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Solvent-free synthesis of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one from Dess–Martin periodinane and its synthetic utility for α-tosyloxylation of ketones

Nandkishor N. Karade *, Girdharilal B. Tiwari, Sandeep V. Shinde, Sumeet V. Gampawar, Jeevan M. Kondre

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, Maharashtra, India

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Abstract

The solvent-free synthesis of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one is reported from Dess–Martin periodinane and *p*-toluenesulfonic acid monohydrate using a grinding technique and is subsequently utilized for the α-tosyloxylation of a range of enolisable ketones.

Keywords: Hypervalent iodine; Dess–Martin periodinane; α-Tosyloxylation; PTSA; Solvent-free reactions

Recent decades have witnessed an exponential growth in the applications of hypervalent iodine reagents in organic synthesis.[1] 2-Iodoxybenzoic acid (IBX) **1** represents one such versatile five-membered hypervalent iodine(V) heterocycle derived from benziodoxole.[2] It has been widely used for various useful oxidative transformations.[3] In 1983, Dess and Martin carried out the reaction of IBX with acetic anhydride at 100 °C for the preparation of triacetoxybenziodoxole **2**.[4] In the following years, triacetate **2** has emerged as a chemoselective reagent of choice for the oxidation of alcohols and in the present literature is commonly referred to as Dess–Martin periodinane (DMP).[5] In contrast to IBX **1** and DMP **2**, the analogous five-membered trivalent iodine heterocycles derived from benziodoxoles have received much less attention. However, the significant contribution of Viktor Zhdankin has led to the development of various trivalent iodine five-membered heterocycles (Fig. 1), such as 1-hydroxy-1,2-benziodoxol-3(1*H*)-one **3**, 1-organosulfonoloxy-1,2-benziodoxol-3(1*H*)-one **4**, 1-cyano-1,2-benziodoxol-3(1*H*)-one **5**, 1-amido-1,2-benziodoxol-3(1*H*)-one **6** and 1-azido-1,2-benziodoxol-3(1*H*)-one **7**.[6] The distinctive feature of these heterocyclic iodanes is their considerable higher stability than their acyclic analogs. These various benziodoxole derivatives have found practical application as reagents for the oxidative functionalization of organic substrates.[7]

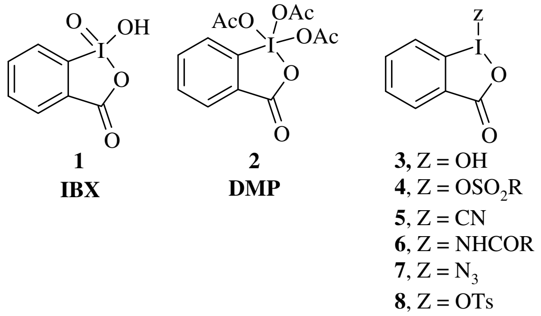

Fig. 1. Benziodoxole-based hypervalent iodine reagents.

The first preparation of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one **8** was reported by Zhdankin et al.

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* Corresponding author. Tel.: +91 2462 266999; fax: +91 2462 29245.
E-mail address: nnkarade2007@rediffmail.com (N. N. Karade).

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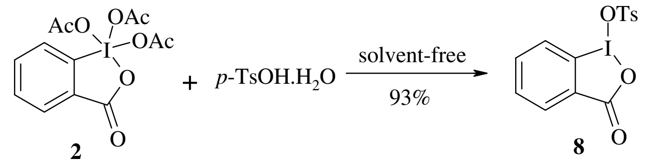
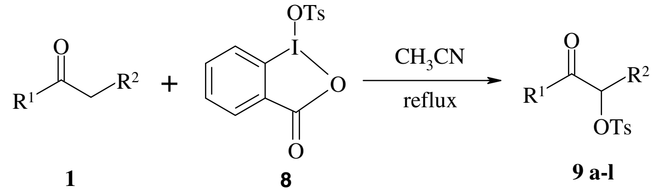


Scheme 1.

Table 1

α-Tosyloxylation of enolisable ketones using 1-(p-toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one in CH_3CN

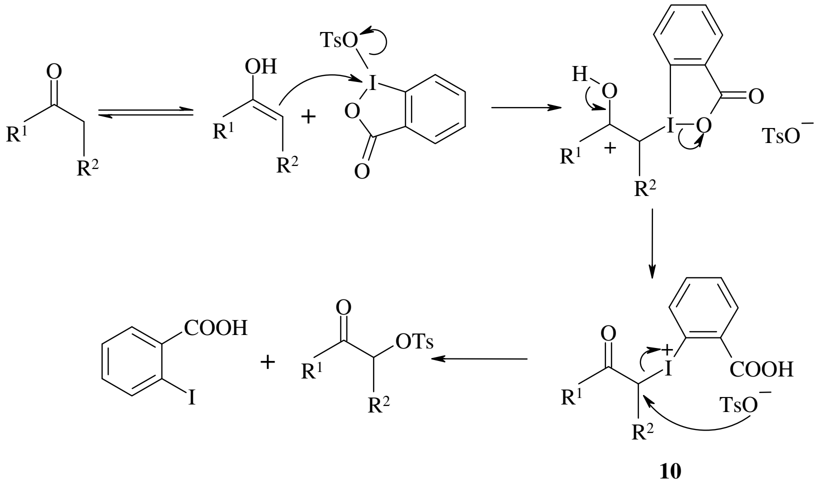


Entry	Product **9**	Reaction time (h)	Yield[a] (%)
a	$C_6H_5COCH_2OTs$	1	88
b	4-$CH_3C_6H_4COCH_2OTs$	1	63
c	4-$CH_3OC_6H_4COCH_2OTs$	1	76
d	2,4-$(CH_3O)_2C_6H_3COCH_2OTs$	1.5	69
e	4-$BrC_6H_4COCH_2OTs$	1	88
f	2-$BrC_6H_4COCH_2OTs$	1.5	67
g	2-$ClC_6H_4COCH_2OTs$	1.5	79
h	4-$NO_2C_6H_4COCH_2OTs$	1.5	73
i	$C_6H_5COCH(CH_3)OTs$	1.5	67
j	α-Tosyloxycyclohexanone	1.5	69
k	$CH_3COCH(OTs)COCH_3$	1.5	71
l	$CH_3COCH(OTs)COOCH_3$	1.5	74

