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Iodobenzene and *m*-Chloroperbenzoic Acid Mediated Oxidative Dearomatization of Phenols

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ABSTRACT

Oxidative dearomatization of 2- and 4-subsituted phenols to their corresponding benzoquinone monoketals by catalytic amount of iodobenzene, and *m*-CPBA as a co-oxidant has been achieved *via in situ* generation of $PhIO_2$, a hypervalent iodine(V) species. The transiently generated orthobenzoquinone monoketals further underwent Diels–Alder reaction with various dienophiles to furnish densly substituted bicyclo[2.2.2]octenones in high selectivities and yields. This methodology features ready availability of reagents, cost effectiveness, safety, brevity, selectivity, diversity and excellent yields.

Introduction

As a powerful tool, the dearomatization[1] of aromatic compounds is an efficient strategy to generate highly reactive intermediates for the facile formation of carbon–carbon, carbon–heteroatom bonds, and to access architecturally complex scaffolds through spontaneous cycloaddition and cascade reactions. The 2- and 4-substituted phenols are by far the most periodically utilized substrates for dearomatization in the presence of nucleophiles to form respective masked *o*-benzoquinones (MOBs) and masked *p*-benzoquinones (MPBs)[2]. Though the simple *o*- and *p*-benzoquinones have high synthetic potential, they undergo notorious reactions limiting their efficacy in organic synthesis. Consequently, their chemistry is mainly explored by masking one of the carbonyl functionalities in the form of MOBs and MPBs. The benzoquinone monoketals are the molecules of wide synthetic utility because of the presence of alkene, diene, carbonyl, enone, dienone and allyl acetal functionalities. With these intrinsic reactive assemblies, they undergo variety of desirable annulation reactions such as Diels–Alder reaction,[3] 1,4-additon,[4] and [3 + 2] cycloaddition.[5] MOBs undergo Baylis–Hillman reaction[6a] and also show umpolung reactivity to access unsymmetrical oxgyenated biaryls[6b] in the presence of Lewis acids. However, the Diels–Alder reaction dominates the MOB chemistry due to their proclivity towards it. MOBs undergo self-dimerization *via* Diels–Alder cycloaddition because of their high reactivity.[7] However, this event can be successively avoided by trapping these MOBs with various external dienophiles to generate highly stereo- and regio-selective bicyclo[2.2.2]octenone scaffolds,[8] which have been considered as building blocks for the synthesis of a myriad of complex biological active molecular ensembles (Figure 1).[9,10]

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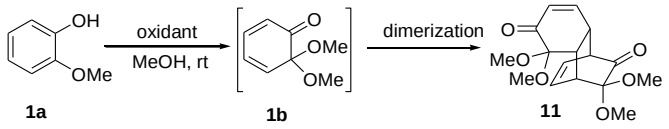
A plethora of strategies[11–14] for the dearomatization of arenols have been emerged to produce these linearly and cross conjugated cyclohexa-2,4-dienones in the presence of appropriate nucleophiles. Among them, hypervalent iodine(III) reagents,[15] due to their mild reactivity and high stability, have proven to be the most accustomed and valuable oxidants for dearomatization.[16] In spite of being less flourished, λ^5-iodanes[17] such as Dess-Martin periodane (DMP)[18a], 2-iodoxybenzoic acid (IBX)[18b] and their analogues documented good synthetic versatility. However, stoichiometric use of these expensive reagents results in the co-production of undesired iodoarenes in equimolar amount. To circumvent these problems, in 2005, the Ochiai[19a] and Kita[19b] independently reported iodine(I) arene-mediated catalytic oxidations using *m*-CPBA as co-oxidant. After that, this concept was reported extensively.[20] Herein we present the studies on the catalytic activity of iodine(I) arene for the dearomatization of phenols to form bicyclo[2.2.2]octenones. The reactions are high yielding and proceed under mild and eco-friendly conditions.

