mixture of compound 3a or 3g along with the corresponding acetal and propanoate and are not found in the others, suggests also that the reaction of 2'-methoxychalcones with no substituent at the 6'-position may proceed via two different intermediates: one is unstable and easily forms the acetal by elimination of the thallium moiety, and another is relatively stable and is

converted gradually into the acetal and propanoate via their thallium complexes. On the basis of the assumption that these intermediates are cyclic thallium complexes such as TM-I and TM-II, the reaction mechanism of the chalcones with no substituent at the 6'-position is proposed as shown in Scheme 3.

The initial complex (TlX) (path 'a') is converted into two intermediates, TM-I and -II, by coordination of the neighbouring 2'-methoxy-group oxygen atom and by attack of the methoxy anion (paths 'b' and 'c'). Path 'b' is accelerated by an increasing electron density of the double bond and proceeds predominantly when the chalcones have methoxy groups at the 2-, 4-, and/or 6-position. The intermediate TM-I forms the acetal A by elimination of the thallium moiety and simultaneous migration of the B ring (path 'd'). On the other hand, TM-II is slowly converted into a mixture of the acetal A and propanoate P via species TlX-A and TlX-C by migration of the B or A ring (paths 'e' and 'f'). The ratio between paths 'e' and 'f' should be dependent on the migratory aptitudes of the B and A rings.

Therefore, the reaction of the 2'-methoxychalcones with methoxy groups at the 2-, 4-, and/or 6-position proceeds mainly via TM-I (paths 'b' and 'd') to give exclusively the corresponding acetal A in high yield. When the 2'-methoxychalcones have no electron-donating group on the B ring, the two intermediates, TM-I and -II, are formed and the propanoate P is slowly produced from the latter intermediate: the product contains an appreciable amount of thallium complexes as well as the products A and P. The other methoxy groups on the A ring, except the 2'-methoxy group, accelerate mainly path 'a' because the electron density of the carbonyl group increases by resonance with the substituents, but the effect is apparently smaller than that of the B ring. In the reaction of the 2'-substituted chalcones such as 7b, 9b and 11b, their reactivities become lower than those of the corresponding 4'-substituted chalcones (Fig. 3) because of both the low coordination ability of the substituents to thallium and the steric hindrance.

