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A novel and convenient approach for tosyloxylation of aromatic ring of some *ortho*-substituted phenolic compounds using [hydroxy(tosyloxy)iodo]benzene

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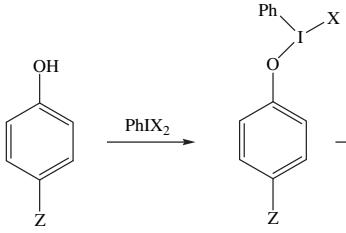
ABSTRACT

The oxidation of some substituted monohydric phenols, containing electron-withdrawing substituents at the *ortho* position to the phenolic group, with [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent) leads to novel tosyloxylation of aromatic ring, thereby offering a convenient synthesis of hitherto unknown 4-tosyloxy-2-substituted phenols.

1. Introduction

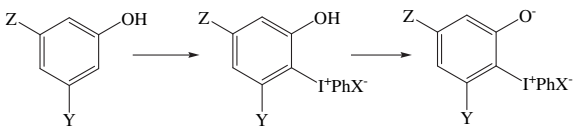
The oxidation of phenols is a key biochemical process in oxidative phosphorylation and it is also important in numerous biosynthetic pathways.[1] There has been considerable interest in developing controlled synthetic transformations involving oxidation of phenolic compounds with a variety of oxidants. Useful reagents include Fermy's salt[2] and a wide variety of other redox-metal based oxidants such as Pb(IV),[3] Tl(III),[4] Mn(III),[5] Cu(II),[6] and Fe(III).[7] Recently, the use of hypervalent iodine reagents has offered very interesting and useful transformations from various phenolic compounds.[8] The beneficial features for the use of hypervalent iodine reagents[9] are their low toxicity, high stability, easy handling, and unique reactivity similar to that of a series of heavy metals. Extensive research studies reported to date in the literature reveal that the process that occurs during the oxidation of phenolic compounds with hypervalent iodine reagents can be divided in two categories. The first category involves ligand exchange of the phenolic proton with the hypervalent iodine reagent to generate the O–I(III) intermediate, which is subsequently transformed to various products, depending upon the reaction conditions (Eq. 1).



(1)

These transformations include oxidation of phenols to quinones and related compounds,[10] formation of spirocyclic compounds,[11] oxygen heterocyclic compounds via oxidative intramolecular participation reactions,[12] and intramolecular carbon–carbon bond formation via phenolic oxidative coupling.[13] All of these reactions are driven by the reduction of iodine (III) to iodine (I).

The second category of these reactions includes formation of stable iodonium salts and ylides, which are important intermediates in organic synthesis. These reactions occur via carbon–I (III) bond formation without loss of iodobenzene (Eq. 2).[14]



(2)

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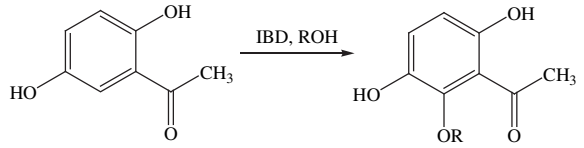
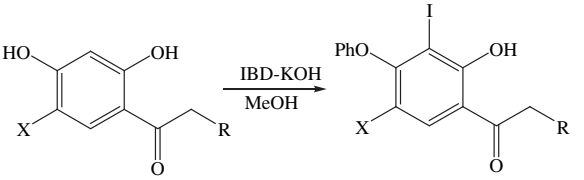
Of the various hypervalent iodine reagents employed for phenolic oxidations, organoiodine(III) reagents namely, iodobenzene diacetate (IBD) and iodobenzene bis(trifluoroacetate) (IBTA) have found versatile and significant applications. In contrast, [hydroxy (tosyloxy)iodo]benzene (HTIB), which is well known for its versatile synthetic utility, particularly tosyloxylation of olefinic and carbonyl compounds,[15] has little been explored for phenolic oxidations.

