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6-Membered Pseudocyclic IBX Acids: Syntheses, X-ray Structural Characterizations, and Oxidation Reactivities in Common Organic Solvents

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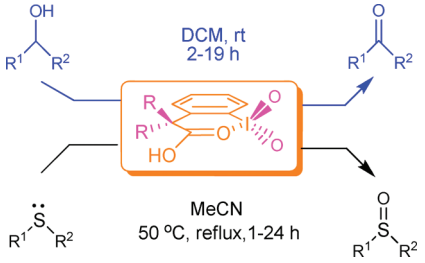

We designed and synthesized λ^5-cyclic periodinanes **1** and **2**, which are homologous to IBX (1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one) by one carbon, to thwart close packing of molecules in the crystal lattice to permit solubility in common organic solvents and to facilitate oxidations with enhanced reactivity. The X-ray crystal structures revealed that both **1** and **2** exist in the solid state as pseudocyclic (**PC**) acids, i.e., **1PC** and **2PC**, and that the molecules in the lattice are less weakly associated as compared to those in the parent IBX due to the twisting introduced via the sp^3 benzylic carbon. Both **1PC** and **2PC** are found to dissolve in palpable amounts in DCM and acetonitrile to allow oxidation of a variety of alcohols and sulfides to carbonyl compounds and sulfoxides in a facile manner. The subtle differences in the sterics due to methyl and ethyl substituents in **1PC** and **2PC** are found to manifest in contrasting reactivities in that the oxidations of alcohols occur faster with **2PC**, while those of sulfides to sulfoxides occur more rapidly with **1PC**.

Introduction

Hypervalent oxidation reagents have gained a lot of importance in recent oxidation chemistry.[1] In particular, IBX—a λ^5-iodane (1-hydroxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]-iodoxol-3-one)—has usurped center stage due to its environmentally benign attributes, easy accessibility, and remarkable reactivity; the latter property continues to be exploited for diverse organic transformations.[2] Two serious limitations, however, with the use of IBX are its insolubility in common organic solvents with the exception of DMSO and explosive nature at high temperatures.[3] A common reason for these two undesirable characteristics has been attributed to the close packing of molecules in the crystal lattice via halogen bonds, hydrogen bonds, and aromatic $\pi-\pi$ stacking interactions.[4] A number of modifications continue to be explored in pursuit of IBX analogues that overcome the

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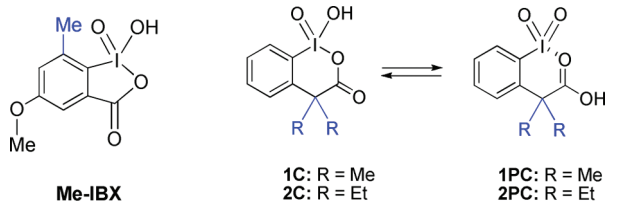
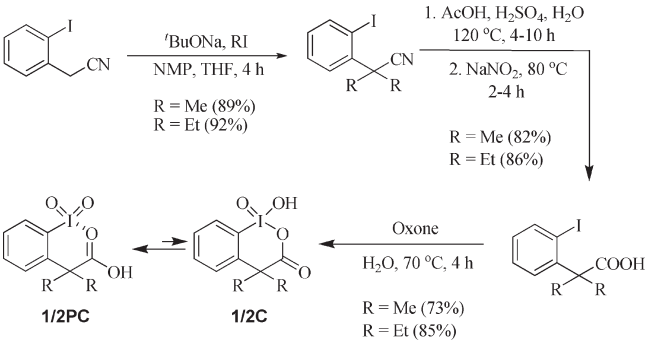
CHART 1