In the reaction of 2',6'-dimethoxychalcones 1 and 2, co-planarity between the A ring and the carbonyl group is no
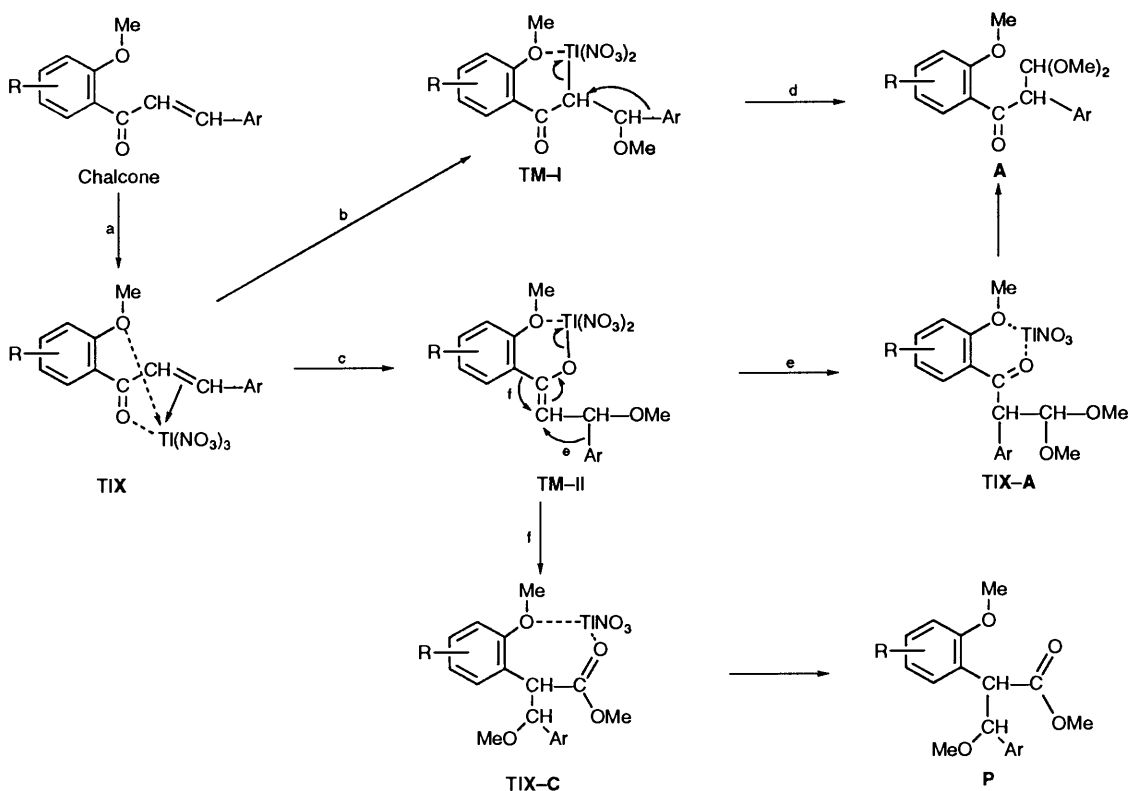
Scheme 3
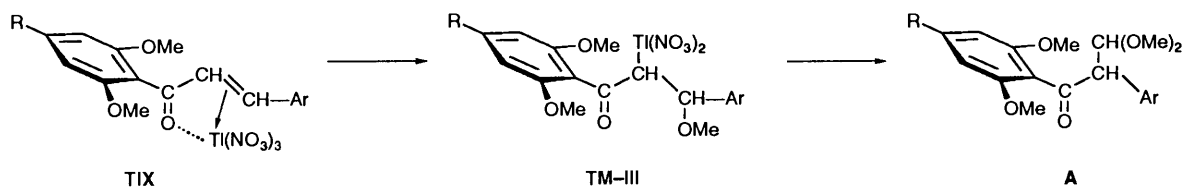
Scheme 4

longer maintained owing to steric hindrance from the 2',6'-dimethoxy groups. This weakens the resonance between the A ring and carbonyl group as well as the interaction between the 2'-methoxy-group oxygen and thallium atoms in the complex (TlX) in Scheme 3: the intermediates such as **TM-I** and **TM-II** are formed hardly at all. The reaction seems to proceed mainly by the process shown in Scheme 4, which is essentially one of the mechanisms proposed by Taylor et al.,[6,13] from the fact that the content of the thallium complexes in the product is small. Thus, the reactivity of the 2',6'-dimethoxychalcones is much lower than those of the corresponding 2'-methoxychalcones. Formation of the propanoate **P** is also suppressed by reduction of the migratory aptitude of the A ring by steric hindrance from the 2',6'-dimethoxy groups.

In another reaction of 2'-hydroxychalcones, i.e. formation of an aurone via the corresponding α-methoxybenzylcoumaranone, the effect of the 2'-hydroxy group is being further elucidated and the results will be presented elsewhere.

Experimental

All m.p.s were determined in glass capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz) or Bruker 400 spectrometer, using tetramethylsilane as internal standard, and chemical shifts are given in δ values. UV and IR spectra were recorded on a Hitachi 124 spectrophotometer in MeOH and a Hitachi 260–10 spectrophotometer by KBr pellet, respectively. Column chromatography

was carried out on Kieselgel 60 (70–230 mesh; Merck). Elemental analyses were performed with a Yanaco CHN-corder, Model MT-5. The chalcones used here were synthesized by usual methods: 2',4-dimethoxychalcone **5b**, m.p. 58–58.5 °C (from MeOH); 4-methoxy-2'-methylchalcone **7b**, m.p. 40–42 °C (from Et₂O–hexane). Analytical values of all chalcones were within 0.3% of theoretical values.

