EurJOC
European Journal of Organic Chemistry

Research Article
doi.org/10.1002/ejoc.202301191

Chemistry Europe
European Chemical Societies Publishing

www.eurjoc.org

New Isoxazole-Substituted Aryl Iodides: Metal-Free Synthesis, Characterization and Catalytic Activity

Rimi,[a] Bhawna Uttam,[a] Viktor V. Zhdankin,[b] and Ravi Kumar*[a]

A series of new isoxazole-substituted aryl iodides **1a**–**1d** have been synthesized by DIB-mediated [3 + 2] cycloaddition reaction of 2-iodo-1,3-bis(prop-2-yn-1-yloxy) benzene (**4**) with corresponding benzaldehyde oximes **5a**–**5d**. Structure of the synthesized aryl iodides **1** were characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS. The structure of **1a** was also confirmed by single-crystal X-ray crystallography. Further, catalytic activity of iodoarenes **1a**–**1d** was screened for the oxidation of hydroquinones and sulfides. On oxidation using aryl iodides **1** with *m*-CPBA as terminal oxidant, hydroquinones afforded benzoquinones while sulfides gave corresponding sulfoxides in good to excellent yields. Iodoarene **1b** showed the best catalytic activity for the oxidation of sulfides and hydroquinones. Moreover, iodoarene **1b**, was also utilized for α-oxytosylation of acetophenones.

Introduction

Hypervalent iodine compounds have been developed as valuable reagents in organic synthesis over the past few decades. Owing to their eco-friendly and mild electrophilic nature and oxidizing ability, these reagents are superior alternatives to toxic heavy metals.[1–2] These reagents have been extensively explored for the various oxidative transformations such as oxidation of alcohols,[3] phenols,[4] sulfides,[5] and C–H functionalization[6] and for the oxidative cyclization to form various heterocyclic moieties.[7–8] Besides the use of hypervalent iodine reagents as stoichiometric reagents, the catalytic use of hypervalent iodine compounds has received much attention in recent years.[9–10] The first hypervalent iodine-catalyzed reaction for electro-chemical gem-difluorination of dithioacetals was reported by Fuchigami and Fujita in 1994.[11] Initially, peracetic acid and some common inorganic oxidants were used, however, *m*-chloroperbenzoic acid (*m*-CPBA) was effectively employed for the *in-situ* generation of hypervalent iodine reagents by the oxidation of iodoarenes. The first hypervalent iodine-catalyzed reaction using *m*-CPBA as a terminal oxidant was independently reported by groups of Ochiai,[12] Kita[13] and Vinod.[14] Subsequently, various reports appeared in the literature regarding iodoarene-catalyzed organic transformations by the use of terminal oxidants.[2,10,15] The oxidation of hydroquinone and sulfides to their corresponding oxidized products is one of the most studied oxidation reactions. During the oxidation of sulfides, most reagents necessitate carefully controlled reaction conditions including the quantity of oxidants because of the formation of sulfones as side products.

Controlling the oxidation of diaryl sulfides to avoid the formation of sulfones has been difficult since the first oxidation to the sulfoxides requires relatively high energy.[16] On the other hand, there are various reports in literature which show that hypervalent iodine(III) compounds such as, PhIO, $PhI(OCOR)_2$, PhI(OH)OTs, $PhICl_2$, PhIO-metalloporphyrin (or Mn(III)-salen complex) etc. are efficient reagents for the selective oxidation of sulfides to sulfoxides.[2,5,17] Certain alternative approaches for the oxidation of sulfides to sulfoxides include electrochemical methods,[18] photocatalytic oxidation using oxygen[19] etc. Besides oxidation reactions, various other valuable reactions such as alkene difunctionalization,[20–21] spiro cyclization of esters and amides[22–23] and oxytosylation and acetylation of ketones[24] have also been studied by the use of iodoarenes as catalysts. Recently, Nachtsheim group developed N-heterocyclic iodoarenes (NHIAs) as efficient organocatalysts in various oxidative transformations.[25] The reported NHIAs showed excellent catalytic activity towards α-oxytosylation of ketones. These results and our continuous interest in the area of HVI compounds prompted us to develop some new iodoarenes and investigate their catalytic activity. With the aim to design some new aryl iodides that exhibit excellent catalytic performance towards the oxidation of diverge range of substrates, a series of new iodoarenes **1a**–**1d** have been synthesized through [3 + 2] cycloaddition reaction of nitrile oxides with 2-iodo-1,3-bis(prop-2-yn-1-yloxy)benzene (**4**). Structures of newly synthesized isoxazole-substituted iodoarenes **1a**–**1d** is given in Figure 1. Further, the catalytic activity of these iodoarenes **1** was investigated for the oxidation of hydroquinone, sulfides as well as for the α-oxytosylation of substituted acetophenones.