drawbacks with IBX.[5] We recently showed that modified Me-IBX (Chart 1) can be employed for oxidation of alcohols and sulfides in common organic solvents such as acetone and acetonitrile; in this case, the so-called hypervalent twisting accelerates the rate of oxidation.[6] In continuation of our interest in exploring the reactions mediated by IBX,[6,7] we were inspired to explore the reactivity of λ^5-cyclic (**C**) periodinanes, **1C** and **2C**, which are homologous to IBX by one carbon. We expected such analogues to exhibit solubility in common organic solvents in addition to improved reactivity based on the following rationale: (i) introduction of additional sp^3 carbon at the benzylic site was expected to render the structure nonplanar and hence preclude stacking interactions in the solid state to facilitate solubility; (ii) the dialkyl groups at the benzylic position were surmised to render the iodine site sterically encumbered to influence the reactivity—the fact that steric acceleration of collapse of the alkoxyperiodinane intermediate in IBX-mediated oxidation of alcohols by the so-called *hypervalent twisting* is well-known;[8] and (iii) the possibility to introduce chirality at the benzylic site in the close proximity of I(V) center was deemed immensely appealing from the point of view of developing chiral λ^5-iodanes for asymmetric oxidations.[5j,9] Herein, we report that the periodinanes **1** and **2** exist in the solid state as pseudocyclic (**PC**) systems, i.e., **1PC** and **2PC**, with no covalent bonding between iodine and oxygen atoms as revealed by X-ray crystallography, yet exhibit high reactivity in common organic solvents for oxidation of alcohols and sulfides. The pseudocyclic IBXs correspond to a different class of λ^5-iodanes, and there is a keen interest,[5a−h] as with cyclic IBXs,[5i−q] to unravel their reactivity in organic oxidations.

SCHEME 1. The Synthetic Routes for the Preparation of 6-Membered IBX Acids 1 and 2



Results and Discussion

Synthesis of Cyclic 6-Membered IBX Acids 1 and 2 and Their X-ray Structural Characterizations. Syntheses of the target oxidation reagents **1** and **2** were accomplished starting from *o*-iodobenzyl cyanide, which was dialkylated[10] and subsequently hydrolyzed to give α-dialkyl-*o*-iodophenylacetic acid.[11] Treatment of the latter with oxone in water at 70 °C led to dimethyl and diethyl λ^5-periodinanes **1** and **2** (Scheme 1).[12]

The single crystals of dimethyl and diethyl homologous IBXs **1** and **2** suitable for X-ray structure determinations were grown from a TFA−DMF (1:2) mixture and DMF, respectively. X-ray intensity data collection followed by structure determination revealed that the asymmetric unit cell in the case of **1** (triclinic, $P\bar{1}$) contains two molecules of the *o*-iodylphenyl-2-methylpropionic acid **1**, i.e., A and B, together with two molecules of trifluoroacetic acid, which was used for crystallization. However, only one molecule was found in the asymmetric unit cell of **2** (tetragonal, $P\bar{4}2_1c$). Further, in both **1** and **2**, the intra- and intermolecular contacts involving iodine and carboxy groups suggest that the pentavalent iodine can only be considered as pseudocyclic, i.e., **1PC**/**2PC**, and not as cyclic iodane, i.e., **1C**/**2C**. This is so despite the fact that intramolecular I···O distances for the two independent molecules in **1PC** and that in **2PC** are 2.404, 2.606, and 2.607 Å. In general, for pseudocyclic iodyl compounds, the I···O distance is higher than 2.60 Å, and any value in the range of 2.20−2.50 Å is considered to classify the molecular system as corresponding to cyclic iodane as opposed to pseudocyclic iodyl derivative.[5p] The O−H···O intermolecular hydrogen bonds involving the carboxy groups unambiguously establish the nature of **1**

