Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2857-2860

Oxidation of 3-Hydroxyflavanones using Polymer-Supported [Hydroxy(tosyloxy)iodo]benzene

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The reaction of polymer-supported [hydroxy(tosyloxy)iodo]benzene with 3-hydroxyflavanones has been described to afford 2,3-dimethoxy-3-hydroxyflavanones. This is a clean oxidation reaction with moderate to high yield.

Key Words: 3-Hydroxyflavanones, Oxidation, Polymer-supported [hydroxy(tosyloxy)iodo]benzene.

INTRODUCTION

Polymer-supported hypervalent reagents are considered important over the simple hypervalent iodine reagents[1,2] because of ease of processing as work-up and purification of the product are reduced to simple separation and the polymer may be recovered, regenerated and recycled[3]. The use of simple hypervalent iodine reagents results in the formation of iodobenzene as the side product which is difficult to remove from the product formed. The polymer-supported hypervalent iodine reagents has been studied for clean organic synthesis with potential application in combinatorial chemistry[4] as well as in the preparation of isoflavones from 2'-hydroxychalcones[5]. Keeping in view of these significances, herein the oxidation of 3-hydroxyflavanones with polymer-supported [hydroxy(tosyloxy)iodo]benzene (PSHTIB) that afforded 2,3-dimethoxy-3-hydroxyflavanones is reported.

EXPERIMENTAL

Melting points are uncorrected. FTIR spectra were recorded in KBr on Shimadzu FTIR 8201 spectrophotometer and ^{1}H NMR spectra on Bruker ACF at 300 MHz using $CDCl_3$. Elemental analysis were determined on Elementar Vario EL III.

3-Hydroxyflavanones (**2**) were synthesized[6] according to modified AFO reaction from 2'-hydroxychalcones (**1**).

Polymer-supported [hydroxy(tosyloxy)iodo]benzene (PSHTIB): Iodination of polystyrene (2% cross linked with divinylbenzene, m.w. = 2,50,000, Aldrich) resulted in the formation of iodopolystyrene which on treatment with acetic anhydride in the presence of 30 % H_2O_2 generated polymer-supported (diacetoxyiodo)benzene (PSDIB)[7-9]. PSDIB was reacted with *p*-toluenesulphonic acid to afford PSHTIB[9].

General procedure

2,3-Dimethoxy-3-hydroxyflavanones (3): To a solution or suspension of flavonols (1.0 mmol) in methanol (40 mL) was added PSHTIB (1.2 mmol, *ca*. loading capacity 1.86 mmol/g). The reaction mixture was stirred at 55-60°C or at refluxing temperature for 0.5-1 h. After the completion of reaction, the solution was filtered while hot and the solid iodopolystyrene was washed with 5-10 mL of hot methanol. The filtrate was concentrated and allowed to cool. The colourless to light yellow coloured compound (2,3-dimethoxy-3-hydroxyflavanones, **3**) separated out, which was filtered and recrystallized from methanol.

3a: m.p. 111-113°C, yield 70%; IR (KBr, cm^{-1}): 1708, 3394; ^{1}H NMR: 2.41 (s, 3H, CH_3), 3.10 (s, 6H, 2 × OCH_3), 7.12-7.17 (m, 2H, C_6-H & C_8-H), 7.31 (d, 2H, J = 8.1 Hz, $C_{3'}$-H & $C_{5'}$-H), 7.61 (t, 1H, J = 7.7 Hz, C_7-H), 7.69 (dd, 2H, J = 8.1 Hz, $C_{2'}$-H & $C_{6'}$-H), 7.95 (dd, 1H, J=1.8 & 8.1 Hz, C_5-H). Anal. Calcd. For $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 67.97; H, 5.31.

3b: m.p. 144-146°C (Lit.[10] 145-148°C), yield 72%; IR (KBr, cm^{-1}): 1701, 3411; ^{1}H NMR: 3.09 (s, 6H, 2 × OCH_3), 7.13 (d, 1H, J = 8.7 Hz, C_8-H), 7.49-7.52 (m, 3H, $C_{3'}$-H, $C_{4'}$-H & $C_{5'}$-H), 7.57 (dd, 1H, J = 2.7 & 8.7 Hz, C_7-H), 7.77-7.80 (m. 2H, $C_{2'}$-H & $C_{6'}$-H), 7.92 (d, 1H, J = 2.7 Hz, C_5-H).