Results and Discussion

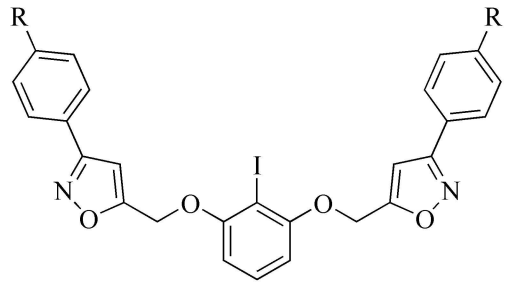
The aryl iodides **1a**–**1d** were synthesized by the procedure as outlined in Scheme 1 using resorcinol **2** as the starting material. The reaction of resorcinol **2** with molecular iodine resulted in the formation of 2-iodoresorcinol **3** which was further treated

[a] *Rimi, B. Uttam, R. Kumar*
Department of Chemistry, J. C. Bose University of Science and Technology, YMCA, Mathura Road, Sector-6, Faridabad 121006, Haryana, India
E-mail: ravi.dhamija@rediffmail.com

[b] *V. V. Zhdankin*
Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota, 55812, United States

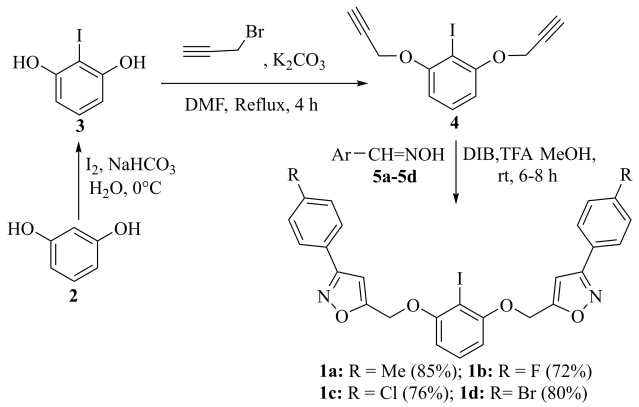
Research Article
doi.org/10.1002/ejoc.202301191

Chemistry Europe
European Chemical Societies Publishing



1a: R = Me; **1b:** R = F; **1c:** R = Cl; **1d:** R= Br

Figure 1. Structure of newly synthesized isoxazole-substituted iodoarenes **1 a-1 d.**

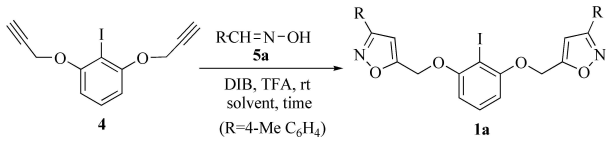


Scheme 1. Synthetic route for isoxazole-substituted iodoarenes **1 a-1 d.**

with propargyl bromide in the presence of K_2CO_3 to form **4** in 70% yield. Finally, [3 + 2] cycloaddition reaction of **4** with *in-situ* generated nitrile oxide, by the reaction of oxime **5 a**–**5 d** with (diacetoxy)iodobenzene (DIB), afforded the corresponding iodoarenes **1 a**–**1 d**.

In initial experiments, the reaction of 4-methyl benzaldehyde oxime (**5 a**, 2.0 eq.) with DIB/TFA and 2-iodo-1,3-bis(prop-2-yn-1-yloxy) benzene (**4**) in acetonitrile afforded the desired iodoarene in 45% yield (Table 1, entry 1). Increasing the concentration of oxime **5 a** (w.r.t alkynes) to 3.0 eq. increased

Table 1. Optimization for the synthesis of **1 a**.



S. No.	Conc. of 5a	Solvent	Time (h)	Yield (%)[a]
1	2.0 eq.	CH_3CN	12	45%
2	2.5 eq.	CH_3CN	10	50%
3	3.0 eq.	CH_3CN	8.5	65%
4	3.0 eq.	C_2H_5OH	8	73%
5	3.0 eq.	CH_3OH	7	85%

[a] Isolated yields.

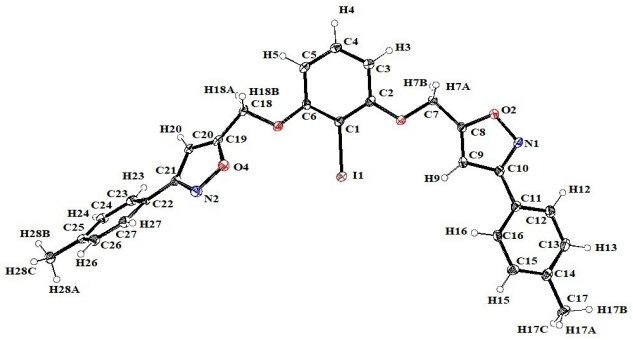


Figure 2. ORTEP drawing of **1 a** (the thermal ellipsoids drawn at the 30% probability level) (CCDC No. 2304049).

the yield of the desired iodoarene **1 a** to 65% (Table 1, entries 2–3). After screening the different solvents (eg., CH_3CN, C_2H_5OH, CH_3OH) as shown in Table 1; best results were obtained with methanol (CH_3OH) which gave iodoarene **1 a** in 85% yield.