At the outset, we were with the idea of using elemental iodine in place of hypervalent iodine(III) species such as DIB or PIFA to oxidise guaiacol (**1a**) in the presence of methanol to form Diels–Alder dimer **11** *via* MOB **1b**. Initially, methanolic solution of guaiacol was treated with elemental iodine and the contents were allowed to stir at room temperature. Even after 24 h, formation of dimer was not observed (Table 1, entry 1). To enhance the oxidizing power of iodine, we supplemented various co-oxidants such as $K_2S_2O_8$, $NaIO_4$, H_2O_2. However, the product formation was not observed in these cases (Table 1, entries 2–4). Even the combination of $K_2S_2O_8$ and $NaIO_4$ with iodine as a co-oxidants proved unsuccessful (Table 1, entry 5) and the use of oxone ($KHSO_5$) also could not give the product **11** (Table 1, entry 6). Gratifyingly, *m*-CPBA successfully works as a co-oxidant with elemental iodine and resulted in the formation of the expected

dimer **11** in 60% yield (Table 1, entry 7), though *m*-CPBA alone was not capable for oxidation (Table 1, entry 8). Interestingly, when iodobenzene is used in place of iodine with *m*-CPBA as terminal oxidant, the Diels–Alder dimer was obtained in remarkably improved yield of 86% (Table 1, entry 9).

Table 1. Initial Optimization of oxidising agents[a,b]



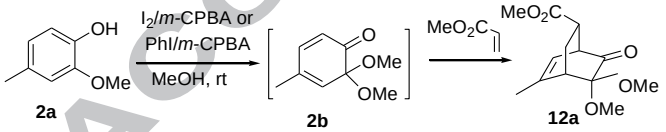
1a **1b** **11**

Entry	Oxidant	Time	Yield (%)[b]
1	I_2	24 h	0
2	$I_2/K_2S_2O_8$	24 h	0
3	$I_2/NaIO_4$	24 h	0
4	I_2/H_2O_2	24 h	0
5	$I_2/NaIO_4/K_2S_2O_8$	24 h	0
6	Oxone	24 h	0
7	I_2/*m*-CPBA	1.5 h	60
8	*m*-CPBA	24 h	0
9	PhI/*m*-CPBA	10 min	86

[a] Reactions were carried out by dissolving **1a** (0.5 mmol, 1 equiv) in methanol (3 mL) followed by the addition of oxidant (1 equiv each) at 25 °C. [b] Isolated yield of **11**.

In order to achieve best reaction conditions, we examined both the oxidizing systems *i.e.* I_2/*m*-CPBA and PhI/*m*-CPBA on our model reaction between creosol (**2a**) and methyl acrylate in methanol to furnish the corresponding Diels–Alder adduct (**12a**). To get the optimized reaction conditions, we performed the reaction under various concentrations of iodine/iodobenzene and *m*-CPBA using methanol as a solvent as shown in Table 2. Initially, we treated the methanolic solution of creosol with 0.5 equiv of iodine and 1 equiv of *m*-CPBA at room temperature and the desired product **12a** was obtained in 50% yield (Table 2, entry 1). Further increase in the amount of iodine did not improve the yield (Table 2, entries 2 and 3). However, rise in *m*-CPBA concentration enhanced the yield up to 76% (Table 2, entries 4–7). Fortunately, the use of 0.5 equiv of iodobenzene instead of iodine furnished **12a** in 86% yield in 30 min (Table 2, entry 8), although 1 equiv of iodobenzene increases the reaction rate without any noticable increase in the yield (Table 2, entry 9). Rise in the concentration of co-oxidant did not improve the yield significantly (Table 2, entry 11). Much to our delight, by lowering the concentration of iodobenzene to 30 mol% the reaction afforded the **12a** in 10 min with 93% yield (Table 2, entry 12) and further decrease in its quantity resulted in slight drop in the reaction rate (Table 2, entry 13).

