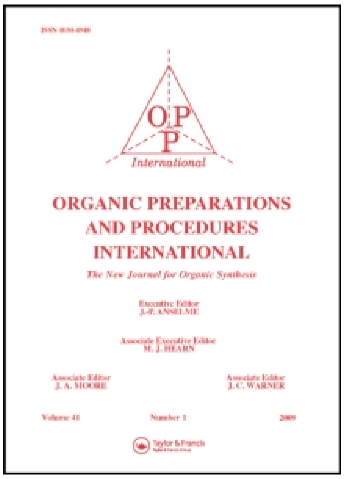

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A CONVENIENT ONE-POT SYNTHESIS OF 2-CINNAMOYLCOUMARAN-3-ONES FROM 2-CINNAMOYLOXYACETOPHENONES USING THALLIUM(III) *p*-TOLUENESULFONATE

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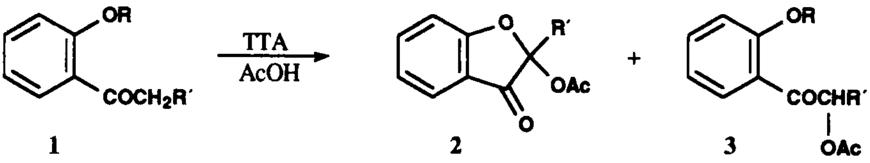
The synthetic utility of thallic salts has been extensively reviewed.[1-5] It has been shown[6] that oxidation of *o*-methoxyacetophenone or *o*-methoxypropiophenone **1** (R = H or CH_3) with thallium(III) acetate (TTA) gives a mixture of coumaran-3-one **2** (R = H 31% and 35%) and α-acetoxy-*o*-methoxyacetophenone (or propiophenone) **3** (R = CH_3 84% and 13%)[6] by neighboring group participation of the methoxy group and by nucleophilic displacement involving the cleavage of weak carbon-thallium bond, respectively. However, **1** (R = H) upon similar treatment affords **2** in 31% (R = H) and 71% (R = CH_3) yield.[6]

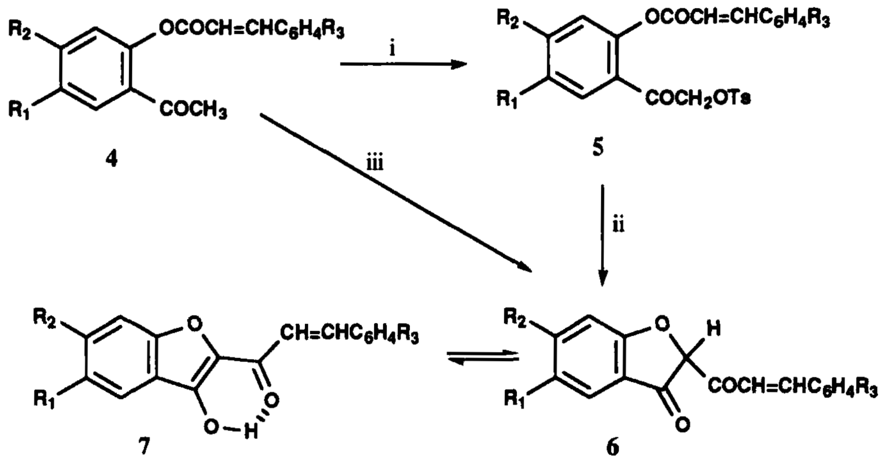


1 2 3

R = R′ = H or CH_3

In continuation of our interest in oxidations using thallium(III) salts[7,8] and with a view to comparing the relative susceptibility of α,β-unsaturated ketone and aralkyl ketone moieties towards thallium(III) reagents, we have examined the oxidation of 2-cinnamoyloxyacetophenones (having both α,β-unsaturated ester and aralkyl ketone moieties) with thallium(III) *p*-toluenesulfonate (TTS); the results are summarized in the scheme below.

