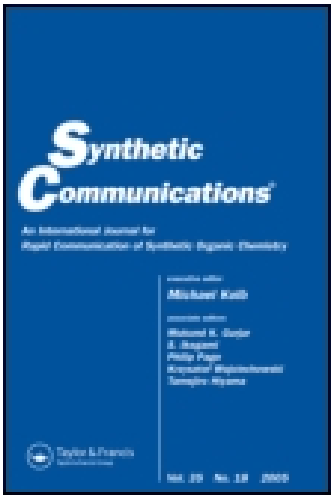

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Thallium(III) p-Tosylate Mediated Oxidative 2,3-Aryl Rearrangement: A New Useful Route to Ipriflavone and Its Analogs

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Thallium(III) *p*-Tosylate Mediated Oxidative 2,3-Aryl Rearrangement: A New Useful Route to Ipriflavone and Its Analogs

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Abstract: A new route for the synthesis of ipriflavone, an antiosteoporotic agent, is described that has four steps and 60% yields starting from resacetophenone (**2**). The key step of the present methodology is thallium(III) *p*-tosylate mediated oxidative 2,3-aryl rearrangement of flavanone to generate the isoflavone ring system of ipriflavone in a highly efficient manner.

Keywords: Flavanones, ipriflavone, isoflavones, oxidative rearrangement, thallium(III) *p*-tosylate

The isoflavones are a subclass of the flavonoids, which are mainly present in the species of the *Leguminosae* family. Often they are called phytoalexins because of their key role in plants' defense against fungal infection.[1] Moreover, these natural products have demonstrated numerous biological activities such as estrogenic,[2] anticancer,[3] antibacterial,[4] antimicrobial,[5] antiulcer,[6] and protein tyrosine kinase inhibiting[7] activities. Isoflavones are also called plant estrogens because they have positive influences on the bone similar to the effect of estrogen, but although estrogen has been associated with an increased risk of cancer, phytoestrogen can help to reduce the risk of cancer.[2] Based on these facts, ipriflavone (7-isopropyloxyisoflavone; **1a**), a derivative of isoflavones

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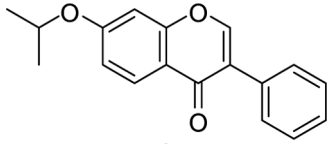
isolated from soy, was developed for the treatment of osteoprosis.[8] Ipriflavone (Fig. 1) had been shown to increase the bone's calcium retention, inhibit bone breakdown, promote the activity of bone-building cells, and reduce the pain of osteoporotic fractures.[9] It is registered as a prescription drug for the treatment for osteoporosis in various European countries and Japan with the trade names Iprosten, Osteofix, and Osten.

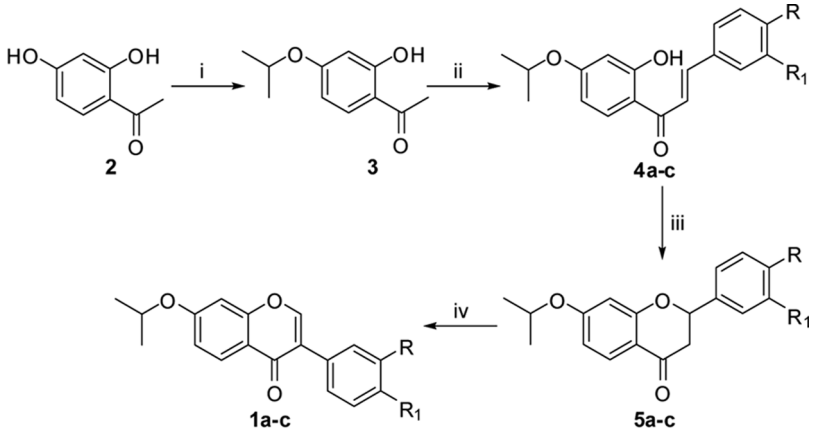
The ipriflavone is synthesized by following three different routes. The first route is the isopropylation of 7-hydroxyisoflavone using isopropyl bromide or isopropyl sulphonate,[10] the second route is the addition of the C_1 unit to 4′-isopropyloxy-2′-hydroxydeoxybenzoin or 2′,4′-dihydroxydeoxybenzoin by using trimethyl orthoformate under different reaction conditions,[11] and the third is the treatment of acid chloride with enamines under mild reaction condition.[12] We have developed a new route for the synthesis of isoflavones by oxidative rearrangement of flavanone using thallium(III) *p*-tosylate (TTS)[13] and thallium(III) perchlorate.[14] To demonstrate the potential utility of this methodology, we synthesized several isoflavones that possessed a natural substitution pattern, which led to the synthesis of several naturally occurring isoflavones.[15] Herein, we further extend the utility of thallium(III) *p*-tosylate for the synthesis of ipriflavone, an antiosteoporotic agent, and its analogs.