Previous investigations from our laboratory have shown that oxidation of some dihydroxy phenols containing enolizable moiety at the *o*-position of phenolic group leads to regioselective oxygenation of aromatic ring[16] and formation of iodonium ylides and their rearrangement[17]depending upon the nature of substrate and reaction condition as outlined in Eqs. 3 and 4, respectively.

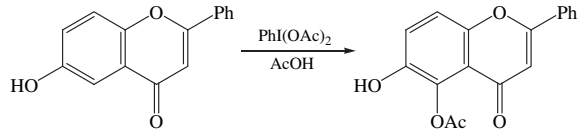


(3)

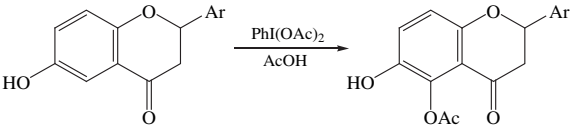


(4)

When applied to 6-hydroxyflavone and 6-hydroxyflavanone, the oxidative approach using IBD in acetic acid provides a convenient route for the synthesis of 5-acetoxylated products (Eqs. 5 and 6).[18]



(5)

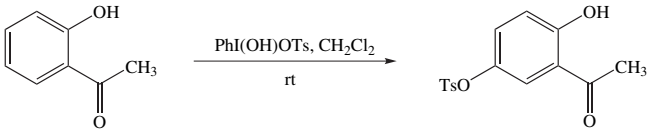


(6)

Encouraged by our previous results and keeping in view that the use of HTIB for oxidation of monohydric phenolic compounds, particularly which contain electron-withdrawing groups has not been explored till date,[19] we have now investigated the oxidation of some substituted monohydric phenols **1** with emphasis on those containing electron-withdrawing substituents ($-NO_2$, $-CHO$, $-CONH_2$, $-COOCH_3$, $-COOPh$) at *ortho* position with HTIB in dichloromethane. The study has led to a novel tosyloxylation of aromatic ring of substituted monohydric phenols **1**, thereby offering a convenient synthesis of hitherto unknown 4-tosyloxy-2-substituted phenols (**2**).

2. Results and discussion

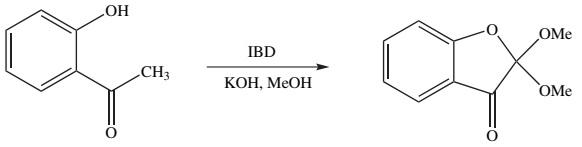
We first selected *o*-hydroxyacetophenone (**1a**), which was treated with 1.1 equiv of HTIB in dichloromethane at room temperature for 3 h. The single product isolated from this reaction was characterized as 2-acetyl-4-tosyloxyphenol (**2a**) on the basis of spectral (IR, ^{1}H NMR) and elemental analytical data (Scheme 1). This was a novel observation, as no such an example of tosyloxylation of phenolic compounds is known in the literature.



1a **2a**

Scheme 1. Reaction of *o*-hydroxyacetophenone (**1a**) with HTIB in dichloromethane.

Further, it is worthwhile to mention that *o*-hydroxyacetophenone on treatment with IBD–KOH in methanol is known to give 2,2-dimethoxycoumaran-3-one (Eq. 7).[12b] We attempted this reaction using IBD in methanol and dichloromethane in the absence of KOH. However, in this experiment only starting *o*-hydroxyacetophenone was recovered.



(7)

Encouraged by this result on tosyloxylation of **1a**, we became interested in examining the impact of the structure of phenolic compounds on the reaction outcome. Accordingly variously substituted monohydric phenols **1b**–**q** were subjected to reaction with HTIB under similar conditions. The results summarized in Table 1, clearly indicate that the reaction is greatly influenced by the electronic effect and position of substituents on the aromatic ring of monohydric phenols. The results of this study are discussed according to the type of phenolic substrates employed.