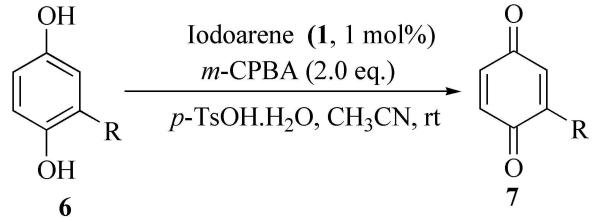
After the optimization of reaction conditions for the synthesis of aryliodide **1 a**, similar synthetic strategy was utilized for the synthesis of other isoxazole-substituted iodoarenes **1 b**–**1 d** using corresponding arylaldehyde oximes **5 b**–**5 d**. The desired iodoarenes **1 b**–**1 d** were obtained in good to excellent yields (72–80%) under the optimal conditions. The structures of new iodoarenes **1 a**–**1 d** were elucidated on the basis of their spectral data, IR, ^{1}H NMR, ^{13}C NMR and HRMS. The solid-state structure of iodoarene **1 a** was also established by single-crystal X-ray crystallography (Figure 2). From XRD data the bond distance between I—O4 and I—O2 was calculated and was found to be 4.615 Å and 6.283 Å, respectively (S1, Figure S1).

Further, the catalytic performance of these synthesized iodoarenes **1 a**–**1 d** was evaluated towards the oxidation of hydroquinone to their corresponding benzoquinone. In preliminary experiments, the oxidation of hydroquinone was investigated using **1 a**–**1 d** (1 mol%) in the presence of *m*-CPBA (2.0 eq.) and acetonitrile as solvent. It was found that about 35% conversion (based on ^{1}H NMR data) of hydroquinone to benzoquinone could be achieved in 15 minutes using **1 b** as catalyst (Table 2, entry 3). When the reaction was performed with iodoarene **1 a**, **1 c** and **1 d** under similar reaction conditions, 18%, 32%, and 28% conversion was achieved respectively (Table 2, entries 2, 4–5). Addition of *p*-toluene sulfonic acid (30 mol%) in the reaction mixture keeping the other reaction conditions similar led to > 90% conversion in 15–20 minutes (Table 2, entries 6–9). This might be due to the *in-situ* formation of more reactive hypervalent iodine species. Conversion of hydroquinone to benzoquinone was confirmed by the ^{1}H NMR of the reaction mixture (S4, Figure S17) which showed the disappearance of peak at δ 6.5 ppm corresponding to the aromatic protons of hydroquinone and a new peak at δ 6.8 ppm was observed corresponding to benzoquinone proton. Similarly, the oxidation of 2-chlorohydroquinone and 2-methylhydroquinone using iodoarenes **1 a**–**1 d** as catalysts under similar reaction conditions afforded the corresponding benzoquinone in excellent yield (Table 2, entries 10–17).

Research Article
doi.org/10.1002/ejoc.202301191

Chemistry Europe
European Chemical Societies Publishing

Table 2. Catalytic oxidation of Hydroquinone.



Entry	1	R	*p*-TsOH.H_2O (eq.)	Time (min)	Yield[a] (%)
1	–	H	–	60	03
2	**1 a**	H	–	15	18
3	**1 b**	H	–	15	35
4	**1 c**	H	–	15	32
5	**1 d**	H	–	15	28
6	**1 a**	H	0.3	20	95
7	**1 b**	H	0.3	15	>99
8	**1 c**	H	0.3	20	>99
9	**1 d**	H	0.3	20	>99
10	**1 a**	Cl	0.3	40	92
11	**1 b**	Cl	0.3	25	>99
12	**1 c**	Cl	0.3	35	>99
13	**1 d**	Cl	0.3	35	96
14	**1 a**	CH_3	0.3	20	95
15	**1 b**	CH_3	0.3	15	>99
16	**1 c**	CH_3	0.3	15	>99
17	**1 d**	CH_3	0.3	20	>99

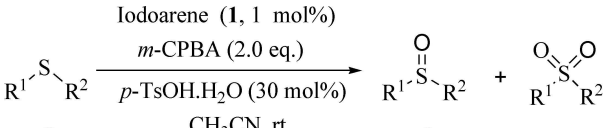
[a] ^{1}H NMR yields/conversions of the products