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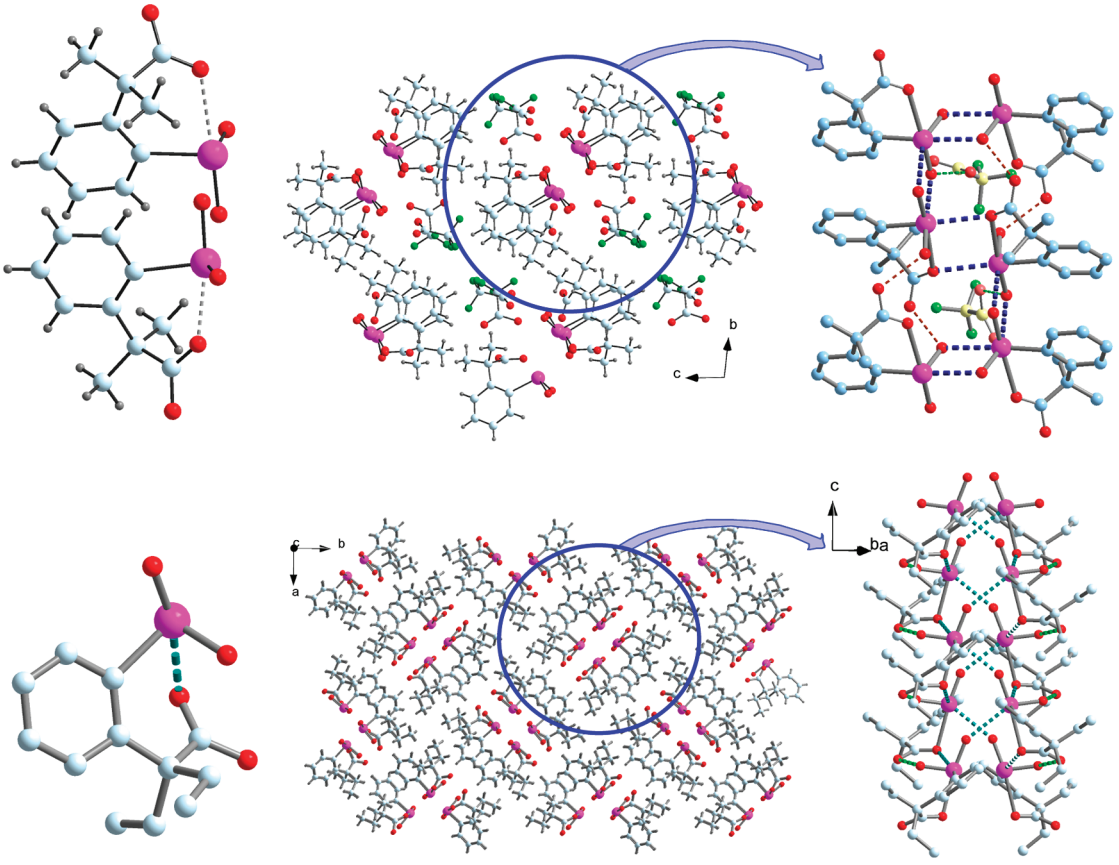


FIGURE 1. The perspective drawings of the molecular structures and crystal packing diagrams of pseudocyclic IBX acids **1PC** (top) and **2PC** (bottom).

and **2** as pseudocyclic (**PC**). The molecular structures of both **1PC** and **2PC** are shown in Figure 1. As expected, the structures are nonplanar with the sp^3 carbon introducing a twist to render the molecules quite skewed. The relevant bond distances and intramolecular contacts for both **1PC** and **2PC** are given in Tables S1 and S2 (Supporting Information).

The crystal packing of **1PC** (Figure 1) reveals the formation of strands that are built up by I···O halogen bonds and O−H···O hydrogen bonds. A closer inspection shows that the centrosymmetric partners of independent molecules A and B are connected by I═O···I halogen bonds; while the iodyl moieties are interconnected for molecules A, iodine and carbonyl oxygen of the carboxy group are involved for molecules B. The centrosymmetrically related pairs of molecules A and B are further O−H···O bonded to make up the strands as shown in Figure 1. The solvent TFA molecules are found to be bound to axial oxygens via O−H···O hydrogen bonds. In **2PC**, one observes helical propagation of molecules (2_1-screw) sustained by I···O and O−H···O bonds. The symmetry related helices are further connected by O−H···O hydrogen bonds in a manner akin to a double helix. What is otherwise noteworthy is that in both **1PC** and **2PC**, the intermolecular association is a lot weaker when compared to that in the parent IBX; in the latter, there exists a 2-dimensional close packing into layers that are further close packed by aromatic stacking interactions.[4]