The synthesis of ipriflavone (**1a**) is illustrated in Scheme 1. Isopropylation of resacetophenone (**2**) with 2-bromopropane in the presence of K_2CO_3 as a base afforded 2-hydroxy-4-isopropyloxyacetophenone (**3**) in 95% yield.[16] The Claisen–Schmidt condensation of **3** with benzaldehyde in KOH-MeOH solution afforded 2′-hydroxy-4′-isopropyloxy-3-phenyl-1-acrylophenone (**4a**) in 80% yield. Similarly, compounds **4b** and **c** were also synthesized from **3** by Claisen–Schmidt condensation with *p*-anisaldehyde and piperonal in excellent yields. The isomerization–cyclization of chalcone **4a** to the corresponding 7-isopropyloxyflavanone (**5a**) was achieved by heating the former in an acidic solution such as hydrochloric acid in acetic acid or sulphuric acid in ethanol, but the yield was very poor, probably because of the deprotection of the isopropyl group, and 7-hydroxyflavanone was obtained as the major product.



1a

Figure 1. Ipriflavone.



Scheme 1. (a) $R = R_1 = H$, Ipriflavone; (b) $R = OMe$, $R_1 = H$; and (c) R, $R_1 = -OCH_2O-$. Reagents and conditions: (i) isopropyl bromide, K_2CO_3, DMF, 80–90°C; 12 h, 95%; (ii) aromatic aldehyde, KOH-MeOH, rt, 24 h, 75–85%; (iii) pyridine-MeOH-H_2O (1:1:1), rreflux, 12 h, 80–90%; and (iv) TTS, MeCN, reflux, 2 h, 92–94%.

Later, it was found that chalcone **4a** can be easily cyclized to 7-isopropyloxyflavanone (**5a**) by refluxing it in a mixture of pyridine–methanol–water (1:1:1) for 12 h in excellent yields. Similarly the chalcones **4b** and **c** were also cyclized to corresponding flavanones **5b** and **c** by heating the former in pyridine–methanol–water (1:1:1) for 12 h.

It was envisioned that the thallium(III) *p*-tosylate mediated oxidative 2,3-aryl rearrangement of flavanone to isoflavone developed by our group[13–15] would provide a convenient access to ipriflavone if the methodology works well with flavanone **5a**. Therefore, 7-isopropyloxyflavanone (**5a**) treated with thallium(III) *p*-tosylate in refluxing acetonitrile for 2 h smoothly underwent oxidative 2,3-aryl rearrangement to afford ipriflavone (**1a**) in excellent yield without deprotection of the isopropyl group. The appearance of the characteristic H-2 proton of isoflavone at δ 7.94 as a singlet and the disappearance of flavanone signals in the aliphatic region in the ^{1}H NMR spectrum of **1a** confirms the formation of an isoflavone nucleus. Similarly, the oxidative 2,3-aryl rearrangement induced by thallium(III) *p*-tosylate was successfully applied to the synthesis of 7-isopropyloxy-4′-methoxyisoflavone (**1b**) and 7-isopropyloxy-3′,4′-methylenedioxyisoflavone (**1c**).