Determination of the Chalcone in the Reaction Mixture.—In a text tube (18φ × 50 mm) with a rubber cap TTN·3H₂O (60 mg, 0.135 mmol: final concentration 33.8 mmol dm⁻³) was dissolved rapidly in stirred 10 mmol dm⁻³ chalcone in MeOH (4 cm³, 0.04 mmol) at 30 °C, and the resultant solution was stirred continuously in a thermostat-controlled water-bath at 30 °C. In the reaction of the chalcones **9b–12b** which have a low solubility in MeOH, a mixture of MeOH (3 cm³) and CHCl₃ (2 cm³) was employed as the reaction solvent. A constant volume (30–40 mm³) of the reaction mixture was removed through the rubber cap with a microsyringe at intervals and was diluted immediately with MeOH to 10 cm³ in a dark-box. The UV spectrum of the solution was measured over the range 250–400 nm, and the decreasing amount of the chalcone was calculated from the change in intensity at the absorption maximum by using the molar extinction coefficients of the chalcone and acetal.

Oxidative Rearrangement of the Chalcones with TTN.—To a solution of the chalcone (1.5 mmol) in MeOH (60–80 cm³), or in a mixture of MeOH and CHCl₃ when the chalcone was not

Table 4 ¹H NMR data for 1,2-diaryl-3,3-dimethoxypropan-1-ones (A1–A12) and methyl 2,3-diaryl-3-methoxypropanoates (P3a, P3g and P6a) in $CDCl_3$ [a]