Further, the catalytic activity of aryl iodide **1 a**–**1 d** were screened for the oxidation of sulfides under similar reaction conditions. During the oxidation of sulfides, sulfoxides were obtained as major product along with small amounts of sulfones. Among all the iodoarenes **1 b** showed best oxidative catalytic activity towards oxidation of sulfides in terms of time taken for oxidation as well as product obtained *i.e.*, sulfoxides as the major product. Reaction of benzyl sulfide with iodoarenes led to the formation of benzyl sulfoxide and benzyl sulfone in 25 min (Table 3, entries 1–4). However, in case of **1 a** and **1 d** benzyl sulfone was obtained as major product (Table 3, entry 1 and 4). In case of oxidation of 2-chloroethyl phenyl sulfide, an exclusive sulfoxide product was obtained in 35 min using **1 b** as catalyst (Table 3, entry 6) while for the other aryl iodides **1 a**, **1 c**–**1 d**, some amount of sulfone was also obtained (Table 3, entries 5 and 7–8). When the oxidation of phenyl sulfide was carried using **1 b**, phenyl sulfoxide obtained in 99% yield and a mixture of sulfoxide and sulfone was observed using **1 a**, **1 c**–**1 d** as catalyst under similar reaction conditions in 45 min (Table 3, entries 9–12).

It was observed that **1 b** showed excellent oxidative catalytic activity towards the oxidation of hydroquinones and sulfides. Excellent catalytic activity of **1 b** prompted us to futher explore its utilization for the α-oxytosylation of acetophenones using *m*-CPBA as a co-oxidant. Initially, α-oxytosylation of acetophenone (**11 a**) was carried with 1 mol% of **1 b** and 2.5 eq. of *m*-CPBA in acetonitrile, but the reaction didn't proceed efficiently even after 24 h (Table 4, entry 2). Increasing the amount of **1 b** enhances the yield of the desired α-oxytosylated product **12 a** (Table 4, entry 3–4). Finally, the desired product was obtained in 90% yield using 20 mol% of the catalyst in 12 h (Table 4, entry 5).

Controlled experiment in the absence of catalyst **1 b** did not afford the desired product even after stirring at room temperature for 48 h (Table 4, entry 1). After the optimal reaction conditions were found, α-oxytosylation of a variety of acetophenone derivatives bearing electron-withdrawing as well as

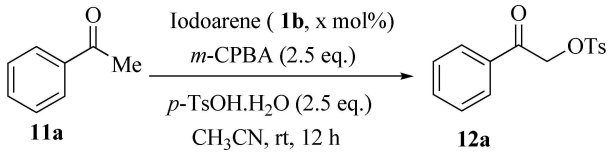
Table 3. Scope for oxidation of sulfides catalyzed by iodoarene **1 a**- **1 d.**



Entry	1	R^1	R^2	9[a]	10[a]
1	**1 a**	Bn	$PhCH_2$	18	82
2	**1 b**	Bn	$PhCH_2$	67	33
3	**1 c**	Bn	$PhCH_2$	62	38
4	**1 d**	Bn	$PhCH_2$	22	78
5	**1 a**	Ph	CH_2CH_2Cl	78	22
6	**1 b**	Ph	CH_2CH_2Cl	96[b]	–
7	**1 c**	Ph	CH_2CH_2Cl	95	05
8	**1 d**	Ph	CH_2CH_2Cl	95	05
9	**1 a**	Ph	Ph	42	58
10	**1 b**	Ph	Ph	>99	–
11	**1 c**	Ph	Ph	85	15
12	**1 d**	Ph	Ph	51	49

[a] ^{1}H NMR yield of the products; [b] isolated yield.

Table 4. Optimization of reaction condition for α-oxytosylation of acetophenones.

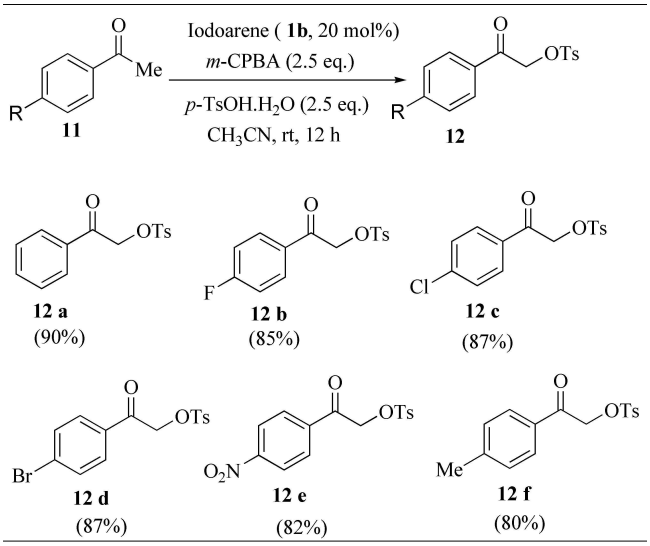


Entry	Iodoarene (1b)	time	yield (%)[a]
1	–	48 h	0
2	1 mol%	48 h	05
3	5 mol%	48 h	30
4	10 mol%	24 h	48
5	20 mol%	12 h	90

[a] isolated yields are given.

Research Article
doi.org/10.1002/ejoc.202301191

Chemistry Europe
European Chemical Societies Publishing



[a] isolated yield of the products

Scheme 2. Substrate scope for α-oxytosylation of acetophenones catalyzed by iodoarene **1 b**.[a]

electron-donating groups was investigated and found that **1 b** efficiently carried out the reaction affording the desired products **12 a**–**12 f** in 80–90 % yield (Scheme 2).

