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Oxidative Cleavage of Olefins by In Situ-Generated Catalytic 3,4,5,6-Tetramethyl-2-iodoxybenzoic Acid/Oxone

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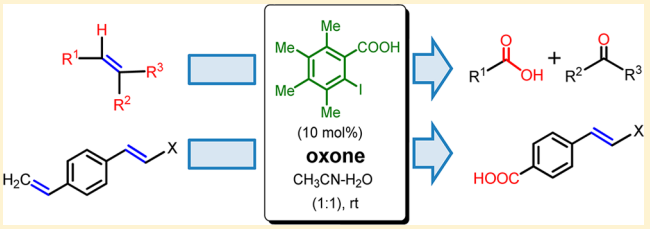
Supporting Information

ABSTRACT: Oxidative cleavage of a variety of olefins to the corresponding ketones/carboxylic acids is shown to occur in a facile manner with 3,4,5,6-tetramethyl-2-iodobenzoic acid (TetMe-IA)/oxone. The simple methodology involves mere stirring of the olefin and catalytic amount (10 mol %) of TetMe-IA and oxone in acetonitrile−water mixture (1:1, v/v) at rt. The reaction mechanism involves initial dihydroxylation of the olefin with oxone, oxidative cleavage by the in situ-generated 3,4,5,6-tetramethyl-2-iodoxybenzoic acid (TetMe-IBX), and oxidation of the aldehyde functionality to the corresponding acid with oxone. Differences in the reactivities of electron-rich and electron-poor double bonds have been exploited to demonstrate chemoselective oxidative cleavage in substrates containing two double bonds.



INTRODUCTION

o-Iodoxybenzoic acid—popularly called IBX—is a more than a century old oxidation reagent.[1] Its cheap availability, ease of handling, and environmentally benign attributes continue to attract the attention of chemists for extensive application in a variety of oxidative transformations.[2] However, the noted disadvantage of IBX is its insolubility in common organic solvents, the root cause of which is traceable to operation of a number of intermolecular interactions[3] that hold molecules very cohesively in the solid state to preclude solvation from overcoming the lattice energy. It is soluble only in a highly polar solvent such as dimethyl sulfoxide (DMSO),[4] which is undesirable from the points of view of difficulty with isolation of product(s) and tedious workup; to avoid the use of DMSO, IBX-mediated reactions are performed at elevated temperatures in a solvent such as ethyl acetate.[5] Furthermore, IBX is known to be explosive on mechanical impact/heating.[6] To overcome these lacunae, development of modified IBXs and catalytic protocols that allow oxidations at ambient conditions by way of in situ generation of IBX in the presence of a terminal oxidant such as oxone is being actively pursued.[7] A catalytic protocol that obviates the use of stoichiometric amounts of IBX was first introduced by Vinod and co-workers for alcohol oxidations with catalytic *o*-iodobenzoic acid and oxone in acetonitrile−water at 70 °C.[7a] Subsequently, Ishihara and co-workers demonstrated oxidation of alcohols using catalytic amounts of *o*-iodobenzenesulfonic acid in the presence of oxone in acetonitrile or nitromethane at 70 °C;[7b] it is noteworthy that generation of I(V) species in the presence of a co-oxidant occurs only at higher temperatures. A variety of reactions catalyzed by hypervalent iodine catalysts have been reported.[8] These include oxidation of phenols to quinones,[8b,c] α,β-dehydrogenation of ketones,[7b] rearrangement of tertiary allylic alcohols to enones,[8d] benzylic oxidation and C−H activation,[8e] etc.

Our own interest has been centered on exploring new reactions mediated by IBX/oxone and developing modified IBXs as well as catalytic protocols that simplify the oxidation chemistry using IBX.[9] We recently showed that the structurally puckered and sterically encumbered TetMe-IBX—generated catalytically in situ from its precursor iodo acid (i.e., TetMe-IA) in the presence of oxone—oxidizes alcohols to the corresponding carbonyl compounds in acetonitrile−water (1:1, v/v) at rt.[9d] The high reactivity of the in situ-generated TetMe-IBX spurred us to explore oxidative cleavage of olefins to corresponding carbonyl compounds. The latter is a transformation of paramount importance in organic synthesis. Vinod et al. showed that olefins can be oxidatively cleaved by using *p*-iodobenzoic acid as a catalyst in the presence of oxone at 60 °C, where [hydroxy(4-carboxyphenyl)iodonium]ion is presumed to be the active species;[10] it is noteworthy that 20 mol % of the iodo acid was employed, and the oxidative cleavage of aliphatic olefins using this procedure was found to be too sluggish. A variety of procedures based on organometallic reagents[11] and metal-free protocols[12,13] have been reported in the literature. While the metal-based reagents are undesirable, metal-free protocols such as ozone present hazards due to explosive property as well as operational difficulties.[12c,d] Noteworthy methodologies for oxidative cleavage that necessitate stoichiometric amounts of the reagents are H_2O_2 with catalytic heteropoly acid adsorbed on aluminum, magnesium or zinc oxide support,[13a] phenyliodonium diacetate (PIDA),[13d] etc. Methodologies involving the use of a stoichiometric amount of