In summary, we have developed a new synthetic route to ipriflavone by oxidative rearrangement of flavanone using thallium(III) *p*-tosylate in four steps and 60% overall yields starting from resacetophenone. The present methodology is also amenable to different substituents at aryl

ring C and would be useful to generate a large number of ipriflavone derivatives.

EXPERIMENTAL

General

Melting points were taken in open capillaries in a sulfuric acid bath and are uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin-Elmer 283 IR spectrophotometer; ^1H NMR spectra were recorded on Brucker DPX-200 using $CDCl_3$ as solvent and residual solvent as the internal standard. Thallium(III) acetate was purchased from Aldrich Chemical Co. (USA), and thallium(III) *p*-tosylate was prepared from thallium(III) acetate as described earlier.[17] All solvents were distilled before use. Thin-layer chromatography (TLC) was performed on silica-gel-coated glass plates and visualized in ultraviolet (UV) light and/or staining with iodine. 2-Hydroxy-4-isopropyloxyacetophenone (**3**) was synthesized by isopropylation of resacetophenone (**2**) in 95% yield by a slightly modified procedure as described in the literature.[16]

2′-Hydroxy-4′-isopropyloxy-3-aryl-1-acrylophenones (3a-c), General Procedure

Compound **2** (1.94 g, 10 mmol) and aromatic aldehyde (10 mmol) were added to a solution of potassium hydroxide (1.23 g, 22 mmol) in methanol (50 mL). The reaction mixture was stirred at room temperature for 24 h and then neutralized with dilute hydrochloric acid and extracted with dichloromethane (2×50 mL). The organic phase was washed with saturated sodium bicarbonate solution (50 mL) followed by water (50 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using petroleum ether–ethyl acetate (19:1) as eluent to give 2′-hydroxy-4′-isopropyloxy-3-aryl-1-acrylophenones (**3a–c**). The characterization data of **3a–c** are given next.

Data for 3a–c

2′-Hydroxy-4′-isopropyloxy-3-phenyl-1-acrylophenone (**3a**)

Yellow crystalline solid; yield 2.26 g (80%); mp 91–92 °C, IR (KBr) $\nu = 3396$ (OH), 1639 cm^{-1} (>C = O); ^1H NMR ($CDCl_3$): δ 1.38 (d, 6H,

$J = 6.0$ Hz), 4.63 (m, 1H, $J = 6.0$ Hz), 6.43–6.45 (m, 2H), 7.39–7.44 (m, 3H), 7.46 (d, 1H, $J = 15.3$ Hz), 7.69 (m, 2H), 7.81 (d, 1H, $J = 9.6$ Hz), 7.86 (d, 1H, $J = 15.3$ Hz), 13.56 (s, 1H); HRMS: m/z = 282.1254 (calcd. for $C_{18}H_{18}O_3$: 282.1256).

2′-Hydroxy-4′-isopropyloxy-3-(4″-methoxyphenyl)-1-acrylophenone (**3b**)

Yellow crystalline solid; yield 2.65 g (85%), mp 102–03 °C; IR (KBr) $\nu = 3400$ (OH), 1641 cm^{-1} (>C = O); ^{1}H NMR ($CDCl_3$): δ 1.37 (d, 6H, $J = 6.0$ Hz), 3.86 (s, 3H), 4.63 (m, 1H), 6.43–6.45 (m, 2H), 6.95 (brd, 2H, $J = 8.7$ Hz), 7.46 (d, 1H, $J = 15.4$ Hz), 7.61 (brd, 2H, $J = 8.7$ Hz), 7.81 (d, 1H, $J = 9.6$ Hz), 7.86 (d, 1H, $J = 15.4$ Hz), 13.52 (s, 1H); HRMS: m/z = 312.1364 (calcd. for $C_{19}H_{20}O_4$: 312.1362).