Conclusions

Herein, a series of new isoxazole-substituted aryl iodides **1 a**–**1 d** *via* [3 + 2] cycloaddition reaction of 2-iodo-1,3-bis(prop-2-yn-1-yloxy) benzene with nitrile oxide have been synthesized under metal-free conditions. The synthesized aryl iodides were characterized by various spectroscopic techniques such as FT-IR, ^{1}H NMR, ^{13}C NMR and HRMS and their catalytic activity was investigated for the oxidation of hydroquinone and sulfides and found that among all **1 b** gave the best results. Moreover, **1 b** was also employed for α-oxytosylation of acetophenones.

Experimental Section

All the chemicals and solvents are used as received without any further purification. All glassware was used after washing with solvent and drying in an oven. Resorcinol, Benzaldehyde, Acetophenone and their derivatives, *p*-toluenesulfonic acid were purchased from CDH. Hydroquinones, sulfides and *m*-CPBA were procured from sigma aldrich. Melting points were determined in open glass capillaries in an electrical melting point apparatus and are uncorrected. The purity of all synthesized compounds was checked by thin layer chromatography (TLC) on silica gel plates using a mixture of petroleum ether and ethyl acetate as eluent using UV chamber as visualizing agents. The infrared (IR) spectra of all synthesized compounds were recorded on Fourier Transform-Infrared spectra (FT-IR) Perkin Elmer Spectrometer (UTAR Two), CIL, JCBUST, YMCA, Faridabad. ^{1}H NMR spectra were recorded on Bruker Avance Neo 500 MHz, 300 MHz and 80 MHz Benchtop NMR Spectrometer at SAIF, P.U., THSTI, Faridabad and CIC, Central University of Haryana, Mahendragarh respectively. ^{13}C NMR spectra were recorded on Bruker Avance Neo 500 MHz, SAIF, P.U. using tetramethylsilane (TMS) as internal standard and HRMS data was recorded on Synapt XS HD Mass spectrometer, SAIF, P.U. Chandigarh. Chemical shifts are expressed in δ ppm. The structural analysis was done using Bruker XRD, D8 Quest Single Crystal Microfocus X-Ray Diffractometer, IIT Kanpur. Abbreviations 's' for singlet, 'd' for doublet, 't' for triplet, and 'm' for multiplet are used for NMR assignments.

Synthesis of 2-iodoresorcinol: 2-iodoresorcinol was synthesized by the procedure reported in the literature.[26] To the ice-cold aqueous solution of resorcinol (0.84 g, 7.63 mmol), iodine (1.938 g, 7.63 mmol) was added in one lot followed by portion-wise addition of sodium bicarbonate (0.640 g, 8.4 mmol) followed by an immediate evolution of carbon dioxide. After the addition of sodium bicarbonate (0.070 g, 8.4 mmol), the reaction mixture was allowed to stir in an ice bath for 30 min. After 30 min., the ice bath was removed and the reaction mixture was stirred at room temperature for 30 min, a brown slurry was formed. The reaction was quenched by 10 % aqueous solution of sodium thiosulfate and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over anhydrous sodium sulfate. The solvent was allowed to evaporate under reduced pressure to give a light brown color solid which was further triturated with ice-cold chloroform to get a cream-coloured solid (yield 1.26 g, 75 %, M.p. 90 °C, Lit. M.p. 99–101 °C).

Synthesis of 2-iodo-1,3-bis(prop-2-yn-1-yloxy) benzene (4): Propargyl bromide (1.5 g, 12.7 mmol) was added to a solution of 2-iodoresorcinol (1 g, 0.42 mmol) in DMF (30 ml) followed by the addition of potassium carbonate (1.75 g, 12.7 mmol). The reaction mixture was refluxed at 60 °C for 4 h. After the completion of reaction (as checked by TLC), reaction mixture was allowed to cool at room temperature, diluted with aqueous sodium chloride solution and extracted with diethyl ether. The etheral layer was washed with brine solution and evaporated under reduced pressure to give shining crystals of light brown color. The structure of **4** was confirmed by ^{1}H and ^{13}C NMR data. (yield 920 mg, 70 %, M.p. 115–117 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.29-7.28 (t, J = 8.3 Hz, 1H), 6.70-6.69 (d, J = 8.3 Hz, 2H), 4.77 (d, J = 2.4 MHz, 4H), 2.52 (t, J = 8.3, MHz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 157.9, 129.5, 106.7, 79.3, 78.1, 76.0, 57.1.