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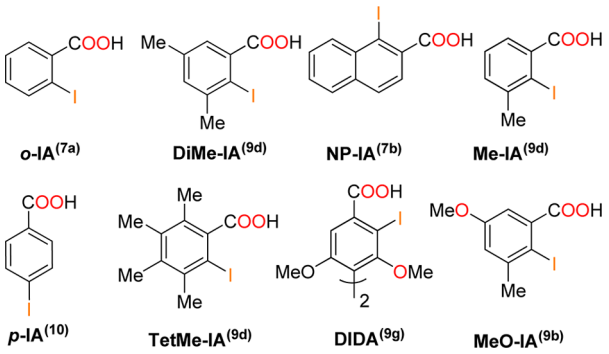
PhIO[13b] and mCPBA[13c] in the presence of ArI as a catalyst have also been developed for oxidative cleavage. We recently showed that olefins can be oxidatively cleaved by oxone itself without the use of any catalyst in acetonitrile−water but at reflux conditions.[9h] Oxone is a cheap and environmentally benign stable triple salt. However, its reactivity at high temperatures limits its application for oxidative cleavage of electron-rich olefins and substrates bearing sensitive functional groups. Herein, we report that the high reactivity of TetMe-IBX, which is generated in situ from its precursor iodo acid (i.e., TetMe-IA) in the presence of oxone, in conjunction with the ability of oxone to carry out dihydroxylation of olefins allows facile oxidative cleavage of a variety of olefins at room temperature; indeed, limitations with oxone as the reagent at high temperatures are overcome due to occurrence of the reaction cascade at rt. It is also shown that electron-rich olefins are selectively cleaved in preference to electron-deficient ones.

RESULTS AND DISCUSSION

At the outset, we set out to identify the iodo acids that allow generation of hypervalent iodine species upon reaction with oxone at rt. In Chart 1 are shown a broad set of iodo acids that

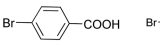
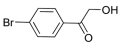
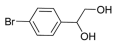
Chart 1



were subjected to screening for their ability to produce hypervalent iodine species in the presence of oxone as a terminal oxidant and catalyze oxidation of *p*-bromostyrene, a representative case. It is noteworthy that the hypervalent iodine species generated from all the iodo acids in Chart 1 have been found to be applicable for oxidation of alcohols. Thus, the oxidation of *p*-bromostyrene was explored with each of these iodo acids employed in 10 mol % together with 3 equiv of oxone in acetonitrile−water (1:1, v/v) at rt. Results of these screening experiments are consolidated in Table 1. While *o*-iodobenzoic acid (*o*-IA) was found to produce the corresponding acid in 20% yield along with the diol in 67% yield after 24 h, *p*-iodobenzoic acid (*p*-IA) led to an insignificant yield of the acid. However, MeO-IA was found to produce the acid in 74% yield. While respectable conversion of *p*-bromostyrene to the corresponding acid was observed with Me-IA, DiMe-IA, and DIDA, remarkable reactivity was found for TetMe-IA; the acid was isolated in 84% yield with a trace amount of the ketol in 12 h. Notably, the formation of only diol was observed without the added catalyst, and no diol was found to be formed when the reaction was conducted with the I(V) reagent (i.e., TetMe-IBX; cf. Supporting Information). It thus emerges that TetMe-IA undergoes oxidation readily to I(V) species, which has been shown to be highly reactive for alcohol oxidations from our previous investigations.[9d]

Spurred by the results observed with TetMe-IA as a catalyst, we examined the oxidation of a variety of olefins. The results are consolidated in Table 2. The parent styrene, under the employed conditions of oxidation, was found to yield benzoic acid in 89% isolated yield (Table 2, entry 1); it should be noted that the reaction of styrene with oxone alone at reflux conditions leads to poor yield of the benzoic acid over a period of 14 h.[9h] The oxidative cleavage with TetMe-IA/oxone was found to work equally well for a variety of electron-rich as well as electron-deficient styrenes, leading to the corresponding benzoic acids in 76−91% yields (entries 2−10). Intriguing results were observed for *o*-substituted styrenes in that the reaction was found to be clean for *o*-Cl- and *o*-Br-substituted styrenes (entries 12 and 13), while *o*-Me-substituted derivative led to a mixture of products (entry 14), where *o*-methylbenzoic acid was obtained only in 11% yield and *o*-methylphenylglyoxylic acid was isolated in 76% yield. *o*-Nitrostyrene was found to react slowly, leading to 52% yield of *o*-nitrobenzoic acid with 27% of the reactant recovered unreacted. Facile cleavage was observed for an aliphatic terminal olefin, that is, 1-tridecene (entry 15). 1,2-Aryl alkyl-substituted olefins yielded good yields of the cleaved products (entries 16 and 17). However, *α*-methylstyrene yielded acetophenone together with benzoic acid; the latter is an overoxidation product of the ketone (entry 21). Cinnamyl alcohol and cinnamyl bromide were found to

Table 1. Results of Catalyst Screening for Oxidative Cleavage of *p*-Bromostyrene as a Representative Case with Oxone as the Terminal Oxidant in Acetonitrile−Water (1:1) Mixture[a]

entry	catalyst	oxone	time (h)	 yield (%)[b]	 yield (%)[b]	 yield (%)[b]
1	***o*-IA**	3	24	20	–	67
2	**MeO-IA**	3	24	74	7	–
3	***p*-IA**	3	24	3	17	66
4	**Me-IA**	3	24	56	22	–
5	**DiMe-IA**	3	20	62	16	–
6	**TetMe-IA**	3	12	84	negligible	–
7	**DiDa-IA**	3	24	55	23	–
8	**NP-IA**	3	24	–	–	84
9	none	3	24	–	–	86
10	**TetMe-IBX**	0	24	–[c]	–[c]	–[c]

[a] *p*-Bromostyrene (0.55 mmol), 10 mol % of the catalyst, and oxone (1.65 mmol) were taken in 10 mL of acetonitrile−water (1:1, v/v) at rt. [b] Isolated yield of *p*-bromobenzoic acid. [c] No reaction.