2′-Hydroxy-4′-isopropyloxy-3-(3″,4″-methylenedioxy)-1-acrylophenone (**3c**)

Yellow crystalline solid: yield 2.45 g (75%); mp 123–24 °C; IR (KBr) $\nu = 3398$ (OH), 1640 cm^{-1} (> C = O); ^{1}H NMR ($CDCl_3$): δ 1.37 (d, 6H, $J = 6.0$ Hz), 4.63 (m, 1H), 6.04 (s, 2H), 6.43–6.45 (m, 2H), 6.86 (d, 1H, $J = 8.0$ Hz), 7.14 (dd, 1H, $J = 1.6$ & 8.1 Hz), 7.18 (d, 1H, $J = 1.6$ Hz), 7.46 (d, 1H, $J = 15.4$ Hz), 7.81 (d, 1H, $J = 9.6$ Hz), 7.86 (d, 1H, $J = 15.4$ Hz), 13.52 (s, 1H); HRMS: m/z = 326.1150 (calcd. for $C_{19}H_{18}O_5$: 326.1154).

7-Isopropyloxyflavanones (**4a–c**), General Procedure

2′-Hydroxy-4′-isopropyloxy-3-aryl-1-acrylophenones (**3a–c**; 300 mg) was dissolved in pyridine–methanol–water (1:1:1; 30 mL), and the reaction mixture was refluxed for 12 h on a hot plate. After completion of the reaction, it was cooled to room temperature, and the solvent was concentrated to 5 mL under reduced pressure. To this, water (50 mL) was added and extracted with chloroform (2 × 25 mL). The organic phase was washed with dilute hydrochloric acid and saturated sodium bicarbonate solution followed by water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was passed through a small bed of basic alumina using ethyl acetate–hexane (1:10) as eluent to give 7-isopropyloxyflavanone (**4a–c**). The characterization data of **4a–c** are presented next.

Data for 4a–c

7-Isopropyloxyflavanone (**4a**)

White crystalline solid; yield 258 mg (86%); mp 132–33 °C; IR (KBr) $\nu = 1685\,cm^{-1}$ (>C = O); ^1H NMR ($CDCl_3$): δ 1.35 (d, 6H, $J = 6.0$ Hz), 2.80 (dd, 1H, $J = 2.9$ & 16.9 Hz), 3.05 (dd, 1H, $J = 12.5$ & 16.9 Hz), 4.58 (m, 1H), 5.43 (dd, 1H, $J = 2.9$ & 12.5 Hz), 6.44 (d, 1H, $J = 2.3$ Hz), 6.57 (dd, 1H, $J = 8.8$ & 2.3 Hz), 7.35–7.51 (m, 5H), 7.85 (1H, d, $J = 8.8$ Hz); HRMS: m/z = 282.1257 (calcd. for $C_{18}H_{18}O_3$: 282.1256).

7-Isopropyloxy-4′-methoxyflavanone (**4b**)

Yield 240 mg (80%), mp 99–100 °C; IR (KBr) $\nu = 1680\,cm^{-1}$ (> C = O); ^1H NMR ($CDCl_3$): δ 1.35 (d, 6H, $J = 6.0$ Hz), 2.79 (dd, 1H, $J = 2.9$ & 16.8 Hz), 3.05 (dd, 1H, $J = 13.3$ & 16.8 Hz), 3.84 (s, 3H), 4.58 (m, 1H), 5.41 (dd, 1H, $J = 2.8$ & 13.3 Hz), 6.43 (d, 1H, $J = 2.3$ Hz, H-8), 6.57 (dd, 1H, $J = 8.8$ & 2.4 Hz), 6.96 (brd, 2H, $J = 8.7$ Hz), 7.46 (brd, 2H, $J = 8.7$ Hz), 7.85 (d, 1H, $J = 8.8$ Hz); HRMS: m/z = 312.1360 (calcd. for $C_{19}H_{20}O_4$: 312.1362).