Synthesis of 5,5′-(((2-iodo-1,3-phenylene) bis(oxy))bis(methylene))bis(3-(p–tolyl)isoxazole) (1 a)

To a solution of *p*-methyl benzaldehyde oxime **5 a** (194 mg, 1.44 mmol) and **4** (150 mg, 0.48 mmol) in methanol, a solution of DIB in methanol along with 3–4 drops of TFA was added dropwise over a period of 1.5 h. The reaction mixture was allowed to stir at room temperature. The progress of the reaction was checked by TLC. Upon completion of the reaction, the solvent was concentrated and a white solid was obtained. The solid was filtered and washed with methanol. The compound was recrystallized from chloroform to get a shining needle-shaped crystal. The structure of the compound **1 a** was confirmed by ^{1}H NMR, ^{13}C NMR, IR and HRMS spectral data. (yield 236 mg, 85 %, M.p. 177–178 °C); FT-IR υ_{max} 2918, 2851, 1617, 1586, 1465; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.68–7.62 (m, 4H), 7.22–7.18 (m, 5H), 6.68 (t, J = 0.9 Hz, 2H), 6.56 (d, J = 8.3 Hz, 2H), 5.21 (d, J = 0.9 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 167.8, 162.5, 158.2, 140.3, 130.2, 129.6, 126.8, 125.9, 106.7, 101.5, 79.5, 63.1, 21.4; HRMS (ESI) m/z calculated for $C_{28}H_{23}IN_2O_4$ $[M+H]^+$ 579.070, found 579.0886.

Synthesis of 5,5′-(((2-iodo-1,3-phenylene) bis(oxy))bis(methylene))bis(3-(4-fluorophenyl) isoxazole) (1 b): Aryl iodide **1 b** was synthesized by the procedure as explained earlier. A white

Research Article
doi.org/10.1002/ejoc.202301191

crystalline solid was obtained which was purified by recrystallization using dichloromethane as solvent. (yield 72%, M.p. 170–172 °C); FT-IR υ_{max} 2932, 2856, 1621, 1589, 1466; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.85–7.78 (m, 4H), 7.30 (t, J=8.3 Hz, 1H), 7.20–7.10 (m, 4H), 6.74 (t, J=0.9 Hz, 2H), 6.64 (d, J=8.3 Hz, 2H), 5.29 (d, J=0.9 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 168.2, 161.7, 158.2, 130.2, 128.9, 128.8, 116.2, 116.0, 106.7, 101.4, 79.5, 63.0; HRMS m/z calculated for $C_{26}H_{17}F_2IN_2O_4$ $[M+H]^+$ 587.020, found 587.0286.

Synthesis of 5,5′-(((2-iodo-1,3-phenylene) bis(oxy))bis(methylene))bis(3-(4-chlorophenyl) isoxazole) (1 c): Aryl iodide **1 c** was synthesized by the procedure as explained earlier. A white solid was obtained which was purified by recrystallization using dichloromethane as solvent. (yield 76%, M.p. 160–162 °C); FT-IR υ_{max} 2928, 2853, 1621 1588, 1466 ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.74–7.66 (m, 4H), 7.45-7.43 (m, 4H), 7.30 (t, J=8.3 Hz, 1H), 6.75 (t, J=0.9 Hz, 2H), 6.64 (d, J=8.3 Hz, 2H), 5.29 (d, J=0.9 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 168.3, 161.6, 158.1, 136.2, 130.2, 129.2, 128.1, 127.2, 106.7, 101.4, 79.4, 63.0; HRMS (ESI) m/z calculated for $C_{26}H_{17}Cl_2IN_2O_4$ $[M+H]^+$/$[M+2+H]^+$/$[M+4+H]^+$ 618.961/620.961/622.96, found 618.9672 /620.9674/622.9665.

Synthesis of 5,5′-(((2-iodo-1,3-phenylene) bis(oxy))bis(methylene))bis(3-(4-bromophenyl) isoxazole) (1 d): Aryl iodide **1 d** was synthesized by the procedure as explained earlier, a white solid was obtained which was recrystallized with dichloromethane to give a white crystalline solid. (yield 80%, M.p. 190–192 °C); FT-IR υ_{max} 2925, 2850, 1616, 1592, 1469; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.74–7.66 (m, 4H), 7.63–7.57 (m, 4H), 7.30 (t, J=8.3 Hz, 1H), 6.75 (s, 2H), 6.64 (d, J=8.3 Hz, 2H), 5.29 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 168.3, 161.7, 158.1, 132.2, 130.2, 128.4, 127.6, 124.5, 106.7, 101.3, 79.4, 63.0; HRMS (ESI) m/z calculated for $C_{26}H_{17}Br_2IN_2O_4$ $[M+H]^+$/$[M+2+H]^+$/$[M+4+H]^+$ 706.860/708.860/710.860, found 706.8707/708.8677/710.8660.

General procedure for the oxidation of hydroquinone: To a solution of hydroquinone (0.2 mmol) in acetonitrile (1 ml), Iodoarene (**1**, 0.002 mmol) *m*-CPBA (0.4 mmol) and *p*-TsOH.H_2O (0.06 mmol) was added and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC and upon completion, the reaction mixture was analysed by ^{1}H NMR.