Table 2. Optimization of reaction conditions[a,b]



2a **2b** **12a**

Entry	I_2 or PhI (equiv)	*m*-CPBA (equiv)	Time (min)	yield (%)[b]
1	I_2/0.5	1	60	50
2	I_2 /1	1	15	55
3	I_2/2	1	10	54
4	I_2/1	1.5	10	65
5	I_2/1	1.7	10	66
6	I_2/1	2	10	68
7	I_2/1	3	10	76
8	PhI/0.5	1.5	30	86
9	PhI/1	1.5	5	86
10	PhI/0.5	2	5	86
11	PhI/0.5	2.5	5	90
12	PhI/0.3	2	10	93
13	PhI/0.2	2	25	92

[a] Reactions were performed by sequential addition of *m*-CPBA to a solution of iodine or iodobenzene in methanol (3 mL) followed by the addition of methanolic solution (2 mL) of creosol (**2a**, 0.5 mmol, 1 equiv) and methyl acrylate (10 mmol, 20 equiv) at rt. [b] Isolated yield of **12a**.

With the optimized reaction conditions in hand (Table 2, entry 12), we explored the generality of this novel synthetic protocol on a range of methoxy phenols bearing different substituents with various dienophiles. In order to have better understanding of reaction mechanism, we performed the oxidation and cycloaddition reactions of MOBs using stoichiometric as well as catalytic amount of iodobenzene. The Diels-Alder reaction of MOBs having different functionalities with electron-deficient dienophiles such as methyl acrylate (MA), methyl vinyl ketone (MVK), methyl methacrylate (MMA) as well as with conjugative dienophiles like styrene afforded the bicyclo[2.2.2]octenone derivatives through *endo* addition in good to excellent yields (Scheme 1). The *in situ* generated MOB **1b** from the parent methoxyphenol *i.e.*, guaiacol (**1a**) was highly reactive and it underwent self-dimerization very rapidly to furnish the dimer **11** in excellent yields up to 96% even in the presence of external dienophiles. In contrast, the reactions of creosol (**2a**) furnished the cycloadducts **12a-c** in excellent yields, except in case of styrene where the bicyclo[2.2.2]octenone **12d** was isolated in 45% yield. The MOBs generated from 2-methoxyphenols bearing electron-withdrawing groups *i.e.*, methyl vanillate (**3a**) and acetovanillone (**4a**) afforded the cycloadducts **13a-d** and **14a-d** in acceptable to high yelds.

The reaction of methyl isovanillate (**5a**) with MA, MVK and styrene provided the cycloadducts **15a,c,d** in good yields, whereas oxidation of **5a** in the presence of MMA furnished substantial amount of dimer **10** along with the Diels–Alder adduct **15b**. Methyl syringate (**6a**) reacted smoothly with MA, MVK and styrene under oxidative-acetalization conditions to afford the cycloadducts **16a,c,d** in very good yields. Due to the less reactivity of MMA, appreciable amount of dimer **20** was formed in its reaction with **6a** (Figure 1).