7-Isopropyloxy-3′,4′-methylenedioxyflavanone (**4c**)

White crystalline solid, yield 270 mg (90%), mp 124–25 °C, IR (KBr) $\nu = 1688\,cm^{-1}$ (>C = O); ^1H NMR ($CDCl_3$): δ 1.35 (d, 6H, $J = 6.1$ Hz), 2.78 (dd, 1H, $J = 2.9$ & 16.8 Hz), 3.06 (dd, 1H, $J = 13.3$ & 16.8 Hz), 4.58 (m, 1H), 5.42 (dd, 1H, $J = 2.9$ & 13.3 Hz), 6.44 (d, 1H, $J = 2.3$ Hz), 6.57 (dd, 1H, $J = 8.8$ & 2.4 Hz), 6.83 (d, 1H, $J = 8.0$ Hz), 6.92 (dd, 1H, $J = 8.2$ & 1.7 Hz), 7.01 (d, 1H, $J = 1.6$ Hz), 7.85 (d, 1H, $J = 8.9$ Hz); HRMS: m/z = 326.1151 (calcd. for $C_{19}H_{18}O_5$: 326.1154).

7-Isopropyloxyisoflavones (1a–c), General Procedure

Thallium(III) *p*-tosylate (800 mg, 1.1 mmol) was added to a solution of 7-isopropyloxyflavanone (**4a–c**; 1 mmol) in acetonitrile (15 mL), and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and diluted with dichloromethane (50 mL), and the separated thallium(I) *p*-tosylate was filtered off and washed with dichloromethane (20 mL). The filtrate was washed with saturated

aqueous solution of sodium hydrogen carbonate (2×50 mL), followed by water, and dried over anhydrous sodium sulfate. The solvent was then distilled off under reduced pressure, and the residue was passed over a small bed of basic alumina and recrystallized from ethyl acetate–hexane (1:9) to afford 7-isopropyloxyisoflavones (**1a–c**). The characterization data of **1a–c** are given next.

Data for 1a–c

Ipriflavone [7-Isopropyloxyisoflavone (**1a**)]

White crystalline solid: yield 258 mg (92%); mp 114–15 °C (lit.[12] mp 115–117 °C), IR (KBr) $\nu = 1640\,cm^{-1}$ (>C = O); ^1H NMR ($CDCl_3$): δ 1.41 (d, 6H, $J = 6.0$ Hz), 4.68 (m, 1H), 6.86 (d, 1H, $J = 2.2$ Hz), 6.96 (dd, 1H, $J = 2.2$ & 8.9 Hz), 7.32–7.48 (m, 3H), 7.52–7.60 (m, 2H), 7.94 (s, 1H), 8.21 (d, 1H, $J = 8.9$ Hz).

7-Isopropyloxy-4′-methoxyisoflavone (**1b**)

White crystalline solid; yield 291 mg (94%); mp 149–51 °C; IR (KBr) $\nu = 1639\,cm^{-1}$ (>C = O); ^1H NMR ($CDCl_3$): δ 1.41 (d, 6H, $J = 6.0$ Hz), 3.84 (s, 3H), 4.67 (m, 1H), 6.83 (d, 1H, $J = 2.0$ Hz), 6.92–6.99 (m, 3H), 7.50 (brd, 2H, $J = 8.7$ Hz), 7.91 (s, 1H), 8.20 (d, 1H, $J = 8.9$ Hz); HRMS: m/z = 310.1202 (calcd. for $C_{19}H_{18}O_4$: 310.1205).

7-Isopropyloxy-3′,4′-methylenedioxyisoflavone (**1c**)

White crystalline solid; yield 305 mg (94%), mp 154–55 °C, IR (KBr) $\nu = 1638\,cm^{-1}$ (>C = O); ^1H NMR ($CDCl_3$): δ 1.41 (d, 6H, $J = 6.0$ Hz), 4.67 (m, 1H), 5.99 (s, 2H), 6.83 (d, 1H, $J = 2.2$ Hz), 6.87 (d, 1H, $J = 8.0$ Hz), 6.94–6.99 (m, 2H), 7.10 (d, 1H, $J = 1.4$ Hz), 7.90 (s, 1H), 8.19 (d, 1H, $J = 8.9$ Hz); HRMS: m/z = 324.0996 (calcd. for $C_{19}H_{16}O_5$: 324.0998).

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