2.1. Phenols containing electron-withdrawing substituents at the *ortho* position

The monohydric phenols, which contain electron-withdrawing substituents ($-NO_2$, $-CHO$, $-CONH_2$, $-COOCH_3$, $-COOPh$) at the *ortho* position on treatment with 1.1 equiv of HTIB in dichloromethane underwent smooth tosyloxylation to the corresponding 4-tosyloxy-2-substituted phenols (**2b**–**f**) (Scheme 2, Table 1, entries 2–6).[20]

Obviously, in all these cases, tosyloxylation occurred at the vacant *para* position with respect to the phenolic hydroxyl group. The reaction of 2-acetyl-4-methylphenol (**1g**), where *para* position was occupied by methyl group occurred according to expectation to give the *ortho* substituted product **2g** in 78% yield (Table 1, entry 7). In case of 1-formyl-2-naphthol (**1h**) tosyloxylation occurred at 6-position to give 1-formyl-6-tosyloxy-2-naphthol (**2h**) in 72% yield (Table 1, entry 8).

2.2. Phenol and phenols containing electron-releasing substituents at the *ortho* position

The phenols, which contain electron-releasing substituents such as CH_3 and OCH_3 at the *ortho* position did not give the tosyloxylated product under the same conditions (Table 1, entries 9 and 10). The reaction was sluggish and formation of complex mixture was observed. Despite making numerous attempts, we were unable to isolate corresponding 4-tosyloxy-2-substituted phenols. The reaction of parent phenol with HTIB also did not give any successful result (Table 1, entry 17). Monitoring the reaction by ^{1}H NMR did not give any indication of tosyloxylation of aromatic ring.

Table 1
Products of the reactions of substituted monohydric phenols with HTIB in dichloromethane at room temperature

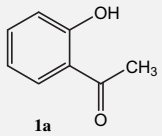
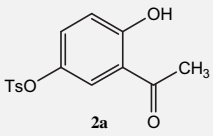
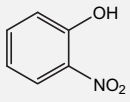
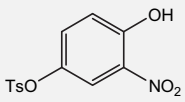
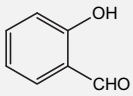
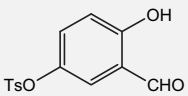
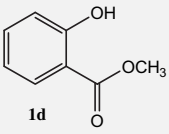
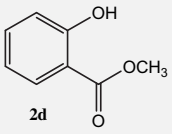
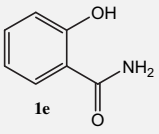
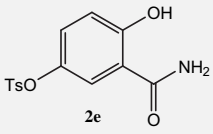
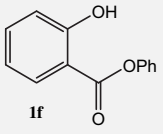
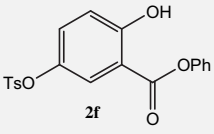
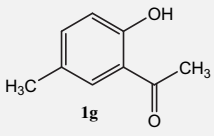
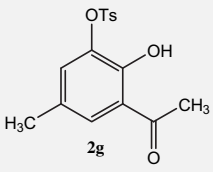
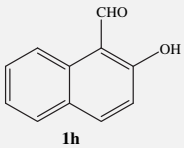
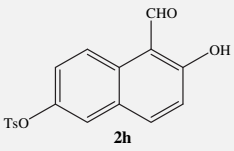
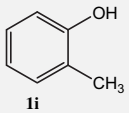
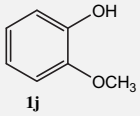
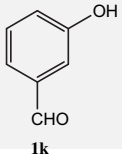
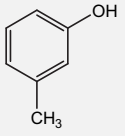
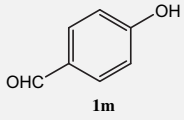
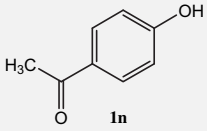
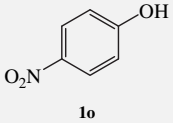
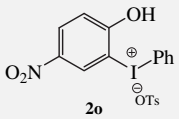
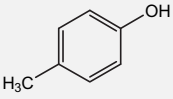
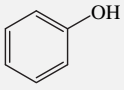
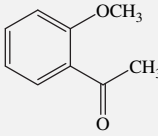
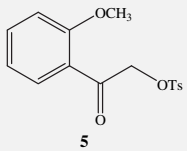
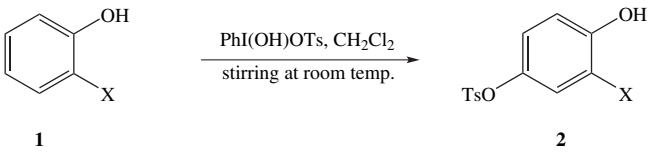
Entry	Substrates	Products[a]	Yield[b] (%)
1	 **1a**	 **2a**	65
2	 **1b**	 **2b**	68
3	 **1c**	 **2c**	64
4	 **1d**	 **2d**	62
5	 **1e**	 **2e**	61
6	 **1f**	 **2f**	58
7	 **1g**	 **2g**	78
8	 **1h**	 **2h**	72
9	 **1i**	c	—
10	 **1j**	c	—
11	 **1k**	d	—