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Table 2. Results of Catalytic Oxidative Cleavage of Olefins by TetMe-IA/Oxone in CH_3CN-H_2O (1:1) Mixture[a]

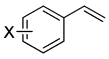
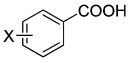
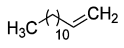
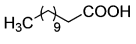
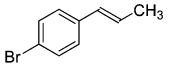
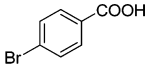
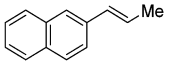
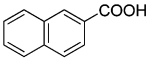
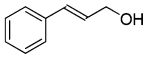
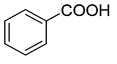
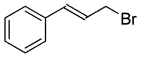
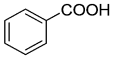
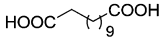
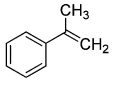
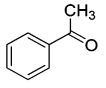
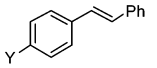
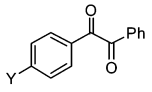
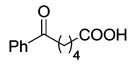
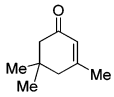
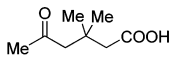
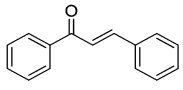
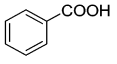
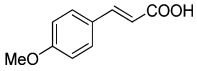
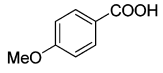
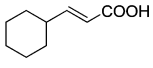
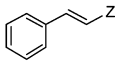
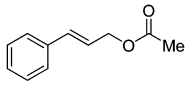
entry	substrate	equiv/ time (h)	product	isolated yield (%)[b]
1	 X = H	3/10		89
2	= *p*-OMe	3/12		76
3	= *p*-Me	3/12		82
4	= *p*-Br	3/12		84
5	= *p*-*t*-Bu	3/14		86
6	= *p*-OBn	3/15		79
7	= *p*-OAc	3/19		88
8	= *p*-NO_2	5/24		77
9	= *p*-CO_2H	5/22		91
10	= *p*-CO_2Me	3/12		82
11	= *o*-NO_2	5/24		43[c]
12	= *o*-Br	5/24		81
13	= *o*-Cl	5/24		79
14	= *o*-Me	5/24		11[d]
15		3/24		86
16		3/13		83
17		3/16		82[e]
18		3/18		86
19		3/18		82
20		4/24		85
21		4/24		43[f]
22		2/8		86
23	 Y = Br	3/24		46[g]
24	= NO_2	5/36		12[h]
25	= CO_2H	5/48		47[i]
26		3/18		85[j]
27		5/24		84
28		4/36		86
29		5/36		87
30		5/24	—[k]	-
31	 Z = COOH	5/24	—[k]	-
32	= CO_2Me	5/24	—[k]	-
33	= CN	5/24	Ph-COOH	4[l]
34		5/24	—[k]	

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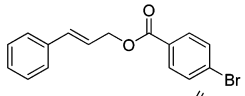
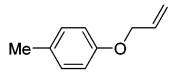
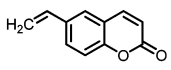
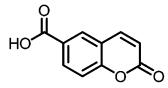
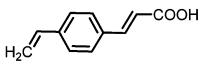
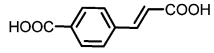
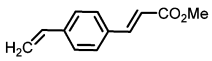
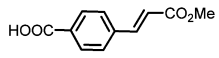
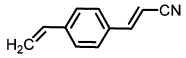
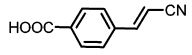
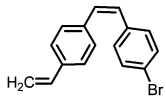
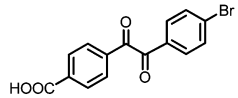
Table 2. continued

entry	substrate	equiv/ time (h)	product	isolated yield (%)[b]
35		5/24	—[k]	
36		5/24	—[k]	

[a]All reactions were carried with 10 mol % of TetMe-IA and oxone in $CH_3CN–H_2O$ (1:1, v/v) mixture at rt. [b]Isolated yields unless mentioned otherwise. [c]27% reactant was recovered. [d]2-Methylphenylglyoxylic acid was isolated in 76% yield. [e]*o*-Carboxycinnamic acid was isolated in 8% yield. [f]Benzoic acid was isolated in 33% yield. [g]Starting compound was recovered in 43% yield. [h]Conversion was ca. 35%, and the corresponding cleaved carboxylic acid was isolated in 9% yield. [i]Conversion was ca. 88%, and the corresponding acid derived from cleavage was isolated in 10% yield. [j]2-Hydroxy-2-phenylcyclohexanone was isolated in 2% yield. [k]No reaction. [l]89% reactant was found unreacted.

Table 3. Chemoselective Oxidations Using TetMe-IA and Oxone in CH_3CN/H_2O[a]

entry	substrate	equiv/ time (h)	product	isolated yield (%)[b]
1		3/16		83
2		3/18		81
3		3/12		85
4		3/14		90
5		5/30		74[c]

[a]All reactions were carried out with 10 mol % of TetMe-IA and 3 equiv of oxone in $CH_3CN–H_2O$ (1:1, v/v) mixture at rt. [b]Isolated yields unless mentioned otherwise. [c]4-[2-(4-Bromophenyl)ethenyl]benzoic acid was isolated in 11% yield.

yield the corresponding oxidative cleavage products in respectable yields (entries 18 and 19). Cyclic dodecene and 1,1-diphenylethylene were found to undergo cleavage, leading to the corresponding diacid and benzophenone in 84 and 85% yields, respectively (entries 20 and 22). 1-Phenylcyclohexene reacted with oxone, leading to the ring-opened keto acid in 85% yield (entry 26). 1,2-Diarylethylenes (i.e., stilbenes) were found to undergo reaction rather sluggishly, leading to 1,2-diketones as one of the products; even after 36–38 h, considerable amounts of starting compounds were recovered unreacted with low yields of oxidative cleavage products, such as carboxylic acids (entries 23–25).

