A New Synthesis of 2-Aroylcoumaran-3-ones by Hypervalent Iodine Oxidation of 2-Acetylphenyl Benzoates Using [Hydroxy(tosyloxy)iodo]benzene

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Hypervalent iodine oxidation of 2-acetylphenyl benzoates **1a–f** using [hydroxy(tosyloxy)iodo]benzene (HTIB), followed by Baker–Venkatraman rearrangement of the resultant 2-[(tosyloxy)acetyl]phenyl benzoates **2a–f** with potassium hydroxide, provides a new convenient and useful synthesis of 2-aroylbenzofuran-3(2*H*)-ones **3a–f**.

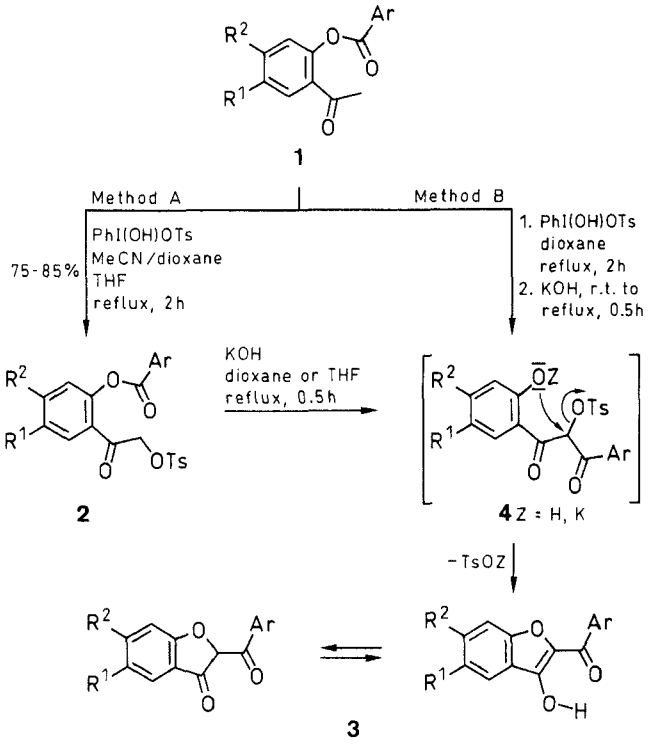
The application of [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent) in organic synthesis and particularly in transformations from carbonyl compounds is a subject of current interest.[1] During our recent investigations on hypervalent iodine oxidation, we realized that HTIB has a great scope for further exploring its synthetic versatility.[2] The present paper demonstrates the utility of HTIB in a new useful synthesis of 2-aroylcoumaran-3-ones (2-aroylbenzofuran-3(2*H*)-ones) **3a–f** which are known to possess a wide range of physiological activity.[3]

Thus, 2-acetylphenyl benzoate **(1a)** was subjected to hypervalent iodine oxidation with HTIB in acetonitrile or dioxane according to the method of Koser et al.[4] to give 2-[(tosyloxy)acetyl]phenylbenzoate **(2a)** as a crystalline solid in 85% yield. Baker–Venkatraman rearrangement (BVR) of **2a** using potassium hydroxide in dioxane according to the standard conditions gave the desired product, 2-benzoylbenzofuran-3(2*H*)-one **(3a)**, in 72% yield. Similarly, 2-acetyl-5-methoxyphenyl benzoate **(1d)** was also transformed into 2-benzoyl-6-methoxybenzofuran-3(2*H*)-one **(3d)** in 70% yield (Method A, Scheme).

To simplify the procedure further, we attempted the conversion **1** → **3** directly by omitting the step of isolation of the intermediates **2** (Method B, Scheme). Interestingly, this approach was also successful and thus variously substituted 2-aroylcoumaran-3-ones **3a–f** were synthesized in 70–82% yields, simply by treating the benzoates **1a–f** with HTIB in dioxane, followed by base-catalysed BVR of **2a–f** (in situ).

It may be noted that the new conversion **1** → **3** is analogous to the most common base-catalyzed BVR of 2-(haloacetyl)phenyl benzoates[5] and probably proceeds via intermediates **4** which in turn result from BVR of **2**. This study provides a new convenient synthesis of **3a–f** directly from readily accessible ketones **1a–f** and the procedure is superior to other well-known literature procedures.[5–7] The most striking and useful feature of the new hypervalent iodine approach is that there exists the possibility of a general and more convenient replacement of the processes which require lachrymatory and difficult to obtain α-halo ketones.