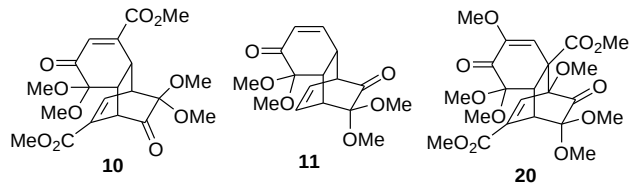
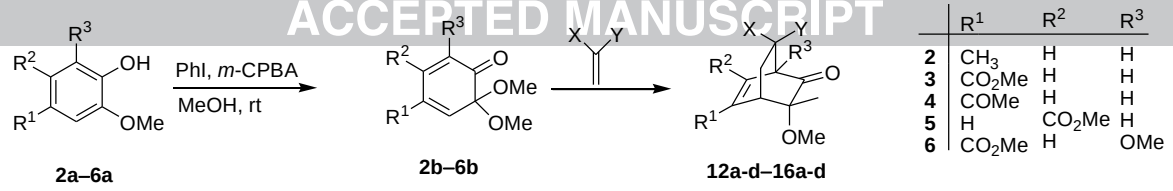
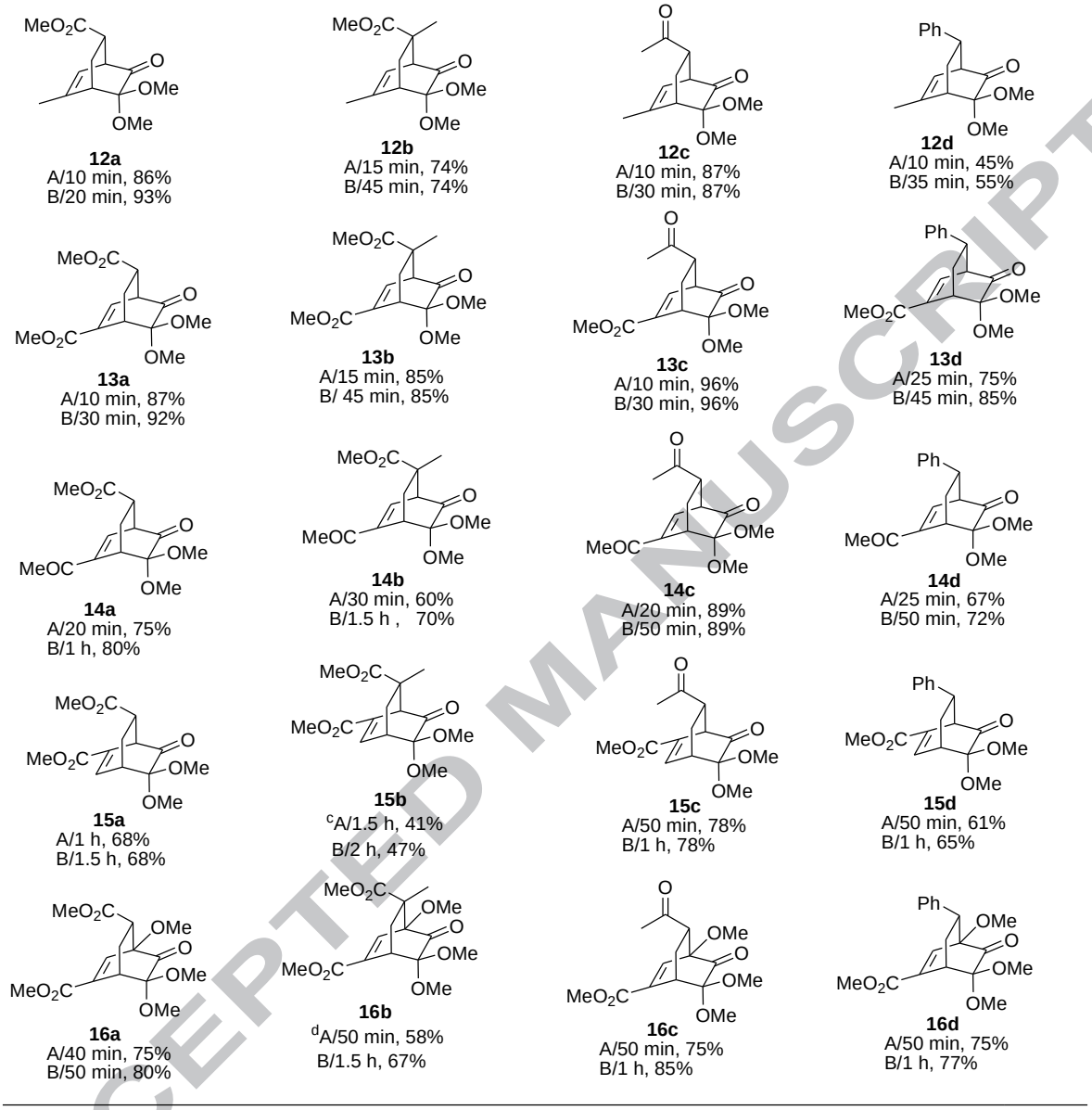


Figure 1. Structures of dimers **10**, **11** and **20**.