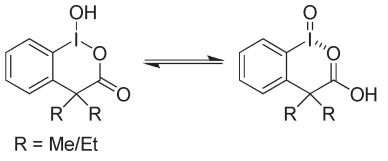
Oxidation of Alcohols and Sulfides with 1PC and 2PC. One of the ways to destroy polymeric network structures associated with pentavalent iodyl arenes that are insoluble has been ortho-substitution, proposed initially by Protasiewicz.[13] On the basis of this concept, Zhdankin and co-workers have synthesized a variety of stable and soluble pseudocyclic 2-iodylbenzenes, and demonstrated their reactivities in the oxidation of alcohols and sulfides.[5a−h,j,p] Some of the notable pseudocyclic IBXs include IBX-amides,[5a] 2-iodoxybenzenesulfamides,[5b] *N*-(2-iodylphenyl)acylamides,[5d] IBX esters,[5e] 2-iodoxybenzenesulfonate esters,[5f] IBX ethers,[5g] *N*-(2-iodylphenyl)tosylamides,[5h] 2-iodylphenyl tosylates,[5h] etc. Of these, only *N*-(2-iodylphenyl)tosylamides, 2-iodylphenyl tosylates, and *N*-(2-iodylphenyl)acylamides correspond to 6-membered pseudocyclic IBXs. It is intriguing that in the present investigation, 1-carbon homologation in **1** and **2** leads to 2-iodylphenylacetic acids instead of cyclic structures as in the case of parent IBX. Presumably, the crystal packing stabilization is higher when the crystallization proceeds through the acyclic form than the cyclic tautomeric form. Notwithstanding the finding that both methyl and ethyl homologous IBXs **1** and **2** exist in their pseudocyclic structures in the solid state, their ability to accomplish oxidation of alcohols and sulfides was explored. As noted earlier, there is lot of continuing interest in exploring the reactivity of pseudocyclic IBXs.[5a−h] Incidentally, 6-membered pseudocyclic IBX homologues are scarce, and their reactivity as oxidation reagents is of fundamental interest.

Initially, the screening studies were carried out with *p*-bromobenzyl alcohol as the substrate. As shown in Table 1,

(13) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, Z. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2007.

oxidation to the corresponding aldehyde was examined with **1PC** and **2PC** in DCM, $CHCl_3$, acetonitrile, acetone, and ethyl acetate as common organic solvents. Typically 1.5 equiv of the reagent was employed for oxidation; although 1.05/1.10 equiv of the reagent was found to be sufficient for DCM, excess reagent, i.e., 1.5 equiv, was uniformly employed to ensure complete conversion of the alcohol in all solvents and to reduce the reaction times; indeed, the excess reagent was found to facilitate complete conversion of less reactive alcohols, Table 2, vide infra. It should be noted that the oxidation of *p*-bromobenzyl alcohol was found to be slow in acetone and ethyl acetate (entries 7−10, Table 1). The oxidation occurred most rapidly in DMSO (entries 11 and 12, Table 1). A perusal of the results in Table 1 show that diethyl analogue, i.e., **2PC**, performs better and that the oxidation occurs in a facile manner in DCM at room temperature; while the conversion of *p*-bromobenzyl alcohol to *p*-bromobenzaldehyde occurred in 6 h with **1PC** (entry 1, Table 1), the oxidation was found to be complete with **2PC** in less than 2.5 h (entry 2). Thus, the oxidation of diverse alcohols was examined at room temperature in DCM as the solvent. As shown in Table 2, a variety of alcohols were readily oxidized to the corresponding carbonyl compounds, the reactions were found to occur considerably faster for diethyl analogue, i.e., **2PC**, than for **1PC**. Insofar as the reactivities are concerned, allylic (entries 7, 8, 13, and 14, Table 2), benzylic (entries 1−6, 11, 12, 19, and 20, Table 2), and secondary alcohols (entries 9, 10, 15, and 16, Table 2) were found to undergo oxidation with comparable rates as reflected from the durations of the reactions, while primary alcohols underwent oxidation over relatively longer times (entries 17 and 18, Table 2).

The reduction products of both **1PC** and **2PC** were identified to be the corresponding I(III) species, viz., 2-(*o*-iodosophenyl)-2-methylpropionic acid and 2-ethyl-2-(*o*-iodosophenyl) butanoic acid, cf. eq 1.

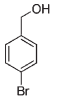
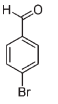


(1)

While the IR spectral analysis indicates the cyclic structure with no evidence for the free carboxyl group, the solution state NMR spectra reveal both cyclic as well as acyclic species in equilibrium (eq 1); one observes two sets of signals in both ^1H and ^{13}C NMR spectra, an observation that has been noted by others as well,[5d] cf. SI.