[a] Isolated yields after chromatography.

by the reaction of 1-hydroxy-1,2-benziodoxol-3(1H)-one **3** with p-toluenesulfonic acid monohydrate in the presence of acetic anhydride.[8] Another noteworthy solvent-free synthesis of **8** involves the grinding of (diacetoxyiodo)benzene, 2-iodobenzoic acid and p-toluenesulfonic acid monohydrate in an agate mortar.[9] In 1987, Toda et al. showed that many reactions (but not all) can be conducted in high yields under solvent-free conditions just by grinding the reactants together.[10] Usually these reactions were carried out on a very small scale in an agate pestle and mortar. We decided to extend this strategy for the reaction between Dess–Martin periodinane and p-toluenesulfonic acid monohydrate (Scheme 1). In a typical experimental procedure, a homogeneous mixture of Dess–Martin periodinane (2 mmol) and p-toluenesulfonic acid monohydrate (2 mmol) was gently ground for 15 min using a pestle and mortar. The formation of acetic acid, and wetting of the reaction mixture was observed. The resulting reaction mixture was washed with diethyl ether to remove liberated acetic acid and dried under high vacuum to afford 1-(p-toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one **8** in 93% yield. The structure of this reagent **8** was established from NMR and mass spectral analysis, and found perfectly in agreement with that reported in the literature.[11]

α-Tosyloxylation of ketones is most frequently achieved using [hydroxy(tosyloxy)iodo]benzene, which is commonly known as Kosser's reagent.[12] The utility of 1-(p-toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one **8** was previously demonstrated for the oxidative nuclear iodination of aromatic rings as well as for the iodotosyloxylation of alkynes.[13] The synthetic application of 1-(p-toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one **8** is hitherto unknown for the α-tosyloxylation of ketones. Herein, we have investigated the ability of **8** for the α-tosyloxylation reaction of enolisable ketones and the results are summarized in Table 1.[14] The method is quite general for the α-tosyloxylation of enolisable ketones and in all the cases good to excellent yields of the products were obtained. Alicyclic ketones such as substituted acetophenones, propiophenone and cyclic ketone such as cyclohexanone underwent the α-tosyloxylation reaction smoothly to afford the corresponding products in reasonable yields. The methodology was also extended to α-tosyloxylation of 1,3-dicarbonyl compounds such as methyl acetoacetate and acetyl acetone to form the respective α-tosyloxy products.



Scheme 2.

A tentative mechanism for the α-tosyloxylation of ketones is shown in Scheme 2. The enol tautomer of the ketone reacts with the electrophilic 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one via ligand exchange to form intermediate **10**, which undergoes reductive elimination of 2-iodobenzoic acid to form the α-tosyloxy ketone.

In conclusion, we have demonstrated an efficient solvent-free synthesis of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one from the readily available Dess–Martin periodinane and *p*-toluenesulfonic acid monohydrate. The α-tosyloxylation of a range of ketones was successfully carried out with 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one in good to excellent yields. The development of other synthetic applications of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one is underway.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.119.

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11. *Experimental procedure for the preparation of 1-(p-toluenesulfonyloxy)-1,2- benziodoxol-3(1H)-one*: A homogeneous mixture of Dess–Martin periodinane (2 mmol) and *p*-toluenesulfonic acid monohydrate (2.1 mmol) was gently ground for 15 min using a pestle and mortar. The liberation of acetic acid and wetting of the reaction mixture was observed. After completion of the reaction, the solid residue was washed with diethyl ether (5 mL) and concentrated in vacuo to afford the analytically pure 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one in 93% yield. Spectral data of 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one **8**: ^{1}H NMR (DMSO): $\delta = 2.35$ (s, 3H, ArCH$_3$), 7.16 (d, 2H, $J = 7.88$ Hz, ArH), 7.66 (d, 2H, $J = 8.08$ Hz, ArH), 7.83 (t, $J = 7.36$ Hz, 1H, ArH), 7.98 (t, $J = 7.36$ Hz, 1H, ArH), 8.15 (d, 1H, $J = 7.48$ Hz, ArH), 8.31 (d, 1H, $J = 7.88$ Hz, ArH); ^{13}C NMR (DMSO): $\delta = 168.45$, 146.58, 143.27, 138.9, 133.53, 132.85, 130.34, 130.10, 128.23, 125.53, 124.55, 20.91; LCMS (M+1): $m/z = 419$.
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14. *Experimental procedure for the α-tosyloxylation of ketones using 1-(p-toluenesulfonyloxy)-1,2-benziodoxol-3(1H)-one*: A mixture of appropriate ketone (1 mmol) and 1-(*p*-toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one **8** (1 mmol) was refluxed in CH$_3$CN (10 mL) for the time period shown in Table 1. After completion of reaction as ascertained by TLC, the mixture was treated with aqueous sodium bicarbonate, extracted with CH$_2$Cl$_2$, dried over anhydrous sodium sulfate, concentrated under vacuum and subsequently chromatographed over silica gel (230–400 mesh) using petroleum ether/ethyl acetate (4:1 v/v) as eluent to afford the α-tosyloxylation product of the ketone.