The 4-halogen substituted MOBs **7b**–**9b** are relatively stable enough and resist self-dimerization. As expected the MOBs with electron-withdrawing halogens at position 4 displayed less reactivity as reflected in the reaction times, though their reactions with all external dienophiles proceeded cleanly, to give the Diels–Alder adducts **17a-c**–**19a-c** in appreciable to very good yields without formation of any dimers. Similarly, these 4-halo guaiacols reacted smoothly with styrene under the reaction conditions to afford the 4-halo adducts **17d**–**19d** in yields up to 90% (Scheme 2).

At the success of oxidative dearomatization of 2-methoxyphenols, next we probed the substrate scope for phenol and *p*-substituted phenol. Keeping the concept of double oxidative dearomatization of phenol to form monoketal in mind, we oxidized phenol using 4 equiv of *m*-CPBA and 30 mol% PhI in the presence of methanol and ethanol in 2–3 h and isolated the MPBs **21** and **22** in 80 and 60% yield, respectively (Scheme 3). After further exploration, we found a clean reaction by using only 2 equiv of *m*-CPBA to furnish the products **21** and **22** in similar yields with easy work up albeit little longer reaction time of 3–4 h.



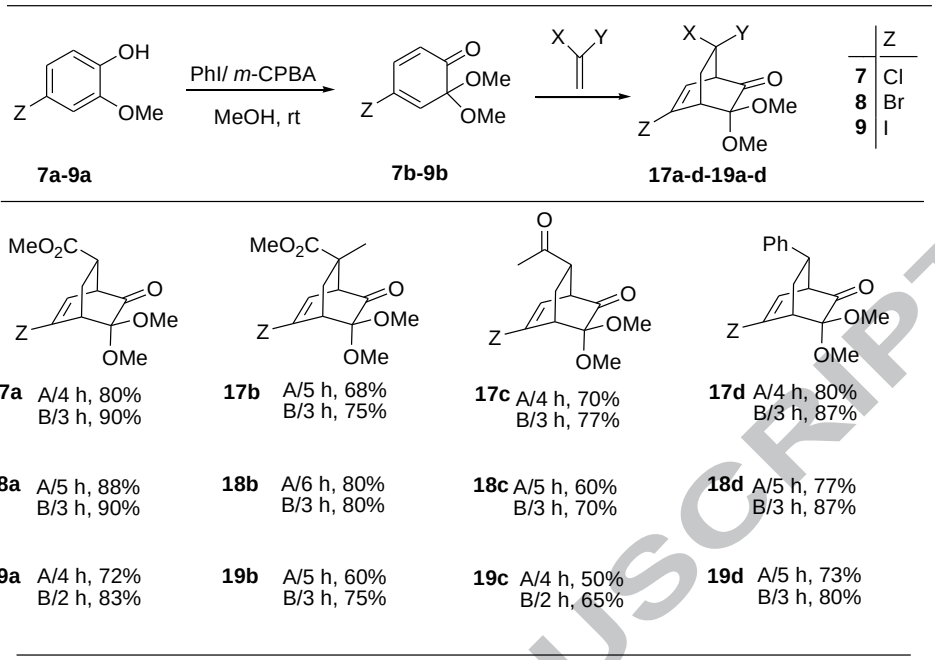


Scheme 1. Oxidative acetalization-Diels–Alder strategy of methoxyphenols **2a**–**6a**[a,b]

[a]Reaction conditions: Method A: a methoxyphenol (**2a**–**6a**, 1 mmol), dienophile (20 equiv), PhI (1 equiv) and *m*-CPBA (1.5 equiv) in methanol (5 mL) at rt. Method B: a methoxyphenol (**2a**–**6a**, 0.5 mmol), dienophile (20 equiv), PhI (30 mol%), and *m*-CPBA (2 equiv) in methanol (3 mL) at rt for the given time. [b]Yield of isolated products. [c]Corresponding dimer **10** was isolated in 57% yield. [d]Corresponding dimer **20** was isolated in 38% yield.