Compd.	Cα-H	Cβ-H	Arom. H in A ring					Arom. H in B ring					-CH(OMe)₂	OMe
			4-H	2-H	6-H	3-H	5-H	4-H	2-H	6-H	3-H	5-H		
A1a	4.47d	5.01d				5.92s (2 H)				7.19 br s (5 H)			3.11s (3 H) 3.39s (3 H)	3.59s (6 H) 3.70s (3 H)
A1b	4.42d	4.95d				5.95s (2 H)			7.18d (2 H)		6.73d (2 H)		3.13s (3 H) 3.38s (3 H)	3.62s (6 H) 3.71s (6 H)
A1c	5.11s (2 H)					5.87s (2 H)				7.4–6.6m (4 H)			3.13s (3 H) 3.43s (3 H)	3.54s (6 H) 3.68s (3 H) 3.59s (3 H)
A1d	4.50d	5.01d				6.02s (2 H)		6.95d'	6.84dd			6.77d	3.20s (3 H) 3.45s (3 H)	3.70s (6 H) 3.84s (3 H) 3.78s (3 H) 3.86s (3 H)
A1e	5.11d	5.00d				5.91s (2 H)			7.16d	6.26d'	6.34dd		3.15s (3 H) 3.46s (3 H)	3.59s (9 H) 3.71s (6 H)
A1f	5.50d	4.98d				5.91s (2 H)						5.85s (2 H)	3.11s (3 H) 3.49s (3 H)	3.57s (6 H) 3.69s (6 H) 3.60s (6 H)
A2a	4.44d	5.04d	c			6.35d (2 H)				7.17br s (5 H)			3.13s (3 H) 3.40s (3 H)	3.58s (6 H)
A2b	4.41d	5.02d				6.3–7.35m (3 H)			7.16d (2 H)		6.71d (2 H)		3.15s (3 H) 3.40s (3 H)	3.60s (6 H) 3.70s (3 H)
A3a	4.98s (2 H)				7.67d	6.28d'	6.36dd			7.0–7.45m (5 H)			3.12s (3 H) 3.36s (3 H)	3.72s (3 H) 3.76s (3 H)
P3a	4.40d	4.59d			7.33d	6.07d'	6.35dd			7.01br s (5 H)			3.20s (3 H)	3.30s (3 H) 3.64s (6 H)
A3b	4.95s (2 H)				7.69d	6.31d'	6.38dd		7.25d (2 H)		6.75d (2 H)		3.13s (3 H) 3.35s (3 H)	3.69s (3 H) 3.78s (3 H) 3.73s (3 H)
A3g	5.03d	5.00d			7.77d	6.38d'	6.49dd		7.34d (2 H)		7.26d (2 H)		3.19s (3 H) 3.41s (3 H)	3.81s (3 H) 3.83s (3 H)
P3g	4.36d	4.58d			7.35d	6.14d'	6.40dd		6.98d (2 H)		7.10d (2 H)		3.22s (3 H)	3.38s (3 H) 3.71s (3 H) 3.73s (3 H)
A4b	4.97s (2 H)				7.28s	6.33s			7.21d (2 H)		6.71d (2 H)		3.14s (3 H) 3.36s (3 H)	3.68s (3 H) 3.82s (3 H) 3.78s (6 H)
A5b	4.93s (2 H)				6.7–7.7m (4 H)				7.25d (2 H)		6.75d (2 H)		3.15s (3 H) 3.39s (3 H)	3.71s (3 H) 3.78s (3 H)
P6a [6]	3.75d	4.65d	7.00d (2 H)			6.66d (2 H)				7.1–7.4m (5 H)			3.23s (3 H)	3.74s (3 H) 3.70s (3 H)
A6b [6]	4.72d	5.01d	7.84d (2 H)			6.74d (2 H)			7.22d (2 H)	6.70d (2 H)			3.17s (3 H) 3.37s (3 H)	3.67s (3 H) 3.72s (3 H)
A7b	4.60d	5.07d			7.1–7.7m (4 H)				7.30d (2 H)		6.83d (2 H)		3.18s (3 H) 3.44s (3 H)	3.74s (3 H) 2.32s (3 H) [b]
A8b	4.79d	5.05d	7.83d (2 H)			7.15d (2 H)			7.31d (2 H)		6.80d (2 H)		3.20s (3 H) 3.40s (3 H)	3.71s (3 H) 2.33s (3 H) [b]
A9b	4.66d	5.01d			7.25–7.5m (4 H)				c		6.85d (2 H)		3.19s (3 H) 3.46s (3 H)	3.76s (3 H)
A10b [6]	4.74d	5.03d	7.86d (2 H)			7.34d (2 H)			7.30d (2 H)		6.82d (2 H)		3.26s (3 H) 3.40s (3 H)	3.73s (3 H)
A11b	4.98d	4.39d			7.1–8.0m (4 H)				7.22d (2 H)		6.78d (2 H)		3.20s (3 H) 3.43s (3 H)	3.73s (3 H)
A12b [6]	4.73d	4.98d	7.97d (2 H)			8.14d (2 H)			7.23d (2 H)		6.77d (2 H)		3.81s (3. H) 3.40s (3 H)	3.71s (3 H)

[a] s, singlet; d, doublet (J 8.0–10.0 Hz); d', doublet (J 2.5–3.0 Hz); dd, double doublet (J 2.5, 8.5 Hz); m, multiplet. [b] The methyl signal. [c] Overlapped with the A- or B-ring aromatic protons.

dissolved completely in MeOH, was added $TTN\cdot3H_2O$ (1.0–1.6 g, 2.2–3.6 mmol), and the mixture was stirred at 30–40 °C until the starting material disappeared by silica gel TLC. Saturated aq. Na_2SO_3 (0.4–0.7 g, 3.1–5.5 mmol) and cooled 2–3% aq. HCl (10–15 cm³) were added to the cooled reaction mixture and the mixture was additionally stirred at 0 °C for 1 h. After the formed precipitate had been filtered off, the filtrate was diluted with cooled water and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and then passed through a short column of silica gel with $CHCl_3$ as eluent. The eluate was evaporated under reduced pressure and the residue was recrystallized to give an acetal. The yields of all acetals except for the products from compounds 3a and 3g were above 70% and the ¹H NMR, m.p. and analytical data are summarized in Tables 4 and 5. The recovered products from the mother liquor of the recrystallization of acetals A3a and A3g were chromatographed on a silica gel column with $CHCl_3$ as eluent to give oily propanoates P3a and P3g, respectively.