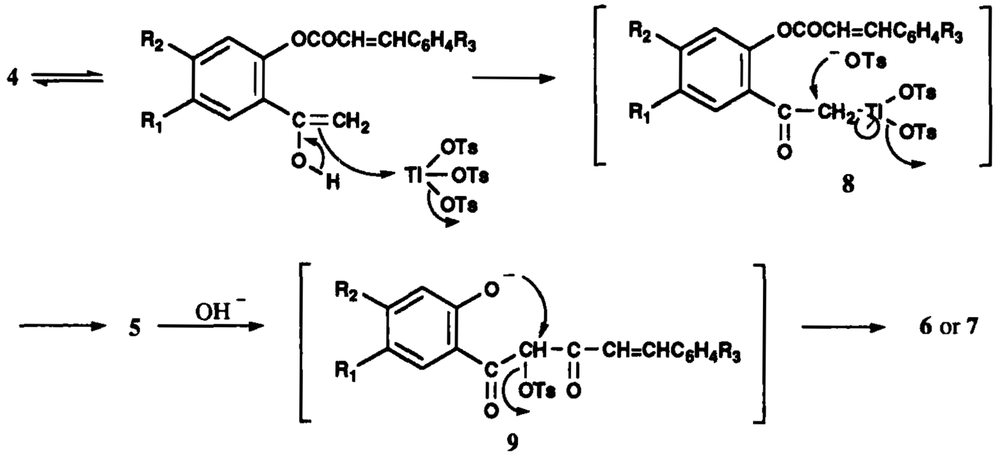
Initial treatment of 2-cinnamoyloxyacetophenones **4** with TTS[9] in refluxing dioxane afforded α-tosyloxy-2-cinnamoyloxyacetophenones **5** in nearly quantitative yield. By the action of powdered KOH in dioxane under the conditions of Baker-Venkataraman transformation,[10,11] **5** yielded 2-cinnamoylcoumaran-3-ones **6** in 70-75% yield. In an alternative one-pot synthesis, compounds **4** were converted into **6** (80-85% yield) by sequential treatment with TTS and powdered KOH without isolation of **5**. The absence of IR absorption peaks in the region 1700-1650 cm^{-1} (C=O stretch in



(i) TTS in dioxane (ii) KOH in dry pyridine
(iii) TTS in dioxane followed by KOH after 30-40 minutes.

-CO-CH=CH-Ar) and the deep violet coloration with Fe^{+3}/EtOH indicate that these molecules exist as chelated structures **7**.

A probable mechanism for the conversion of **4** to **6** is outlined in the Scheme below. In analogy with our earlier proposed mechanism,[9] the reaction is initiated by an electrophilic attack of TTS upon the enol form of **4** to give an intermediate **8**. Intermolecular nucleophilic displacement involving the cleavage of weak carbon-thallium bond by tosylate leads to the formation of **5**. Base-catalyzed transformation of **5** affords **9**, which undergoes intramolecular nucleophilic displacement of tosylate leading to the formation of **6**.



The present oxidative transformation of **4** into **6** is better than earlier existing methods because of high yields and selectivity towards oxidation of the α-position of the *ortho* acyl moiety without affecting the olefinic double bond.

TABLE. Conversion of **4a-f** to **6a-f** using TTS.

No.	Products	Yield[a] %	mp. (lit mp.) (°C)	Analysis Found C	(calculated) H
5a	$R_1 = R_2 = R_3 = H$	92	109-110[c]	65.93 (66.05)	4.49 (4.59)
5b	$R_1 = Cl; R_2 = R_3 = H$	96	126-127[c]	61.13 (61.21)	3.92 (4.04)
5c	$R_1 = CH_3; R_2 = R_3 = H$	93	112[c]	66.69 (66.67)	4.53 (4.49)
5d	$R_1 = Cl; R_2 = CH_3; R_3 = H$	90	112[c]	61.82 (61.91)	4.24 (4.33)
6a	$R_1 = R_2 = R_3 = H$	70 (80)	152-153 (154)[14]	—	—
6b	$R_1 = Cl; R_2 = R_3 = H$	72 (78)	160-161	68.40 (68.34)	3.65 (3.68)
6c	$R_1 = CH_3; R_2 = R_3 = H$	70 (82)	119 (119)[14]	—	—
6d	$R_1 = Cl; R_2 = CH_3; R_3 = H$	70 (82)	180-182[c]	69.21 (69.12)	4.19 (4.16)
6e	$R_1 = R_2 = H; R_3 = OCH_3$	(80)[b]	132 (135)[14]	—	—
6f	$R_1 = CH_3; R_2 = H; R_3 = OCH_3$	(82)[b]	210 (211)[14]	—	—