Table 1 (*continued*)

Entry	Substrates	Products[a]	Yield[b] (%)
12	 **1l**	c	—
13	 **1m**	d	—
14	 **1n**	d	—
15	 **1o**	 **2o**	82
16	 **1p**	c	—
17	 **1q**	c	—
18	 **4**	 **5**	92

[a] Satisfactory spectral data were obtained on all the products.
[b] Isolated yields after purification by column chromatography.
[c] Reaction was sluggish.
[d] No reaction.



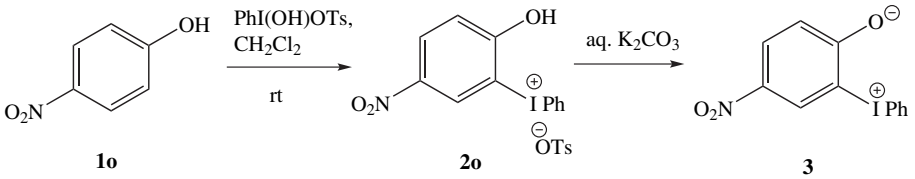
1 **2**

X = NO_2 (**b**); CHO (**c**); $COOCH_3$ (**d**); $CONH_2$ (**e**); COOPh (**f**)

Scheme 2. Reaction of 2-substituted phenol derivatives (**1b**–**f**) with HTIB leading to formation of 4-tosyloxy-2-substituted phenol derivatives (**2b**–**f**).

2.3. Phenols containing electron-withdrawing and electron-releasing substituents at the *para* position

The phenols, which contain electron-withdrawing substituents at the *para* position (Table 1, entries 13–15) also did not follow the same trend. When the reaction of *p*-nitrophenol was carried out under similar reaction conditions, the 2-hydroxy-5-nitrodiphenyliodonium tosylate (**2o**) was obtained in 82% rather than any tosyloxylated product (Table 1, entry 15). The tosylate **2o** on basification with aqueous potassium carbonate resulted in the formation of ylide **3** (Scheme 3).



Scheme 3. Reaction of *p*-nitrophenol (**1o**) with HTIB.

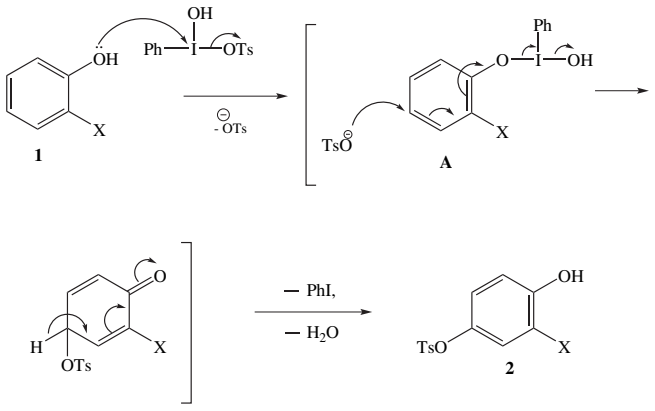
Similar iodonium ylides/salts have previously been reported by Kokil and Nair by the reaction of *p*-nitrophenol with IBD in acetic acid.[14b] To our surprise *p*-hydroxyacetophenone and *p*-hydroxybezaldehyde under similar conditions did not give neither tosyloxylated product nor iodonium salt/ylide (Table 1, entries 13 and 14). In the case of *p*-cresol, the reaction was also sluggish (Table 1, entry 16).