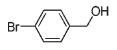
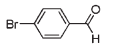
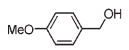
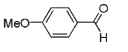
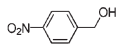
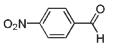
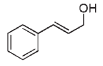
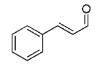
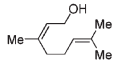
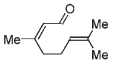
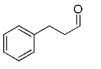
Buoyed by the reactivity of pseudocyclic IBXs **1** and **2** in the oxidation of alcohols at rt and selectively in the case of primary alcohols, we examined the oxidation of a few select sulfides. The oxidations were performed in a neutral solvent such as acetonitrile by employing 1.1 equiv of **1PC**/**2PC**. While the reactions were found to be sluggish at rt, the sulfoxides were found to be formed at higher temperatures. The dialkyl sulfide such as ethyl *n*-octyl sulfide reacted in 1−3 h with **1PC** and **2PC** to yield the corresponding sulfoxide in a quantitative yield (entries 1and 2, Table 3). The methyl phenyl sulfide reacted likewise to afford the sulfoxide in ca. 80% isolated yield (entries 3 and 5, Table 3). While the unsubstituted diphenyl sulfide and *p*-methoxy-substituted

TABLE 1. Results of Solvent Screening Studies for the Oxidation of Representative *p*-Bromobenzyl Alcohol to *p*-Bromobenzaldehyde with Pseudocyclic IBX Acids 1PC and 2PC[a]

entry	substrate	reagent	solvent	product	time (h)	yield[b] (%)
1		**1PC**	DCM		6.0	94
2		**2PC**	DCM		2.3	93
3		**1PC**	$CHCl_3$		8.0	84
4		**2PC**	$CHCl_3$		6.0	85
5		**1PC**	CH_3CN		6.0	92
6		**2PC**	CH_3CN		5.0	91
7		**1PC**	acetone		13.0	90
8		**2PC**	acetone		8.5	90
9		**1PC**	EtOAc		24.0	55[c]
10		**2PC**	EtOAc		24.0	81
11		**1PC**	DMSO		1.2	91
12		**2PC**	DMSO		1.0	90

[a]All reactions were conducted on 0.5−1.0 mmol of the alcohol at room temperature (25−30 °C). [b]Isolated yields. [c]40% unreacted starting compound was isolated.

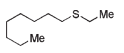
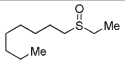
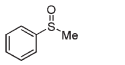
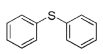
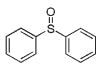
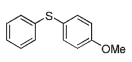
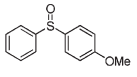
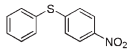
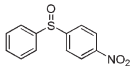
TABLE 2. Results of Oxidation of a Variety of Alcohols to the Corresponding Carbonyl Compounds with Pseudocyclic IBX Acids 1PC and 2PC in DCM at Room Temperature[a]

entry	substrate	reagent	product	time (h)	yield[b] (%)
1		**1PC**		6.0	94
2		**2PC**		2.3	93
3		**1PC**		6.0	93
4		**2PC**		2.0	95
5		**1PC**		6.0	96
6		**2PC**		2.7	97
7		**1PC**		8.0	95
8		**2PC**		4.0	95
9		**1PC**		9.0	96
10		**2PC**		2.5	97
11		**1PC**		9.5	83
12		**2PC**		5.0	86
13		**1PC**		6.5	81
14		**2PC**		3.5	79
15		**1PC**		3.0	93
16		**2PC**		1.5	94
17		**1PC**		19.0	84
18		**2PC**		13.0	80
19		**1PC**		4.0	61[c]
20		**2PC**		4.0	70[c]

[a]All reactions were conducted on 0.5−1.0 mmol of the alcohol at room temperature (25−30 °C). [b]Isolated yields. [c]Reactions were performed at 20 °C.

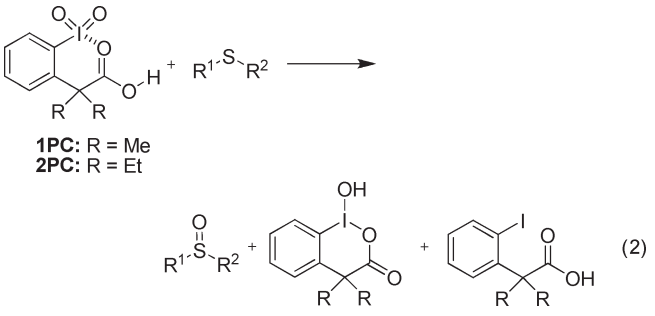
analogue were found to be oxidized, albeit the former over a longer period of time (entries 7−10, Table 3), the oxidation of *p*-nitro analogue was found to be extremely sluggish (entries 11 and 13, Table 3). Nonetheless, a limited, yet meaningful set of substrates show clearly that the pseudocyclic IBXs **1PC** and **2PC** serve as oxidation reagents for the oxidation of dialkyl and e-rich diarylsulfides under neutral conditions. It is noteworthy that overoxidation to sulfones