While the electron-rich *p*-methoxycinnamic acid underwent oxidative cleavage over a period of 36 h to afford *p*-methoxybenzoic acid in 86% isolated yield, the unsubstituted cinnamic acid was found to be unreactive even after 24 h (entries 29 and 31). While cyclic enone and chalcone were found to undergo cleavage leading to the corresponding products in 84 and 86% yields, respectively (entries 27 and 28), *α*,*β*-unsaturated carboxylic acids, nitriles, and esters were found to be unreactive under the employed conditions (entries 30–33). Intriguingly, allyl and cinnamyl esters were found to be unreactive (entries 34–36). ^{1}H NMR monitoring studies of the reactions of these substrates revealed no evidence for formation of the dihydroxy intermediates (cf. Figures S37 and S38, Supporting Information).

As mentioned at the outset, we have recently reported that oxone itself can be employed to cleave olefins but at the reflux conditions of acetonitrile–water (1:1, v/v);[9h] the high temperature at which the reactions occur with oxone alone is highly detrimental and renders the protocol limited in its scope.[9h] We have shown that this procedure is disadvantageous for methoxy-substituted arylolefins, olefins that contain benzylic carbons, and esters. The present protocol involving the use of TetMe-IA is mild in terms of the reaction conditions. Consequently, all the drawbacks associated with oxone as the reagent are overcome. As may be seen from the results in Table 2, substrates that contain methoxy-substituted arenes are not affected at rt (entries 2, 6, and 29). While alkylarenes lead to messy reactions with products arising from oxidation of the

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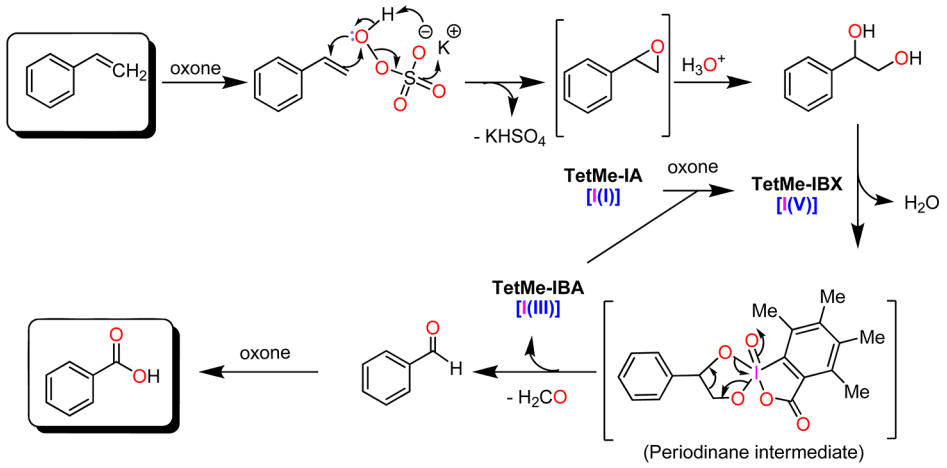
Scheme 1. Mechanism of Oxidative Cleavage of Styrene



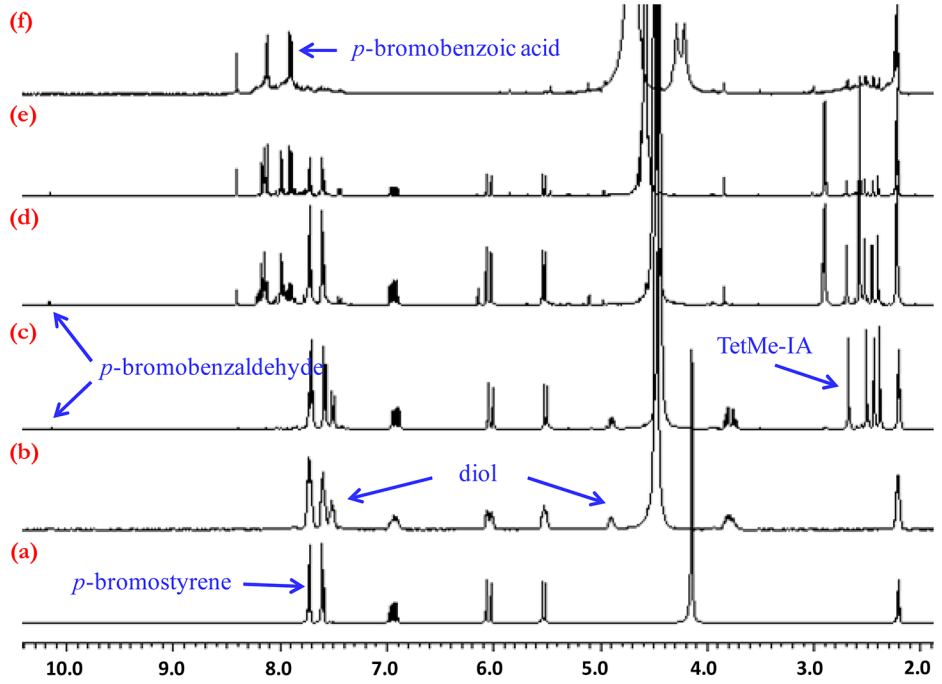


Figure 1. ^{1}H NMR monitoring of oxidation of *p*-bromostyrene with oxone (3 equiv) in $CD_3CN–D_2O$ (1:1) at rt: (a) 0 h, before addition of oxone, (b) 2 h after addition of oxone, (c) upon introduction of TetMe-IA, (d) after 4 h, (e) after 8 h, (f) after 14 h.

alkyl groups and esters undergoing hydrolysis at the reflux conditions with oxone in acetonitrile–water mixture,[9h] alkylarenes and ester functionalities are unaffected with the present protocol at rt (entries 3, 6, 7, 10, and 14).