3c: m.p. 118-120°C, yield 65%; IR (KBr, cm^{-1}): 1716, 3440; ^{1}H NMR: 2.42 (s, 3H, CH_3), 3.10 (s, 6H, 2 × OCH_3), 7.12 (d, 1H, J = 8.7 Hz, C_8-H), 7.31 (d, 2H, J = 8.1 Hz, $C_{3'}$-H & $C_{5'}$-H), 7.56 (dd, 1H, J = 2.1 & 8.7 Hz, C_7-H), 7.66 (m. 2H, $C_{2'}$-H & $C_{6'}$-H), 7.91 (d, 1H, J = 2.7 Hz, C_5-H). Anal. Calcd. For $C_{18}H_{17}O_5Cl$: C, 61.99; H, 4.91. Found: C, 60.61; H, 4.61.

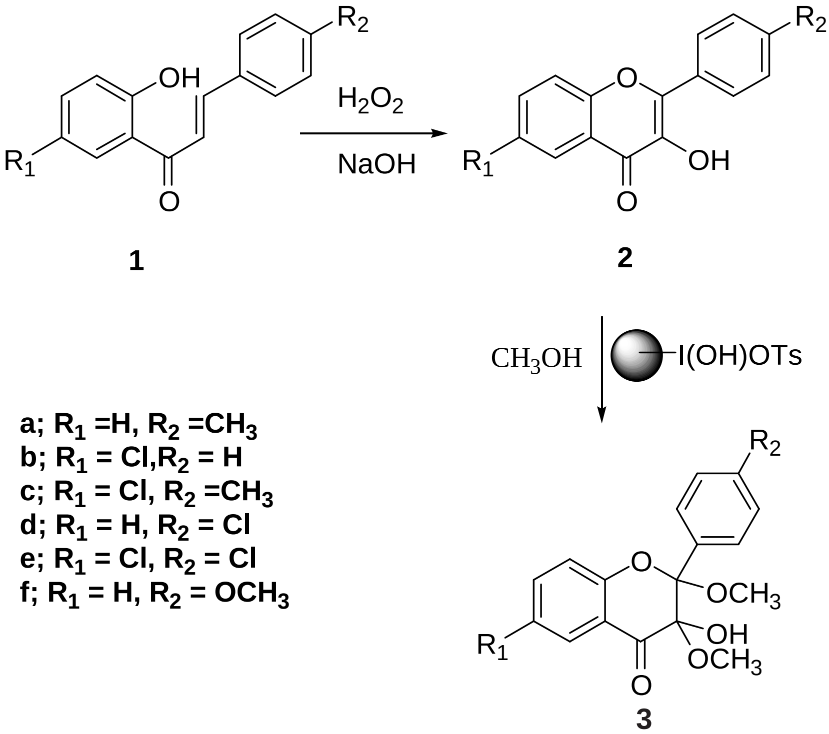
3d: m.p. 156-157°C (Lit.[11] 156-159°C), yield 80%; IR (KBr, cm^{-1}): 1703, 3465; ^{1}H NMR: 3.07 (s, 6H, 2 × OCH_3), 7.13-7.18 (m, 2H, C_6-H , C_8-H), 7.43-7.47 (m, 2H, $C_{3'}$-H & $C_{5'}$-H), 7.59-7.65 (m, 1H, C_7-H), 7.71-7.76 (m. 2H, $C_{2'}$-H & $C_{6'}$-H), 7.92 (dd, 1H, J = 1.5 & 7.8 Hz, C_5-H).

3e: m.p. 171-173°C (Lit.[10] 170-173°C), yield 76%; IR (KBr, cm^{-1}): 1716, 3436; ^{1}H NMR: 3.05, 3.07 (s, s, 3H, 3H, 2 × OCH_3), 7.11 (dd, 1H, J = 3.0 Hz, C_8-H), 7.46 (m, 2H, $C_{3'}$-H & $C_{5'}$-H), 7.57 (dd, 1H, J = 2.7 &7.7 Hz, C_7-H), 7.69-7.74 (m. 2H, $C_{2'}$-H & $C_{6'}$-H), 7.90 (d, 1H, J = 2.6 Hz, C5-H).