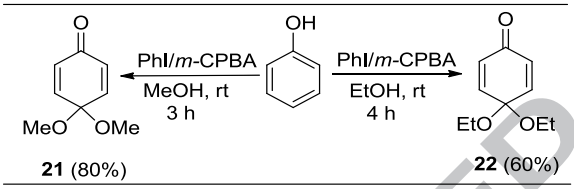
Having established an efficient protocol for dearomatization of phenol and 2-methoxyphenols, we extended this strategy by carrying out the oxidation of 4-methoxyphenol with PhI/*m*-CPBA in methanol to afford masked *p*-benzoquinone **21** in 86% yield (Scheme 4). Similarly, 4-alkyl substituted phenols were oxidized to the corresponding cross conjugated cyclohexadienones **23** and **24** in very good yields.

.Although a relatively low yield was observed in the reactions of phenols bearing bulky isopropyl and *tert*-butyl group wherein the corresponding phenol was added at 50 °C to improve the yield of **23b** and **24c** to 70 and 61%, respectively. The reaction also tolerates phenyl group to furnish corresponding cyclohexadienones **23d** in 83% yield. To further evaluate the efficacy of the present protocol, we carried out the oxidative dearomatization of 4-substituted phenols using ethanol as an external nucleophile to obtain the corresponding dienones **24a-d** in good yields. It turned out that the methodology shows unique general reactivity (Scheme 4).



Scheme 2. Reaction of 4-halo guaiacols with olefinic compounds[a,b]

[a]Reaction conditions: Method A: a 4-halo-2-methoxyphenol (**7a**–**9a**, 1 mmol, 1 equiv), dienophile (20 mmol), PhI (1 equiv) and *m*-CPBA (1.5 equiv) in methanol (5 mL) at rt. Method B: a 4-halo-2-methoxyphenol (**7a**–**9a**, 0.5 mmol, 1 equiv), dienophile (10 mmol), PhI (30 mol%), and *m*-CPBA (2 equiv) in methanol (3 mL) at rt for the given time. [b] Yield of isolated products.

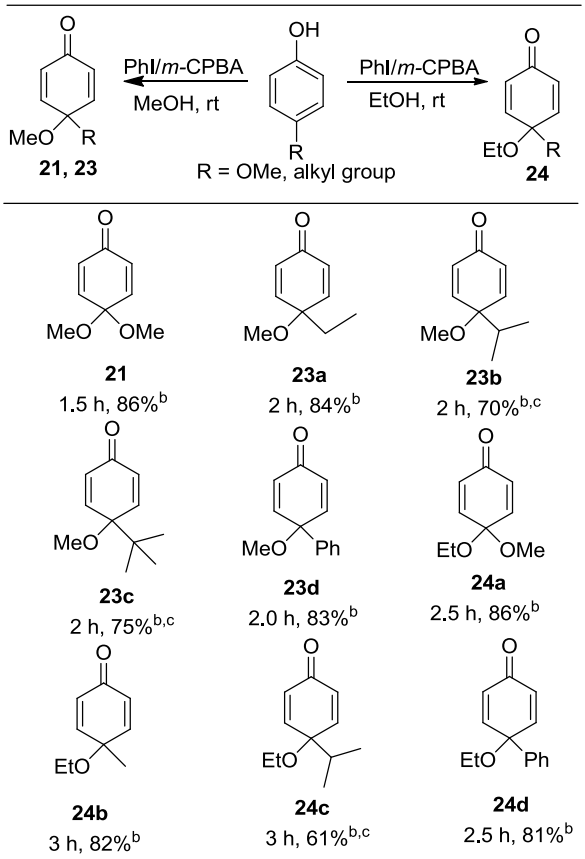


Scheme 3. Dearomatization of phenol[a]