All reagents were of commercial quality from freshly opened containers. Reagent quality solvents were used without further purification. Melting points were taken in open capillaries and are uncorrected.



1–4	R^1	R^2	Ar	1–4	R^1	R^2	Ar
a	H	H	Ph	**d**	H	OMe	Ph
b	Cl	H	Ph	**e**	H	OMe	4-$MeOC_6H_4$
c	Cl	Me	Ph	**f**	Cl	H	4-$MeOC_6H_4$

Table. 2-Aroylbenzofuran-3(2*H*)-ones **3a–f** Prepared According to Methods A, B

3	Yield (%)[a] A	Yield (%)[a] B	mp (°C)	Molecular Formula or Lit. mp (°C)
a	72	80	81–82	81–82[8]
b	–	82	138–139	138–139[8]
c	–	75	153–154	153–154[8]
d	70	74	128–130	129–130[8]
e	–	70	184–186	$C_{17}H_{14}O_5$[b] (298.3)
f	–	75	135–137	$C_{16}H_{11}O_4Cl$[b] (302.7)

[a] Yield of isolated product **3** with respect to the quantity of 2′-aroyloxyacetophenones **1** used.

[b] **3e**: IR (Nujol): $\nu = 1600\ cm^{-1}$ (C=O, s). ^1H NMR ($CDCl_3$): $\delta = 3.86$ (s, 6H, OCH_3), 6.90–8.40 (m, 8H); **3f**: IR (Nujol): $\nu = 1606\ cm^{-1}$ (C=O, s). ^1H NMR ($CDCl_3$): $\delta = 3.90$ (s, 3H, OCH_3), 6.70–8.20 (m, 8H).
The found and calculated elemental analysis (C, H) agreed within ±0.4%.

Conversion of 2-Acetylphenyl Benzoates 1- to 2-Aroylbenzofuran-3(2*H*)-ones 3a–f; General Procedures:

Method A (via isolation of **2a,d**):

Step 1: 2-[(Tosyloxy)acetyl]phenyl Benzoates **2**: HTIB (1.96 g, 5.0 mmol) was added to a stirrred solution of ketone **1** (5.0 mmol) in MeCN/dioxane/THF (20 mL) and the mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure. The crude product was crystallized using EtOH to give compound **2**.

2-[(Tosyloxy)acetyl]phenyl Benzoate (**2a**): yield: 85%; mp 106–108 °C.

IR (Nujol): ν = 1740, 1720 cm^{-1} (C=O, s).

^1H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 5.10 (s, 2 H, $C\underline{H}_2OTs$), 7.15–8.30 (m, 13 H_{arom}).

5-Methoxy-2-[(tosyloxy)acetyl]phenyl Benzoate (**2d**): yield: 75%; mp 132–134 °C.

IR (Nujol): ν = 1743, 1702 cm^{-1} (C=O, s).

^1H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 5.05 (s, 2 H, $C\underline{H}_2OTs$), 7.1–8.3 (m, 12 H_{arom}).

Step 2: 2-Aroylbenzofuran-3(2H)-ones **3**: To a solution of **2** (10.0 mmol) in dioxane (20 mL) or THF (25 mL) was added KOH (0.6–1.2 g, 10.0–20.0 mmol) and was refluxed for 0.5 h. The mixture was then cooled down and was poured into dil. H_2SO_4. The compounds **3** separated out as yellow crystalline solid, which were recrystallized with EtOH (Table).

Method B (directly from benzoates **1**): To a stirred solution of ketone **1** (5.0 mmol) in dioxane (25 mL) was added HTIB (1.96 g, 5.0 mmol) and the mixture was refluxed for 2 h. On cooling the mixture to r.t., KOH (3.4 g, 60.0 mmol) was added and the mixture was then refluxed gently with frequent shaking for another 30 min. The resulting mixture was cooled to r.t. and the contents were poured into dil. H_2SO_4 (40 mL) and extracted with $CHCl_3$ (4 × 25 mL). The combined organic extract was dried (Na_2SO_4) and evaporated in vacuo. The crude product containing iodobenzene was crystallized with EtOH. The characterization data of **3a–f** thus prepared were given in the Table.

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