As is evident from the results in Table 2, the oxidative cleavage is not observed for electron-deficient olefins that cannot undergo epoxidation followed by ring opening to yield the corresponding diols (vide infra); notably, the same olefins do lead to diols in the presence of oxone upon heating. Capitalizing on the difference in the reactivities of electron-rich and electron-deficient olefins to undergo epoxidation with oxone at rt, chemoselective oxidative cleavage of electron-rich double bonds in the presence of electron-poor double bonds was explored. Incidentally, there are only a few reports of chemoselective epoxidation and are virtually unknown with the exception of reactions employing ozone; even with the latter, there are only scant reports in the literature.[14] In Table 3 are shown our results of chemoselective cleavage of olefins with TetMe-IA as a catalyst in the presence of oxone as a co-oxidant at rt.

When 6-vinyl-2*H*-chromen-2-one was employed as the substrate at the employed reaction conditions, 2-oxo-2*H*-chromene-6-carboxylic acid was isolated in 83% yield (Table 3, entry 1). Clearly, cleavage of the vinyl group occurs with the cyclic electron-deficient double bond untouched. In a similar manner, electron-rich double bonds were found to undergo cleavage in substrates that simultaneously contain a functionality such as α,β-unsaturated ester/acid/nitrile; the acids were produced in 81–90% isolated yields (entries 2–4). The reaction of 4-bromostilbene was earlier found to be sluggish, leading to the corresponding benzil, but not the benzoic acid derived from oxidative cleavage, suggesting thereby that the latter does not occur at rt. Thus, chemoselective oxidative cleavage of the isolated double bond in (*Z*)-1-ethenyl-4-[2-(4-bromophenyl)ethenyl]benzene was examined. Indeed, the vinyl double bond underwent cleavage to the corresponding acid

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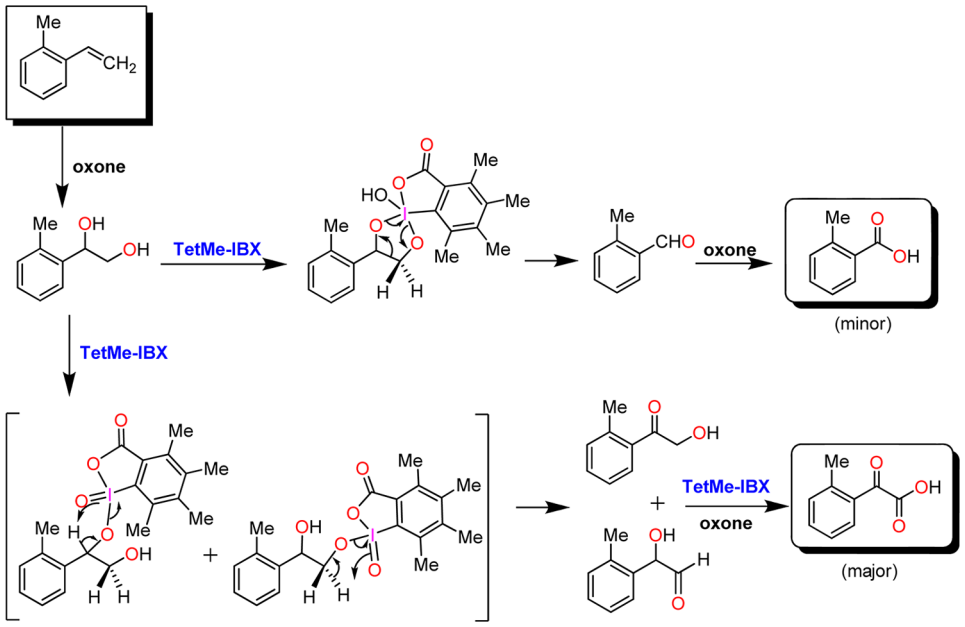
Scheme 2. Mechanism of Oxidation of *o*-Methylstyrene

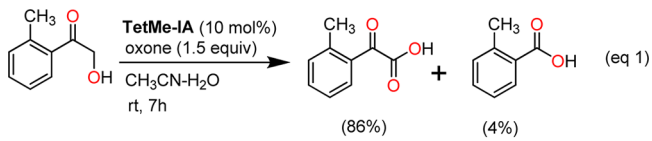


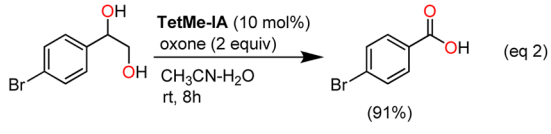
with concomitant oxidation of the stilbene double bond, leading to 4-[2-(4-bromophenyl)-2-oxoacetyl]benzoic acid in 74% isolated yield when oxone was employed in 5 equiv and the reaction was run for 30 h. However, when the reaction was carried out with 3 equiv of oxone and over a period of 18 h, a mixture of products, namely, (*E*)-4-[2-(4-bromophenyl)-ethenyl]benzoic acid (37%) and 4-[2-(4-bromophenyl)-2-oxoacetyl]benzoic acid (45%), was isolated.