TABLE 3. Results of Oxidation of Sulfides with 1PC and 2PC in Acetonitrile[a]

entry	substrate	reagent	time (h)	product	conv. (%)	yield[b] (%)
1		**1PC**	1.0		100	95[c]
2		**2PC**	3.0		100	92[c]
3		**1PC**	2.2		100	78
4		**1PC**	1.5		100	80[d]
5		**2PC**	2.7		100	79
6		**2PC**	1.7		100	83[d]
7		**1PC**	24.0		82	71[e]
8		**2PC**	24.0		80	69[e]
9		**1PC**	3.0		100	84
10		**2PC**	4.5		100	82
11		**1PC**	60.0		45	44[f]
12		**1PC**	24.0		54	49[d,f]
13		**2PC**	60.0		16	15[g]
14		**2PC**	24.0		56	50[d,f]

[a]All reaction were carried out on 0.5−1 mmol of the sulfide in acetonitrile at reflux by employing 1.1 equiv of the reagent, unless mentioned otherwise. [b]Isolated yields based on consumed starting compound. [c]The reaction was carried out at 50 °C. [d]The reagent (0.55 equiv) and TFA (5 equiv) were employed and the reactions were conducted at room temperature in $CHCl_3$. [e]Ca. 20% unreacted starting compound was recovered. [f]Ca. 45−50% starting compound was recovered. [g]The reaction was too sluggish, and 84% unreacted starting compound was recovered.

was observed for none of the cases. The ^{1}H NMR monitoring studies of the oxidations with **1PC** and **2PC** revealed the formation of their iodo acid precursors together with 2-(*o*-iodosophenyl)-2-methylpropionic acid or 2-ethyl-2-(*o*-iodosophenyl)butanoic acid−I(III) species (eq 2).



(2)

The formation of 2-(*o*-iodophenyl)-2-methylpropanoic acid or 2-ethyl-2-(*o*-iodophenyl)butanoic acid suggests that the intermediate I(III) species also undergoes further reduction.[14] This process, however, appears to be substrate-dependent as suggested by the formation of iodo acid in varying amounts (ca. 10−50%); it is for this reason that the reagent was employed in 1.1 equiv uniformly for the sulfide to sulfoxide oxidations. Quite remarkably, the oxidation was found to occur very rapidly in the presence of added TFA. For example, the oxidation of methyl phenyl sulfide and *p*-nitrophenyl phenyl sulfide was found to occur with 0.55 equiv of **1PC** and **2PC** (entries 4 and 6, Table 3), see the SI. Even the less reactive *p*-nitrophenyl phenyl sulfide underwent reaction at rt (entries 12 and 14, Table 3). The end product of iodine reagent was found to be 2-(*o*-iodophenyl)-2-methylpropionic acid/2-ethyl-2-(*o*-iodophenyl)butanoic acid, which suggests 4e-reduction in the overall conversion of sulfides to sulfoxides.

Mechanistic Considerations. Insofar as alcohol oxidations are considered, the results of oxidations with **1PC**/**2PC** are indeed very facile and occur at rt when compared with the reactivities reported for other pseudocyclic analogues.[5a−h] In particular, **2PC** is found to work better than **1PC**. The reverse is found to hold true for sulfide oxidations. In addition to these intriguing observations, the question that springs up is: which of the two species, i.e., cyclic (**C**) and pseudocyclic (**PC**) in Chart 1, is responsible for oxidation, although pseudocyclic structure is revealed by X-ray crystallography in the solid state. The ^{1}H NMR analyses in DMSO did not reveal any evidence for the presence of two species, while IR analyses in DCM were not possible due to poor solubilities (0.36 g/L for **1PC** and 0.45 g/L for **2PC**). The possibility that the cyclic species in equilibrium may contribute to the overall observed oxidations to some degree cannot be ruled out. We believe that the origin of contrasting differences in the reactivities of dimethyl (**1PC**) and diethyl (**2PC**) homologous IBXs in regard to alcohol and sulfide oxidations should be traceable to the way the sterics associated with methyl and ethyl groups exert influence on the rate-determining steps of the two oxidation reactions, which clearly appear to follow distinct mechanisms.