General procedure for the oxidation of sulfides: To a solution of sulfides (0.2 mmol) in acetonitrile (1 ml), iodoarene **1 a-1 d** (0.002 mmol), *m*-CPBA (0.4 mmol) and *p*-TsOH. H_2O (0.06 mmol) was added and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC and after the completion; the reaction was quenched with aqueous solution of $Na_2S_2O_3$ and extracted with chloroform. The organic layer was washed with sodium bicarbonate solution and evaporated under reduced pressure to get the corresponding oxidized products.

General procedure for the α-oxytosylation of acetophenones: To a solution of acetophenone (0.2 mmol) in acetonitrile (1.5 ml), iodoarene **1 b** (0.02 mmol), *m*-CPBA (0.5 mmol) and *p*-TsOH. H_2O (0.5 mmol) was added and the reaction mixture was stirred at room temperature for 12 h. After the completion, the reaction was quenched with 5% aqueous solution of $Na_2S_2O_3$ and extracted with chloroform. The organic layer was washed with saturated solution of sodium bicarbonate and evaporated under reduced pressure to get α-oxytosylated acetophenone.

2-oxo-2-phenylethyl 4-methylbenzenesulfonate (12 a):[27] White solid; M.p. 81–82 °C, Lit. M.p. 90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.86 (m, 4H), 7.60 (t, J =7.5 Hz, 1H), 7.47 (t, J=7.5 Hz, 2H), 7.34 (d, J=8.0 Hz, 2H), 5.47 (s, 2H), 2.41 (s, 3H).

2-(4-fluorophenyl)-2-oxoethyl 4-methylbenzene sulfonate (12 b): White solid; M.p. 115–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86–7.91 (m, 2H), 7.82–7.86 (m, 2H), 7.35 (d, J=8.1 Hz, 2H), 7.17–7.11 (m, 2H), 5.21 (s, 2H), 2.45 (s, 3H).

2-(4-chlorophenyl)-2-oxoethyl 4-methylbenzene sulfonate (12 c):[27] White solid; M.p. 121–123 °C, Lit. M.p. 125 °C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.83 (d, J=3.3 Hz, 1H), 7.73 (d, J=3.9 Hz, 2H), 7.41 (m, 5H), 5.16 (s, 2H), 2.41 (s, 3H).

2-(4-bromophenyl)-2-oxoethyl 4-methylbenzene sulfonate (12 d):[28] Pale yellow solid; M.p. 128–130 °C, Lit. M.p. 132–133 °C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.77 (d, J=8.3 Hz, 2H), 7.59 (d, J=2.2 Hz, 4H), 7.27 (d, J=9.1 Hz, 2H), 5.13 (s, 2H), 2.38 (s, 3H).

2-(4-nitrophenyl)-2-oxoethyl 4-methylbenzene sulfonate (12 e):[27] Yellow solid; M.p. 135–136 °C, Lit. M.p. 139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30–8.34 (m, 2H), 8.01–8.04 (m, 2H), 7.82–7.85 (m, 2H), 7.37 (d, J=8.0 Hz, 2H), 5.23 (s, 2H), 2.46 (s, 3H).

2-oxo-2-(*p*–tolyl)ethyl 4-methylbenzene sulfonate (12 f):[27] Red solid; M.p. 75–77 °C, Lit. M.p. 82–83 °C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.76-7.98 (m, 3H), 7.34-7.47 (m, 5H), 5.31 (s, 2H), 2.52 (s, 3H), 2.48 (s, 3H).

Acknowledgements

RK is highly thankful to DST, Government of India for the DST PURSE grant (SR/PURSE/2022/126) and J. C. Bose University of Science & Technology for seed grant (R&D/SG/2020-21/166). RK and BU acknowledge financial support from DST, Haryana (HSCSIT/R&D/2022/164). BU acknowledges DST, Government of India for SERB-POWER Grant, {SPG/2021/004027}. Rimi is grateful to J. C. Bose University of Science & Technology for the award of University Research Fellowship. V.V.Z. is thankful to NSF (CHE-2243793) for support of his research on hypervalent iodine chemistry at University of Minnesota Duluth. The authors also acknowledge the Central Instrumentation Laboratories (CIL) of J. C. Bose University of Science & Technology for providing the instrumentation facilities.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aryl iodide · oxidation · oxytosylation · hydroquinone · sulfides

[1] a) T. Wirth, Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis. [In: Top. Curr. Chem., 2016, p. 373], Springer-Verlag, **2016**; b) V. V. Zhdankin, Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds, Wiley, **2013**.