Mechanism of Oxidation of Olefins. It is well-known that the reaction of olefins with oxone produces epoxides and diols depending on basic and acidic conditions, respectively.[15] As the solution of oxone in acetonitrile−water (1:1, v/v) is strongly acidic, pH ≈3−4, the initially formed epoxides should be expected to open up to afford the corresponding diols (Scheme 1). Indeed, the latter were isolated in a number of cases when the reactions were stopped midway or when the reactions were conducted without TetMe-IA as an added catalyst (e.g., entry 9, Table 1). Further, for *o*-methylstyrene, 1-*o*-tolylethane-1,2-diol was isolated in 87% when the reaction was run without the catalyst. The fact that the diols are produced by the reaction of oxone with olefins such as styrene in CH_3CN-H_2O (1:1, v/v) has also been shown by us previously.[9h]

The reaction of *p*-bromostyrene, a representative olefin, with TetMe-IA/oxone in CD_3CN-D_2O (1:1, v/v) as monitored by ^1H NMR spectroscopy is shown in Figure 1. As can be seen, the formation of 1-(4-bromophenyl)ethane-1,2-diol occurs within 2 h after the addition of oxone. Upon introduction of TetMe-IA to the reaction mixture, one observes the disappearance of the signals corresponding to the diol with concomitant appearance of new signals at δ 2.6, 2.8, 8.0, and 8.3, which presumably correspond to the periodinane complex; evidently, TetMe-IA undergoes oxidation to I(V) species (i.e., TetMe-IBX) at rt, which subsequently participates in the oxidation to form a cyclic periodinane. The signals corresponding to aldehyde and acid appear gradually, which we believe are a consequence of decomposition of the periodinane complex (Scheme 1). The fact that the initially formed aldehyde undergoes oxidation rapidly to carboxylic acid under the employed reaction conditions is well-known.[16] As the diols are quickly decomposed oxidatively to aldehydes, which further undergo rapid oxidation, the formation of diols from the olefins appears to be rate-determining. The fact that the reactions of electron-deficient olefins with TetMe-IA/oxone proceed slowly is in good agreement with this reasoning.

The result observed with *o*-methylstyrene clearly brings out the role of sterics (entry 14, Table 2). Oxidative cleavage of this substrate leads predominantly to *o*-methylphenylglyoxylic acid (76%) with *o*-toluic acid formed only in 11% yield. Clearly, the sterics prohibit cleavage followed by oxidation. We have isolated the 1,2-diol and subjected it independently to oxidation to establish the fact that it is the 1,2-diol which is an intermediate in the reaction of *o*-methylstyrene with TetMe-IA/oxone leading to the glyoxylic acid and *o*-toluic acid. With 3 equiv of oxone and 10 mol % of TetMe-IA, the reaction of the 1,2-diol at rt led to *o*-methylglyoxylic acid in 87% isolated yield along with *o*-toluic acid as a minor product in 7% yield. This suggests that the *o*-methyl group hinders the formation of cyclic periodinane derived from in situ-generated TetMe-IBX, which may decompose to *o*-toluic acid (Scheme 2). We have verified from an independent experiment that the oxidation of *o*-methyl-α-hydroxyacetophenone with TetMe-IA (10 mol %)/oxone (1.5 equiv) at rt leads to glyoxylic acid and *o*-toluic acid in 86 and 4% yields, which attests to the fact that the sterically hindered acyloins do not decompose predominantly to *o*-toluic acid (eq 1); notably, the reaction was found not to





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occur even after 24 h without the added TetMe-IA catalyst and with just oxone alone. In contrast, the oxidation of sterically unhindered diol, that is, 1-(4-bromophenyl)ethane-1,2-diol, under conditions similar to those employed for *o*-methylstyrene led to *p*-bromobenzoic acid in 91% yield within 8 h (eq 2).

Given that chloro and bromo substituents at *o*-position do not influence as that of the methyl group, a subtle difference is evidently obviating the oxidative cleavage. Otherwise, a range of olefins including the moderately poor ones are found to be oxidatively cleaved with TetMe-IA/oxone to the corresponding acids under mild conditions at rt.

The fact that oxidative cleavage of the diols—generated by the reaction of olefins with oxone—does not occur at all or occurs with lower efficiencies with all other iodo acids other than TetMe-IA in Chart 1 should be understood from the unique attributes inherent to TetMe-IA. In the latter, the consecutive methyl groups render the iodo acid to be sufficiently electron-rich as to facilitate its oxidation with oxone at rt to I(V) species. We have shown earlier that the steric relay between the consecutive methyl groups in TetMe-IBX renders it to be twisted and that the twisting enhances its solubility in common organic solvents.[9d] Thus, the room temperature oxidation of TetMe-IA to TetMe-IBX in conjunction with enhanced solubility of the latter is responsible for the facile domino oxidative cleavage of olefins at rt with catalytically in situ-generated modified IBX and oxone.

■ CONCLUSIONS

A catalytic protocol that works at rt for oxidative cleavage of olefins has been developed based on in situ-generated hypervalent I(V) and oxone. From the screening of a number of iodo acids that lead to hypervalent I(V) species on oxidation with oxone in CH_3CN-H_2O at rt, TetMe-IA was identified as the reactive catalyst. It has been shown that olefins undergo facile oxidative cleavage with 10 mol % of TetMe-IA/oxone at rt. Mechanistically, the olefins undergo initial epoxidation followed by ring opening to 1,2-diols with oxone as the reagent in CH_3CN-H_2O. The in situ-generated I(V) species is surmised to decompose the diols into carbonyl compounds. The aldehydes thus produced undergo further oxidation to acids with oxone. The procedure that involves mere stirring of the substrate and the catalyst in CH_3CN-H_2O (1:1, v/v) mixture at rt with incremental addition of oxone is simple, convenient, and cost-effective for oxidative cleavage of olefin to corresponding carbonyl compounds. For substrates that contain both electron-rich and electron-deficient double bonds, chemoselective cleavage of electron-rich olefins has been demonstrated.