Oxidative Rearrangement of the Chalcone 3g (Separation of the Thallium Complexes A, B, and C).—A mixture of chalcone 3g (615 mg) and $TTN\cdot3H_2O$ (1.8 g, 2 mol equiv.) in MeOH (100 cm³) was stirred at 30 °C for 24 h (the chalcone 3g dissolved after 3–4 h). To the cooled mixture was added aq. Na_2SO_3 (1.5 g), the mixture was stirred at 0 °C for 1 h, and then 2% aq. HCl was added to the stirred mixture. After 5 min, the precipitate was filtered off and the filtrate was diluted with water and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, passed through a short column of silica gel, and eluted successively with $CHCl_3$ and then with EtOAc. The $CHCl_3$ eluate was rechromatographed on a silica gel column with $CHCl_3$ to give propanoate P3g (15 mg, 2%) and acetal A3g (250 mg, 34%) [ν_{max}/cm^{-1} 1660; λ_{max}^{MeOH}/nm (log ε) 274 (4.07) and 308 (3.95); $\delta_C(CDCl_3)$ 54.8, 55.3, 55.5 and 55.7 (OMe × 4), 59.6, 107.2 and 197.4 (C^{β}, C^{α} and C=O), 98.4, 105.4, 121.0, 133.4, 160.5 and 164.7 (A ring: C-3, -5, -1, -6, -4 and -2); 128.4 (2 C), 130.7 (2 C), 132.9 and 134.3 (B ring: C-3, -5, -2, -6, -4 and -1)]. The EtOAc eluate was rechromatographed with

Table 5 1,2-Diaryl-3,3-dimethoxypropan-1-ones

Compd.	M.p. (°C)	Recryst. solvent	Formula	Found (%)		Required (%)	
				C	H	C	H
A1a	102–103	MeOH	$C_{20}H_{24}O_6$	66.6	6.6	66.65	6.71
A1b	133–134	MeOH	$C_{21}H_{26}O_7$	64.7	6.45	64.60	6.71
A1c	121–122	MeOH	$C_{21}H_{26}O_7$	64.4	6.65	64.60	6.71
A1d	104–105	MeOH	$C_{22}H_{28}O_8$	62.55	6.6	62.84	6.71
A1e	122–123	MeOH	$C_{22}H_{28}O_8$	63.1	6.8	62.84	6.71
A1f	129–130	MeOH–Et$_2$O	$C_{23}H_{30}O_9$	61.5	6.8	61.32	6.71
A2a	95–96	CHCl$_3$–MeOH	$C_{19}H_{22}O_5$	68.9	6.6	69.07	6.71
A2b	113–114	MeOH	$C_{20}H_{24}O_6$	66.4	6.6	66.65	6.71
A3a [a]	91–92	CHCl$_3$–MeOH	$C_{19}H_{22}O_5$	68.8	6.7	69.07	6.71
A3b	69–70	MeOH	$C_{20}H_{24}O_6$	66.6	6.8	66.65	6.71
A3g	68–69	CHCl$_3$–MeOH	$C_{19}H_{21}ClO_5$	62.35	5.7	62.55	5.80
A4b	88–89	MeOH	$C_{21}H_{26}O_7$	64.5	6.6	64.60	6.71
A5b	75–76	MeOH	$C_{19}H_{22}O_5$	69.1	6.6	69.07	6.71
A6b [6]	72–73	Et$_2$O–hexane	$C_{19}H_{22}O_5$	68.8	6.7	69.07 [b]	6.71 [b]
A7b	45–46	Et$_2$O–hexane	$C_{19}H_{22}O_4$	72.7	6.9	72.59	7.05
A8b	90–91	MeOH	$C_{19}H_{22}O_4$	72.5	6.9	72.59	7.05
A9b	49–50	Et$_2$O–hexane	$C_{18}H_{19}ClO_4$	64.7	5.6	64.57	5.72
A10b [6]	54–55	aq. MeOH	$C_{18}H_{19}ClO_4$	64.5	5.7	64.57 [b]	5.72 [b]
A11b	93–94	Et$_2$O–hexane	$C_{18}H_{19}NO_6$	62.7	5.7	62.60	5.55
A12b [6]	71–72	Et$_2$O	$C_{18}H_{19}NO_6$	62.8	5.8	62.60 [b]	5.55 [b]

[a] The yield was 44%. [b] Calculated values for known compounds.

a silica gel column with CHCl$_3$–EtOAc (2:1–1:2) and the following complexes were isolated from fractions 1–3.