a) The yields in parenthesis are based upon the isolated solid products in alternate procedure (without isolating **5a-d**) whereas, others are based upon the two-step conversion of **4** to **6** involving isolation of intermediate **5**. b) **5e-f** were not isolated. c) Satisfactory IR and ^1H NMR spectral data were obtained.

EXPERIMENTAL SECTION

Melting points were determined in Thiele tube (sulfuric acid bath) in open capillaries and are uncorrected. IR spectra were recorded as nujol mulls on a Perkin-Elmer 842 IR spectrophotometer and ^1H NMR spectra were determined on a Perkin-Elmer R-32 instrument using $CDCl_3$ as solvent and TMS as an internal standard. All the 2-cinnamoyloxyacetophenones **4a-f** were synthesized according to the procedure reported in the literature.[14]

Two-step Conversion of 4 to 6.

Conversion of 2-Cinnamoyloxyacetophenones 4 to α-Tosyloxy-2-cinnamoyloxyacetophenones 5. Method A.- To a solution of 2-cinnamoyloxyacetophenone (**4a**, 0.01 mol) in dry dioxane (20 mL) was added thallium(III) *p*-toluenesulfonate (TTS, 0.011 mol).[8,9] The reaction mixture was then refluxed for 30 min. (the progress of the reaction was monitored by tlc), cooled to room temperature and poured into ice-cold water. The precipitate obtained was extracted with CH_2Cl_2 (2x50 mL) and washed with saturated aq. $NaHCO_3$ followed by water (3x50 mL). The organic layer was dried

($MgSO_4$) and evaporated *in vacuo* to afford **5a** (92% yield), mp. 109-110°.

A similar procedure was employed for the conversion of **4b-d** to **5b-d** and the results are summarized in the Table.

Method B.- Conversion of 4 to 5 *via in situ* Formation of TTS.- A mixture of *p*-TSA (0.036 mol), TTA (0.011 mol) and **4a** (0.010 mol) in dry dioxane (20 mL) was refluxed for 30 min. The reaction mixture after work up as above afforded **5a** in 90% yield.

A similar procedure was employed for the conversion of **4b-d** to **5b-d** and the results are given in the Table.

Conversion of α-Tosyloxy-2-cinnamoyloxyacetophenones 5 to 6.- A mixture of **5a** (0.010 mol) and powdered KOH (0.040 mol) in dry pyridine (20 mL) was stirred at 40-50° for 1-2 hrs, cooled to room temperature and poured into a mixture of ice and conc. HCl. The precipitate obtained was extracted with CH_2Cl_2 (2x50 mL). The organic layer was washed with saturated aq. $NaHCO_3$ followed by water (3x50 mL) and dried ($MgSO_4$). The solid obtained after evaporation of the solvent under *vacuo* was crystallized from ethanol-acetic acid to afford **6a**, mp. 153-154°, mmp. 153°, lit.[14] mp. 154°.

A similar procedure was employed for the conversion of **5b-d** to **6b-d** and the results are summarized in the Table.

One-pot Transformation of 4a-f to 6a-f *via in situ* Formation of TTS and 5a-f.- A mixture of TTA (0.011 mol), *p*-TSA (0.036 mol) and **4a** (0.010 mol) in dioxane (20mL) was refluxed for 30 min; the progress of the reaction was monitored by tlc. After cooling to room temperature, powdered KOH (0.040 mol) was added to the mixture which was then heated at 50° for 1 hr with constant stirring. The resulting solution after work up as above afforded **6a** in 80% yield.

A similar procedure was employed for the transformation of **4b-f** to **6b-f**, and the results are given in the Table.

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