2.4. Phenols containing electron-withdrawing and electron-releasing substituents at the *meta* position

Unfortunately, the method for tosyloxylation of phenols was not applicable to the *m*-substitued phenols. While in the case of *m*-hydroxybezaldehye (Table 1, entry 11) only starting *m*-hydroxybezaldehyde was recovered, the reaction of *m*-cresol (Table 1, entry 12) resulted in a complex mixture without affording any desired tosyloxylated product.

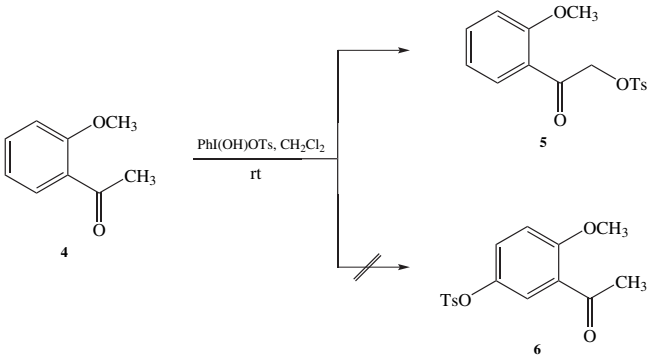
2.5. Mechanistic considerations

It is evident from the results of the present study, summarized in Table 1 that it is necessary to have electron-withdrawing substituents at the *ortho* position of the phenolic group for the successful tosyloxylation of aromatic ring. Although, actual role of various electron-withdrawing substituents is not clear and detailed understanding of the reaction mechanism awaits further study, the plausible mechanism suggested for the tosyloxylation of phenols is analogous to the reported studies on hypervalent iodine oxidation of phenols[21] and is outlined in Scheme 4. The mechanism probably involves Type **A** intermediate, in which the phenolic oxygen initially reacts with iodine of HTIB. This is followed by the nucleophilic attack of $^{-}$OTs at the *para* (or *ortho* when *para* position is not vacant) position of phenol ring to give the tosyoxylated product **2**, together with iodobenzene.

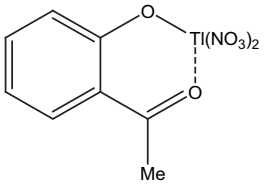


Scheme 4. Plausible mechanism for the formation of 4-tosyloxy-2-substituted phenols (**2**).

It may be mentioned that Kita et al. in 1994,[22] determined the SET oxidation ability of IBTA toward phenyl ethers, affording the corresponding aromatic cation radicals. Since then, they have utilized IBTA as selective and efficient oxidizing agent that enables a variety of direct C–H functionalization of aromatic and hetero aromatic rings. Koser et al. have also suggested SET mechanism for oxidative-substitution reaction of polycyclic aromatic hydrocarbons with HTIB in dichloromethane.[15i] Thus, we considered the possibility of SET mechanism for tosyloxylation of phenols under study. In order to determine whether the reaction involves phenolic group, we carried out the reaction of *o*-methoxyacetophenone (**4**) in place of *o*-hydroxyacetophenone with HTIB in dichloromethane under similar reaction conditions. However, the reaction afforded α-tosyloxyketone **5** rather than *p*-tosyloxylated product **6** in 92% yield (Scheme 5). This experiment suggested that the ring tosyloxylation could not proceed without phenolic group and therefore probably proceeds via ligand exchange between phenolic group and HTIB as shown in Scheme 4. It is also relevant to mention that involvement of the intermediate of the Type **B** (similar to Type **A**) has been suggested in on thallium(III) mediated oxidation of some *o*-hydroxyacetophenones (based upon ^{1}H NMR measurements).[23]



Scheme 5. Reaction of *o*-methoxyacetophenone (**4**) with HTIB.