Complex **C** (fraction 1): 270 mg (27%); m.p. 216–220 °C (decomp.) (from MeOH); v_{max}/cm^{-1} 1750; λ_{max}^{MeOH}/nm (log ε) 242sh (4.25), 287sh (4.10) and 291 (4.13); δ_C(CDCl$_3$) 50.4, 84.1 and 172.9 (C$^{\alpha}$, C$^{\beta}$ and C=O); 51.9, 55.3, 55.8 and 57.0 (ester OMe, 2-OMe, 4-OMe and β-OMe); 127.7 (2 C), 129.2 (2 C), 133.0 and 137.4 (B ring: C-3, -5, -2, -6, -4 and -1) [Found: C, 46.8; H, 4.2. (C$_{19}$H$_{21}$ClO$_5$)$_2$ TlCl requires C, 47.06; H, 4.33%].

Complex **B** (fraction 2): 185 mg (19%); m.p. 124–129 °C (solidified; contained appreciable amounts of complexes **A** and **C**) [Found: C, 46.3; H, 4.2. (C$_{19}$H$_{21}$ClO$_5$)$_2$ TlCl requires C, 47.06; H, 4.33%].

Complex **A** (fraction 3): 58 mg (6%); m.p. 139–142 °C (triturated with Et$_2$O); v_{max}/cm^{-1} 1650br; λ_{max}^{MeOH}/nm (log ε) 243 (4.79), 273 (4.39) and 307 (4.24); δ_C(CDCl$_3$) 59.4, 107.3 and 196.8 (C$^{\beta}$, C$^{\alpha}$ and C=O); 54.4, 55.0, 55.9 and 56.0 (OMe × 4); 128.4 (2 C), 130.8 (2 C), 132.8 and 134.4 (B ring; C-3, -5, -2, -6, -4 and -1) [Found: C, 47.0; H, 4.15. (C$_{19}$H$_{21}$ClO$_5$)$_2$TlCl requires C, 47.06; H, 4.33%].

Reaction in MeOH–CHCl$_3$. Chalcone **3g** (0.5 g) was treated with TTN·3H$_2$O (1.5 g) in a mixture of MeOH (50 cm^3) and CHCl$_3$ (10 cm^3) at 30 °C for 24 h and then worked up by a method described above (Table 1).

Hydrolysis of Complex **C**.—A solution of complex **C** (100 mg) in MeOH (10 cm^3) containing 5% aq. HCl (0.5 cm^3) was stirred at 30 °C for 1 h, diluted with water, and then extracted with CHCl$_3$. The extract was passed through a short column of silica gel and the eluate was evaporated under reduced pressure to give propanoate **P3g** (68 mg, 90%), m.p. 74–75 °C (from hexane); v_{max}/cm^{-1} 1740; λ_{max}^{MeOH}/nm (log ε) 280 (3.49) and 286 (3.46); δ_C(CDCl$_3$) 52.0, 55.2 (2 C) and 57.0 (OMe of ester, arom. OMe × 2 and β-OMe); 49.3, 85.2 and 173.4 (C$^{\alpha}$, C$^{\beta}$ and C=O); 98.4, 104.5, 115.6, 129.0, 157.7 and 160.2 (A ring: C-3, -5, -1, -6, -2 and -4); 127.5 (2 C), 129.0 (2 C), 133.1 and 137.2 (B ring:

C-3, -5, -2, -6, -4 and -1) (Found: C, 62.4; H, 5.7. C$_{19}$H$_{21}$ClO$_5$: C, 62.55; H, 5.80%).

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