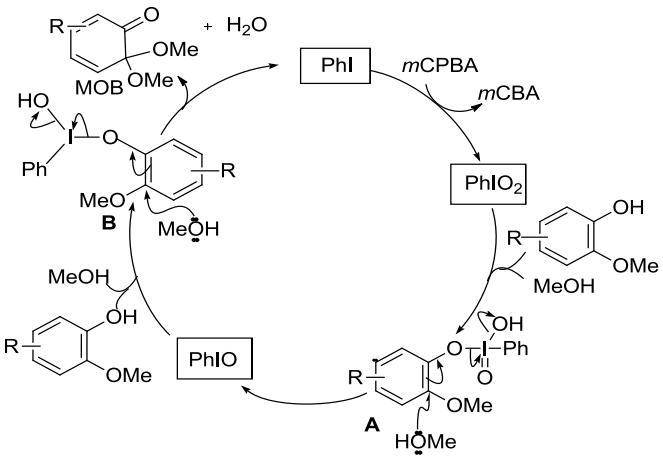
[a]Reactions were performed with phenol (0.5 mmol, 1 equiv), PhI (30 mol%), and *m*-CPBA (2.0 mmol) in solvent (3 mL) at rt.

In an effort to understand the course of the reaction, we performed the reaction between iodobenzene and *m*-CPBA in methanol for 10 min, then the reaction mixture was filtered to afford a white solid which was found to be iodoxybenzene ($PhIO_2$)[21a] {mp: 234–235 °C, IR: ν_{max} 763, 737, 731, 714 cm^{-1}, HRMS (ESI^+): m/z calcd for $PhIO_2Na$ $[M+Na]^+$: 258.9353, found: 258.9226}. To further support the role of $PhIO_2$ as an intermediate, we have prepared $PhIO_2$ and PhIO according to the literature procedure[21b] and carried out the oxidation of **2a** with these synthesized hypervalent iodine reagents. It was observed that the reaction of **2a** with $PhIO_2$ in methanol was completed in 15 min and afforded **12a**, whereas the reaction with PhIO did not reach to completion even after 3–4 h.

Proposed mechanism for the reaction is outlined in Scheme 5. Initially, *m*-CPBA oxidizes iodobenzene *in situ* to generate electrophilic hypervalent iodine(V) species $PhIO_2$. Then the nucleophilic oxygen of phenol attacks on the electrophilic iodine(V) centre of $PhIO_2$ to produce species **A**. After the attack of one molecule of methanol on electrophilic carbon, the species **A** collapses to MOB through dearomatization accompanying the release of water and an iodine(III) species PhIO. The latter participates in the oxidation of arenol into another molecule of MOB *via* species **B**. The influence of the nucleofugality of the phenyliodanyl group helps the two-electron reduction of the iodine(III) center with simultaneous regeneration of PhI which further involves in the catalytic cycle. Thus formed MOB undergoes [4 + 2] cycloaddition either with dienophile to afford Diels–Alder adduct or participates in the self-dimerization event with another molecule of MOB.



Scheme 4. Dearomatization reactions of 4-subsituted phenols[a]
[a]Reactions were performed with 4-substitued phenols (0.5 mmol), PhI (30 mol%), *m*-CPBA (2 mmol) in solvent (3 mL) at rt. [b] Yield of isolated products. [c] Reactions done at 50 °C.



Scheme 5. Proposed reaction mechanism

Conclusions

In summary, we have thrived a clean and efficient protocol for the dearomatization of phenols using catalytic iodobenzene in the presence of *m*-CPBA as terminal oxidant. The *in situ* generated $PhIO_2$ readily transform 2- and 4-subsituted phenols to MOBs and cross conjugated cyclohexadienones, respectively, and the *in situ* generated MOBs underwent Diels–Alder reaction with various dienophiles to give bicyclo[2.2.2]octenone scaffolds. Thus we unraveled a new horizon for the generation of benzoquinone monoketals.