Conclusions

6-Membered homologues of IBXs **1** and **2** were designed to overcome the insolubility of parent IBX in common organic solvents and influence oxidation reactivity via sterics. The X-ray crystal structure analyses revealed the structures of homologous IBXs to be pseudocyclic in the solid state, i.e., **1PC** and **2PC**. The X-ray crystal packing analyses show that the molecules are twisted due to the sp^3 carbon at the benzylic site, which is doubly alkylated. The nonplanarity seemingly renders the crystal packing rather less cluttered in comparison to that in parent IBX. Both pseudocyclic IBXs **1** and **2** are found to exhibit comparable, but palpable solubility in common organic solvents to permit oxidation of diverse alcohols and sulfides in common organic solvents. In alcohol oxidations, **2PC** is found to perform better than **1PC**, while the latter is found to be better for sulfide oxidations. This difference in reactivities should be a result of the influence of sterics associated with methyl and ethyl groups on the seemingly contrasting mechanisms of oxidation of alcohols and sulfides. The results demonstrate the viability to manipulate the reactivities by steric effects. Given that the substituents in structures **1** and **2** at the benzylic site evidently modify the reactivity and that the chirality can be introduced readily to develop chiral IBXs, analogous chiral oxidation reagents are likely to be very promising for enantioselective oxidations. We are continuing our efforts to develop chiral IBXs for application in enantioselective oxidation chemistry.

(14) The reduction product, i.e., I(III) species, failed to oxidize the alcohols. Further, 0.55 equiv of the IBX acid (**1PC**/**2PC**) was found to be sufficient for complete conversion of a sulfide such as methyl phenyl sulfide to the corresponding sulfoxide in the presence of TFA, cf. SI. These two considerations preclude the possibility of disproportionation of I(III) species to I(V) and I(I), and hence as the origin of I(I) species in sulfide oxidations.

Experimental Section

Preparation of 2-(2-Iodophenyl)-2-methylpropanenitrile.[15] A solution of 6.64 g (4.2 equiv, 69.13 mmol) of ^{t}BuONa in 22 mL of a 1:1 mixture of 1-methylpyrrolidin-2-one (NMP) and THF was cooled to 0 °C under nitrogen atmosphere. Into this solution was introduced 4.0 g (1.0 equiv, 16.46 mmol) of *o*-iodobenzylcyanide followed by 4.65 mL (4.5 equiv, 74.07 mmol) of methyl iodide dropwise. The reaction mixture was allowed to stir for 4 h at rt. Subsequently, the reaction was quenched with water at ice cold condition and extracted with $CHCl_3$. The combined extracts were dried over anhydrous Na_2SO_4 and solvent stripped in vacuo. Silica gel column chromatography of the residue led to the isolation of 3.97 g of 2-(2-iodophenyl)-2-methylpropanenitrile (yield 89%). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 6H), 6.99 (td, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H), 7.38 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.45 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 8.03 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H).

Preparation of 2-(2-Iodophenyl)-2-methylpropanoic Acid. A solution of 4.0 g (1.0 equiv, 14.76 mmol) of 2-(2-iodophenyl)-2-methylpropanenitrile in a mixture of AcOH (15 mL) and 60% H_2SO_4 (30 mL) was heated at 120 °C for 2 h. The reaction mixture was allowed to cool to room temperature. Subsequently, 5.09 g (5.0 equiv, 73.80 mmol) of $NaNO_2$ was added slowly, and the reaction mixture was heated at 90 °C for another 2 h. After the completion of the reaction, it was poured into crushed ice, and the mixture was filtered (yield 82%). Colorless solid; mp 134−136 °C; IR (KBr) cm^{-1} 2982, 1692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 6H), 6.93 (td, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1H), 7.33−7.42 (m, 2H), 7.92 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 50.0, 98.6, 127.0, 128.2, 128.5, 141.9, 145.6, 182.9; ESI-MS + m/z calcd for $C_{10}H_{11}IO_2$ 290.9882 [M + H], found 290.9884.

Preparation of 2-(2-Iodylphenyl)-2-methylpropanoic Acid, 1PC. To a solution of 12.72 g (2 equiv, 20.68 mmol) of oxone in 50 mL of distilled water was added 3.0 g (1.0 equiv, 10.34 mmol) of 2-(2-iodophenyl)-2-methylpropanoic acid gradually. The stirring was continued for 4 h at 70 °C. The product, i.e., 2-(2-iodylphenyl)-2-methylpropanoic acid (**1PC**), was obtained as a colorless solid, which was filtered, washed with cold acetone, and dried (2.43 g, yield 73%). Mp 161−163 °C; IR (KBr) cm^{-1} 3445, 2493, 2980, 1657, 1207, 752, 732; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.63 (s, 6H), 7.57−7.62 (m, 3H), 8.16−8.18 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 29.0, 46.3, 127.1, 127.5, 128.2, 131.9, 144.6, 148.3, 179.7; ESI-MS + m/z calcd for $C_{10}H_{11}IO_4$ 322.9780 [M + H], found 322.9782.