■ EXPERIMENTAL SECTION

Solvents were distilled prior to use, and double distilled water was used for the reaction. All the reactions were carried out in an open atmosphere without any precaution. The products were isolated by column chromatography with a silica gel of 100−200 μm particle size. NMR spectra were recorded with 400 and 500 MHz spectrometers. IR spectra were recorded on an FT-IR spectrophotometer. Mass spectral analyses were carried out with ESI-Q^{TOF} instrument.

General Procedure for the Oxidative Cleavage of Olefins. To a solution of the olefin (ca. 1.0 mmol) in 10−16 mL of acetonitrile−water (1:1) mixture was added 10 mol % of TetMe-IA followed by oxone (2−5 mmol) incrementally over the entire duration of the reaction. Progress of the reaction in each case was monitored by TLC analysis. After completion of the reaction as judged from TLC analysis, the organic matter was extracted with ethyl acetate. The combined organic extract was dried over anhyd Na_2SO_4 and concentrated in vacuo. The residue was subjected to a short-pad silica gel column chromatography to isolate pure product(s). All the products were characterized by their ^{1}H NMR spectral data (cf. Supporting Information).

Characterization Data of Oxidation Products. *Benzoic Acid.*[9h] Colorless solid; R_f (25% EtOAc/petroleum ether) 0.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (t, J = 7.3 Hz, 2H), 7.62 (t, J = 7.8 Hz, 1H), 8.12 (d, J = 7.3 Hz, 2H).

p-Methoxybenzoic Acid.[9h] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.95 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H).

p-Toluic Acid.[9h] Colorless solid; R_f (25% EtOAc/petroleum ether) 0.37; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 7.4 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 8.1 Hz, 2H).

p-Bromobenzoic Acid.[9h] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.48; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H).

p-Nitrobenzoic Acid.[9h] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.32; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, J = 8.8 Hz, 2H), 8.33 (d, J = 8.8 Hz, 2H).

o-Bromobenzoic Acid.[9h] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.49; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38−7.43 (m, 2H), 7.72(d, J = 8.2 Hz, 1H), 8.02 (dd, J_1 = 7.3 Hz, J_2 = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 122.6, 127.3, 130.1, 132.5, 133.6, 134.9, 170.8.

Acetophenone.[9d] Colorless liquid; R_f (10% EtOAc/petroleum ether) 0.59; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.61 (s, 3H), 7.46 (t, J = 7.3 Hz, 2H), 7.54−7.59 (m, 1H), 7.96 (dd, J_1 = 8.5 Hz, J_2 = 1.4 Hz, 2H).

Benzophenone.[9f] Colorless solid; R_f (10% EtOAc/petroleum ether) 0.45; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (t, J = 7.8 Hz, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.8 (d, J = 8.2 Hz, 4H).

2-Hydroxy-2-phenylcyclohexanone.[9a] Colorless liquid; R_f (25% EtOAc/petroleum ether) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.7−1.87 (m, 4H), 2.02−2.1 (m, 1H), 2.4−2.45 (m, 2H), 2.97−3.01 (3, 1H), 7.28 (m, 5H).

p-tert-Butylbenzoic Acid.[17] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.5; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35 (s, 9H), 7.49 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.6 Hz, 2H).

p-(Benzyloxy)benzoic Acid.[18] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.14 (s, 2H), 7.03 (d, J = 8.5 Hz, 2H), 7.33−7.45 (m, 5H), 8.06 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 70.2, 114.7, 121.2, 127.5, 128.3, 128.7, 132.5, 136.0, 163.4, 171.6.

p-Acetoxybenzoic Acid.[19] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 7.21 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H).

o-Cholrobenzoic acid.[20] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.38 (m, 1H), 7.46−7.52 (m, 2H), 8.03 (d, J = 8.7 Hz, 1H).

o-Nitrobenzoic Acid.[9h] Colorless solid; R_f (10% CH_3OH/EtOAc) 0.31; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68−7.73 (m, 2H), 7.86−7.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 123.9, 125.9, 130.4, 132.58, 132.6, 148.9, 169.0.

o-Toluic Acid.[9h] Colorless solid; R_f (25% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.26 (m, 2H), 7.45 (m, 1H), 8.06 (dd, J = 7.5 Hz, J_1 = 1.8 Hz, 1H).

2-Methylphenylglyoxylic Acid. Colorless solid; R_f (10% CH_3OH/EtOAc) 0.3; mp 279−283 °C (decomp); IR (KBr) cm^{-1} 3432, 2927, 1686, 1632; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.48 (s, 3H), 7.22−7.25 (m, 2H), 7.36−7.37 (m, 1H), 7.71−7.73 (m, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.2, 126.0, 131.8, 131.9, 132.0, 134.6, 138.9, 170.8, 199.8; ESI-MS$^-$ m/z calcd for $C_9H_7O_3$ 163.0395 [M − H$^+$], found 163.0395.