General Procedure for the Diels–Alder Reaction of MOBs 1b–9b with dienophiles:

Method A: To a stirred solution of iodobenzene (204 mg, 1 mmol, 1 equiv) in dry methanol (3 mL) dry *m*-CPBA (374 mg, 2 mmol, 1.5 equiv) was added followed by addition of methanolic solution (2 mL) of guaiacol derivatives (1 mmol). To the resulting yellow colour solution, dienophile (20 mmol, 20 equiv) was added and stirred the reaction mixture at room temperature for 10 min to 5 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated *in vacuo.* The mixture was washed with a saturated aqueous solution of $NaHCO_3$ and extracted twice (2 x 20 mL) with CH_2Cl_2. The combined organic layers were washed with brine, filtered, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using EtOAc (10–20%) in hexanes to afford the pure cycloadducts **12a-d**–**19a-d**.

Method B: To a stirred solution of iodobenzene (30 mol%) in dry methanol (2 mL) dry *m*-CPBA (249 mg, 1 mmol, 2 equiv) was added followed by addition of methanolic solution (1 mL) of guaiacol derivatives (0.5 mmol). To the resulting yellow colour solution dienophile (10 mmol, 20 equiv) was added and stirred the reaction mixture at room temperature for 20 min to 3 h. After the completion of the reaction as monitored by TLC, the solvent was evaporated *in vacuo*. The mixture was washed with a saturated aqueous solution of $NaHCO_3$ and extracted twice (2 x 20 mL) with CH_2Cl_2. The combined organic layers were washed with brine, filtered, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using EtOAc (10–20%) in hexanes to afford the pure cycloadducts **12a-d**–**19a-d**. The NMR data of the compounds from the current study is comparable with that of the compounds reported in literature.[22]

General Procedure for the formation of 2,5-cyclohexadienones 21–**24:** To a stirred solution of iodobenzene (30 mol%) in dry methanol (2 mL) dry *m*-CPBA (249 mg, 1 mmol, 2 equiv) was added followed by addition of phenol and its *p*- ubstituents. The resulting yellow colour solution was stirred at the given temperature for 2–6 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated *in vacuo*. The mixture was washed with a saturated aqueous solution of $NaHCO_3$ and extracted twice (2 x 20 mL) with CH_2Cl_2. The combined organic layers were washed with brine, filtered, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using EtOAc (10–20%) in hexanes to afford the pure cyclohexadienones **21**–**24**.

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Graphical Abstract

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Iodobenzene and *m*-Chloroperbenzoic Acid Mediated Oxidative Dearomatization of Phenols

Neha Taneja and Rama Krishna Peddinti *

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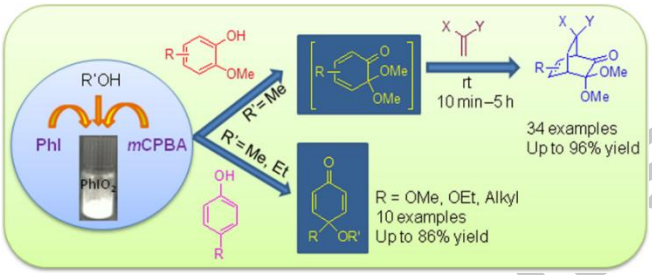

Highlights of the Work

- Explored easy accessible and cost-effective iodobenzene–*m*CPBA reagent system.
- Dearomatization of phenols to the corresponding cyclohexadienones has been studied.
- The methodology is clean and efficient and avoids the coproduction of iodoarenes.
- Overcomes the stoichiometric amount of expensive hypervalent iodine reagents.
- Oxidation–Diels–Alder protocol furnishes bicyclo[2.2.2]octenones in high yields.