3f: m.p. 161-163°C (Lit.[11] 162-164°C), yield 80%; IR (KBr, cm^{-1}): 1685, 3460; ^{1}H NMR: 3.00, 3.06 (s, s, 3H, 3H, 2 × OCH_3), 3.85 (s, 3H, OCH_3), 6.95-7.00 (m, 2H, $C_{3'}$-H & $C_{5'}$-H), 7.11-7.16 (m, 2H, C_6-H , C_8-H), 7.60 (ddd, 1H, J = 1.4 &7.8 Hz, C_7-H), 7.67-7.71 (m. 2H, $C_{2'}$-H & $C_{6'}$-H), 7.93 (dd, 1H, J = 1.9 & 8.0 Hz, C_5-H).

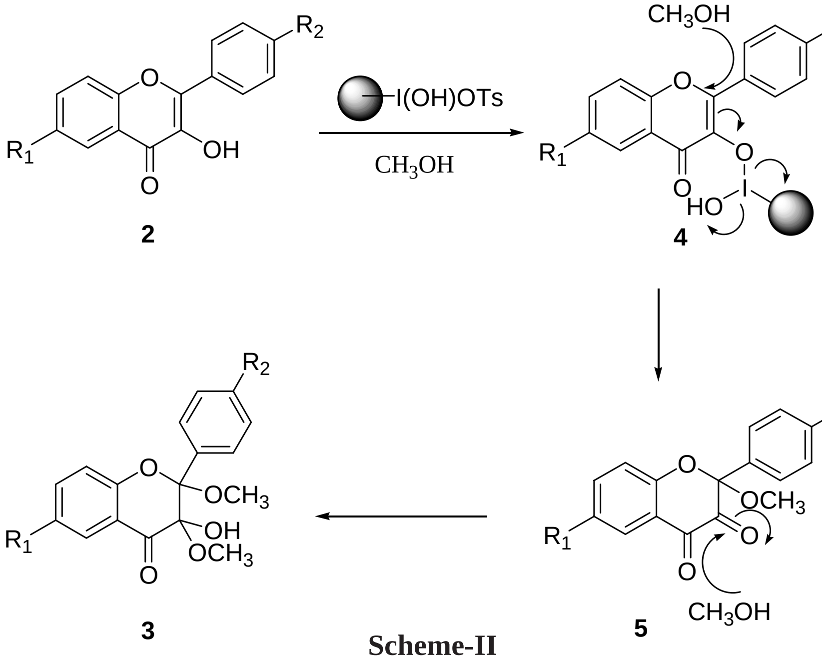
RESULTS AND DISCUSSION

The reaction of 2'-hydroxychalcones (**1**) with hydrogen peroxide generated the 3-hydroxyflavanones (**2**), which on oxidation with PSHTIB yielded the corresponding 2,3-dimethoxy-3-hydroxyflavanones (**3**) in moderate to high yield (**Scheme-I**). After completion of reaction, the product was filtered and purified by column chromatography in some cases. The structure assignment of 2,3-dimethoxy-3-hydroxyflavanones was based on physical characteristics and spectroscopic (IR and NMR) data. The presence of bands at 1708 and 3394 cm^{-1} in IR spectrum were due to (C=O) str. and OH str. in **3a**, whereas the same bands were at 1606 and 3284 cm^{-1} in **2a** thereby confirming its oxidation. In ^1H NMR spectrum of **3a**, both methoxy groups resonated at δ 3.10. The complete assignment of other protons was found to be in agreement with the structure (**3a**) and are presented in experimental.



Scheme-I

The mechanism involves first attack of C_3-OH on PSHTIB resulting in the formation of intermediate (**4**) that underwent reductive elimination of iodopolystyrene by the attack of methanol on C_2 generating 3,4-diketone (**5**). The 3,4-diketone (**4**) is selectively attacked *in situ* at C_3 by methanol yielding 2,3-dimethoxy-3-hydroxyflavanones (**3**) (**Scheme-II**).



Scheme-II

The use of polymer-supported [hydroxy(tosyloxy)iodo]benzene (PSHTIB) is advantageous over the toxic lead(IV)acetate which cause similar transformation. The results are also comparable to the use of simple HTIB where removal of iodobenzene after completion of reaction is little problematic. PSHTIB utilized in these reactions can be regenerated back by treatment of recovered iodopolystyrene with peracetic acid followed by *p*-toluenesulphonic acid.

ACKNOWLEDGEMENT

The authors are grateful to CSIR, New Delhi for financial support.

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(*Received*: 25 April 2006; *Accepted*: 23 January 2007) AJC-5333