2-Naphthoic Acid.[21] Colorless solid; R_f (25% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.63 (m, 2H), 7.92−7.99 (m, 3H), 8.06 (dd, J = 7.5 Hz, J_1 = 1.8 Hz, 1H), 8.73 (s, 1H).

o-Carboxycinnamic Acid.[9f] Colorless solid; R_f (10% MeOH/EtOAc) 0.2;^{1}H NMR (acetone-d_6, 400 MHz), δ 6.39 (d, J = 15.9 Hz,

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1H), 7.52 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 8.55 (d, J = 15.9 Hz, 1H).

6-Phenyl-6-oxohexanoic Acid.[9h] Colorless solid; R_f (75% EtOAc/petroleum ether) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.74−1.81 (m, 4H), 2.42 (t, J = 6.9 Hz, 2H), 3.01 (t, J = 6.9 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.7 Hz, 2H).

(E)-4-(3-Methoxy-3-oxoprop-1-enyl)benzoic Acid.[22] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.5; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.83 (s, 3H), 6.55 (d, J = 16 Hz, 1H), 7.62 (d, J = 8 Hz, 2H), 7.72 (d, J = 16 Hz, 1H), 8.12 (d, J = 8 Hz, 2H).

(E)-4-(2-Carboxyethenyl)benzoic Acid.[23] Colorless solid; R_f (20% MeOH/EtOAc) 0.5; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.64 (d, J = 16.05 Hz, 1H), 7.63 (d, J = 16.0 Hz, 1H), 7.8 (d, J = 8.3 Hz, 2H), 8.12 (d, J = 8.3 Hz, 2H).

3,3-Dimethyl-5-oxohexanoic Acid.[24] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 6H), 2.14 (s, 3H), 2.45 (s, 2H), 2.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.1, 30.0, 32.6, 44.4, 52.2, 177.2, 208.9.

1-(4-Bromophenyl)-2-phenylethane-1,2-dione.[25] Yellow solid; R_f (10% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.54 (m, 2H), 7.65−7.7 (m, 3H), 7.84 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H).

Dodecanoic Acid.[9h] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.86 (t, J = 6.6 Hz, 3H), 1.2−1.31 (m, 16H), 1.58−1.66 (m, 2H), 2.33 (t, J = 7.5 Hz, 2H).

(E)-4-(2-Cyanoethenyl)benzoic Acid.[26] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.4; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.6 (d, J = 16.6 Hz, 1H), 7.71−7.77 (m, 3H), 7.97 (d, J = 8.6 Hz, 2H).

p-(Methoxycarbonyl)benzoic Acid.[27] Colorless solid; R_f (50% EtOAc/petroleum ether) 0.4; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.88 (s, 4H), 8.06 (s, 4H).

Dodecanedioic Acid.[28] Colorless solid; R_f (10% MeOH/EtOAc) 0.4; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.21−1.24 (m, 12H), 1.46−1.47 (m, 4H), 2.18 (t, J = 9.15, 4H).

4-(2-(4-Bromophenyl)-2-oxoacetyl)benzoic Acid. Yellow solid; R_f (20% MeOH/EtOAc) 0.4; mp >300 °C; IR (KBr) cm^{-1} 1688, 1665; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.86−7.89 (m, 4H), 8.05 (d, J = 8.05, 2H), 8.13 (d, J = 8.05, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 129.9, 130.53, 130.59, 131.6, 132.1, 133.1, 135.5, 136.85, 166.8, 193.4, 193.8; ESI-MS$^-$ m/z calcd for $C_{15}H_8O_4Br$ 330.9605 [M − H$^+$], found 330.9605.

1-(4-Bromophenyl)-2-hydroxyethanone.[29] Colorless solid; R_f (20% EtOAc/petroleum ether) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 2H), 7.66 (d, J = 8.7, 2H), 7.78 (d, J = 8.7, 2H).

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione.[30] Yellow solid; R_f (10% EtOAc/petroleum ether) 0.5; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.55 (t, J = 7.8 Hz, 2 H), 7.71 (t, J = 7.3 Hz, 1 H), 7.90 (m, 2 H), 8.17 (m, 2 H), 8.36 (m, 2 H).

(E)-4-[2-(4-Bromophenyl)ethenyl]benzoic Acid.[31] Colorless solid; R_f (25% EtOAc/petroleum ether) 0.5; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.64−6.65 (m, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.31(d, J = 8.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H).

2-Oxo-2H-chromene-6-carboxylic Acid. Colorless solid; R_f (50% EtOAc/petroleum ether) 0.5; mp 251−254 °C, IR (KBr) cm^{-1} 3096, 2929, 1750, 1682, 1622; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 6.58 (d, J = 12.0 Hz, 1H), 7.48 (d, J = 10.8 Hz, 1H), 8.10−8.13 (m, 1H), 8.19 (d, J = 12.0 Hz, 1H), 0.8.35 (d, J = 2.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 117.3, 117.4, 119.2, 127.5, 130.7, 133.0, 144.6, 156.7, 160.0, 166.7; ESI-MS$^-$ m/z calcd for $C_{10}H_5O_4$ 189.0187 [M − H$^+$], found 189.0181.

4-(2-Phenyl-2-oxoacetyl)benzoic Acid.[30] Yellow solid; R_f (10% MeOH/EtOAc) 0.3; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.64 (t, J = 7.8 Hz, 2H), 7.81 (t, J = 7.6, 1H), 7.95 (d, J = 7.4 Hz, 2H), 8.04 (t, J = 8.3 Hz, 2H), 8.14 (d, J = 8.3 Hz, 2H).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectral reproductions for the products of oxidations and ^{1}H NMR spectral reproductions for monitoring of the oxidations of *p*-bromostyrene, *o*-methylstyrene, 1-(allyloxy)-4-methylbenzene, and (*E*)-3-(4-bromophenyl)allyl acetate. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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