3. Conclusion

The tosyloxylation of phenols reported in this study demonstrates an interesting application of HTIB in aromatic substitution of certain phenolic compounds containing electron-withdrawing substitution at their *ortho* position. The noteworthy features of this study are:

(i) Oxidation of monohydric phenols **1** containing electron-withdrawing substituents at *ortho* position with 1 equiv of HTIB offers a novel and efficient route for their tosyloxylation at *para* position. The tosyloxy derivatives **2a**–**h** obtained from this study are hitherto unknown and seem to be useful precursors for further transformations such as carbon–carbon coupling reaction such as arylation of enolates derived from carbonyl compounds.[24]

(ii) In enolizable ketones, $COCH_3$ group, which is prone to undergo α-tosyloxylation remains intact under the reaction conditions.[25]
(iii) In the case of *o*-hydroxybenzamide (**2e**), $CONH_2$ group does not undergo Hoffmann reaction to produce the amine with HTIB, as reported earlier.[26]
(iv) The reaction conditions are mild and further oxidative-substitution of phenolic group is not observed.

4. Experimental section

4.1. General information

Melting points (mp) were taken in open capillaries and are uncorrected. The IR spectra were recorded on Perkin–Elmer IR1800 spectrophotometer. The ^1H NMR spectra were recorded in $CDCl_3$ on Bruker 300 MHz instrument with TMS as an internal standard. The data are reported as follows: chemical shift in parts per million (δ) and coupling constant (Hz). Elemental analyses were carried out in Perkin–Elmer 2400 instrument. PhI(OH)OTs (HTIB, Koser's reagent) was prepared according to the literature method.[27] Solvents and all starting materials were obtained from commercial suppliers and were used without further purification.

4.2. Typical procedure for synthesis of 4-tosyloxy-2-substituted phenols (2)

To a stirred solution of *o*-hydroxyacetophenone (**1a**, 136 mg, 1.0 mmol) in dichloromethane (50 ml) was added HTIB (431 mg, 1.1 mmol) in one portion. The resulting mixture was allowed to stir at room temperature. HTIB was highly insoluble in dichloromethane, gradually disappeared as the reaction proceeded. The stirring was allowed to continue for about 3 h. After completion of the reaction (as monitored by TLC), the crude product **2a** was purified by column chromatography on silica gel using 1:10 EtOAc–Petroleum ether as eluent; mp 102–103 °C, yield, 280 mg (65%), entry 1, Table 1.

4.2.1. 2-Acetyl-4-tosyloxyphenol ***2a***. Colorless crystals; mp 102–103 °C; IR (KBr): 3450, 1651, 1483, 1377, 1285, 1167, 1089, 1024 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H, CH_3 of ^-OTs), 2.52 (s, 3H, CH_3), 6.87 (d, 1H, *J*=9.0 Hz), 7.01 (dd, 1H, *J*=9.0, 2.7 Hz), 7.35 (d, 2H, *J*=8.1 Hz), 7.37, (d, 1H, *J*=2.7 Hz), 7.71 (d, 2H, *J*=8.1 Hz), 12.15 (s, 1H, OH); elemental analysis calcd (%) for $C_{15}H_{14}O_5S$: C, 58.82; H, 4.58; found: C, 58.91; H 4.43.

Other derivatives were prepared in a similar manner. The characterization data of the compounds prepared in this study is given as under.

4.2.2. 2-Nitro-4-tosyloxyphenol ***2b***. Yellow crystals; mp 112–113 °C; IR (KBr): 3432, 1528, 1490, 1381, 1358, 1259, 1177, 1089, 1005 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 7.11 (d, 1H, *J*=9.0 Hz), 7.29 (dd, 1H, *J*=9.0, 3.0 Hz), 7.36 (d, 2H, *J*=8.1 Hz), 7.68 (d, 1H, *J*=3.0 Hz), 7.73 (d, 2H, *J*=8.1 Hz), 10.49 (s, 1H, OH); elemental analysis calcd (%) for $C_{13}H_{11}NO_6S$: C, 50.49; H, 3.56; found: C, 50.38; H, 3.58.