Preparation of 2-Ethyl-2-(2-iodophenyl)butanenitrile.[16] A similar procedure as described above with ethyl iodide led to 2-ethyl-2-(2-iodophenyl)butanenitrile in 92% isolated yield. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.6 Hz, 6H), 2.02 (m, 2H), 2.72 (m, 2H), 6.98 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H).

Preparation of 2-Ethyl-2-(2-iodophenyl)butanoic Acid. As described above for the dimethyl analogue, 6.50 g (1.0 equiv, 21.74 mmol) of 2-ethyl-2-(2-iodophenyl)butanenitrile was taken in a mixture of AcOH (30 mL) and 60% H_2SO_4 (40 mL) and heated at 120 °C overnight. The reaction mixture was allowed to cool to rt. Subsequently, 6.0 g (4.0 equiv, 86.96 mmol) of $NaNO_2$ was added and heating was continued at 90 °C for another 2 h. Later, the reaction mixture was poured into crushed ice and the product was filtered under cold conditions (yield 86%). Colorless solid; mp 153−155 °C; IR (KBr) cm^{-1} 2979, 2637, 1701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, J = 7.6 Hz, 6H), 2.03 (m, 2H), 2.33 (m, 2H), 6.92 (t, J = 7.5 Hz, 1H), 7.29−7.36 (m, 2H), 7.94 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.5, 25.8, 56.9, 98.7, 127.5, 128.4, 129.2, 142.3, 143.0, 181.3; ESI-MS + m/z calcd for $C_{12}H_{15}IO_2$ 319.0195 [M + H], found 319.0195.

Preparation of 2-Ethyl-2-(2-iodylphenyl)butanoic Acid, 2PC. To a solution of 11.6 g (2.0 equiv, 18.87 mmol) of oxone in 50 mL of distilled water at 70 °C was added 3.0 g (1.0 equiv, 9.43 mmol) of 2-ethyl-2-(2-iodophenyl)butanoic acid slowly. The stirring was continued at 70 °C for 4 h. 2-Ethyl-2-(2-iodylphenyl)-butanoic acid (**2PC**) was obtained as a colorless solid (2.8 g, yield 85%). Mp 166−168 °C; IR (KBr) cm^{-1} 3435, 2978, 2469, 2227, 1646, 798, 737; ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.62 (t, J = 7.3 Hz, 6H), 2.05−2.13 (m, 4H), 7.53−7.57(m, 3H), 8.18−8.20 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 9.3, 31.4, 55.0, 127.1, 128.1, 130.1, 131.4, 141.6, 148.5, 178.7; ESI-MS + m/z calcd for $C_{12}H_{15}IO_4$ 348.9937 [M − H], found 348.9934.

General Procedure for Oxidation of Alcohols with 1PC and 2PC in DCM. In a typical experiment, 0.5−1.0 mmol of the alcohol in 10.0 mL of DCM was stirred for 5−10 min and to this was introduced 1.5 equiv of **1PC**/**2PC**. The reaction mixture was stirred for the appropriate duration at room temperature (see Table 2). The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the solid material from the reaction mixture was filtered in vacuo. Concentration of the filtrate afforded the product, which was subjected to silica gel column chromatography to isolate the pure product.

General Procedure for Oxidation of Sulfides with 1PC and 2PC in CH_3CN. In a typical experiment, 0.5−1.0 mmol of the sulfide was taken in 10.0 mL of CH_3CN and to it 1.1 equiv of modified IBX (**1PC/2PC**) was introduced. The reaction mixture was stirred for the appropriate duration and temperature (see Table 3). The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the solid material from the reaction mixture was filtered in vacuo. Concentration of the filtrate afforded the product, which was subjected to silica gel column chromatography to isolate the pure product.

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Supporting Information Available: Characterization data, spectra for the products, ^{1}H and ^{13}C spectral reproductions for **1PC** and **2PC**, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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