[2] a) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328–3435; b) M. Elsherbini, T. Wirth, *Chem. Eur. J.* **2018**, *24*, 13399–13407; c) R. Rimi, S. Soni, B. Uttam, H. China, T. Dohi, V. V. Zhdankin, R. Kumar, *Synthesis* **2022**, *54*, 2731–2748.
[3] a) Z. Shahamat, F. Nemati, A. Elhampour, *React. Funct. Polym.* **2020**, *146*, 104415; b) M. Uyanik, K. Ishihara, *Chem. Commun.* **2009**, 2086–2099.
[4] a) X. Xiao, *Synlett* **2021**, *32*, 752–762; b) R. Kumar, F. V. Singh, N. Takenaga, T. Dohi, *Chem. Asian J.* **2022**, *17*, e202101115.
[5] H. Tohma, T. Maegawa, Y. Kita, *Arkivoc* **2003**, *6*, 62–70.
[6] a) S. R. Kandimalla, S. P. Parvathaneni, G. Sabitha, B. V. Subba Reddy, *Eur. J. Org. Chem.* **2019**, *2019*, 1687–1714; b) R. Narayan, A. P. Antonchick, *Chem. Eur. J.* **2014**, *20*, 4568–4572.
[7] a) A. Yoshimura, A. Saito, M. S. Yusubov, V. V. Zhdankin, *Synthesis* **2020**, *52*, 2299–2310; b) A. Dahiya, A. K. Sahoo, N. Chakraborty, B. Das, B. K. Patel, *Org. Biomol. Chem.* **2022**, *20*, 2005–2027.
[8] S. E. Shetgaonkar, M. Krishnan, F. V. Singh, *Mini-Rev. Org. Chem.* **2021**, *18*, 138–158.
[9] F. V. Singh, S. E. Shetgaonkar, M. Krishnan, T. Wirth, *Chem. Soc. Rev.* **2022**, *51*, 8102–8139.
[10] S. Soni, V. Kumar, K. Kikushima, T. Dohi, V. V. Zhdankin, R. Kumar, *Arkivoc* **2022**, *2022*, 27–56.
[11] T. Fuchigami, T. Fujita, *J. Org. Chem.* **1994**, *59*, 7190–7192.
[12] M. Ochiai, Y. Takeuchi, T. Katayama, T. Sueda, K. Miyamoto, *J. Am. Chem. Soc.* **2005**, *127*, 12244–12245.
[13] T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem. Int. Ed.* **2005**, *44*, 6193–6196.
[14] A. P. Thottumkara, M. S. Bowsher, T. K. Vinod, *Org. Lett.* **2005**, *7*, 2933–2936.
[15] a) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073–2085; b) Z. Zhao, L. H. Britt, G. K. Murphy, *Chem. Eur. J.* **2018**, *24*, 17002–17005; c) X. Li, G. Li, Y. Cheng, Y. Du, *Phys. Sci. Rev.* **2021**, *7*, 237–300.
[16] D. Kaiser, I. Klose, R. Oost, J. Neuhaus, N. Maulide, *Chem. Rev.* **2019**, *119*, 8701–8780.
[17] M. Ochiai, K. Miyamoto, *Eur. J. Org. Chem.* **2008**, *2008*, 4229–4239.
[18] N. Amri, T. Wirth, *J. Org. Chem.* **2021**, *86*, 15961–15972.
[19] a) M. Forchetta, F. Sabuzi, L. Stella, V. Conte, P. Galloni, *J. Org. Chem.* **2022**, *87*, 14016–14025; b) S. Wang, L. Tang, B. Cai, Z. Yin, Y. Li, L. Xiong, X. Kang, J. Xuan, Y. Pei, M. Zhu, *J. Am. Chem. Soc.* **2022**, *144*, 3787–3792.
[20] X. Li, P. Chen, G. Liu, *Beilstein J. Org. Chem.* **2018**, *14*, 1813–1825.
[21] J. H. Lee, S. Choi, K. B. Hong, *Molecules* **2019**, *24*, 2634.
[22] H. Sasa, K. Mori, K. Kikushima, Y. Kita, T. Dohi, *Chem. Pharm. Bull.* **2022**, *70*, 106–110.
[23] F. V. Singh, P. B. Kole, S. R. Mangaonkar, S. E. Shetgaonkar, *Beilstein J. Org. Chem.* **2018**, *14*, 1778–1805.
[24] M. Uyanik, *Iodine Catalysis in Organic Synthesis* **2022**, 275–298.
[25] a) A. Boelke, E. Lork, B. J. Nachtsheim, *Chem. Eur. J.* **2018**, *24*, 18653–18657; b) A. Boelke, B. J. Nachtsheim, *Adv. Synth. Catal.* **2020**, *362*, 184–191.
[26] S.-I. Tsujiyama, K. Suzuki, *Org. Synth.* **2007**, *84*, 272.
[27] Y. Yamamoto, Y. Kawano, P. H. Toy, H. Togo, *Tetrahedron* **2007**, *63*, 4680–4687.
[28] M. S. Khanna, C. P. Garg, R. P. Kapoor, *Tetrahedron Lett.* **1992**, *33*, 1495–1498.

Manuscript received: November 19, 2023
Revised manuscript received: December 7, 2023
Accepted manuscript online: December 11, 2023
Version of record online: January 24, 2024