4.2.3. 2-Formyl-4-tosyloxyphenol ***2c***. Brownish crystals; mp 219–220 °C; IR (KBr): 3455, 2866, 1666, 1473, 1374, 1265, 1172, 1083, 1003 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H, CH_3), 6.88 (d, 1H, *J*=9.0 Hz), 7.01 (dd, 1H, *J*=9.0, 2.8 Hz), 7.28 (d, 1H, *J*=2.8 Hz), 7.34 (d, 2H, *J*=8.4 Hz), 7.71 (d, 2H, *J*=8.4 Hz), 9.78 (s, 1H, –CHO), 10.96 (s, 1H, OH); elemental analysis calcd (%) for $C_{14}H_{12}O_5S$: C, 57.53; H, 4.11; found: C, 57.61; H, 4.03.

4.2.4. 2-Carbamethoxy-4-tosyloxyphenol ***2d***. Brownish crystals; mp 91–92 °C; IR (KBr): 3445, 1682, 1490, 1384, 1259, 1175, 1083, 1004 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.86 (s, 3H, -OCH_3), 6.78 (d, 1H, *J*=9.0 Hz), 6.87 (dd, 1H, *J*=9.0, 2.9 Hz), 7.26 (d, 2H, *J*=8.4 Hz), 7.50 (d, 1H, *J*=2.9 Hz), 7.63 (d, 2H, *J*=8.4 Hz), 10.66 (s, 1H, OH); elemental analysis calcd (%) for $C_{15}H_{14}O_6S$: C, 55.90; H, 4.35; found: C, 55.84; H 4.21.

4.2.5. 2-Carbamoyl-4-tosyloxyphenol ***2e***. Brownish crystals; mp 145–146 °C; IR (KBr): 3466, 3340, 3219, 1654, 1450, 1372, 1258, 1179, 1095, 1029 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H, CH_3), 6.11 (br s, 2H, $-NH_2$), 6.79 (d, 1H, *J*=9.0 Hz), 6.89 (dd, 1H, *J*=9.0, 2.0 Hz), 7.21 (d, 1H, *J*=2.0 Hz), 7.33 (d, 2H, *J*=8.1 Hz), 7.68 (d, 2H, *J*=8.1 Hz), 12.17 (s, 1H, OH); elemental analysis calcd (%) for $C_{14}H_{13}NO_5S$: C, 54.72; H, 4.23; found: C, 54.61; H 4.13.

4.2.6. 2-Carbaphenoxy-4-tosyloxyphenol ***2f***. Brownish crystals; mp 105–106 °C; IR (KBr): 3442, 1691, 1487, 1377, 1256, 1178, 1083, 1004 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3), 6.79 (d, 1H, *J*=9.0 Hz), 6.88 (dd, 1H, *J*=9.0, 2.9 Hz), 7.23 (d, 2H, *J*=8.1 Hz), 7.33 (m, 3H), 7.39 (m, 2H), 7.56 (d, 1H, *J*=2.9 Hz), 7.63 (d, 2H, *J*=8.1 Hz), 10.71 (s, 1H, OH); elemental analysis calcd (%) for $C_{20}H_{16}O_6S$: C, 62.50; H, 4.17; found: C, 62.55; H, 4.06.

4.2.7. 2-Acetyl-4-methyl-6-tosyloxyphenol ***2g***. Colorless crystals; mp 121–122 °C; IR (KBr): 3451, 1648, 1469, 1374, 1260, 1172, 1085, 1003 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 7.31, (d, 2H, *J*=8.1 Hz), 7.40 (d, 1H, *J*=1.8 Hz), 7.44 (d, 1H, *J*=1.8 Hz), 7.84, (d, 2H, *J*=8.1 Hz), 12.02 (s, 1H, OH); elemental analysis calcd (%) for $C_{16}H_{16}O_5S$: C, 60.00; H, 5.00; found: C, 59.89; H, 5.08.

4.2.8. 1-Formyl-6-tosyloxy-2-naphthol ***2h***. Colorless crystals; mp 152–153 °C; IR (KBr): 3410, 2834, 1672, 1444, 1293, 1247, 1170, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 7.11 (d, 1H, *J*=6.9 Hz), 7.15 (dd, 1H, *J*=6.9, 21.8 Hz), 7.25 (d, 2H, *J*=6.3 Hz), 7.41 (d, 1H, *J*=1.8 Hz), 7.66 (d, 2H, *J*=6.3 Hz), 7.81 (d, 1H, *J*=6.9 Hz), 8.19 (d, 1H, *J*=6.9 Hz), 10.67 (s, 1H, –CHO), 13.05 (s, 1H, OH); elemental analysis calcd (%) for $C_{18}H_{14}O_5S$: C, 63.16; H, 4.09; found: C, 62.99; H, 4.01.

4.3. Synthesis of 2-hydroxy-5-nitrodiphenyliodonium ylide 3

4.3.1. 2-Hydroxy-5-nitrodiphenyliodonium tosylate ***2o***. To a stirred solution of *p*-nitrophenol (**1o**, 347 mg, 2.5 mmol) in dichloromethane (50 ml) was added HTIB (1077 mg, 2.8 mmol) in one portion. The resulting mixture was allowed to stir at room temperature. HTIB, initially insoluble in dichloromethane, gradually disappeared as the reaction proceeded. After stirring the reaction mixture for 2 h the yellow colored solid was separated out and filtered; yield 632 mg (82%); mp 191–192 °C; IR (KBr): 3448, 1540, 1490, 1381, 1352, 1250, 1180, 1089, 1005 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 2.37 (s, 3H, CH_3), 7.21–7.24 (m, 3H), 7.53 (d, 2H, *J*=7.8 Hz), 7.67–7.70 (m, 3H), 8.19 (d, 2H, *J*=7.8 Hz), 8.39 (dd, 1H, *J*=8.7, 2.7 Hz), 9.10 (d, 1H, *J*=2.7 Hz).

4.3.2. 2-Hydroxy-5-nitrodiphenyliodonium ylide ***3***. The suspension of tosylate **2o** (513 mg, 1.0 mmol) with aqueous potassium carbonate (10 ml, 10%) was stirred at room temperature for 30 min. The resulting yellow colored solid was filtered and washed with water; yield 325 mg (95%); mp 131–132 °C (lit.[13b] mp 133 °C); IR (KBr): 3460, 1550, 1461, 1381, 1259, 1010 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 6.35 (d, 1H, *J*=9.3 Hz), 7.49–7.54 (m, 2H), 7.64–7.68 (m, 1H), 7.94 (d, 1H, *J*=9.1 Hz), 8.10 (d, 2H, *J*=7.5 Hz), 8.38 (d, 1H, *J*=2.7 Hz).

4.4. Synthesis of *o*-methoxy-α-tosyloxyacetophenone 5

To a stirred solution of *o*-methoxyacetophenone (**4**, 150 mg, 1.0 mmol) in dichloromethane (40 ml) was added HTIB (431 mg, 1.1 mmol) in one portion. The resulting mixture was allowed to stir

at room temperature for about 3 h. The solvent was evaporated in vacuo. The gummy mass so obtained was triturated with pet ether (60–80 °C) to remove iodobenzene. The resulting colorless solid was thoroughly washed with water to remove *p*-toluenesulphonic acid formed as a byproduct. The solid was recrystallized with acetonitrile to give the pure *o*-methoxy-α-tosyloxyacetophenone as colorless crystalline solid (**5**, yield 294 mg, 92%); mp 91–92 °C; IR (KBr): 1660, 1571, 1461, 1381, 1348, 1271, 1167, 1078, 1003 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 5.27 (s, 2H, CH_2), 6.97–7.06 (m, 2H), 7.36 (d, 2H, *J*=8.1 Hz), 7.55 (td, 1H, *J*=8.4, 1.8 Hz), 7.86 (dd, 1H, *J*=8.4, 1.8 Hz), 7.91 (d, 2H, *J*=8.1 Hz); elemental analysis calcd (%) for $C_{16}H_{16}O_5S$: C, 60.00; H, 5.00; found: C, 59.83; H, 5.09.

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